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KINETIC AND NUCLEAR MAGNETIC RELAXATION STUDIES IN TRIVALENT PHOSPHORUS HALIDES

by

© Anna Diana Jordan

A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

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STUDIES IN TRIVALENT PHOSPHORUS HALIDES

submitted by Anna Diana Jordan in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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September 11th 1970.

To Robert

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ABSTRACT

The work described in this thesis is composed of two parts: a study of redistribution reactions for three trivalent phosphorus halide systems, and a study of the mechanisms governing the phosphorus nuclear magnetic relaxation in four phosphorus trihalides.

The gas phase reaction between PF_3 and PCl_3 to yield PF_2Cl and $PFCl_2$, and the disproportionation of PF_2Cl were studied by infrared spectroscopy. Redistribution occurred only to a limited extent after 24 hr at 300°C.

The reaction between PCl_3 and PBr_3 to yield PBr_2Cl and $PBrCl_2$, in the neat liquid, was studied by ^{31}P nmr spectroscopy. Contrary to previous reports indicating that this reaction attained equilibrium within 15 min at 25°C, it was found to have a lower limit of 10.5 days for the half-life at 70°C. A kinetic study of the reaction was complicated by non-reproducible results, which appeared to originate from catalysis by traces of water. For the catalyzed reaction, the rate of production or disappearance of a given species was first-order in that species. A study of the equilibrium constant for the redistribution indicated that the reaction is essentially thermoneutral.

The reaction between CF_3PCl_2 and CF_3PBr_2 to yield CF_3PBrCl, in the neat liquid, was studied by ^{19}F nmr spectroscopy. This reaction was also catalyzed by traces of water, however, the kinetics of the catalyzed reaction did not show any consistent first-order behaviour. A study of the temperature dependence of the equilibrium constant for the redistribution indicated that the reaction is thermoneutral.

Nuclear magnetic relaxation studies were carried out at 40.5 MHz for ^{31}P in PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 in a mixture of these species in equilibrium in the neat liquid. Both the transverse, $1/T_2$, and longitudinal, $1/T_1$, relaxation rates were measured as a function of temperature. A study of the $1/T_2$ for ^{35}Cl in PCl_3, in a mixture with PBr_3, as a function of temperature, yielded a value of 2.34×10^{-12} sec at 25°C for the reorientational correlation time. This was then used to calculate the value of $1/T_2$ for ^{79}Br in PBr_3.

The $1/T_2$ for ^{31}P is controlled by a scalar interaction mechanism of the second kind for all the species. The values of $1/T_2$ for ^{35}Cl in PCl_3 and for ^{79}Br in PBr_3 were used in conjunction with the values of $1/T_2$ for ^{31}P in PCl_3 and PBr_3 to calculate the values of the $P-^{35}Cl$ and $P-^{79}Br$ scalar coupling constants, 128.9 Hz and 248.6 Hz respectively.

The high temperature region of the $1/T_1$ for ^{31}P is controlled by a spin-rotation mechanism for all the species. On the basis of this, the spin-rotation coupling constants for PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 were calculated to be 3.00, 3.99, 5.67, and 9.13 kHz respectively.

The low temperature region of the $1/T_1$ for ^{31}P is consistent with contributions from dipolar, scalar interaction, and anisotropic chemical shift mechanisms. It is shown that the anisotropic chemical shift contribution, which has generally been disregarded in the interpretation of $1/T_1$ data, is quite significant for PBr_3 and PCl_3.

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CHAPTER I

INTRODUCTION

1. A Review of Redistribution Reactions in Group VA Compounds

Reactions involving the interchange of substituents between molecules have been known since the 19th century. It was only in 1939, however, that the nature of these reactions was recognized by Calingaert.[1] He introduced the term "redistribution reaction" to describe those reactions in which there was a random exchange of ligands between organometallic compounds. Such reactions are also referred to as displacement, disproportionation, rearrangement, reorganization, and scrambling reactions.

The most general definition of a redistribution reaction is that of a process "in which bonds change in relative position but not in total number or formal charge."[2] In intermolecular redistribution reactions two or more kinds of substituents interchange positions on one or more kinds of central atom or moiety, this process eventually leading to an equilibrium state.

Redistribution reactions are often encountered among the compounds of nontransitional elements in groups II to VII.[3,4,5,6,7] Several review articles dealing with different aspects of redistribution reactions involving group VA compounds have appeared.[4,5,6,7,8,9] Most of the work in this field has been carried out from either a preparative or thermodynamic point of view. Few systems have been studied kinetically, hence the kinetic trends are poorly defined, and the mechanistic considerations are only speculative. This review is an attempt to

document all the redistribution reactions that are known to occur among group VA compounds, excluding nitrogen. A special emphasis is placed on stating the conditions used, the extent and duration of the reaction and, where available, any thermodynamic and kinetic parameters. The review deals only with reactions in which there is a redistribution of two monofunctional substituents about a given central atom or moiety.

Redistribution reactions among P(III), As(III), Sb(III), and Bi(III) compounds are compiled in Tables I, II, III and IV respectively; those among P(V), As(V), and Sb(V) compounds are compiled in Tables V, VI, and VII respectively. Redistribution reactions of substituents between two oxidation states of a given central atom are compiled in Table VIII. All the equations are written in the conventional manner to represent the reactants used on the left hand side, and the products obtained on the right hand side. The equilibrium constants are reported for the appropriate ratio of products to reactants, as given by the equations. Unless otherwise stated, the reactions were studied in the absence of solvent. The tables contain a comprehensive survey of the literature, however, they may not be entirely complete because redistribution reactions are often not indexed as such.

The relationship between the free energy change and the enthalpy change, entropy change, and equilibrium constant for a reaction is given by the following expression:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -RT\ln K \ . \qquad (I.1)$$

TABLE I

P(III) Redistribution Reactions

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$PF_3 + PCl_3 \rightleftarrows PF_2Cl + PFCl_2$	350		hours	10	See also ref 11.
$3PF_2Br \rightleftarrows 2PF_3 + PBr_3$	-78		days	12	10% reaction in 10 days.
$3PFBr_2 \rightleftarrows PF_3 + 2PBr_3$	room temp		days	12	
$3PF_2I \rightleftarrows 2PF_3 + PI_3$	20		minutes	13	Rate of decomposition
	25		days	14	depends on initial concentration of PF_2I.
$PCl_3 + PBr_3 \rightleftarrows PCl_2Br + PClBr_2$	room temp		1-1.5 hr	15	See also ref 16,17,18,19
	25	7.1 (9)	< 15 min	22	20,21.
$PCl_3 + PI_3 \rightleftarrows PCl_2I + PClI_2$	room temp			23	
$PBr_3 + PI_3 \rightleftarrows PBr_2I + PBrI_2$	room temp		minutes	24	See also ref 25.

TABLE I (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$PFCl_2 + PFBr_2 \rightleftarrows 2PFClBr$	room temp	3.7 (4)	4 hr	26	No new compounds detected even after 1 year. See also ref 27.
$4PFBr_2 + 3PCl_3 \rightleftarrows 2PFCl_2 + 2PFClBr + PCl_2Br + PClBr_2 + PBr_3$	room temp		4 days	15	See also ref 26.
$3PF_2CN \rightleftarrows 2PF_3 + P(CN)_3$	-20		hours	28	
$5(CF_3)_2PI \rightleftarrows 3(CF_3)_3P + CF_3PI_2 + PI_3$	205		~ 48 hr	29	
$5CF_3PI_2 \rightleftarrows (CF_3)_3P + 3(CF_3)_2PI + PI_3$	240		~ 48 hr	29	
$CF_3PF_2 + CF_3PCl_2 \rightleftarrows 2CF_3PFCl$	60		days	30	CF_3PFCl detected after 18 hr.
$2CF_3PFCl \rightleftarrows CF_3PF_2 + CF_3PCl_2$	room temp	very large	>2 days	30	

TABLE I (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$PCl_3 + P(NCS)_3 \rightleftarrows PCl_2(NCS) + PCl(NCS)_2$	25	9.2 (9)	∿ 12 hr	31	
$PBr_3 + P(NCS)_3 \rightleftarrows PBr_2(NCS) + PBr(NCS)_2$	25	8.7 (9)	< 12 hr	31	
$PCl_3 + P(NCO)_3 \rightleftarrows PCl_2(NCO) + PCl(NCO)_2$	80		>24 days	31	
$PCl_3 + P(OC_2H_5)_3 \rightleftarrows PCl_2(OC_2H_5) + PCl(OC_2H_5)_2$	100	4.8×10^5 (9)	∿156 hr	32	
$PCl_3 + P(OC_6H_5)_3 \rightleftarrows PCl_2(OC_6H_5) + PCl(OC_6H_5)_2$	180	59 (9)	∿ 12 hr	22	Products detected after ∿ 12 hr at room temp. See also ref 33.
$PBr_3 + P(OC_6H_5)_3 \rightleftarrows PBr_2(OC_6H_5) + PBr(OC_6H_5)_2$	180	22 (9)	∿ 12 hr	22	Products detected after ∿ 12 hr at room temp.

TABLE I (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$PCl_3 + 2P[N(CH_3)_2]_3 \rightleftarrows 3PCl[N(CH_3)_2]_2$	100	very large	∿20 min	34	The equilibrium lies completely to the right.
$2PBr_2[N(CH_3)_2] \rightleftarrows PBr[N(CH_3)_2]_2 + PBr_3$	150		∿6 hr	34	
$PCl_3 + P[N(C_2H_5)_2]_3 \rightleftarrows PCl_2[N(C_2H_5)_2] + PCl[N(C_2H_5)_2]_2$	25	$\sim 6\times10^{13}$ (9)	seconds	35	$t_{1/2} < 30$ sec, $\Delta H = -17.5$ kcal mol^{-1}. Mole ratios of reactants must be 1:1.
$PCl_3 + PCl[N(C_2H_5)_2]_2 \rightleftarrows 2PCl_2[N(C_2H_5)_2]$	25	$\sim 25\times10^{6}$ (3)	seconds	35	$t_{1/2} < 30$ sec, $\Delta H = -10$ kcal mol^{-1}.
$CH_3PCl_2 + CH_3P[N(CH_3)_2]_2 \rightleftarrows 2CH_3PCl[N(CH_3)_2]$	25	very large	seconds	35	$t_{1/2} < 30$ sec.
$CH_3PBr_2 + CH_3P[N(CH_3)_2]_2 \rightleftarrows 2CH_3PBr[N(CH_3)_2]$	25	very large	seconds	35	$t_{1/2} < 30$ sec.

TABLE I (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$CH_3PCl_2 + CH_3P[N(C_2H_5)_2]_2 \rightleftarrows 2CH_3PCl[N(C_2H_5)_2]$	25	$1x10^{10}$ (4)	seconds	35	$t_{1/2}$ < 30 sec, $\Delta H = -12.8$ kcal mol^{-1}.
$3PCl_3 + 4CH_3P[N(C_2H_5)_2]_2 \rightleftarrows PCl_2[N(C_2H_5)_2] + PCl[N(C_2H_5)_2]_2 + 2CH_3PCl_2 + 2CH_3PCl[N(C_2H_5)_2] + P[N(C_2H_5)_2]_3$	25			35	$t_{1/2}$ < 30 sec.
$4CH_3PCl_2 + 3P[N(C_2H_5)_2]_3 \rightleftarrows PCl_3 + PCl_2[N(C_2H_5)_2] + PCl[N(C_2H_5)_2]_2 + 2CH_3PCl[N(C_2H_5)_2] + 2CH_3P[N(C_2H_5)_2]_2$	25		seconds	35	$t_{1/2}$ < 30 sec.
$PCl_3 + P(SC_4H_9)_3 \rightleftarrows PCl_2(SC_4H_9) + PCl(SC_4H_9)_2$	120	21.1 (9)	48 hr	36	
$P(OCH_3)_3 + P(OC_2H_5)_3 \rightleftarrows P(OCH_3)_2(OC_2H_5) + P(OCH_3)(OC_2H_5)_2$	120	6.92 (9)	10-15 hr	36	With traces of HCl as catalyst.

TABLE I (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$P(SCH_3)_3 + P(SC_4H_9)_3 \rightleftarrows P(SCH_3)_2(SC_4H_9) + P(SCH_3)(SC_4H_9)_2$	120	9.27 (9)	< 3 days	36	With traces of HCl as catalyst.
$P(OC_6H_5)_3 + P[N(C_2H_5)_2]_3 \rightleftarrows P(OC_6H_5)_2[N(C_2H_5)_2] + P(OC_6H_5)[N(C_2H_5)_2]_2$	100	4.2×10^4 (9)	~156 hr	32	
$CH_3P(OC_2H_5)_2 + CH_3P(OC_8H_{17}) \rightleftarrows 2CH_3P(OC_2H_5)(OC_8H_{17})$				37	

TABLE II

As(III) Redistribution Reactions

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$AsF_3 + AsCl_3 \rightleftarrows AsF_2Cl + AsFCl_2$	room temp	4.8×10^{-5} 2.3×10^{-5} (9)	seconds	38	Rate increased on addition of pyridine, Cl^- and F^- ions. See also ref 39.
$AsCl_3 + AsBr_3 \rightleftarrows AsCl_2Br + AsClBr_2$				39	See also ref 40.
$AsCl_3 + (CF_3)_3As \rightleftarrows CF_3AsCl_2 + (CF_3)_2AsCl$	210		~20 hr	41	Reaction does not occur at 165°C after 9 hr, nor at 195°C after 14 hr.
$AsI_3 + (CF_3)_3As \rightleftarrows CF_3AsI_2 + (CF_3)_2AsI$	220		hours	42	See also ref 43.
$2AsCl_3 + (C_6H_5CH_2)_3As \rightleftarrows 3C_6H_5CH_2AsCl_2$				44	

TABLE II (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$AsCl_3 + (CH_2CH)_3As \rightleftarrows CH_2CHAsCl_2 + (CH_2CH)_2AsCl$	100		∿ 5 hr	45	
$AsBr_3 + (CH_2CH)_3As \rightleftarrows CH_2CHAsBr_2 + (CH_2CH)_2AsBr$	60-130		0.5-3 hr	45	
$2AsBr_3 + (CH_3CH_2)_3As \rightleftarrows 3CH_3CH_2AsBr_2$				45	
$2C_6H_5AsCl_2 \rightleftarrows (C_6H_5)_2AsCl + AsCl_3$	256	5.7×10^{-2}	∿18 hr	46	A negligible amount of
	304	7.0×10^{-2} (0.33)	∿10 hr	46	$(C_6H_5)_3As$ is formed. $k_f = 3.22\times10^{-6}$ M^{-1} sec^{-1} at 256°C, ΔH = 2.6 kcal mol^{-1}.
	220	4.52×10^{-2}	∿45 hr	47	Second-order mechanism
	240	5.74×10^{-2}	< 8 hr	47	for 90% of reaction.
	260	6.5×10^{-2} (0.33)	< 6 hr	47	$k_f = 8.51\times10^{-6}$ M^{-1} sec^{-1} at 260°C, E_{af} = 37.0 kcal mol^{-1}, ΔH = 4.8 kcal mol^{-1}.

TABLE II (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$2(C_6H_5)_2AsCl \rightleftarrows C_6H_5AsCl_2 + (C_6H_5)_3As$	252	5.9×10^{-2}	>25 hr	46	A negligible amount of $AsCl_3$ is formed. $k_f = 0.89\times10^{-6}$ M^{-1} sec^{-1} at 252°C, E_{af} = 37.4 kcal mol^{-1}, ΔH = 3.8 kcal mol^{-1}. Reaction catalyzed by metals.
	304	8.2×10^{-2} (0.33)		46	
	273	4.68×10^{-2} (0.33)		47	
$AsCl_3 + (C_6H_5)_3As \rightleftarrows C_6H_5AsCl_2 + (C_6H_5)_2AsCl$	350	large		48	See also ref 49,50.
$AsBr_3 + (C_6H_5)_3As \rightleftarrows C_6H_5AsBr_2 + (C_6H_5)_2AsBr$	350		∿3 hr	48	
$AsI_3 + (C_6H_5)_3As \rightleftarrows C_6H_5AsI_2 + (C_6H_5)_2AsI$	350		∿6 hr	48	

TABLE II (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$AsF_3 + As[N(CH_3)_2]_3 \rightleftarrows AsF_2[N(CH_3)_2] + AsF[N(CH_3)_2]_2$	37 28	$\sim 6 \times 10^{9}$ $\sim 1 \times 10^{12}$ (9)	$\sim$0.1 sec	51 51	A second-order mechanism is indicated. $k_f \sim 10^2$ M^{-1} sec^{-1} at 25°C, $\Delta H = -5.6$ kcal mol^{-1}.
$2AsF_2[N(CH_3)_2] \rightleftarrows AsF_3 + AsF[N(CH_3)_2]_2$	37	very small	seconds	51	The equilibrium lies to the left.
$2AsF[N(CH_3)_2]_2 \rightleftarrows AsF_2[N(CH_3)_2] + As[N(CH_3)_2]_3$		large	seconds	51	The equilibrium lies to the right.
$AsCl_3 + As[N(CH_3)_2]_3 \rightleftarrows AsCl_2[N(CH_3)_2] + AsCl[N(CH_3)_2]_2$	37	3×10^{8} (9)	<0.02 sec	51	A second-order mechanism is indicated. $k_f \sim 10^2$ M^{-1} sec^{-1} at 25°C, $E_{af} \sim 5$ kcal mol^{-1}, $\Delta H = -13.7$ kcal mol^{-1}.

TABLE II (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$AsBr_3 + As[N(CH_3)_2]_3 \rightleftarrows AsBr_2[N(CH_3)_2] + AsBr[N(CH_3)_2]_2$	37	3×10^{11} (9)	<0.01 sec	51	The reaction order is greater than two. $k_f \sim 10^2$ M^{-1} sec^{-1}, $E_{af} \sim 5$ kcal mol^{-1}, $\Delta H \sim -14.5$ kcal mol^{-1}.
$AsF_3 + As(OCH_3)_3 \rightleftarrows AsF_2(OCH_3) + AsF(OCH_3)_2$	37	7.7×10^2		51	A second-order mechanism is indicated. $k_f \sim 10^2$ M^{-1} sec^{-1} at 25°C, $E_{af} \sim 2$ kcal mol^{-1}, $\Delta H = -4.1$ kcal mol^{-1}.
	28	9.1×10^2 (9)	~0.02 sec	51	
$AsCl_3 + As(OCH_3) \rightleftarrows AsCl_2(OCH_3) + AsCl(OCH_3)_2$	37	1.6×10^4 (9)	<0.2 sec	51	A second-order mechanism is indicated. $k_f \sim 10^2$ M^{-1} sec^{-1} at 25°C, $E_{af} \sim 2$ kcal mol^{-1}, $\Delta H = -7.2$ kcal mol^{-1}.

TABLE II (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$AsBr_3 + As(OCH_3)_3 \rightleftarrows AsBr_2(OCH_3) + AsBr(OCH_3)_2$	37	6.9×10^3 (9)	<0.1 sec	51	A second-order mechanism is indicated. $k_f \sim 10^2$ M^{-1} sec^{-1} at 25°C, $E_{af} \sim 2$ kcal mol^{-1}, $\Delta H = -4.4$ kcal mol^{-1}.
$As(OCH_3)_3 + As[N(CH_3)_2]_3 \rightleftarrows As(OCH_3)_2[N(CH_3)_2] + As(OCH_3)[N(CH_3)_2]_2$	37	33.5 (9)	minutes	51	Reaction also studied in CCl_4.
$AsBr_3 + As(OOCCH_3) \rightleftarrows AsBr_2(OOCCH_3) + AsBr(OOCCH_3)_2$				52	

TABLE III

Sb(III) Redistribution Reactions

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$SbCl_3 + (CH_3)_3Sb \rightleftarrows CH_3SbCl_2 + (CH_3)_2SbCl$	72 100			53 53	Initial rates in dimethylformamide indicate that reaction is first-order in each reactant. $k_f = 6.7\times10^{-5}$ M^{-1} sec^{-1} at 72°C, $\Delta H^{\ddagger} = 18$ kcal mol^{-1}, $\Delta S^{\ddagger} = -25$ eu.
$SbCl_3 + (CH_2CH)_3Sb \rightleftarrows CH_2CHSbCl_2 + (CH_2CH)_2SbCl$		large		45	
$SbBr_3 + (CH_2CH)_3Sb \rightleftarrows CH_2CHSbBr_2 + (CH_2CH)_2SbBr$	65		∿30 min	45	
$SbCl_3 + (C_6H_5)_3Sb \rightleftarrows C_6H_5SbCl_2 + (C_6H_5)_2SbCl$				50	See also ref 54.

TABLE III (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$3(CF_3)_2SbCl \rightleftarrows 2(CF_3)_3Sb + SbCl_3$				55	
$5(CF_3)_2SbBr \rightleftarrows 3(CF_3)_3Sb + CF_3SbBr_2 + SbBr_3$	20		< 17 hr	55	
$2(CF_3)_3Sb + SbI_3 \rightleftarrows 3(CF_3)_2 SbI$	120		~7 days	55	
$5(CF_3)_2SbI \rightleftarrows 3(CF_3)_3Sb + CF_3SbI_2 + SbI_3$	20		~6 months	55	

TABLE IV

Bi(III) Redistribution Reactions

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$BiCl_3 + BiI_3 \rightleftarrows BiCl_2I + BiClI_2$	25	0.58 (9)		56	Reaction studied in dioxane. See also ref 57.
$2BiCl_3 + (CH_3)_3Bi \rightleftarrows 3CH_3BiCl_2$				58	Reaction studied in glacial acetic acid.
$2BiBr_3 + (CH_3)_3Bi \rightleftarrows 3CH_3BiBr_2$				58	Reaction studied in ether.
$2BiCl_3 + (C_2H_5)_3Bi \rightleftarrows 3C_2H_5BiCl_2$			fast	58	Reaction studied in glacial acetic acid.
$2BiBr_3 + (C_2H_5)_3Bi \rightleftarrows 3C_2H_5BiBr_2$				58	Reaction studied in ether.
$2BiBr_3 + (C_4H_9)_3Bi \rightleftarrows 3C_4H_9BiBr_2$				59	Reaction studied in ether.
$2BiBr_3 + (iso\text{-}C_5H_{11})_3Bi \rightleftarrows 3(iso\text{-}C_5H_{11})BiBr_2$				59	Reaction studied in ether.

TABLE IV (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$BiCl_3 + 2(C_6H_5)_3Bi \rightleftarrows 3(C_6H_5)_2BiCl$				60	Reaction studied in ether. See also ref 61.
$BiBr_3 + 2(C_6H_5)_3Bi \rightleftarrows 3(C_6H_5)_2BiBr$			fast	61	Reaction studied in ether.
$BiBr_3 + (C_6H_4Cl)_3Bi \rightleftarrows C_6H_4ClBiBr_2 + (C_6H_4Cl)_2BiBr$				62	Reaction studied in ether.

TABLE V

P(V) Redistribution Reactions

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$2OPF_2(NCS) \rightleftarrows OPF_3 + OPF(NCS)_2$	65	large	∿1 hr	63	See also ref 64.
$CH_3P(O)F_2 + CH_3P(O)Cl_2 \rightleftarrows 2CH_3P(O)FCl$	100		∿2 weeks	65	
$2PF_5 + (CF_3)_3PF_2 \rightleftarrows 3CF_3PF_4$	100	large	∿4 hr	66	
$5CF_3PF_4 \rightleftarrows 3PF_5 + (CF_3)_2PF_3 + (CF_3)_3PF_2$	25			66	Disproportionates 5% per month.
$2(CF_3)_2PF_3 \rightleftarrows CF_3PF_4 + (CF_3)_3PF_2$	25			66	Disproportionates 10% per day.
$2PCl_5 + 3PBr_5 \rightleftarrows PCl_4Br + 2PCl_2Br_3 + 2PClBr_4$				17	Polybromochlorides also formed.

TABLE V (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$OPCl_3 + OPBr_3 \rightleftarrows OPCl_2Br + OPClBr_2$	130	7.22 (9)	<1 week	67	See also ref 68.
$SPCl_3 + SPBr_3 \rightleftarrows SPCl_2Br + SPClBr_2$	130	8.04 (9)	<1 week	67	
$OPCl_3 + OP(NCS)_3 \rightleftarrows OPCl_2(NCS) + OPCl(NCS)_2$	130	7.51 (9)	∿156 hr	69	
$SPBr_3 + SP(NCS)_3 \rightleftarrows SPBr_2(NCS) + SPBr(NCS)_2$	150	1.62	∿154 hr	69	
$OPH(OCH_3)_2 + OPH(OC_3H_7)_2 \rightleftarrows 2OPH(OCH_3)(OC_3H_7)$	room temp		∿2 months	70	
$OPH(OCH_3)_2 + OPH(OC_2H_5)_2 \rightleftarrows 2OPH(OCH_3)(OC_2H_5)$	150	3.50 (4)	<12 hr	36	Less than 5% reaction after 3 months at room temp. Catalyzed by acid and not by base.

TABLE V (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$OP(OCH_3)_3 + OP(OC_2H_5)_3 \rightleftarrows OP(OCH_3)_2(OC_2H_5) + OP(OCH_3)(OC_2H_5)_2$	200	12.8 (9)	<7 days	36	No reaction after 3 months at room temp even with HCl as catalyst, but reaction complete in 6 days with $NaOCH_3$ as catalyst.
$OP(OCH_3)_3 + OP(OC_6H_5)_3 \rightleftarrows OP(OCH_3)_2(OC_6H_5) + OP(OCH_3)(OC_6H_5)_2$				36	(OCH_3) and (OC_6H_5) exchange slower than (OCH_3) and (OC_2H_5) exchange.
$2OPCl_3 + OP(OH)_3 \rightleftarrows 3OPCl_2(OH)$	25		~2 months	71	Condensed species are formed when the mole percent of $OPCl_3$ is less than 50.

TABLE V (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$OPCl_3 + CH_3P(S)Cl_2 \rightleftarrows CH_3P(O)Cl_2 + SPCl_3$	230	0.71,0.83 (1)	hours	72	
$OPCl_3 + C_6H_5P(S)Cl_2 \rightleftarrows C_6H_5P(O)Cl_2 + SPCl_3$	230	0.56,0.59 (1)	hours	72	
$SPCl_3 + CH_2ClP(O)Cl_2 \rightleftarrows CH_2ClP(S)Cl_2 + OPCl_3$	230	3.6 (1)	hours	72	
$SPCl_3 + (CH_3)(CH_2Cl)P(O)Cl \rightleftarrows (CH_3)(CH_2Cl)P(S)Cl + OPCl_3$	150	13.5 (1)	∿1 day	72	Some decomposition also occurs.
$OPBr_3 + SPCl_3 \rightleftarrows OPCl_3 + SPBr_3$	230	6.7 (1)	hours	72	$OPCl_2Br$, $OPClBr_2$, $SPCl_2Br$, $SPClBr_2$ also formed.
$(CH_3NPF_3)_2 + (CH_3NPCl_3)_2 \rightleftarrows (CH_3NP)_2F_xCl_{5-x}$	110		∿48 hr	73	All the possible compounds for x = 1 to 5 are formed.

TABLE VI

As(V) Redistribution Reactions

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$(CH_3)_3AsF_2 + (CH_3)_3AsCl_2 \rightleftarrows 2(CH_3)_3AsFCl$	-53	5.4 (4)	<0.1 sec	74	Reaction studied in $CHCl_3$.
$(CH_3)_3AsF_2 + (CH_3)_3AsBr_2 \rightleftarrows 2(CH_3)_3AsFBr$			<0.1 sec	74	Reaction in $CHCl_3$ too fast at -60°C to distinguish 3 signals in the nmr spectrum.
$(CH_3)_3AsCl_2 + (CH_3)_3AsBr_2 \rightleftarrows 2(CH_3)_3AsClBr$			<0.1 sec	74	Reaction in $CHCl_3$ too fast at -60°C to distinguish 3 signals in the nmr spectrum.
$(C_6H_5CH_2)_3AsF_2 + (C_6H_5CH_2)_3AsCl_2 \rightleftarrows 2(C_6H_5CH_2)_3AsClF$	-47	10 (4)	<0.1 sec	74	Reaction studied in $CHCl_3$.

TABLE VII

Sb(V) Redistribution Reactions

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$(CH_3)_3SbF_2 + (CH_3)_3SbCl_2 \rightleftarrows 2(CH_3)_3SbFCl$	35	3.9	<0.1 sec	74	Reaction studied in $CDCl_3$.
	60	4.2	<0.1 sec	74	See also ref 75.
		(4)			
$(CH_3)_3SbF_2 + (CH_3)_3SbBr_2 \rightleftarrows 2(CH_3)_3SbFBr$	0	2.8	<0.1 sec	74	Reaction studied in $CDCl_3$.
	35	3.2	<0.1 sec	74	See also ref 75.
	60	3.6	<0.1 sec	74	
		(4)			
$(CH_3)_3SbF_2 + (CH_3)_3SbI_2 \rightleftarrows 2(CH_3)_3SbFI$	0	1.1	<0.1 sec	74	Reaction studied in $CDCl_3$.
	35	1.5	<0.1 sec	74	See also ref 75.
	60	1.7	<0.1 sec	74	
		(4)			
$(CH_3)_3SbCl_2 + (CH_3)_3SbBr_2 \rightleftarrows 2(CH_3)_3SbClBr$	0	3.3	<0.1 sec	74	Reaction studied in $CDCl_3$.
	35	3.5	<0.1 sec	74	See also ref 75.
	60	3.7	<0.1 sec	74	
		(4)			

TABLE VII (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$(CH_3)_3SbCl_2 + (CH_3)_3SbI_2 \rightleftarrows 2(CH_3)_3SbClI$	0	2.1	<0.1 sec	74	Reaction studied in $CDCl_3$.
	35	2.3	<0.1 sec	74	See also ref 75.
	65	2.9	<0.1 sec	74	
		(4)			
$(CH_3)_3SbBr_2 + (CH_3)_3SbI_2 \rightleftarrows 2(CH_3)_3SbBrI$	0	2.9	<0.1 sec	74	Reaction studied in $CDCl_3$.
	35	3.0	<0.1 sec	74	See also ref 75.
	65	3.3	<0.1 sec.	74	
		(4)			
$(C_6H_5CH_2)_3SbF_2 + (C_6H_5CH_2)_3SbCl_2 \rightleftarrows 2(C_6H_5CH_2)_3SbFCl$	-37	6.4	<0.1 sec	74	Reaction studied in $CDCl_3$.
		(4)			
$(C_6H_5)_3SbF_2 + (C_6H_5)_3SbCl_2 \rightleftarrows 2(C_6H_5)_3SbFCl$	35	9.0	<0.1 sec	74	Reaction studied in $CDCl_3$.
		(4)			
$(C_6H_5)_3SbF_2 + (C_6H_5)_3SbBr_2 \rightleftarrows 2(C_6H_5)_3SbFBr$	35	4.0	<0.1 sec	74	Reaction studied in $CDCl_3$.
		(4)			

TABLE VII (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$(C_6H_5)_3SbF_2 + (C_6H_5)_3SbI_2 \rightleftarrows 2(C_6H_5)_3SbFI$	35	1.0 (4)	<0.1 sec	74	Reaction studied in $CDCl_3$.

TABLE VIII

Mixed Valence Redistribution Reactions

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$PCl_3 + PCl_5^* \rightleftarrows PCl_3^* + PCl_5$	0.1		~160 days	76	Reaction studied in CCl_4.
	25		~ 14 days	76	Rate = $k_f[PCl_5]$,
	50		~ 2 days	76	$k_f = 10.6 \times 10^{-3}$ hr^{-1} at 25°C, E_{af} = 15.9 kcal mol^{-1}. HCl acts as a catalyst.
$3PCl_3 + 3OPBr_3 \rightleftarrows OPCl_3 + OPCl_2Br + OPClBr_2 + PCl_2Br + PClBr_2 + PBr_3$	200		~ 1 week	21	
$3PBr_3 + 3OPCl_3 \rightleftarrows OPCl_2Br + OPClBr_2 + OPBr_3 + PCl_3 + PCl_2Br + PClBr_2$	200		days	21	
$3OPCl_3 + 3P(OC_6H_5)_3 \rightleftarrows OPCl_2(OC_6H_5) + OPCl(OC_6H_5)_2 + OP(OC_6H_5)_3 + PCl_3 + PCl_2(OC_6H_5) + PCl(OC_6H_5)_2$	300		weeks	21	

TABLE VIII (Cont'd)

Reactions	T(°C)	K	Time reqd	Ref	Remarks
$Sb^*Cl_3 + SbCl_5 \rightleftarrows SbCl_3 + Sb^*Cl_5$	50.1		days	77	Reaction studied in CCl_4.
	68.4		days	77	Rate = $k_1[SbCl_5]$ +
	81.0		days	77	$k_2[SbCl_3][SbCl_5]$.
					See also ref 78, 79.

The number and type of bonds remain the same in a redistribution reaction. If it is assumed that the bond energy between the central atom and each of the substituents is independent of the nature of the other substituents on the central atom, then the enthalpy change of the reaction will be zero. Such reactions are termed thermoneutral. The free energy change is governed by the entropy of mixing, and a random distribution of substituents takes place:

$$\Delta G^{o}_{rand} = -T\Delta S^{o}_{rand} = -RT\ln K_{rand} \quad . \qquad (I.2)$$

The distribution of molecules in a random redistribution reaction can be calculated statistically from the laws of probability,[67,7] and therefore the value of K_{rand} may be obtained. The experimental equilibrium constant of a reaction may be compared to the equilibrium constant for random reorganization, in order to determine whether the reaction is "random" or "non-random." It follows that reactions for which the equilibrium constant varies from the random value are expected to have a measurable enthalpy change. In Tables I to VIII the value of the equilibrium constant for random reorganization, K_{rand}, is placed in brackets next to the experimental value, where available.

There are many examples of redistribution reactions in P(III) compounds, and some trends can be detected. When the two exchanging substituents are of the same type, both halogen, ethoxy, or mercapto, the redistribution is essentially random. When the two exchanging substituents, however, are of different type as for dialkylamino-

halogen, alkoxy- or phenoxy-halogen, mercapto-halogen, or dialkylamino-phenoxy, then the redistribution is highly non-random, and favours the formation of the mixed compounds. The largest deviations from random behaviour are found for the PCl_3-$P[N(C_2H_5)_2]_3$ and CH_3PCl_2-$CH_3P[N(C_2H_5)_2]_2$ systems. The above observations for the redistribution of unlike substituents in P(III) compounds also apply to the redistribution of unlike substituents in As(III) compounds. Again the non-random redistribution of molecules is strongly in favour of the formation of the mixed compounds, and the most non-random behaviour is again exhibited by the dialkylamino-halogen exchanges. The only study of exchange between like substituents in As(III) compounds has been that of the AsF_3-$AsCl_3$ system.[38] This system is rather unique in that the distribution of molecules is very non-random, and in favour of the unmixed species. Too few systems involving Sb(III) or Bi(III) systems have been studied, thus even qualitative observations cannot be made. The trends for redistribution in P(III) and As(III) compounds are in agreement with the concept that, for very different types of ligands, there will be considerable rehybridization of the central atom when these ligands are interchanged. In other words, the bonding of a ligand to the central atom depends on the type of other substituents on that atom. The bond energy of a particular bond will therefore be dependent on the rest of the environment, hence the reaction will not be thermoneutral.

Almost all the reactions studied for pentavalent compounds have

involved the redistribution of two like substituents. For P(V) compounds there is an essentially random distribution of molecules, whereas for As(V) and Sb(V) compounds some redistributions are of random behaviour and others are not. However, the departure from random redistribution is never large.

Kinetic parameters are known for very few reactions, most of the rate data being in the form of the time required to attain equilibrium. Even when the data are available, a comparison between the systems is difficult because the conditions are not duplicated. Moreover, in certain systems[51] it was suspected that catalytic impurities could have been playing a role in determining the rate of the reaction. For all these reasons it is difficult to obtain meaningful kinetic trends in this field, but some general trends appear.

The rate of redistribution varies with the nature of the central atom, increasing with increase in the electropositive character of the atom; hence, the rates decrease in the order Sb > As > P. Few reactions between P(V) compounds have been studied, but in general they are slower than the corresponding reactions between P(III) compounds. The exchange of substituents between a given central atom in two oxidation states was extremely slow.

The rate of redistribution for a given central atom depends on the nature of the substituents. For the redistribution of like substituents between P(III) compounds, the rates decreased in the order halogen > alkoxy > mercapto. Within the halogen compounds, the rates

decreased in the order Br > Cl > F. When the exchanging ligands on P(III) compounds were not of the same type, the fastest rates were found for the halogen-dialkylamino exchanges. The reactivity with PCl_3 decreased in the order $P[N(C_2H_5)_2]_3 >> P(NCS)_3 >> P(OC_2H_5)_3$ and $P[N(C_2H_5)_2]_3 >> P[N(CH_3)_2]_3 > P(OC_6H_5)_3 \sim P(SC_6H_5)_3 >> P(CH_3)_3$. No trends in the rates of exchange between substituents of the same type on As(III) compounds can be given, because only the AsF_3-$AsCl_3$ system has been studied; redistribution was quite fast. The reactivity with $AsCl_3$ decreased in the order $As[N(CH_3)_2]_3 \sim As(OCH_3)_3 >> AsF_3 > (CH_2CH)_3As >> (CF_3)_3As > (C_6H_5)_3As$. The reactivity of halogens with $As(OCH_3)_3$ decreased in the order $AsF_3 > AsBr_3 > AsCl_3$, however, the differences between them were not large and the authors[51] did not place much relevance on the quantitative results. In the same study it was shown that the reactivity of the halogens with $As[N(CH_3)_2]_3$ was independent of the halogen used. It seems, therefore, that the nature of the halogen plays a relatively unimportant role in redistribution reactions for As(III) compounds.

The mechanisms governing redistribution reactions are still in the speculative stage.[4] It has been generally assumed that the reactions are bimolecular, and proceed through a four-centre bridged mechanism. This mechanism is favourable for exchange between compounds whose central atoms have strong electron-acceptor character and whose substituents have strong electron-donor character. The results of the dimethylamino-halogen and methoxy-halogen exchanges[51] on As(III)

mentioned in the above paragraph, were found to be consistent with second-order kinetics. For these reactions, an ionic mechanism could be postulated. The rate determining step could be the attack of an electrophilic arsenic cation, derived from the halide, on the nucleophilic nitrogen or oxygen in $As[N(CH_3)_2]_3$ or $As(OCH_3)_3$. Clearly, much more work in this field is required before reasonable mechanistic trends can be proposed.

The original project undertaken was to study the kinetics of exchange between halogens on triply connected phosphorus. From the preceeding observations on this system, discussed above, these exchanges are expected to be relatively slow, hence conventional kinetic techniques could be used. The ultimate goal was to derive the rate law for the exchange and obtain the kinetic and thermodynamic parameters, with the hope of proposing a reasonable mechanism for each system. The work included a study of the exchange between PF_3 and PCl_3, between PCl_3 and PBr_3, and between CF_3PCl_2 and CF_3PBr_2. However, initial aspirations were not realized due to the complexity of the systems. It is hoped, nevertheless, that the nature and reactivity of these reactions have been partially elucidated.

2. Nuclear Magnetic Relaxation in Liquids

The mechanisms by which magnetic nuclei relax in the nuclear magnetic resonance (nmr) experiment have been the object of numerous studies in recent years. The studies of relaxation phenomena in liquids have been especially useful in yielding some insight into the nature of the liquid state. The theory of nuclear magnetic relaxation and the mechanisms governing it have been discussed and reviewed by several authors.[80,81,82,83,84,85]

When a nuclear spin system is placed in a strong magnetic field, H_o, a Zeeman splitting of the nuclear energy levels occurs and a Boltzmann distribution of nuclear spins is established among the energy levels. In the nmr experiment, energy is absorbed by the nuclear spin system when a radiofrequency field H_1, rotating about H_o in a plane perpendicular to it and of the appropriate frequency ω_o, known as the Larmor frequency, is applied. Since the population of nuclear spins in the lower energy levels exceeds that of the higher energy levels, this absorption of energy causes the transfer of some nuclei from the lower to the higher energy states, thus perturbing the normal Boltzmann distribution or thermal equilibrium of nuclear spins. Because spontaneous emission of energy is negligible, the only path by which the nuclear spin system can be restored or relaxed to its thermal equilibrium, is through transitions caused by fluctuating magnetic fields oscillating at the Larmor frequency. These magnetic fields are in turn caused by magnetic interactions between the nuclear spins and the surrounding electrons and nuclei composing the entire sample;

this is often called the lattice or heat reservoir. The rate at which the thermal equilibrium is restored is governed by characteristic relaxation times for the particular nuclear spin system.

The rate of decay of the nuclear magnetization to its thermal equilibrium has been described quantitatively by Bloch in the so-called "Bloch equations."[86] These equations combine the effects of Larmor precession and nuclear relaxation:

$$\frac{dM_z}{dt} = -\frac{M_z - M_o}{T_1} \quad , \tag{I.3a}$$

$$\frac{dM_x}{dt} = \omega_o M_y - \frac{M_x}{T_2} \quad , \tag{I.3b}$$

$$\frac{dM_y}{dt} = -\omega_o M_x - \frac{M_y}{T_2} \quad . \tag{I.3c}$$

M_z, M_x, and M_y refer to the z, x, and y components of magnetization at a given time, where z is the component parallel to the main magnetic field; M_o is the equilibrium magnetization in the z direction; ω_o is the Larmor frequency; T_1 is the characteristic time for the decay of the M_z component to M_o, and is known as the spin-lattice or longitudinal relaxation time; and T_2 is the characteristic time for the decay of the M_x and M_y components to zero, and is known as the spin-spin or transverse relaxation time.

Certainly the best definition of T_1 and T_2 is in terms of the Bloch equations presented above, where T_1 determines the approach to

equilibrium of the component of magnetization lying parallel to the magnetic field, while T_2 determines the loss of phase coherence of the nuclear spin system. Transverse relaxation alone is incapable of causing an energy transfer between the nuclear spin system and the lattice. Longitudinal relaxation always brings about transverse relaxation, thus T_1 is always greater than, or equal to, T_2.

Longitudinal and transverse relaxation both depend on the existence of perturbing magnetic fields at the nucleus. However, longitudinal relaxation with a characteristic time T_1 can only occur when these magnetic fields fluctuate with time due to the thermal motion of the nuclei, whereas transverse relaxation with a characteristic time T_2 is not dependent on these fluctuations for its existence; although it can be modified by such fluctuations, it is most effective in the absence of thermal motions. In a system in which the magnetic field fluctuations are very slow due to restricted motion of the nuclei, as in the case of very viscous liquids and solids, T_1 is very long while T_2 is very short. When the magnetic field fluctuations are very rapid, as in the case of non viscous liquids, T_1 decreases considerably whereas T_2 increases. In most liquids the magnetic field fluctuations are so rapid that the interactions between nuclei alone are ineffective in causing relaxation of the transverse components of magnetization. M_x and M_y then relax by the same mechanism as M_z, and the equality $T_1 = T_2$ applies. In this situation, the frequency of magnetic fluctuations is much larger than the Larmor frequency. This may be expressed by the mathematical condition that:

$$\omega_o \tau_c << 1 \quad , \qquad (I.4)$$

where ω_o is the Larmor frequency, and τ_c is the characteristic time for the magnetic fluctuation. This condition is often referred to as the extreme narrowing condition.

The mechanisms by which the nuclei are relaxed were first presented in detail in the pioneering study by Bloembergen, Purcell, and Pound.[81,87] These mechanisms were confirmed, refined and supplemented by various authors who will be mentioned in the course of this chapter. The following section will deal with a presentation of the relaxation mechanisms most commonly encountered in diamagnetic liquids; the dipolar, anisotropic chemical shift, quadrupolar, scalar coupling, and spin-rotation mechanisms.

Relaxation of a nucleus by direct dipole-dipole interactions with other magnetic nuclei is probably one of the most frequently encountered relaxation mechanisms, especially for protons in organic liquids.[88,89,90,91,92] The dipolar relaxation mechanism may be illustrated for the simple case of two magnetic nuclei, i and j, whose magnetic moments are separated by a distance r, where r makes an angle Θ with the main magnetic field. The dipolar interactions between the two nuclei are modulated by fluctuations in r and Θ due to the random thermal motions. One can immediately distinguish between two types of dipolar interactions; the intramolecular and intermolecular. The dipolar relaxation between nuclei in the same molecule is termed intramolecular. The distance r is fixed but the

angle Θ varies because of the rotational motion of the molecule, hence this is frequently called a rotational dipolar mechanism. The dipolar relaxation between nuclei in different molecules is termed intermolecular. In this case, both r and Θ may vary due to the translational or diffusional motion of the molecules, in addition to the rotational motion which is important for the intramolecular interaction. The intermolecular dipolar mechanism is often referred to as a translational dipolar mechanism. Thus the dipole-dipole interactions act as time dependent perturbations on the Zeeman energy levels of the nuclei, and produce transitions between these energy levels which result in the relaxation of the nuclear magnetization.

The contribution of intramolecular and intermolecular dipolar interactions to the relaxation of a nucleus were first formulated by Bloembergen, Purcell and Pound[81] for the interaction between two identical nuclei of spin 1/2. Except for some minor modifications the same results were obtained by Kubo and Tomita,[93] using a different theoretical approach, and by Solomon.[94] These results were generalised by Gutowsky and Woessner[88] for interactions between many nuclei of different spins. The total relaxation resulting from the interaction of spin i with j ($i = j$) and k ($i \neq k$) is given by:[80,82,95]

$$\frac{1}{T_1} = \frac{1}{T_1(ij)} + \frac{1}{T_1(ik)} \; ; \quad \frac{1}{T_2} = \frac{1}{T_2(ij)} + \frac{1}{T_2(ik)} \; . \qquad \text{(I.5)}$$

The intramolecular dipolar contribution to the relaxation,

$1/T_{1D}$ and $1/T_{2D}$, is given by:[80,82,95]

$$\frac{1}{T_{1D}} = \{\frac{2}{5}\hbar^2\gamma_i^4 I_i(I_i+1)(\Sigma_j r_{ij}^{-6}) + \frac{4}{15}\hbar^2\gamma_i^2[\Sigma_k \gamma_k^2 I_k(I_k+1)r_{ik}^{-6}]\} \times$$

$$\{\frac{\tau_D}{1+\omega_o^2\tau_D^2} + \frac{4\tau_D}{1+4\omega_o^2\tau_D^2}\} \quad , \qquad \text{(I.6)}$$

$$\frac{1}{T_{2D}} = \{\frac{2}{10}\hbar^2\gamma_i^4 I_i(I_i+1)(\Sigma_j r_{ij}^{-6}) + \frac{4}{30}\hbar^2\gamma_i^2[\Sigma_k \gamma_k^2 I_k(I_k+1)r_{ik}^{-6}]\} \times$$

$$\{3\tau_D + \frac{5\tau_D}{1+\omega_o^2\tau_D^2} + \frac{2\tau_D}{1+4\omega_o^2\tau_D^2}\} \quad , \qquad \text{(I.7)}$$

where Σ_j are summations over nuclei of the same kind as i, the relaxing nucleus, and Σ_k are summations over all other nuclei; $\hbar$ is Planck's constant divided by 2π; γ is the magnetogyric ratio; I is the nuclear spin; r is the internuclear distance; ω_o is the Larmor frequency of the nucleus i; and τ_D is the correlation time for intramolecular dipolar interaction.

The correlation time τ_D is found to be of the order of 10^{-12} sec, and the radiofrequencies usually used are $< 2\pi \times 10^8$ sec^{-1}, hence the extreme narrowing condition $\omega_o\tau_D << 1$, may be applied. Equations (I.6) and (I.7) then reduce to:

$$\frac{1}{T_{1D}} = \frac{1}{T_{2D}} = 2\hbar^2\gamma_i^2\{\gamma_i^2 I_i(I_i+1)(\Sigma_j r_{ij}^{-6}) + \frac{2}{3}[\Sigma_k \gamma_k^2 I_k(I_k+1)r_{ik}^{-6}]\}\tau_D \quad . \qquad \text{(I.8)}$$

The correlation time τ_D is the rotational correlation time of the molecule, which is of the order of the time a molecule takes to turn through one radian. Bloembergen, Purcell, and Pound (BPP)[81] proposed that τ_D can be calculated to a reasonable approximation by considering the molecule as a rigid sphere, of radius a, imbedded in a viscous liquid, and undergoing a 'rotational' Brownian motion. This assumption was made in analogy to the theory of translational Brownian motion in viscous liquids, thus τ_D is given by:

$$\tau_D = \frac{1}{6D} \quad . \tag{I.9}$$

D is the 'rotational' diffusion coefficient, and it is related to the viscosity η by the relation:

$$D = \frac{kT}{8\pi\eta a^3} \quad , \tag{I.10}$$

where k is Boltzmann's constant and T the absolute temperature. Thus:

$$\tau_D = \frac{4\pi\eta a^3}{3kT} \quad . \tag{I.11}$$

The correlation time τ_D is closely related to the Debye correlation time for dielectric dispersion, τ, and it is found that $\tau_D = \tau/3$. Because of this relationship, equation (I.11) is often referred to as the Debye-BPP equation. It is often used to calculate τ_D, even though it is a generalisation from the treatment of translational motion.

The intermolecular dipolar contribution to the relaxation, $1/T_{1D}'$ and $1/T_{2D}'$, has the same form as the intramolecular contribution.

When the extreme narrowing condition applies, it is given by:[82]

$$\frac{1}{T_{1D}'} = \frac{1}{T_{2D}'} = 2\hbar^2\gamma_i^2\{[\sum_j \gamma_i^2 I_i(I_i + 1)(r_{ij}')^{-6}] + \frac{2}{3}[\sum_k \gamma_k^2 I_k(I_k + 1)(r_{ik}')^{-6}]\}\tau_D' \quad . \tag{I.12}$$

The only difference in equations (I.8) and (I.12) is in the terms which are primed, r' and τ_D'. The correlation time for the intermolecular dipolar interaction τ_D', is mainly the translational correlation time for molecules in a spherical shell of radius r' + dr' centered at the relaxing nucleus i. One definition of τ_D' is the time it takes for the nucleus i to move a distance r' relative to the other nucleus, j or k. The motion is three-dimensional and the molecules containing the nucleus i and the nucleus j or k are considered both to be moving, hence τ_D' may be calculated using the theory for translational Brownian motion. This approach to τ_D' gives:[80,82,88,96]

$$\tau_D' = \frac{(r')^2}{12D'} \quad . \tag{I.13}$$

D' is the translational diffusion coefficient, and it is related to the viscosity η by the Stokes-Einstein relation:

$$D' = \frac{kT}{6\pi\eta a} \quad , \tag{I.14}$$

where k is Boltzmann's constant, T is the absolute temperature, and a is the radius of the molecules, considered to be spherical. Thus:

$$\tau_D' = \frac{\pi\eta a(r')^2}{2kT} \quad , \tag{I.15}$$

where r' is taken as the radius of closest approach, 2a, of two spherical molecules. Substituting for τ_D' in equation (I.12) by (I.15) for the case of spherical molecules with the atoms situated on the surface of a sphere, where $r_{ij}' = r_{ik}' = r'$, and summing over the individual contributions by integrating over a volume from infinity to the radius of closest approach, 2a, yields:

$$\frac{1}{T_{1D}'} = \frac{1}{T_{2D}'} = 2\hbar^2\gamma_i^2\{[\Sigma_j\gamma_i^2 I_i(I_i+1)] + \frac{2}{3}[\Sigma_k\gamma_k^2 I_k(I_k+1)]\} \times$$

$$\int_\infty^{r'=2a} (r')^{-6}[\frac{\pi\eta a(r')^2}{2kT}][4\pi(r')^2 dr']N \quad , \tag{I.16}$$

$$\frac{1}{T_{1D}'} = \frac{1}{T_{2D}'} = \frac{4\pi^2\hbar^2\gamma_i^2\eta aN}{kT}[\Sigma_j\gamma_i^2 I_i(I_i+1) + \frac{2}{3}\Sigma_k\gamma_k^2 I_k(I_k+1)](r')^{-1} \quad , \tag{I.17}$$

where N is the number of molecules per cm^3. The substitution of 2a for r' yields the equation for spherical molecules. This result is often used for the case where the molecules are non-spherical by justifying that $r_{ij}' \simeq r_{ik}' \simeq r'$ to a good approximation. However, a better approximation is to substitute for the appropriate radii in equation (I.17) to give the more general form:

$$\frac{1}{T_{1D}'} = \frac{1}{T_{2D}'} = \frac{4\pi^2\hbar^2\gamma_i^2\eta aN}{kT}\left[\sum_j \gamma_i^2 I_i(I_i+1)(r_{ij}')^{-1} + \right.$$

$$\left. \frac{2}{3}\sum_k \gamma_k^2 I_k(I_k+1)(r_{ik}')^{-1}\right] \quad . \qquad \text{(I.18)}$$

This equation may be expressed in terms of the intramolecular correlation time, τ_D' by substituting for η from the Debye-BPP equation. More sophisticated approaches [80,95,97,98] in which both the effects of translation and rotation are considered yield different expressions for $1/T_{1D}'$ however, the qualitative features of the equations remain the same.

Both the intramolecular and intermolecular contributions to the relaxation, $1/T_{1D}$ and $1/T_{1D}'$, are directly proportional to τ_D, which is in turn a function of η/T from the theory presented above. Since η increases as the temperature decreases, $1/T_{1D}$ and $1/T_{1D}'$ increase with decreasing temperature. For nuclei relaxing by a dipolar mechanism, a check of the dependence of the relaxation rate on η/T should give a good indication as to the validity of the treatment of correlation times in terms of a Brownian motion. However, viscosity data are quite scarce, and the theory is often not tested.

In this section the correlation time for rotation has been presented for the case of spherical molecules undergoing isotropic reorientations. Few molecules, however, can be considered truly spherical. Several authors [99,100,101,102,103] have been concerned with considering the effects on the relaxation terms due to anisotropic rotational reorientation in which the molecule can have

different rotational diffusion constants for the different major axes. However, this has not really improved the Stokes hydrodynamic method for calculating rotational diffusion constants, which is still used because of its simplicity.

Relaxation of a nucleus may occur through an anisotropic chemical shift interaction. This relaxation mechanism was first proposed by McConnell and Holm[104] and Gutowsky and Woessner.[88] The chemical shift in a nucleus may be different for different orientations of the molecule relative to the main magnetic field; in other words, the chemical shift is anisotropic. As a result, when the molecule reorients in solution the magnetic field at the nucleus fluctuates. These fluctuations bring about relaxation of the nucleus.

The chemical shift may be considered as the sum of an isotropic and an anisotropic part, only the latter being effective in the relaxation mechanism. The anisotropy of the chemical shift in the z, x, and y directions may be denoted by $\delta_{z'}$, $\delta_{x'}$, and $\delta_{y'}$ respectively. It has been shown by Abragam[80] that if these components are expressed in terms of $\delta_{z'}$ and an asymmetry parameter η according to the relationship:

$$\delta_{z'} \; ; \; \delta_{x'} = -\frac{1}{2}(1 - \eta)\delta_{z'} \; ; \quad \delta_{y'} = -\frac{1}{2}(1 + \eta)\delta_{z'} \qquad \text{(I.19)}$$

then, the anisotropic chemical shift contribution to the relaxation, $1/T_{1A}$ and $1/T_{2A}$, is given by:

$$\frac{1}{T_{1A}} = \frac{6}{40}\gamma^2 H_o^2 \delta_{z'}^2 \left(1 + \frac{\eta^2}{3}\right)\left(\frac{2\tau_A}{1 + \omega_o^2 \tau_A^2}\right) \quad , \qquad \text{(I.20)}$$

$$\frac{1}{T_{2A}} = \frac{1}{40}\gamma^2 H_o^2 \delta_{z'}^2 \left(1 + \frac{\eta^2}{3}\right)\left(8\tau_A + \frac{6\tau_A}{1 + \omega_o^2 \tau_A^2}\right) , \qquad (I.21)$$

where γ is the magnetogyric ratio of the nucleus; H_o is the main magnetic field strength; ω_o is the Larmor frequency; and τ_A is the correlation time for the anisotropic chemical shift interaction. The correlation time τ_A is the correlation time for the rotation of the molecule, and hence the same as τ_D. Under conditions of extreme narrowing, where $\omega_o \tau_A << 1$, equations (I.19) and (I.20) reduce to:

$$\frac{1}{T_{1A}} = \frac{12}{40}\gamma^2 H_o^2 \delta_{z'}^2 \left(1 + \frac{\eta^2}{3}\right)\tau_A , \qquad (I.22)$$

$$\frac{1}{T_{2A}} = \frac{14}{40}\gamma^2 H_o^2 \delta_{z'}^2 \left(1 + \frac{\eta^2}{3}\right)\tau_A . \qquad (I.23)$$

This result represents the rather unusual feature that even in the extreme narrowing case the ratio of $1/T_{2A}$ to $1/T_{1A}$ is 7:6.

Since the correlation time τ_A is the rotational correlation time, the temperature dependence features of the anisotropic chemical shift relaxation rate, $1/T_{1A}$, are the same as those for the dipolar relaxation rate, $1/T_{1D}$; $1/T_{1A}$ increases with decrease in temperature. This mechanism, however, has the distinguishing feature of being proportional to H_o^2.

Proton chemical shifts are too small for their anisotropy to be important enough to produce effective relaxation. For fluorine, on the other hand, the anisotropic chemical shift contribution has been

found to be more significant.[84,88,105] However, due to the difficulty in obtaining the values of δ_z, and η, this relaxation mechanism has not been studied in any detail.

The importance of relaxation by a quadrupolar interaction mechanism was first demonstrated by Bloembergen, Purcell, and Pound[81] in a mixture of H_2O and D_2O. Nuclei with spin greater than 1/2 possess an electric quadrupole moment, and relax by the interaction of the electric quadrupole moment with an asymmetric electric field gradient at the nucleus.[106] The nuclear electric quadrupole moment is a measure of the deviation of the nuclear charge distribution from spherical symmetry, and it is oriented in a fixed direction due to the polarization of the nucleus by the main magnetic field. The field gradient at the nucleus, however, due to the electrons in the bonds fluctuates in orientation because of molecular motion. Thus, the quadrupolar interaction is a function of the orientation of the nucleus with respect to its electrostatic environment.

The general equation describing the quadrupolar contribution to the relaxation, $1/T_{1Q}$ and $1/T_{2Q}$, is complex and only its form under extreme narrowing conditions is presented here:[80]

$$\frac{1}{T_{1Q}} = \frac{1}{T_{2Q}} = \frac{3}{40} \frac{2I + 3}{I^2(2I - 1)} \left(1 + \frac{\tilde{\eta}^2}{3}\right) \left(\frac{e^2qQ}{\hbar}\right)^2 \tau_Q \quad , \qquad \text{(I.24)}$$

where I is the nuclear spin; $\tilde{\eta}$ is an asymmetry parameter, which is a measure of the departure of the electric field gradient at the nucleus from spherical symmetry; $e^2qQ/\hbar$ is the product of the

nuclear electric quadrupole moment and the electric field gradient, in rad sec^{-1}, and called the quadrupole coupling constant; and τ_Q is the correlation time for the quadrupolar interaction.

The quadrupolar relaxation mechanism is modulated only by the rotation of the molecule, therefore τ_Q is the rotational correlation time which has already been designated as τ_D for the dipolar relaxation and τ_A for the anisotropic chemical shift relaxation correlation times. The quadrupolar interaction is the most effective relaxation mechanism for nuclei possessing a quadrupole moment. For covalently bonded quadrupolar nuclei especially, the electric field gradients are quite large and the quadrupolar interaction may be two or three orders of magnitude larger than any other interaction. Thus mechanisms other than quadrupolar do not contribute significantly to the relaxation time.[107,108] In such cases, the relaxation may be so rapid as to broaden the nmr signal considerably, sometimes to the extent that the signal cannot be detected.[109] For this reason, few studies of the relaxation phenomena of quadrupolar nuclei other than deuteron have been undertaken;[107,110,111] quadrupole coupling constants are small enough for deuteron compounds, allowing this nucleus to be studied conveniently.[100,112,113,114]

Relaxation of a nucleus by a scalar spin-spin coupling interaction between two kinds of nuclear spins is another commonly encountered mechanism. Abragam[80] considers two types of relaxation mechanisms of this kind, depending on whether the scalar interaction is modulated by chemical exchange[111] or by the rapid relaxation of

the non-resonant nuclear spin.[115,116,117] The former is referred to as a scalar relaxation mechanism of the first kind, and the latter as a scalar mechanism of the second kind.

The contribution of the scalar interaction mechanism of the second kind to the relaxation of a spin I coupled to a spin S, $1/T_{1Sc}$ and $1/T_{2Sc}$, is given by:[80]

$$\frac{1}{T_{1Sc}} = \frac{2}{3} A^2 N_S S(S+1) \left(\frac{\tau_2}{1 + (\omega_I - \omega_S)^2 \tau_2^2}\right) , \qquad \text{(I.25)}$$

$$\frac{1}{T_{2Sc}} = \frac{1}{3} A^2 N_S S(S+1) \left(\tau_1 + \frac{\tau_2}{1 + (\omega_I - \omega_S)^2 \tau_2^2}\right) , \qquad \text{(I.26)}$$

where A is the scalar coupling constant; S is the spin quantum number of the non resonant nucleus; ω_I and ω_S are the Larmor frequencies of nuclei I and S respectively; N_S is the number of S nuclei to which nucleus I is coupled; and τ_1 and τ_2 are the longitudinal and transverse relaxation times for the nucleus S.

For a scalar interaction mechanism of the first kind the correlation time for the exchange, τ_e, is substituted for τ_1 and τ_2 in (I.25) and (I.26). This mechanism will not be further discussed here.

The scalar interaction mechanism of the second kind is most often encountered for nuclei S of spin larger than 1/2. Such nuclei relax rapidly by a quadrupolar mechanism, as has been mentioned above.

Since in most cases $(\omega_I - \omega_S)\tau_2 >> 1$ and the coupling constant A is often small, the contribution of this relaxation mechanism to

$1/T_1$ is usually quite negligible and therefore rarely observed.[118,119] The contribution to $1/T_2$, however, is given by:

$$\frac{1}{T_{2Sc}} = \frac{1}{3} A^2 N_S S(S + 1)\tau_1 \quad . \tag{I.27}$$

Since τ_1, the longitudinal relaxation time for nucleus S, is inversely proportional to τ_Q, the correlation time for the quadrupolar interaction, and since τ_Q increases as the temperature decreases, then $1/T_{2Sc}$ increases, with increasing temperature.

The interaction of a nuclear magnetic moment with the magnetic field produced at the nucleus due to the rotation of the molecule containing the nucleus is called a spin-rotation interaction. The possibility of relaxation by a spin-rotation interaction mechanism was pointed out by Bloembergen, Purcell, and Pound.[81] It was not until much later, however, that the importance of such a mechanism was first recognized by Gutowsky and co-workers[105] for the relaxation of hydrogen and fluorine nuclei in a series of fluorinated hydrocarbons.

When a molecule rotates, the motion of the electrons and the nuclei do not exactly follow each other, with the result that a rotating electric field is produced at the nucleus. This in turn generates a magnetic field, proportional to the rotational angular momentum, which can interact with the nuclear magnetic moment. Motion of the molecule causes continual alterations in the magnitude and direction of the rotational angular velocity, thus causing relaxation. The effectiveness of this mechanism depends on the

rotational angular momentum, the correlation time for the rotational angular velocity, and the strength of the interaction between the electric field and the nucleus, as expressed by the spin-rotation coupling constant C. The spin-rotation coupling constant is a tensor quantity, but because of the short correlation time for the interaction only an average value is observed by the nucleus.

The contribution of the spin-rotation interaction to the relaxation was developed by Brown, Gutowsky and Shimomura[84] and by Hubbard[120] using different models. Brown et al [84] proposed a model in which the molecule remains in the same orientation until it makes a sudden jump to a new uncorrelated orientation at random times. The spin-rotation interaction leading to relaxation takes place during these jumps when the molecule is actually rotating. Hubbard,[120] on the other hand, treated the problem by assuming that the reorientation of the molecule occurs by a Brownian diffusion model. The formulation of the relaxation time is insensitive to the model assumed for the reorientation of the molecule, since equivalent results are obtained for the two models.

The contribution of the spin-rotation interaction to the relaxation of identical spin 1/2 nuclei at equivalent positions in spherical liquid molecules as derived by Hubbard,[120] $1/T_{1SR}$ and $1/T_{2SR}$, is given by:

$$\frac{1}{T_{1SR}} = \frac{2}{3} kT\hbar^{-2} I(2C_{\perp}^{2} + C_{\parallel}^{2}) \left(\frac{\tau_{SR}}{1 + \omega_o^{2}\tau_{SR}^{2}}\right) , \qquad (I.28)$$

$$\frac{1}{T_{2SR}} = \frac{1}{3} kT\hbar^{-2} I(2C_{\perp}^{2} + C_{||}^{2})(\tau_{SR} + \frac{\tau_{SR}}{1 + \omega_o^{2}\tau_{SR}^{2}}) \quad , \qquad (I.29)$$

where k is Boltzmann's constant; T is the absolute temperature; $\hbar$ is Planck's constant divided by 2π; I is the moment of inertia which for non-spherical molecules is given by $(I_x + I_y + I_z)/3$ where I_x, I_y, and I_z are the principal moments of inertia in the x, y, and z directions respectively; $(2C_{\perp}^{2} + C_{||}^{2})$ describes the diagonalized components of the spin rotation coupling constants, where $C_{\perp} = C_{xx} = C_{yy}$ and $C_{||} = C_{zz}$; and τ_{SR} is the correlation time for the interaction. In the terms involving I and C the z axis is defined as directed from the centre of the molecule to the resonant nucleus. Under extreme narrowing conditions where $\omega_o\tau_{SR} << 1$, equations (I.28) and (I.29) simplify to:

$$\frac{1}{T_{1SR}} = \frac{1}{T_{2SR}} = \frac{2}{3} kT\hbar^{-2} I(2C_{\perp}^{2} + C_{||}^{2})\tau_{SR} \quad . \qquad (I.30)$$

The correlation time τ_{SR} may be considered as the time during which a particular angular velocity is maintained. Qualitatively, one might expect that as the temperature is increased the frictional torque on the molecule decreases and hence the angular velocity is maintained for a longer time. Thus τ_D and τ_{SR} are expected to be inversely proportional to each other. It was shown by Hubbard[120] that, for a spherical molecule undergoing rotational Brownian motion, and for $\tau_{SR} << \tau_D$:

$$\tau_D\tau_{SR} = \frac{I}{6kT} \quad , \qquad (I.31)$$

where I is the moment of inertia; k is Boltzmann's constant; and T is the absolute temperature. This equation is often referred to as the Hubbard equation, and it indicates that τ_{SR} has the opposite temperature dependence to τ_D. It has been shown that for a rotational diffusion model τ_D is proportional to η/T, thus τ_{SR} is proportional to $1/\eta$ and $1/T_{1SR}$ increases with increasing temperature. An alternative derivation of equations (I.30) and (I.31) has been given by Green and Powles.[121]

The spin-rotation coupling constant can be obtained from microwave and molecular beam experiments. Usually, the values of $C_\perp$ and $C_{||}$ are not known independently and the average value, C_{Av}, is obtained where:

$$C_{Av} = \frac{1}{3}(2C_\perp + C_{||}) \quad . \tag{I.32}$$

In order to calculate the value of $1/T_{1SR}$, the quantity $(2C_\perp^2 + C_{||}^2)$ is needed. This value is related to C_{Av} by:[97,98]

$$(2C_\perp^2 + C_{||}^2) = 3C_{Av}^2 + \frac{2}{3}(C_\perp - C_{||})^2 \quad . \tag{I.33}$$

Therefore, unless $C_\perp$ and $C_{||}$ are equal, the value of $(2C_\perp^2 + C_{||}^2)$ is larger than $3C_{Av}^2$. Thus, instead of using a known value of C_{Av} in order to obtain τ_{SR} from equation (I.30), most authors assume the validity[122,123] of the "Hubbard equation" to obtain the value of τ_{SR} needed to calculate $(2C_\perp^2 + C_{||}^2)$. Unlike the rotational correlation time, which can also be obtained from dielectric dispersion experiments,

the spin-rotation correlation time is easily obtained only by nmr.

Nuclear relaxation by a spin-rotation interaction mechanism has been encountered for both hydrogen[124,125,126,127] and fluorine[84,91,97,128] nuclei. The importance of this mechanism is much greater[84,91,96,128] for fluorine than for hydrogen nuclei due to the larger fluorine spin-rotation coupling constants. Spin-rotation contributions to the relaxation of phosphorus[118,119,129] and arsenic[117] nuclei have recently been shown to be significant.

For most nuclei in a molecular environment, relaxation is accomplished through more than just one mechanism. All the contributions from the various interactions must be added. Thus for a nucleus which can relax by any of the mechanisms discussed here, the total relaxation rate, $1/T_1$, is given by:

$$1/T_1 = 1/T_{1D} + 1/T_{1D}' + 1/T_{1A} + 1/T_{1Q} + 1/T_{1Sc} + 1/T_{1SR} , \quad (I.34)$$

and the same applies for $1/T_2$. The usual method for determining and separating the various contributions is to study the relaxation rate over as large a temperature range as possible. The data is commonly plotted as $\ln(1/T_1)$ or $\ln(1/T_2)$ versus $10^3/T$, in $^\circ K^{-1}$. From the temperature dependence of the relaxation certain contributions can be differentiated. The quadrupolar interaction mechanism is of course only applicable for nuclei with a quadrupole moment, for which this is the dominant mechanism. Nuclei which are coupled to quadrupolar nuclei will usually have a large contribution to $1/T_2$ from a scalar

coupling interaction mechanism. The contribution to $1/T_1$ is negligible unless the nucleus is studied at low enough frequencies. The anisotropic chemical shift contribution to the relaxation is usually very small and therefore often neglected. Thus, for most cases the problem simplifies to that of separating the contributions due to intramolecular and intermolecular dipolar interactions or the two dipolar interactions and the spin-rotation interaction. The separation may be accomplished by several techniques.[85] For example, the relaxation mechanisms for a proton in a molecule could be elucidated by a study of the relaxation rate of the proton as a function of its concentration in a non-interacting solvent, or its perdeutero analogue solvent, or by the study of the relaxation of a different nucleus in the molecule, or by a combination of these methods.

The investigation of the mechanisms governing the nuclear magnetic relaxation of phosphorus in the series of compounds PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3 was undertaken. In order to make direct comparisons between these compounds it was necessary to study the relaxation rates in a medium of uniform viscosity. This was easily accomplished by using a sample containing a mixture of all four compounds. A sample of equivalent viscosity containing only PBr_3 and PCl_3 was also studied in order to note any differences in the PBr_3 and PCl_3 relaxation rates in conjunction with the absence of intermolecular effects due to PBr_2Cl and $PBrCl_2$. During the course

of this work, the results of separate studies on the phosphorus relaxation rate, $1/T_1$, in PCl_3[118,130] and PBr_3[119] were published. For both of these compounds, the contributions to the longitudinal relaxation are due to spin-rotation and dipolar interaction mechanisms. For the PBr_3, an additional contribution due to a scalar coupling interaction mechanism with the bromine nucleus was detected at low frequencies. In the present work the results of both the longitudinal and transverse relaxation rates of phosphorus in PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3, in conjunction with the results of the transverse relaxation rate of chlorine in PCl_3 are presented with the aim of providing a more complete picture of the relaxation mechanisms in these compounds.

The experimental methods for obtaining the values of the longitudinal and transverse relaxation rates for the phosphorus and chlorine nuclei will be discussed in detail in the next chapter. Since relatively standard methods are used, only a brief outline of the theoretical background of relaxation rate measurements will be presented here.

It can be shown [86] from a solution of the Bloch equations that the signal intensity for the absorption mode, v, for a Lorentzian line shape function is a function of both T_1 and T_2:

$$v \propto \frac{\omega \chi_o H_o \gamma H_1 T_2}{1 + T_2^2(\omega_o - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} \quad , \qquad \text{(I.35)}$$

where χ_o is the equilibrium magnetic susceptibility; H_o is the main magnetic field strength; H_1 is the oscillating field strength; γ is

the magnetogyric ratio; ω_o is the Larmor frequency; and ω is the angular frequency. The term $(1 + \gamma^2 H_1^2 T_1 T_2)^{-1}$ in equation (I.35) is known as the saturation factor. Under optimum conditions, the absorption spectrum is displayed using a value of H_1 small enough so as not to cause saturation. Thus $\gamma^2 H_1^2 T_1 T_2 << 1$ and equation (I.35) reduces to:

$$v \propto \frac{\omega \chi_o H_o \gamma H_1 T_2}{1 + T_2^2 (\omega_o - \omega)^2} \quad . \tag{I.36}$$

The value of $1/T_2$ can be obtained from a measurement of the full line width at half-maximum intensity:

$$2\pi W_{\frac{1}{2}\ max} = \frac{2}{T_2} \quad , \tag{I.37}$$

where $W_{\frac{1}{2}\ max}$ is in Hz. For very large values of $1/T_2$, the signal-to-noise ratio can be enhanced by displaying the signal as the first derivative of the Lorentzian absorption function.[131] The value of $1/T_2$ can be obtained from a measurement of the peak to peak separation, S:

$$2\pi S = \frac{2}{\sqrt{3} T_2} \quad , \tag{I.38}$$

where S is in Hz. The value of $1/T_2$ obtained from equations (I.37) and (I.38) are in units of sec^{-1}, since T_2 is a measure of time.

The effect of saturation on the signal intensity is made use of in the experimental determination of T_1, the simplest method of

which is the saturation recovery or direct method. This method has the added advantage that it can be carried out on an ordinary nmr spectrometer. It is best suited for relaxation times of between 0.2 to 25 secs. As will be seen, this condition was fulfilled by the system under study, hence this method is quite satisfactory.

Briefly, the sample at resonance is saturated by the application of a sufficiently strong radiofrequency field, H_1, so that $\gamma H_1 >> (T_1 T_2)^{-\frac{1}{2}}$. When the amplitude of H_1 is suddenly reduced to a non-saturating value, the intensity of the absorption mode, v, recovers exponentially with a time constant which is essentially T_1 if $T_1 << T_2$.[132] The recovery of the signal in a homogeneous field for the case of $T_1 < T_2$ is given by:

$$v_t = v_\infty \{1 - \frac{1}{T_1 - T_2} [T_1 \exp(-t/T_1) - T_2 \exp(-t/T_2)]\} , \quad (I.39)$$

where v_∞ is the final non-saturated value of the signal intensity, and v_t is the signal intensity at any time t. If $T_1 << T_2$, the exponent containing T_2 decays fast leaving a simple exponential decay:

$$v_t = v_\infty [1 - \exp(-t/T_1)] \quad . \quad (I.40)$$

The integrated form of this expression is given by:

$$\ln(v_\infty - v_t) = - t/T_1 \quad , \quad (I.41)$$

and the value of $1/T_1$ in sec^{-1} is obtained from the plot of $\ln(v_\infty - v_t)$ versus time. In the present system $T_2 << T_1$ and thus equation (I.41) is applicable.

CHAPTER II

EXPERIMENTAL TECHNIQUES

1. Preparation and Purification of Compounds

All preparations and purifications of compounds were carried out in a vacuum system using standard vacuum techniques.[133] The temperature of traps was maintained with appropriate slush baths.

Phosphorus trifluoride, PF_3, (Penninsular ChemResearch, Inc.) was vacuum distilled through traps cooled to -131°C and -196°C and was trapped at -196°C. The PF_3 was then distilled into a tube containing trimethylamine, $(CH_3)_3N$, with which it was allowed to react in order to remove traces of silicon tetrafluoride, SiF_4, as the solid $(CH_3)_3NSiF_4$. The volatile products were then vacuum distilled through traps cooled to -131°C and -196°C, and the PF_3 was trapped at -196°C. The PF_3 was then transferred into a storage bulb equipped with a stopcock.

Phosphorus trichloride, PCl_3, (Mallinckrodt Chemical Works) was vacuum distilled through traps cooled to -45°C, -95°C, and -196°C. The PCl_3 was collected at -95°C, transferred into a break-seal tube, and sealed.

Phosphorus tribromide, PBr_3, (Matheson Coleman & Bell) was vacuum distilled through traps cooled to 6°C, -45°C, and -196°C. The PBr_3 was collected at -45°C, transferred into a break-seal tube, and sealed.

Hydrogen chloride, HCl, (Matheson of Canada, Ltd.) was vacuum distilled through traps cooled to -131°C and -196°C. The HCl was collected at -196°C and transferred into a storage bulb equipped with a stopcock.

Dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$, was prepared by the fluorination of the corresponding chloride with a suspension of sodium fluoride in tetramethylene sulfone.[134] The $(CH_3)_2NPF_2$ was purified by a vacuum distillation through traps cooled to -79°C, -119°C, and -196°C. The compound was trapped at -119°C and transferred into an ampoule, where it was stored.

Chlorodifluorophosphine, PF_2Cl, was prepared by the gas phase reaction of stoichiometric amounts of dimethylaminodifluorophosphine and hydrogen chloride.[13] The products were vacuum distilled through traps cooled to -131°C, -160°C, and -196°C. Pure PF_2Cl, trapped at -160°C, was either transferred into an ampoule, sealed and kept frozen, or stored frozen in a trap on the vacuum line.

Di-iodotrifluoromethylphosphine, CF_3PI_2, was prepared by the reaction of red phosphorus, iodine, and trifluoroiodomethane in a Carius tube.[135] The yield of CF_3PI_2 is low, the bulk of the product being a mixture of iodobistrifluoromethylphosphine, $(CF_3)_2PI$, and tristrifluoromethylphosphine, $(CF_3)_3P$. The products of the reaction were vacuum distilled through traps cooled to -45°C, -84°C, -116°C, and -196°C. The material which collected at -45°C contained CF_3PI_2 contaminated with $(CF_3)_2PI$ and iodine. This fraction was further purified by a vacuum distillation through traps cooled to -25°C, -45°C, and -196°C. CF_3PI_2, only slightly contaminated with iodine, was collected at -45°C, transferred into an ampoule and sealed. This was very slow, but the most effective method of purification.

Dichlorotrifluoromethylphosphine, CF_3PCl_2, was prepared[29] by

reacting CF_3PI_2 with excess mercuric chloride, $HgCl_2$, in a sealed tube for about one day at room temperature. At the end of this period the volatile products of the reaction were distilled onto a fresh batch of $HgCl_2$, in order to insure the complete conversion of the CF_3PI_2 to CF_3PCl_2. After allowing the reaction to proceed for another day, the contents were distilled under vacuum through traps cooled to -45°C, -116°C, and -196°C. The $(CF_3)PCl_2$ was collected at -116°C, transferred into a break-seal tube, and sealed.

Dibromotrifluoromethylphosphine, CF_3PBr_2, was prepared in the same way as CF_3PCl_2, except for the use of mercuric bromide, $HgBr_2$, instead of $HgCl_2$. The products of the reaction were distilled under vacuum through traps cooled to -45°C, -84°C, and -196°C. The CF_3PBr_2 was collected at -84°C, transferred into a break-seal tube, and sealed.

The aquopentamminecobalt(III) bromide was obtained from Dr. R.B. Jordan, and was prepared according to the procedure in reference 136.

All other compounds used without purification were commercially available chemicals of reagent grade quality.

The purity of each of the compounds used in the kinetic and relaxation studies was established by an infrared spectrum. In addition, molecular weight determinations were made for PF_3, PCl_3, PF_2Cl, CF_3PCl_2, and CF_3PBr_2. Although mass spectra of all the compounds were taken, they were not used to determine their purity because traces of water in the instrument partially hydrolyzed some of the compounds.

2. Sample Preparation Techniques

All samples were prepared in vacuum systems using high vacuum techniques.

All the work on the PF_3-PCl_3 system was carried out in a vacuum system constructed with Pyrex tubing, vacuum cup stopcocks, and ground glass joints. The stopcocks were lubricated with KEL-F #90 grease in preference to Apiezon "N", because the latter dissolved to a certain extent in PCl_3. Compounds for the PF_3-PCl_3 system and the PF_2Cl hydrolysis study were weighed out, distilled into a 30 ml reaction tube, and sealed.

The preliminary work on the PCl_3-PBr_3 system was carried out on the grease-lubricated system. The required amount of each compound was weighed out, distilled into an nmr tube, sealed, and kept frozen in liquid nitrogen until ready for use. It was later found necessary to construct a grease-free vacuum system out of Pyrex tubing and Fisher & Porter 1¼ mm needle valves. The procedure for preparing samples on this system was far more complicated and time consuming. Break-seal tubes containing PBr_3, and PCl_3, and nmr tubes were sealed to outlets, leading from needle valves on the system, and the whole apparatus evacuated for at least 24 hr. At the end of this period the break-seals were broken, and each compound was purified again according to the procedure described in the previous section. The compounds were stored frozen at liquid nitrogen temperature in traps on the vacuum system. Since the compounds could not be weighed out in this system, an nmr tube was used as a measuring device. One of

the compounds was distilled into this tube, and the quantity needed was estimated by the height of the liquid in the tube. The compound was then transferred into the nmr sample tube, and the procedure was repeated for the second compound. The nmr tube was then sealed, and stored frozen in liquid nitrogen. This method for measuring the amount of compounds needed was found to be quite reproducible.

In order to make up a sample containing a known amount of water an nmr tube, equipped with a break-seal on a side arm, was used. The sample was made up in the usual manner, and the tube was sealed above the break-seal to an outlet on a separate grease-free manifold. This manifold was then connected to an outlet on the grease-lubricated system and evacuated overnight. A known amount of water was obtained by allowing water vapour to expand into a chamber of known volume, contained between two stopcocks. The water was then distilled into the sample tube, after breaking the break-seal, and the sample sealed off.

A more convenient method of adding small amounts of water made use of the fact that the complex $[Co(NH_3)_5H_2O]Br_3$ liberates water quantitatively on heating, according to the equation:

$$[Co(NH_3)_5H_2O]Br_3 \xrightarrow{\Delta} [Co(NH_3)_5Br]Br_2 + H_2O \quad . \qquad \text{(II.1)}$$

The apparatus used to make up the samples is shown in Figure 1. A weighed amount of complex was put in tube A, and the top of the tube sealed off. The apparatus was connected to the grease-lubricated system by the ground glass joint, evacuated overnight, and sealed at

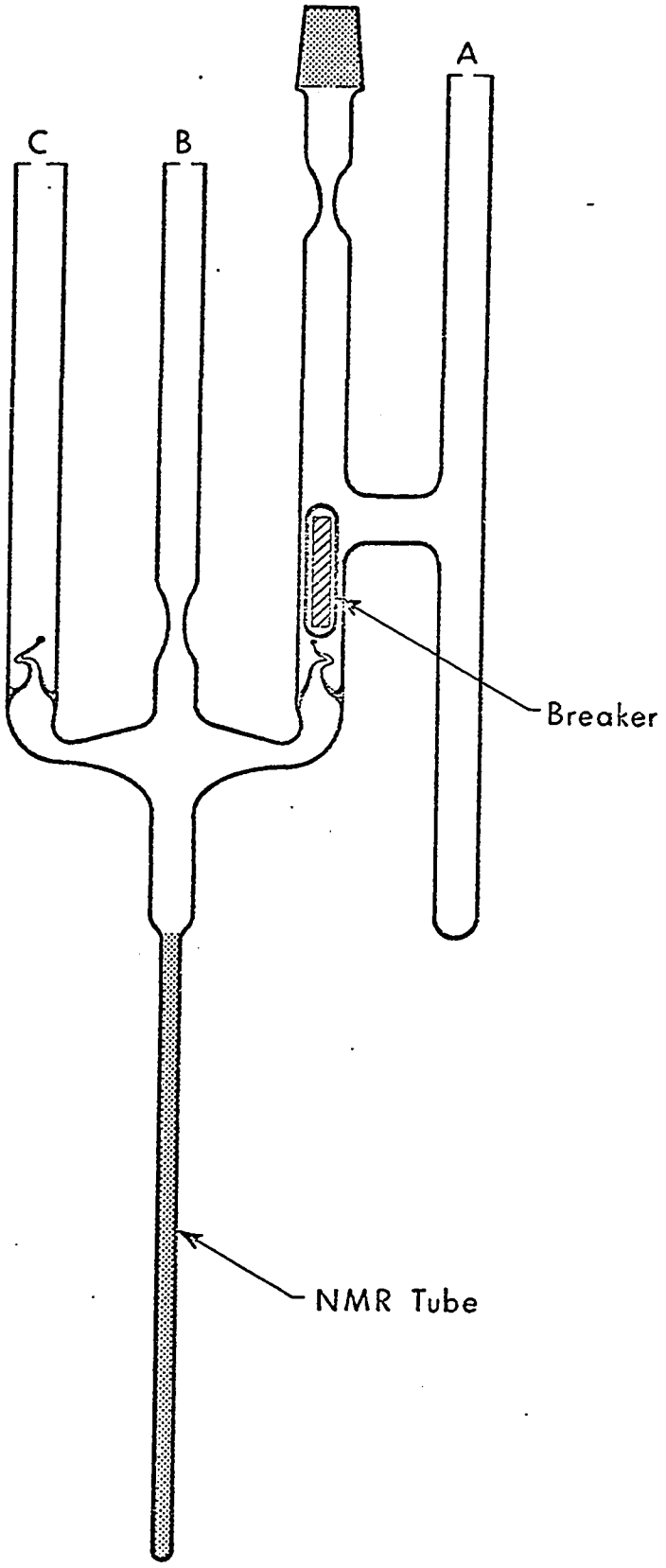


Figure 1: Diagram of the apparatus used for the preparation of samples containing two components and water.

the constriction. The apparatus was then sealed onto an outlet on the grease-free system at B. The usual procedure was used to distill the required amounts of PCl_3, or PBr_3, or both compounds into the nmr tube, and the apparatus was sealed off at the constriction. The nmr tube was frozen in liquid nitrogen and tube A was immersed in a bath at 100°C for one hour. The break-seal between tube A and the nmr tube was broken, and the water was distilled into the nmr tube. At this point, if both the PCl_3 and PBr_3 had originally been distilled into the nmr tube, it was sealed off. If on the other hand, only one of the compounds was present, the nmr tube was warmed up to room temperature and the contents allowed to react. The apparatus was then sealed onto an outlet on the grease-free system at C and evacuated. The second compound was distilled into the nmr tube, after breaking the break-seal. The nmr tube was then sealed off, and kept frozen in liquid nitrogen.

All preparations and purifications for the CF_3PCl_2-CF_3PBr_2 system were carried out in the grease-lubricated system. All the samples however were prepared in the grease-free system in the same way as that described for the PCl_3-PBr_3 samples.

3. Instrumental Techniques Used

Infrared spectra covering the range 4000-400 cm^{-1} were recorded on a Perkin-Elmer 337 spectrophotometer, using an 8 cm gas cell equipped with potassium bromide windows. Infrared spectra down to 200 cm^{-1} were recorded on a Perkin-Elmer 421 dual grating spectrophotometer, using a 8 cm gas cell equipped with caesium bromide windows. The salt windows were stuck on the cell faces with a thin layer of hot paraffin wax. Paraffin was used in preference to Kel-F grease because it maintained a much better vacuum. All infrared measurements were made at room temperature.

Mass spectra were recorded on an MS-9 instrument operating at an ionizing voltage of 70 eV. The instrument could be used with a room temperature inlet, a heated inlet, or a direct probe inlet, depending on the volatility of the compound.

All proton and fluorine nmr spectra were recorded on a Varian A-56/60 instrument, equipped with a variable temperature probe and a Varian V6040 temperature controller. Phosphorus nmr spectra were initially recorded on a Varian HA-60 instrument operating at 24.3 MHz. The majority of the phosphorus nmr spectra was recorded on a Varian HA-100 instrument operating at 40.5 MHz. The instrument was equipped with a variable temperature probe and a Varian V6040 temperature controller. All measurements of relaxation times were made at 40.5 MHz. Chlorine nmr spectra were recorded on the Varian HA-60 instrument operating at 5.9 MHz. The instrument was equipped with a variable temperature probe and a Varian V4343 temperature controller. In all

the variable temperature probes the desired temperature was attained by the standard gas circulation technique. For temperatures below -30°C, nitrogen gas was circulated through a copper coil immersed in liquid nitrogen. For temperatures above 30°C, the copper coil was immersed in water at room temperature. Temperatures between 30°C and -30°C were the most difficult to regulate, and were achieved by immersing the copper coil in a slush bath which maintained a temperature of either -63°C or -96°C. The temperature of the probe was accurately measured by means of a Leeds & Northrup potentiometer, with a copper-constantan thermocouple in an nmr tube containing ethanol. By frequently checking the pressure of the nitrogen flow, and the level of liquid nitrogen or the consistency of the slush bath around the copper coil, the temperature was known to an accuracy of ±1°C. Samples for proton, fluorine, and phosphorus spectra were prepared in 5 mm o.d. nmr tubes. Samples for chlorine spectra were prepared in 10 mm o.d. tubes, designed to fit the probe.

Overlapping peaks in the phosphorus nmr spectra were resolved on a Dupont 310 curve resolver, assuming that a standard Lorentzian function described each peak. Values of the relative areas of each peak were read off an integrator with 100 divisions. The precision with which readings could be made was ±0.5 divisions.

The density determinations were made by measuring the height of a weighed amount of compound in an nmr tube, calibrated with respect to volume and height. The readings were taken with a Griffin & George cathetometer. The nmr tube was placed in a glass vessel through which

water was circulated from a constant temperature bath. The temperature in the vessel was measured with a thermometer.

4. Experimental Procedure for the Study of the Redistribution Reactions

The PF_3-PCl_3 System

The reaction of PF_3 and PCl_3, the disproportionation of PF_2Cl, and the hydrolysis of PF_2Cl were studied in the gas phase. The compounds were sealed in tubes, and allowed to stand at a particular temperature for a prescribed period of time. The contents were then analyzed by infrared spectroscopy. Mass spectra and nmr spectra were often used for additional characterization.

An attempt was made to obtain quantitative results by the comparison of the intensities of certain infrared bands to the corresponding calibration of concentration versus infrared band intensity for the pure compound. Although the individual compounds obeyed Beer's law, mixtures of certain compounds did not, and quantitative determinations by means of infrared band intensities could not be done. This will be discussed in greater detail with reference to a specific example, in the section on results.

The PCl_3-PBr_3 System

The kinetics of the reaction of PCl_3 with PBr_3 was studied in the liquid phase by ^{31}P nmr spectroscopy. The samples were made up in nmr tubes, as described previously, and stored frozen in liquid nitrogen. A uniform procedure for studying all the samples was used. The sample was thawed as fast as possible, the contents were thoroughly mixed by shaking the tube, and the tube was placed in the probe. The zero time for the reaction was taken to be 3 min after the contents in the nmr tube had thawed. The time was recorded on each scan, and the time for

the reaction was taken at the midpoint between the PBr_3 and PCl_3 peaks. With the combination of sweep width and sweep time used, the spectrum could be scanned every 6 min. This frequency was fast enough for most of the reactions studied. The reaction was usually followed to about 90% completion, and the sample was then kept in a constant temperature bath until an infinite time spectrum was recorded. The temperature was measured at least twice during the course of the reaction.

The variation of the equilibrium constant with temperature, for the PCl_3-PBr_3 system, was determined from the study of the spectra of samples that were equilibrated at the desired temperatures. The samples were kept in a constant temperature bath for a period of at least ten half-lives, as determined from their kinetic results. The majority of the data was obtained from the infinite time measurements of the reactions.

The usual technique for recording nmr spectra is to lock on the frequency of a reference peak, and to scan the spectrum in HA-mode with a frequency or field sweep. In this system an internal standard was avoided, in order to eliminate the possibility of contaminating the reactants; an external standard was ruled out, because it decreased the signal-to-noise ratio by a factor of two. The spectra were thus recorded by scanning in HR-mode with a field sweep. The disadvantage of scanning without a lock signal is that the field is not as steady. The spectra were recorded by scanning upfield and downfield alternately. A comparison of the distance between the PBr_3 and PCl_3 peaks in two consecutive scans indicated the direction in which the field was

drifting, and the necessary adjustments were made. The instrument was carefully set up on a sample already at equilibrium, and the drift was checked throughout a kinetic run.

A typical spectrum[22] of a PCl_3-PBr_3 sample at equilibrium is given in Figure 2. Each species gives rise to one peak, the area under which is a measure of its relative concentration in the mixture. The areas cannot be integrated satisfactorily in HR-mode, moreover, the PBr_3 and PBr_2Cl peaks are too close to give a sharp separation between their integrated signals. The areas under each peak were obtained with the help of an analog curve resolver. The four species could not be resolved simultaneously. A small horizontal gain was needed in order to fit the PBr_3 curve, whereas maximum horizontal gain was necessary for the PCl_3 curve. The PBr_3 and PBr_2Cl curves were resolved separately from the $PBrCl_2$ and PCl_3 curves. The areas under each set of curves were compared to those of standard Lorentzian curves. The true areas of the standard curves were known, thus the relative area or mole fraction of each species in a spectrum was obtained. There is no significant overlap between the PBr_2Cl and $PBrCl_2$ curves, hence very little error involved in resolving the spectrum in two sections.

The CF_3PCl_2-CF_3PBr_2 System

The kinetics of the reaction of CF_3PCl_2 with CF_3PBr_2 was studied in the liquid phase by ^{19}F nmr spectroscopy. The samples were made up in nmr tubes, as described previously, and stored frozen in liquid nitrogen until ready for use. The procedure for studying the kinetics of the system, and the variation of the equilibrium constant with temperature

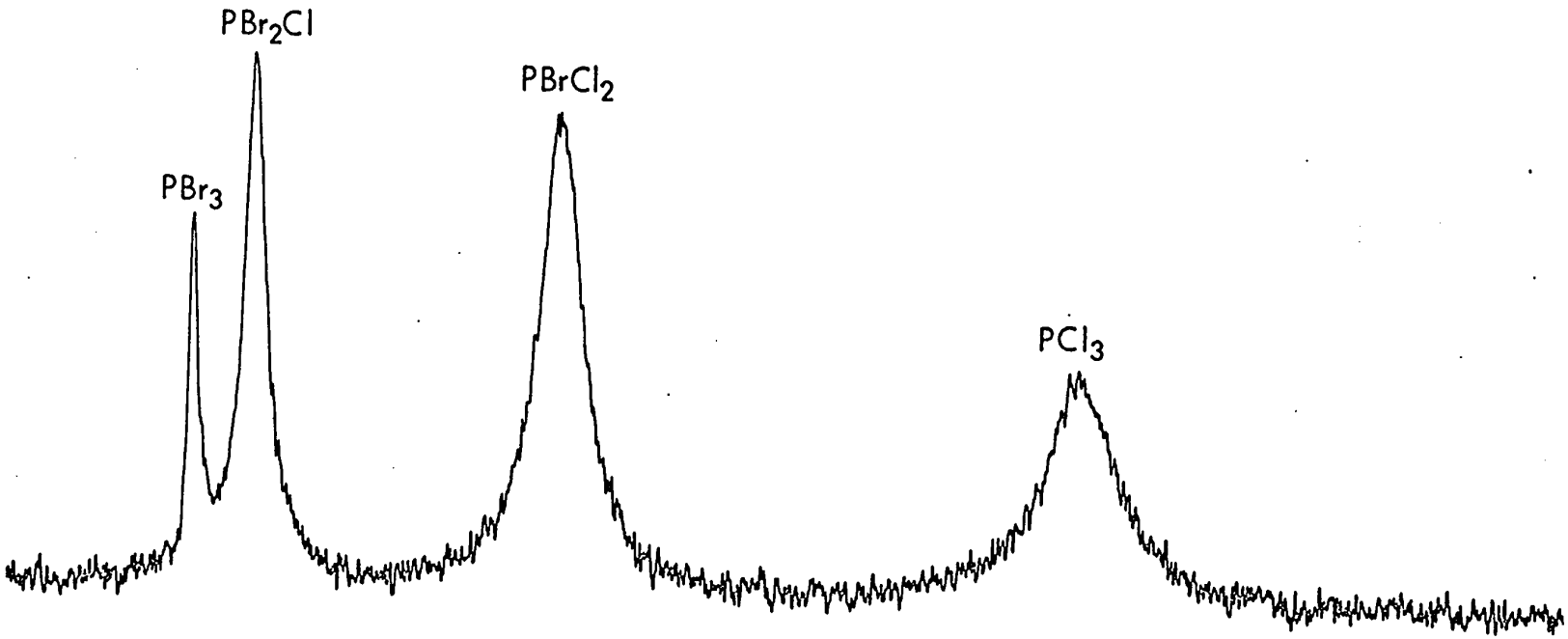


Figure 2: ^{31}P nmr spectrum at 35°C in a sample containing PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3.

was identical to that used for the PCl_3-PBr_3 system.

The spectrum of a CF_3PCl_2-CF_3PBr_2 sample consists of three well separated doublets, corresponding to the three species in the mixture. The reaction was studied by recording the integrated signal of the spectrum. The average height of each doublet was used to obtain the relative concentration or mole fraction of each species in the mixture.

5. Experimental Procedure for the Study of Nuclear Relaxation Times

Measurement of the ^{35}Cl Transverse Relaxation Times

The reciprocal of the transverse relaxation time for the ^{35}Cl nucleus in PCl_3 was determined at four temperatures. The $1/T_2$ values were obtained from measurements of the peak to peak separation of the derivative spectrum, as described in the introduction.

The samples were placed in the probe at the desired temperature for 45 min, in order to reach thermal equilibrium. The frequency of the radiofrequency unit was always synchronized with the frequency from the output of a frequency synthesizer. The spectrum was recorded, and the frequency changed by 20 KHz while the field was being swept. A spectrum was recorded at the new frequency. Thus the distance between the centre of each spectrum was separated by 20 KHz. This yielded a calibration for the spectra in KHz per cm. The spectrum was recorded with upfield and downfield scans, and an average peak to peak separation in KHz was obtained. The temperature was measured before and after recording the spectra.

Measurement of the ^{31}P Transverse Relaxation Times

The reciprocal of the transverse relaxation time for the ^{31}P nucleus in PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 was determined from 80°C to -106°C. The $1/T_2$ values for each species were obtained from measurements of the linewidth at half-height of the absorption signal, as described in the introduction. The instrument was carefully adjusted to attain maximum signal intensity, and radiofrequency values well below the saturation level were used, in order to avoid inhomogeneity and

saturation broadening. This is especially important for the PBr_3 and PBr_2Cl signals which have small linewidths.

The samples were placed in the probe at the desired temperature for 15 min or more, in order to reach thermal equilibrium. For each temperature, an upfield and a downfield scan of the whole spectrum, and several scans of the PBr_3-PBr_2Cl section of the spectrum at larger sweep widths were recorded. An average linewidth at half-height in cm was obtained for each species. The temperature was measured before and after recording the spectra.

In order to obtain values of linewidths in units of Hz, the spectra had to be calibrated in terms of Hz per cm. To this effect, a PBr_3-PCl_3 sample was made up in an nmr tube containing phosphorus trioxide, P_4O_6, sealed in a capillary tube. The sample was allowed to come to equilibrium, and the spectrum was recorded from 30°C to 80°C. The chemical shift of each signal, relative to P_4O_6, was measured, and an average value over the temperature range studied was obtained. The chemical shift difference between the PBr_3 and $PBrCl_2$ signals was used to calibrate all the spectra in Hz per cm.

Measurement of the ^{31}P Longitudinal Relaxation Times

The reciprocal of the longitudinal relaxation time for the ^{31}P nucleus in PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 was determined from 80°C to -100°C. The $1/T_1$ values for each species were obtained by the saturation recovery method, the basis of which has been described in the introduction. In order to enhance the signal to noise ratio, the experiments were performed in a homogeneous field.

The measurements were made by repetitively sweeping over the resonance signal with a sweep period of 1.9 sec and a radiofrequency field H_1 small enough to avoid saturation. The value of H_1 was then increased by 40 decibels, and then suddenly reduced to its original value, within one sweep through the resonance. The signal was observed as it returned to its original non-saturated level. A typical spectrum is shown in Figure 3. A semi-logarithmic plot of the difference between the final signal intensity, v_∞, and the signal intensity at time t, v_t, against time, yielded a straight line of slope $-1/T_1$.

The samples were placed in the probe at the desired temperature for 15 min or more in order to reach thermal equilibrium. For each species, three to six saturation recovery scans were run, the data from all scans plotted on one graph, and the best straight line drawn. In this manner the reproducibility of the experiments could be estimated.

The resonance signals of the $PBrCl_2$ and PCl_3 were separated from each other and from the PBr_2Cl signal at all temperatures, thus $1/T_1$ values for each species could be determined independently. This was also the case for the PBr_3 and PBr_2Cl signals below 40°C. However above 40°C these two signals could not be scanned separately, and the saturation recovery spectra contained both signals. A plot for each species could be made easily, however, because of the large difference in their final intensity. For temperatures between 40°C and -30°C, the $1/T_1$ values for PBr_3 and PBr_2Cl were obtained by performing the experiments on each signal separately, and on both of them together. Figure 3 gives representative spectra for one such determination at 0.3°C. The

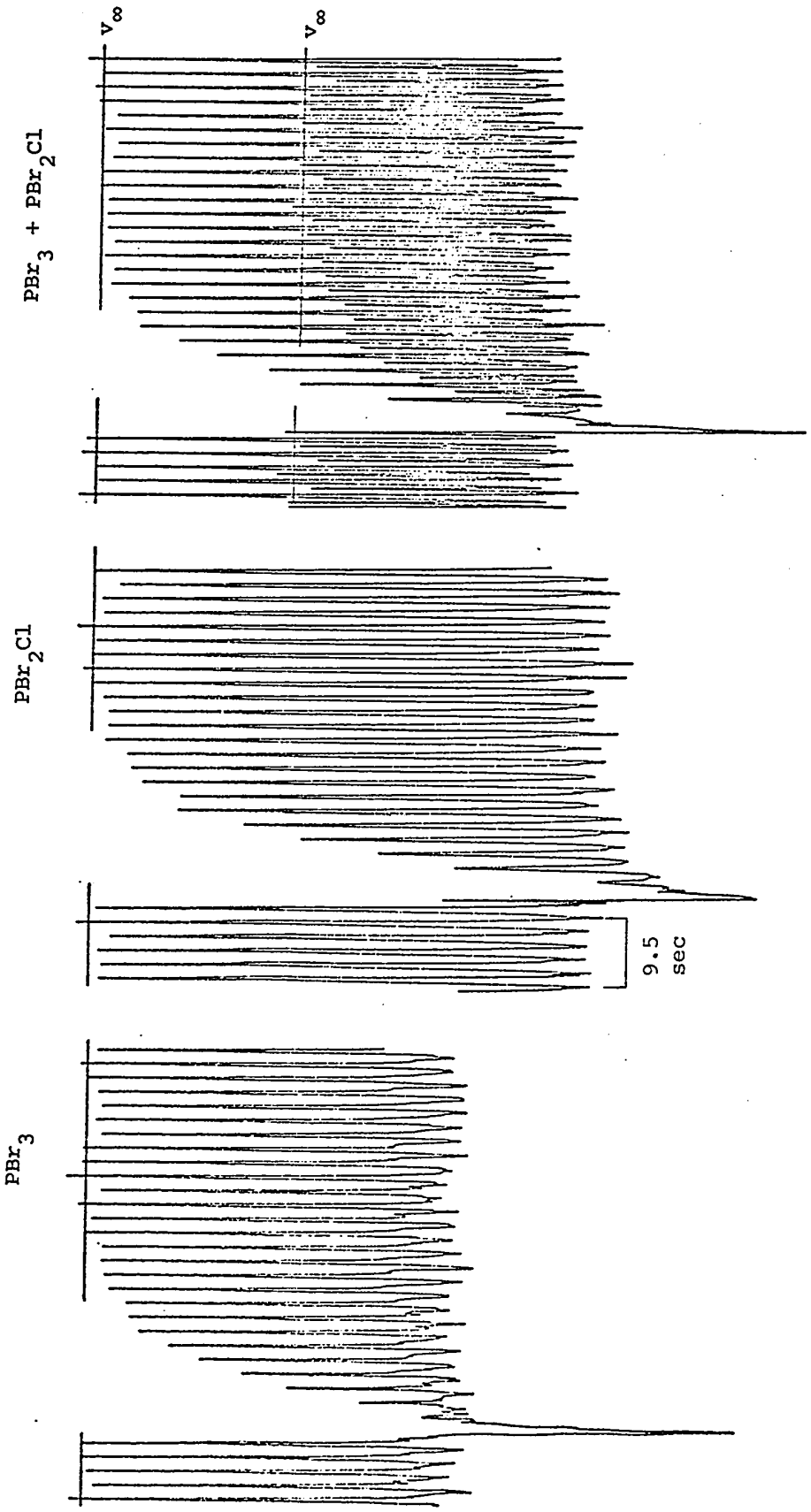


Figure 3: ^{31}P nmr saturation recovery spectra at 0.3°C for PBr_3, PBr_2Cl, and a mixture of PBr_3 and PBr_2Cl.

temperature was measured before and after each set of experiments for the species at a particular temperature.

CHAPTER III

RESULTS AND DISCUSSION OF REDISTRIBUTION REACTIONS

1. Kinetics and Hydrolysis of the PF_3-PCl_3 System

Booth and Bozarth[10] have shown that when PF_3 and PCl_3 are allowed to react at 350-400°C over several hours, small amounts of PF_2Cl and $PFCl_2$ are formed. These authors also indicated that $PFCl_2$ was much more stable than PF_2Cl. One may conclude therefore that either the reaction of PF_3 with PCl_3 is very slow, or that the equilibrium distribution of molecules is very much in favour of the unmixed species. It was of interest to elucidate the thermodynamics and kinetics for this redistribution reaction.

It was initially proposed to study the kinetics of the disproportionation of PF_2Cl in the gas phase, by measuring the change in intensity with time of the bands in the infrared spectrum which are due to the compound PF_3. Table IX gives the infrared spectra of PF_3,[137] PF_2Cl,[28] $PFCl_2$,[138] PCl_3,[139] and of some other phosphorus compounds which will be encountered later on. The spectra of all the compounds, except for PCl_3, were determined in the gaseous phase. For bands which have a PQR structure only the frequency of the Q branch was reported, and for those which have a PQQ'R structure the midpoint between the Q and Q' branches was given. If the four molecules of the PF_3-PCl_3 system are put together, there is a considerable overlap of their spectral bands. However, certain strong bands are free of overlap and may be used for intensity measurements; these are the 892 cm^{-1} and 487 cm^{-1} bands of PF_3, and the 507.4 cm^{-1} band of PCl_3. The intensities of these bands were measured as a

TABLE IX

Infrared Frequencies of Certain Phosphorus Compounds

PF_3 [137]	PF_2Cl [28]	$PFCl_2$ [138]	PCl_3 [139]	OPF_3 [140]	F_2POPF_2 [28]	OPF_2H [141]
1781 (w)	864.5 (s)	838 (s)	507.4	1417.7 PQR	1077 (w)	2500 (w) PQR
1713 (w)	853.5 (s)	521 (s)	493.5	994	976.1 (s)	1377 (s) PQQ'R
1375 (w)	543.7 (s) PQR	512 (s)	260.1	872.8 PQR	853 (s) PQR	1020 (w) PQQ'R
1238 (w)	412.2 (s) PQR	328 (m)	189.0	483.2	682 (m)	993.5 (s)
1196 (w)	404	268		473.2	519 (m)	932 (s) PQQ'R
892 (s) PQR	302			462	515	892 (s) PQR
860 (s)	259			335.6 PQR	460 (w)	510.5 (m) PQR
831 (m)					359 (w)	491 (w)
487 (m) PQR						388 (m) PQR
344 (m)						

function of a known quantity of pure PF_3 or PCl_3, and were found to obey Beer's law individually.

Freshly prepared PF_2Cl was condensed into an infrared cell, and the spectrum was scanned at room temperature for 48 hr. The bands at 892 cm^{-1} and 487 cm^{-1}, attributed to the formation of PF_3, as well as a band at 510 cm^{-1}, believed to be due to the formation of PCl_3, increased with time. However, the band at 510 cm^{-1} was a sharp one, in contrast to the rather broad band at about 507 cm^{-1} obtained for pure PCl_3. Moreover, in addition to the expected bands for PF_3 and PF_2Cl, the characteristic spectrum of HCl[142] centered at 2885 cm^{-1}, a band at 1030 cm^{-1} attributable to SiF_4,[143] and a rather broad band at around 975 cm^{-1} were obtained. A mass spectrum of the total sample indicated that the main products were PF_2Cl, PF_3, and HCl. There was no PCl_3, and only minute traces of $PFCl_2$ were detected. There were, however, several peaks which indicated the presence of one compound containing P, F, and O, and another compound containing P, F, O, and H. This experiment therefore indicated that hydrolysis had taken place, rather than a disproportionation.

In order to eliminate the possibility of a hydrolysis occurring from moisture in the grease around the stopcock on the infrared cell, or from imperfect vacuum, PF_2Cl was condensed into tubes which were sealed. After a certain period of time the contents were analyzed by either a mass spectrum, or an infrared spectrum, or both.

Several samples of PF_2Cl were analyzed after being allowed to react at room temperature for 3 hr, 24 hr, and 3 days. They all

contained the same products as were obtained in the preliminary experiment mentioned above. That is, the compounds present were PF_3, HCl, SiF_4, unreacted PF_2Cl, maybe a trace of $PFCl_2$, and the same oxygen containing compounds. The mass spectra of these unknown species indicated the presence of molecules having the empirical formulae F_4P_2O and F_2POH. Even samples which were allowed to react for 21 days at room temperature gave no indication of PCl_3. Because there was always an excess of PF_2Cl, it was concluded that the disproportionation of PF_2Cl was extremely slow at room temperature, if it occurred at all, and that it hydrolyzed readily with traces of moisture.

When the PF_2Cl was heated at 70°C for 12 hr, still no disproportionation was detected. In an attempt to identify the hydrolysis products, a sample of PF_2Cl was heated at 100°C for 33 hr. Quite fortuitously, this experiment coincided with other work in the laboratory concerning the synthesis and characterization of OPF_2H.[141] When the contents of the tube which was heated at 100°C were distilled through traps cooled to -95°, -130°, -160°, and -196°C, the product which trapped at -95°C was pure OPF_2H, as indicated by infrared and mass spectral properties identical to those of the directly synthesized material. Similar treatment of the other fractions indicated the presence of OPF_2H and traces of HCl at -130°C; PF_2Cl, F_2POPF_2,[28] and traces of OPF_2H and HCl at -160°C; and PF_3, PF_2Cl, HCl, and traces of OPF_2H and F_2POPF_2 at -196°C. The infrared spectra of OPF_2H and F_2POPF_2 are given in Table IX. One of the strongest bands in OPF_2H at 892 cm^{-1} coincides with a band due to PF_3 at 892 cm^{-1}, and another

strong band at 510 cm^{-1} is quite close to the band due to PCl_3 at 507 cm^{-1}. It seems clear now why the presence of small amounts of OPF_2H was not identified in the original infrared spectra.

Before continuing the study of the disproportionation of PF_2Cl, it was necessary to elucidate the nature of the hydrolysis reaction which had not previously been investigated.

Nearly equimolar quantities of PF_2Cl (0.95 mmol) and H_2O (1.1 mmol) were allowed to react at room temperature in a sealed tube for 24 hr. Analysis of the products indicated a volatile fraction consisting only of PF_3, HCl, and SiF_4, and a sticky solid, which was identified as phosphorous acid, H_3PO_3, by its proton nmr spectrum in CD_3CN, and its mass spectrum. The nmr spectrum showed the expected pattern of a singlet and doublet with a coupling constant, J_{PH} = 699 cps, in agreement with that of a sample of commercially available H_3PO_3. The integration of singlet to doublet areas gave the expected ratio of 2:1. The mass spectral pattern of the material was also in good agreement with that of a sample of H_3PO_3. A similar reaction, allowed to proceed for 48 hr gave the identical products.

Because the products obtained in the hydrolysis of PF_2Cl with trace amounts of water were quite different from those obtained with equimolar ratios of water and PF_2Cl, it was of interest to study the products resulting from intermediate quantities of water. PF_2Cl (0.79 mmol) and H_2O (0.33 mmol) were allowed to react at room temperature for 12 days. The contents were then vacuum distilled through traps cooled to -95°, -160°, and -196°C. Analysis of each fraction indicated

the presence of OPF_2H, PCl_3, and traces of HCl at -95°C; PF_2Cl, $PFCl_2$, PCl_3, OPF_2H, and traces of HCl at -160°C; and PF_3, PF_2Cl, HCl, and traces of SiF_4 at -196°C. The oily liquid left behind in the reaction tube was H_3PO_3. The formation of disproportionation products in this reaction was rather unexpected, in view of the fact that earlier experiments had shown that the disproportionation of PF_2Cl did not proceed at room temperature even after 21 days.

The hydrolysis of PF_2Cl with equimolar quantities of water proceeded to completion. The stoichiometry of the reaction could not definitely be established because of the difficulty of separating the mixtures of PF_3, HCl, and trace quantities of SiF_4 which are produced. Measurements of infrared band intensities do not give a quantitative measure of the concentrations of the products because this mixture does not obey Beer's law, even though the individual compounds do. It was shown in a separate set of experiments that the concentrations of a known quantity of PF_3 and HCl in a mixture were consistently larger when calculated from the intensity of their infrared bands.

From the above, it became clear that the disproportionation could be studied only if even trace amounts of water were removed from the system. This was achieved by condensing thionyl chloride, $SOCl_2$, in the reaction tubes, which were then sealed and heated at 300°C for 24 hr. After evacuating the contents thoroughly, no hydrolysis of PF_2Cl was detected after heating the PF_2Cl in such "pretreated" tubes. This dehydrating procedure was therefore used for all the reaction tubes.

When PF_2Cl was heated at 100°C for 40 hr, no disproportionation was detected; likewise, a mixture of PF_3 and PCl_3 did not redistribute after 24 hr at 100°C. When the temperature was increased to 200°C, there was no disproportionation of PF_2Cl after 24 hr, with only a trace of the hydrolysis products, OPF_2H, F_2POPF_2, PF_3, HCl, and SiF_4 being formed; however, the reaction of PF_3 with PCl_3 at 200°C for 24 hr yielded a small amount of PF_2Cl and traces of HCl. When the temperature was increased further to 300°C, PF_2Cl disproportionated after 24 hr to give very small amounts of $PFCl_2$ and PCl_3 and the same hydrolysis products as for the reaction at 200°C; the reaction of PF_3 and PCl_3 at 300°C for 24 hr yielded only small amounts of PF_2Cl and $PFCl_2$. At even higher temperatures the reaction of PF_3 and PCl_3 gave larger quantities of the redistribution products, but there was considerably more etching of the glass, as indicated by the presence of SiF_4 and OPF_3. It was clear that trace hydrolysis of PF_2Cl could not be entirely eliminated even with rigorous dehydration of reaction tubes with $SOCl_2$. Water may be picked up from other sections of the vacuum system and condensed into the reaction tubes, or it may be difficult to remove it completely with chemical treatment to allow the use of long reaction times in the disproportionation study.

These results seem to indicate that PF_2Cl is kinetically very stable. Likewise, the redistribution of PF_3 and PCl_3 is extremely slow. As a result, little can be said about the thermodynamic stability of the PF_2Cl and $PFCl_2$ with respect to that of PF_3 and PCl_3. These reactions would have to be carried out over periods of months at

temperatures ranging between 200°C and 300°C, in order to obtain an equilibrium distribution of products.

The present studies, moreover, indicated that PF_2Cl is extremely susceptible to hydrolysis. Trace amounts of water yielded the products HCl, PF_3, OPF_2H, F_2POPF_2, and traces of SiF_4; equimolar quantities of PF_2Cl and H_2O yielded only HCl, PF_3, H_3PO_3, and SiF_4; at intermediate ratios of PF_2Cl to H_2O the products are HCl, PF_3, OPF_2H, and SiF_4. It is reasonable to suggest that the first step yields OPF_2H and HCl, according to the reaction:

$$PF_2Cl + H_2O \rightarrow OPF_2H + HCl \quad . \qquad \text{(III.1)}$$

When excess PF_2Cl is present the OPF_2H may react with it to form F_2POPF_2 and HCl, according to the reaction:

$$OPF_2H + PF_2Cl \rightarrow F_2POPF_2 + HCl \quad . \qquad \text{(III.2)}$$

The OPF_2H may also decompose to yield PF_3 and H_3PO_3, according to (III.3). This reaction has been reported[141] to proceed to 92% completion in 14 days at room temperature.

$$3OPF_2H \rightarrow 2PF_3 + H_3PO_3 \qquad \text{(III.3)}$$

Thus, according to reactions (III.1), (III.2), and (III.3), the hydrolysis of PF_2Cl with traces of water would be expected to yield OPF_2H, F_2POPF_2, PF_3, HCl, and H_3PO_3. These products agree with the results obtained except for H_3PO_3, whose presence was not detected. On the other hand, the hydrolysis of PF_2Cl with equimolar quantities of water would be

expected to yield only the products of reactions (III.1), and (III.3); OPF_2H, PF_3, HCl, and H_3PO_3. However, OPF_2H is not detected among the products for this reaction, probably because it decomposes or reacts readily with other compounds available. The presence of SiF_4 in all the reactions studied may be explained by the formation of HF from the hydrolysis[141] of OPF_2H, according to the reaction:

$$OPF_2H + 2H_2O \rightarrow H_3PO_3 + 2HF \ . \qquad \text{(III.4)}$$

The HF then attacks the glass, according to the reaction:

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \ . \qquad \text{(III.5)}$$

2. Kinetic Studies of the PCl_3-PBr_3 System

The only kinetic information on the redistribution in the PCl_3-PBr_3 system is not very specific. Delwaulle and Bridoux[15] indicated that the reaction of PCl_3 with PBr_3 at room temperature reached equilibrium in 1-1½ hr. Van Wazer[22] and his co-workers have stated that the reaction is complete in less than 15 min at 25°C. Even though these time estimates were quite different, it was reasonable to assume that the kinetics of this reaction could be studied by the change in the ^{31}P spectrum of the system with time. The preparation of samples, kinetic procedure, and technical aspects of this system have been discussed in detail in the experimental section of the thesis.

Although the reaction of PCl_3 and PBr_3 leading to the equilibrium state is probably a complex one, a study of initial reaction rates could reveal the rate law for the reaction:

$$PCl_3 + PBr_3 \rightarrow PBr_2Cl + PBrCl_2 \quad . \qquad \text{(III.6)}$$

Before proceeding with the description of the experiments carried out and the results obtained, it is of interest to investigate some of the mechanisms that can be postulated when the order of the reaction is determined.

One possible mechanism would be an ionic mechanism, in which the dissociation of PCl_3 or PBr_3 into ions is the slow step. It is followed by the attack of an ion on an undissociated species or another ion. The dissociation of PCl_3 could be occurring by a unimolecular or bimolecular mechanism:

$$PCl_3 \rightleftarrows PCl_2^+ + Cl^- \quad , \qquad \text{(III.7)}$$

$$2PCl_3 \rightleftarrows PCl_2^+ + PCl_4^- \quad . \qquad \text{(III.8)}$$

A set of analogous reactions can be written for PBr_3. The overall rate law might be quite complex, but the initial rate of the reaction would depend only on the concentration of the rate initiating species, raised to the appropriate power. In other words, a rate order of one with respect to PCl_3 and zero with respect to PBr_3 would favour the dissociative reaction (III.7), whereas a rate order of two with respect to PCl_3 and zero with respect to PBr_3 would favour the dissociative reaction (III.8). Of course, both PCl_3 and PBr_3 may be dissociating, but it is the species that dissociates fastest which would be the rate initiating species. Also, it would be quite coincidental if both species dissociated at the same rate, thereby causing initial rates to be dependent on the concentration of both species.

In the liquid state the phosphorus trihalides exhibit very low conductivities, indicating that they ionize only to a limited extent. Recently Dillon and Waddington[144] have prepared some alkylammonium salts of the PBr_4^- ion. This is the first example of a negative halogen ion of the phosphorus trihalides. No evidence for the existence of positive ions of trivalent phosphorus, such as PBr_2^+, has yet been reported.

Another possible mechanism for the reorganization reaction would involve the formation of a radical in the rate determining step. The radical formed would then react by attacking a free molecule or another radical. Reactions for the dissociation of PCl_3 into radicals may be

written in the same manner as for the dissociation of PCl_3 into ions:

$$PCl_3 \rightleftarrows PCl_2^{\cdot} + Cl^{\cdot} \quad , \qquad \text{(III.9)}$$

$$2PCl_3 \rightleftarrows PCl_2^{\cdot} + PCl_4^{\cdot} \quad . \qquad \text{(III.10)}$$

A study of initial rates would indicate whether the PCl_3 or the PBr_3 species is rate initiating. A differentiation between reactions (III.9) and (III.10) would be made on the same basis as for reactions (III.7) and (III.8) in the ionic mechanism. In fact, chemical methods would have to be used to differentiate between an ionic mechanism and a radical mechanism, because both exhibit the same kinetics at the beginning of the reaction.

In 1945 Kharash[145] and co-workers proposed that the reaction of PCl_3 with $CH_2{=}CHC_6H_{13}$ to yield $PCl_2CH_2CHClC_6H_{13}$ occurred via the $PCl_2^{\cdot}$ radical. When PCl_3 was flash photolyzed[146] the spectrum of the $PCl^{\cdot}$ radical, believed to originate from a $PCl_2^{\cdot}$ radical, was observed. The flash photolysis of PBr_3[146,147], however, did not yield the same product. Recently Kokoszka and Brinckman[148] obtained the epr spectra of $PCl_2^{\cdot}$ and $PCl_4^{\cdot}$ radicals, formed when PCl_3 is irradiated with a 200w ultraviolet light. From the ratio of the integrated spectra of $PCl_2^{\cdot}$ and $PCl_4^{\cdot}$ they were able to propose the following scheme:

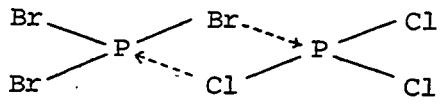
$$4PCl_3 \rightarrow 4PCl_2^{\cdot} + 4Cl^{\cdot} \qquad \text{(III.11a)}$$

$$3Cl^{\cdot} + 3PCl_3 \rightarrow 3PCl_2^{\cdot} + 3Cl_2 \qquad \text{(III.11b)}$$

$$Cl^{\cdot} + PCl_3 \rightarrow PCl_4^{\cdot} \quad . \qquad \text{(III.11c)}$$

If reaction (III.11a) can occur with weak ultraviolet radiation, and the PBr_3 molecule is substituted for the PCl_3 in reactions (III.11b) and (III.11c), then this mechanism could yield the mixed halides.

The mechanism which is most often favoured for redistribution reactions is one which proceeds through the formation of a four-centre transition state. For PBr_3 and PCl_3, this is depicted as:



The initial step would yield PBr_2Cl and $PBrCl_2$, but the overall reaction could be quite complex, since bridged intermediates could ideally be formed between any two compounds, thus:

$$PBr_3 + PCl_3 \rightleftarrows PBr_2Cl + PBrCl_2 \quad , \qquad \text{(III.12)}$$

$$PBr_2Cl + PBr_3 \rightleftarrows 2PBrCl_2 \quad , \qquad \text{(III.13)}$$

$$PBrCl_2 + PCl_3 \rightleftarrows 2PBr_2Cl \quad . \qquad \text{(III.14)}$$

The initial reaction rate law for such a mechanism would be expected to be first-order in each of the reactants. There has been no evidence of dimer formation between phosphorus trihalides, however, such a bridged reactive intermediate might well exist.

A quick semi-quantitative estimate of the overall reaction rate may be obtained from the half-life of the reaction. Therefore, reactions will be compared in terms of their half-lives which are reported as the average of the values obtained from the change in concentration with

time for each species.

The concentration-time data for samples 1 to 35 are given in the Appendix A in Tables AI to AXXXV respectively. These samples represent only those for which the reaction was followed to completion. At this point, it is pertinent to indicate the accuracy of these results. The largest errors are found for PBr_2Cl and $PBrCl_2$ at the beginning of the reaction where their relative abundance, compared to PBr_3 and PCl_3, is small. It has been mentioned previously that the areas of the nmr curves of each species can be read with a precision of ±0.5 divisions on the integration from the curve resolver. This leads to a precision of ±0.005 in the values of mole fractions obtained for each species. The percentage error is therefore large in the early stages of the reaction. However, because spectra were recorded frequently and many values were obtained, these errors cancel each other and smooth curves can be drawn through the plots of concentration against time.

Originally all samples were prepared on a grease-lubricated vacuum system. From the measured weight of PCl_3 and PBr_3 and their respective density,[149] the molar concentration of each species could be determined.

The mole fractions of PCl_3 and PBr_3 in samples 1, 2, and 3 were, respectively: 0.49, 0.51; 0.65, 0.35; and 0.34, 0.66. The half-life of the reaction at 41°C was 55, 17, and 4.5 min for samples 1, 2 and 3 respectively. Since these results were not consistent, samples 4 and 5, containing the same mole fractions as sample 3, were prepared. The half-lives obtained, 140 min and 79 min respectively

at 41°C, clearly showed that the results were not reproducible. Samples 6, 7, and 8, prepared on the same day and containing the same amounts of PCl_3 and PBr_3, reacted with very different rates at the same temperature.

During the course of preparing the samples, it was noticed that the reactants dissolved small amounts of the vacuum system grease which ran into the nmr tube. In order to prevent grease from entering the nmr tube, a sample was prepared by distilling the reactants into the sample tube through a U-tube attachment. This reaction proceeded much more slowly than any of the previous ones, in fact reorganized products were detected only after 30 min. However, an attempt to reproduce this result with a sample containing the same amounts of reactants failed; this reaction was even slower. These experiments indicated that the presence of grease had a catalytic effect on the reaction. A sample to which a small dab of KEL-F #90 grease had been added reacted so fast that the reaction had reached equilibrium by the time the first spectrum was obtained. This result clearly demonstrated the necessity of preparing the samples in a grease-free system.

One drawback in preparing samples on a grease-free system is that the compounds cannot be weighed, and hence the initial molar concentration of the reactants cannot be determined. However, the initial mole fractions of the reactants may be determined after the spectra are recorded and resolved. The initial mole fractions can be obtained from the first spectrum scanned, but these results are not accurate if the reaction proceeds fast, and the errors are larger at the very beginning of the reaction. A much more satisfactory procedure

is to obtain the initial mole fractions from the spectrum of the sample at equilibrium. The total chlorine content of the sample, Cl_T, can be calculated from the mole fractions of the chlorine containing species according to (III.15):

$$Cl_T = 3N_{PCl_3} + 2N_{PCl_2Br} + N_{PClBr_2} \quad , \qquad \text{(III.15)}$$

where N denotes mole fractions.

The initial mole fraction of PCl_3, iN_{PCl_3}, is then given by:

$$iN_{PCl_3} = Cl_T/3 \quad . \qquad \text{(III.16)}$$

The initial mole fraction of PBr_3, iN_{PBr_3}, is obtained by subtraction of iN_{PCl_3} from unity.

Initial mole fractions, calculated by the method described above, are compared to the values obtained from weight measurements of the reactants in Table X for samples 1 to 8. The agreement is excellent, confirming the reliability of this approach. If molar concentrations are required, they can be calculated from the initial mole fractions of PCl_3 and PBr_3, their molecular weights, their densities,[149] and the total volume of liquid. The latter can reliably be obtained from an independent calibration of the volume occupied by a certain height of liquid in an nmr tube.

All samples discussed from this point onwards were prepared on a grease-free system. Two samples containing the same amounts of reactants were prepared, in order to check the reproducibility of the results. The reactions, carried out at 60°C, were extremely slow. The reactions

TABLE X

Experimental[a] and Calculated[b] Initial Mole Fractions of PCl_3 and PBr_3

Sample[c]	iN_{PCl_3} expl	iN_{PCl_3} calcd	iN_{PBr_3} expl	iN_{PBr_3} calcd
1	0.49	0.50	0.51	0.50
2	0.65	0.65	0.35	0.35
3	0.34	0.35	0.66	0.65
4	0.36	0.37	0.64	0.63
5	0.37	0.38	0.63	0.62
6	0.59	0.60	0.41	0.40
7	0.58	0.59	0.42	0.41
8	0.58	0.60	0.42	0.40

[a] Obtained by separately weighing PCl_3 and PBr_3.

[b] Calculated from mole fractions of all species at equilibrium.

[c] For equilibrium mole fractions of samples 1 to 8 see Tables AI to AVIII.

were not followed to completion, because the time required to detect the products in each sample, namely 10 hr and 19 hr, indicated that the problem of reproducibility had not yet been solved, even though the bulk of the catalysis had been eliminated. It was clear that the reaction rate was considerably slower than had originally been believed. The fact that the reaction was catalyzed could be useful in postulating the mechanism for the exchange, if the nature of the catalyst could be determined.

The first attempt in the direction of isolating the catalyst for the reaction was to make a sample containing a simple compound which would approximate the composition of KEL-F #90 grease, $Cl-(CF_2CFCl)_n-Cl$.[150] Sample 9 containing 0.02 ml 1,1,2-trichloro-1,2,2-trifluoroethane, $CFCl_2CF_2Cl$, taken directly from a reagent bottle without purification, attained equilibrium in about 8 hr at 33°C. This sample, compared to the preceeding ones in which the products were barely detectable after 10 to 19 hr at 60°C, suggested that $CFCl_2CF_2Cl$ was a catalyst for the reaction. However, in order to check the above results, two samples containing the same amounts of reactants and $CFCl_2CF_2Cl$, which had been vacuum distilled through traps cooled to -63°C and -196°C, were prepared. The choice of traps was guided by the fact that any water present in the sample would collect at -63°C, while the $CFCl_2CF_2Cl$ would be trapped at -196°C. The samples prepared from fractionated $CFCl_2CF_2Cl$ did not yield any detectable products within one hour at 33°C, thereby suggesting that the catalyst was probably water and not $CFCl_2CF_2Cl$.

Two samples containing duplicate amounts of PCl_3 and PBr_3 and 0.02 ml water were prepared, in order to determine directly whether water was a catalyst. At 35°C both samples attained equilibrium in less than 30 min, thus illustrating that water is a good catalyst for the exchange.

The above result indicated that sufficient water may be adsorbed on the glass to provide a catalytic effect on the redistribution reaction. Moreover, in the grease-lubricated system traces of water may be present in the grease and may be picked up during the transfer of reactants. For this reason, reactions in samples which had been prepared on a grease-lubricated system were much faster than in those which had been prepared on a grease-free system. For complete removal of water, baking of the glassware for several hours is necessary. The results obtained from the study of the PF_3-PCl_3 system did indicate that glassware had to be heated at 300°C for 24 hr in order to remove the water. It is likely then that some water may still be present in samples prepared on a grease-free system, despite the precautions taken, but a uniform surface water concentration is not to be expected.

Water, when added to the mixture of PCl_3 and PBr_3, catalyzes the exchange reaction. The phosphorus halides are known[151] to hydrolyze to phosphorous acid and the corresponding hydrohalic acid and the catalyst, therefore, could be any of the products H_3PO_3, HCl, and HBr, as well as water itself. Two carefully dried samples containing the same quantities of reactants were therefore prepared; one contained 0.06 mmol HCl and the other 0.05 mmol HBr. At 35°C no products

were detected within 30 min, indicating that HCl and HBr do not catalyze the reaction. The question of whether H_3PO_3 catalyzes the reaction is a much more difficult one to answer, because H_3PO_3 is extremely deliquescent, and it is doubtful that it can be obtained free of water. However, a sample containing H_3PO_3, which had been heated at 90°C for 30 min and pumped on for 24 hr, was prepared. The half-life of the reaction was approximately 15 min at 35°C. This experiment is inconclusive insofar as the H_3PO_3 could still have contained some water.

Although the rates of the reactions of samples containing the same concentration of reactants were not reproducible, even when the samples were prepared on a grease-free system, it was of interest to obtain a lower limit to the half-life of the reaction. Samples 10 and 11 proceeded with a half-life of 5 days and 3 days respectively at 60°C. Samples 12 and 13 proceeded with a half-life of 10.7 days and 10.5 days respectively at 70°C. It seems ironic that the reactions that were carried out at 70°C were slower than those at 60°C. This, however, emphasizes again that the catalysis has not yet been completely eliminated. The mole fraction versus time plots for samples 10 to 13 are given in Figures 4 to 7 respectively, for all the species. The plots are representative of most of the reactions studied in this system.

Because of the difficulty of obtaining an uncatalyzed reaction of PCl_3 and PBr_3, a study of the kinetics of the reaction as a function of the catalyst concentration was undertaken. By first determining the order of the reaction with respect to the catalyst concentration, it would then be possible to determine the order of the reaction with

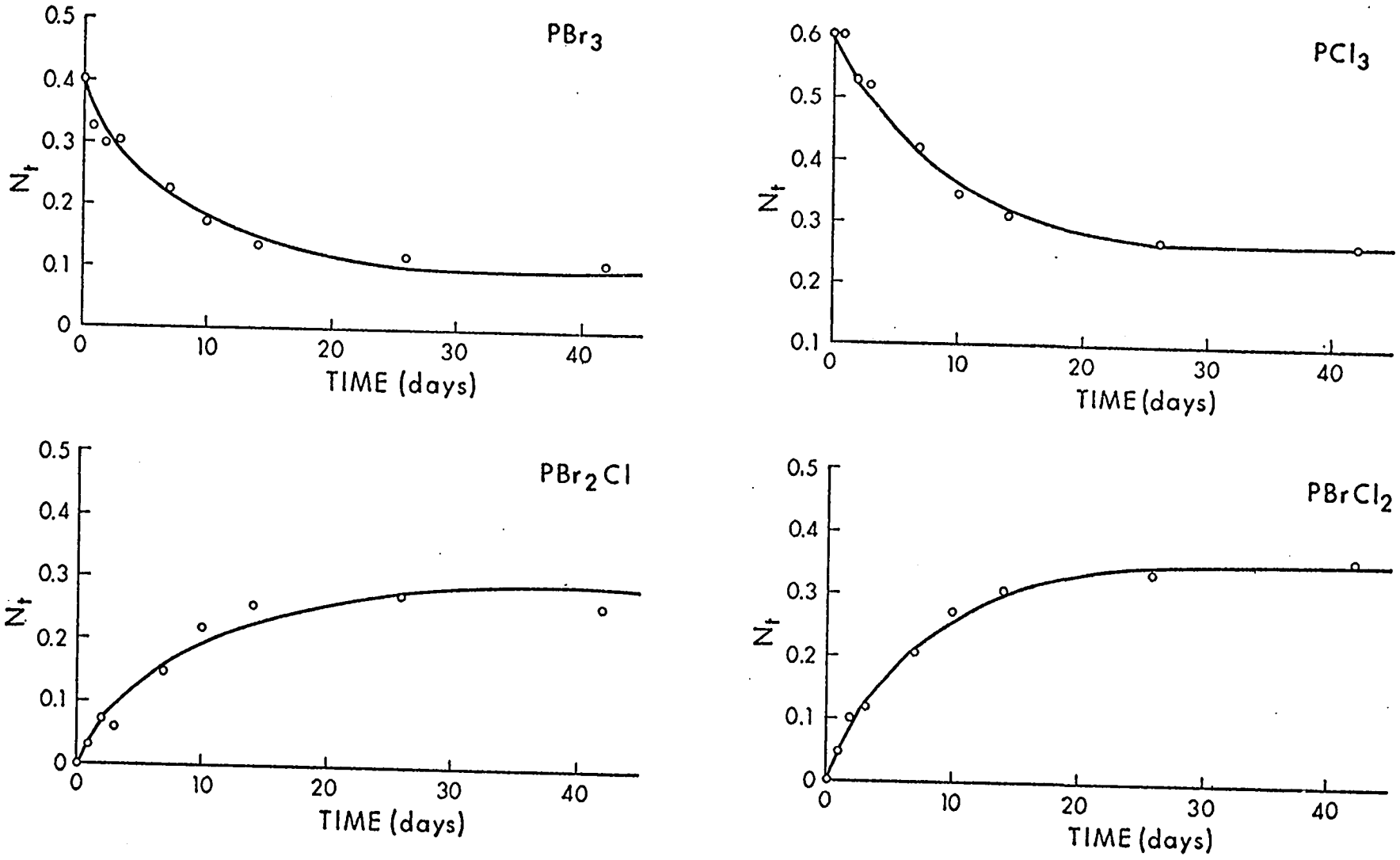


Figure 4: Variation of mole fraction with time for the PCl_3-PBr_3 reaction in sample 10 at 60°C.

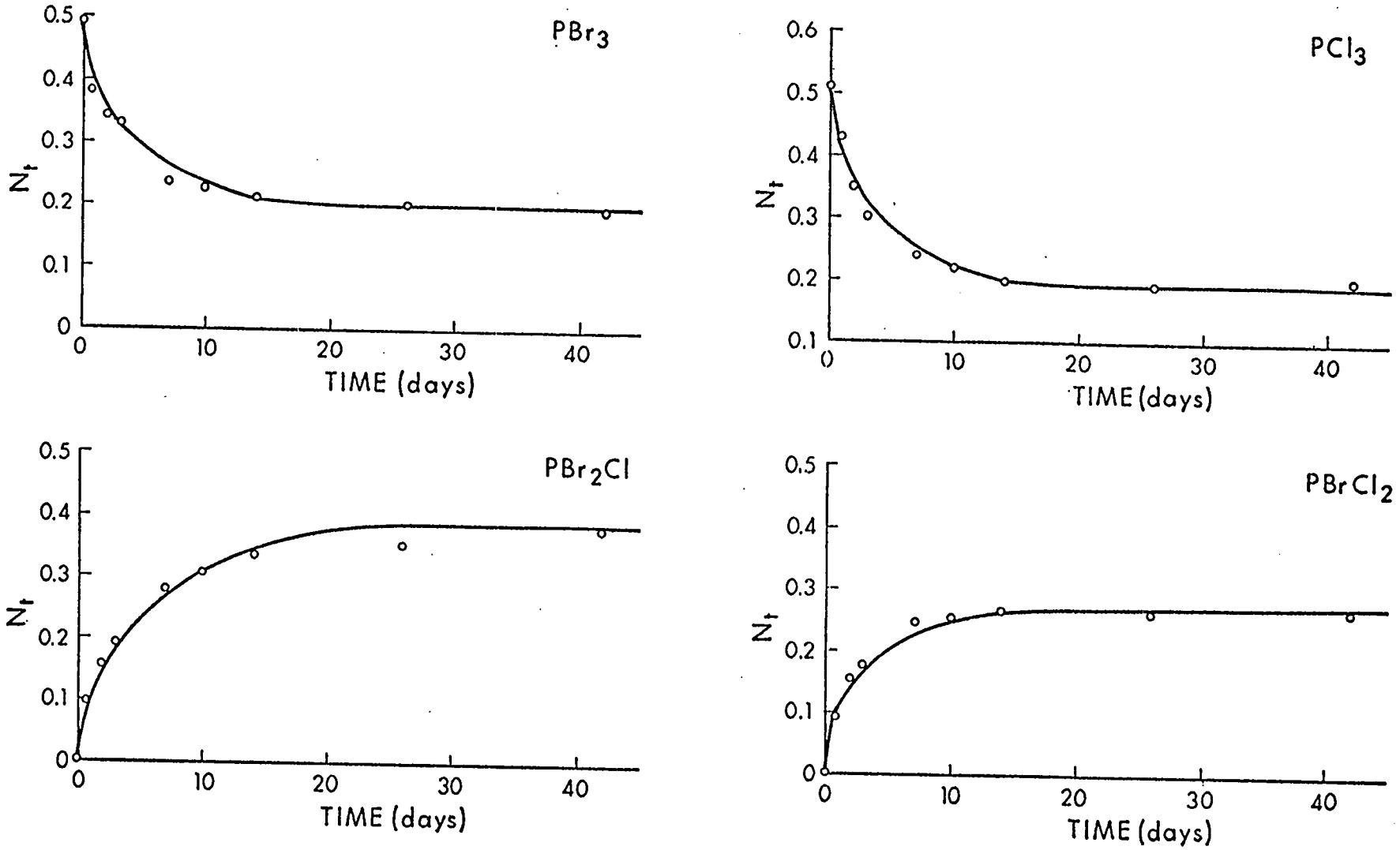


Figure 5: Variation of mole fraction with time for the PCl_3-PBr_3 reaction in sample 11 at 60°C.

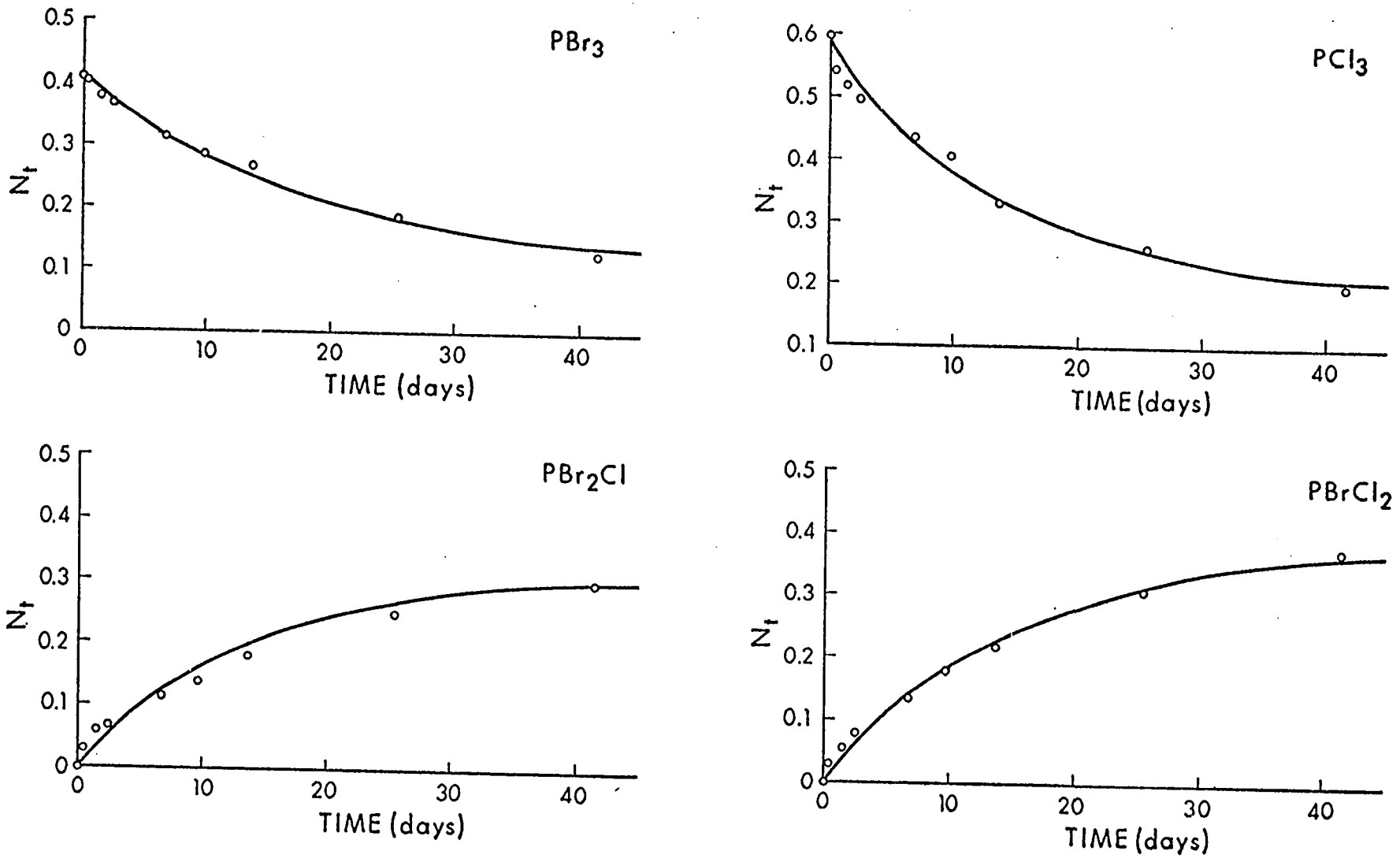
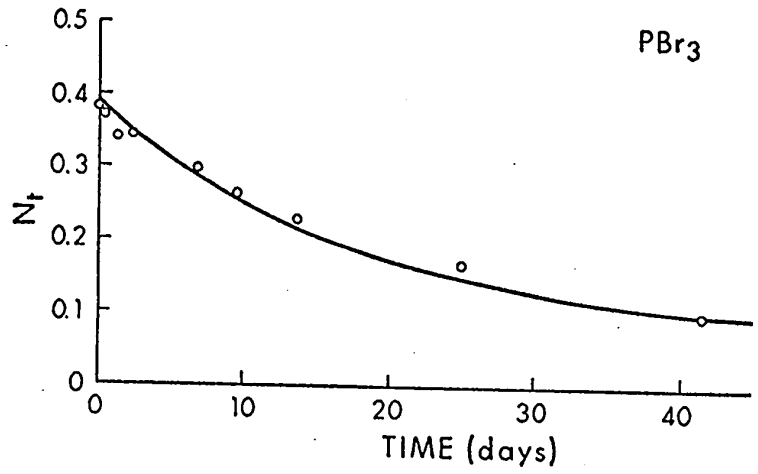
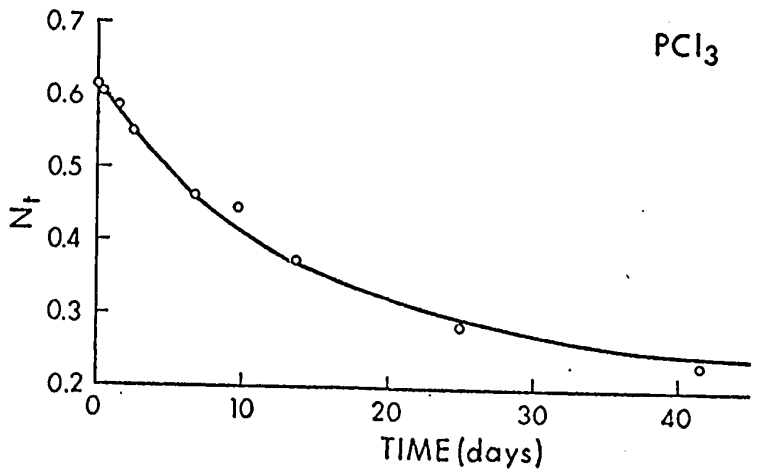
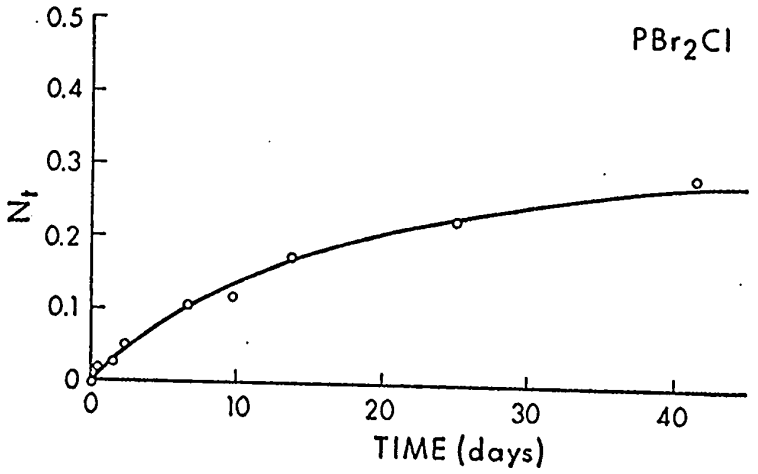


Figure 6: Variation of mole fraction with time for the PCl_3-PBr_3 reaction in sample 12 at 70°C.







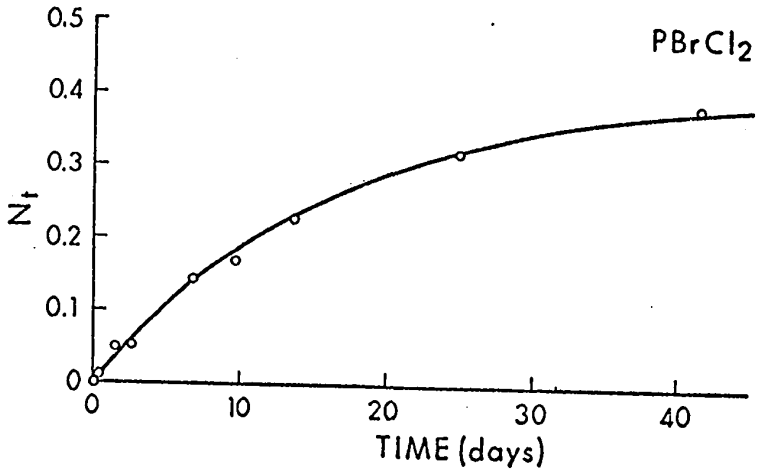


Figure 7: Variation of mole fraction with time for the PCl_3-PBr_3 reaction in sample 13 at 70°C.

respect to the PCl_3 and PBr_3 concentrations.

In order to determine the dependence of the rate of the reaction on the water concentration, the concentration of water is varied while that of the reactants is kept constant. For all subsequent samples, an attempt was made to keep the concentration of PCl_3 and PBr_3 constant. The mole fractions of PCl_3 and PBr_3, as calculated from the equilibrium distribution of all species and a constant height of liquid in the nmr tube, indicated that this was accomplished with reasonable consistency.

The water concentration was originally measured by allowing its vapour to expand into a known volume, as described in the chapter on experimental techniques. Unless otherwise stated, the water was introduced into the sample tube after the addition of the reactants. Sample 14, containing 0.0303 mmol H_2O, reacted with a half-life of 33 min at 35°C. Water concentrations of 0.0606 mmol and 0.125 mmol caused the reaction to proceed at too rapid a rate to be accurately measured. Samples 15, 16, and 17, prepared on the same day and containing 0.0132, 0.0193, and 0.0258 mmol H_2O respectively, reacted with a half-life of 78, 27, and 11 min respectively at 35°C. The results of these three samples were qualitatively consistent with each other, but did not agree with the result of sample 13. In another attempt, samples 18, 19, and 20, prepared on the same day and containing 0.0064, 0.0130, and 0.0193 mmol H_2O respectively, reacted with a half-life of 150, 22, and 12.5 min respectively at 35°C. The results of these three samples were certainly not in agreement with the previous ones, indicating that again the samples were not reproducible.

In all the water containing samples mentioned to date the water had been added after the PBr_3 and PCl_3, in that order. When the samples are thawed, the water probably comes into contact with the PCl_3 prior to the PBr_3, even though the sample tubes are shaken vigorously. However, the amount of each reactant that originally comes in contact with H_2O is probably not reproducible. If the nature of the catalyst, or the mechanism of the catalyzed reaction, or both of these are different for water attacking PCl_3 and PBr_3, then the discrepancies encountered above could be explained. In order to check for this possibility, samples 21 and 22, in which water was allowed to react for 2 hr with the PBr_3 prior to the addition of the PCl_3, and samples 23 and 24, in which water was allowed to react for 2 hr with the PCl_3 prior to the addition of PBr_3, were prepared. All the samples contained approximately 0.0125 mmol H_2O. At 35°C the half-life of the reaction was 44 min and 12 min for samples 21 and 22 respectively, and 89 min and 34 min for samples 23 and 24 respectively. In view of the non-reproducibility of results in identical samples no conclusions could be made. However, the results may be due to an inability to control completely the quantity of water added by this method.

In all further samples the water was added by heating a known amount of $[Co(NH_3)_5H_2O]Br_3$, as described in the section on experimental procedure. This method should yield an accurately known quantity of water, which could be introduced in the absence of interfering stopcocks which hamper the transfer. Samples 25, 26, 27 and 28, containing 0.00759, 0.0145, 0.0148, and 0.0215 mmol H_2O respectively, were

prepared. At 35°C their respective half-lives were 36, 6, 20.5, and 15.5 min. Sample 26 seemed to be out of order with respect to the other three samples. The experiment was repeated by preparing samples 29, 30, and 31, containing 0.00796, 0.0147, and 0.0213 mmol H_2O respectively. At 35°C their respective half-lives were 14.6, 11.3 and 14.3 min. Even though the results for samples 28 and 31 are in agreement, no other correspondence is observed. It may be worth pointing out that the reactions in general proceed faster in the samples prepared by adding water from the complex than in the corresponding samples to which water was added by the volumetric measurement of its vapour. This may indicate that not all of the expected quantity of water was being added by the volumetric method.

Finally, four samples, all containing approximately 0.0146 mmol H_2O, were prepared in which the water was allowed to react with one of the reactants prior to the addition of the other reactant. In samples 32 and 33 the water was allowed to react with PCl_3 for 2 hr, and in samples 34 and 35 it was allowed to react with PBr_3 for 2 hr. Samples 32 and 33 reacted with a half-life of 75 min and 125 min respectively, while samples 34 and 35 reacted with a half-life of 16 min and 30 min respectively at 35°C. In this set of experiments again identical samples did not yield duplicate results. The reactions in which water had been allowed to react with PBr_3 proceeded much faster than those in which water had been allowed to react with PCl_3. However, in view of the non-reproducibility of data, no conclusions can be drawn.

The mechanistic possibilities mentioned at the beginning of this

chapter cannot be tested, because the rate law for the PCl_3-PBr_3 reaction was not obtained. It was found that the reaction was catalyzed by water or one of the products of the hydrolysis of the reactants. It was not possible to determine the order with respect to the catalyst, nor was it possible to determine the order with respect to the reactants, because of experimental difficulties encountered. However, an attempt was made to determine the order of the catalyzed reaction by graphical methods. The first-order plot of $\ln|N_t - N_e|$ against t, where N_t is the mole fraction of a particular species at a particular time, t, and N_e is the mole fraction of that species at equilibrium, was constructed for each of the four molecules in a kinetic run. The success of this first attempt was overwhelming. Of the 35 samples whose reactions had been followed to completion 30 gave first-order plots over 90% of the reaction, for all species. Although the order of the reaction with respect to the catalyst is still unknown, the rate determining step in the formation or decomposition of a particular species is first-order in that species, for all the molecules.

The first-order plots for the species in samples 10 to 13, which were the slowest reactions studied, are given in Figures 8 to 11 respectively. They are representative of all the first-order plots obtained. For all those samples that obeyed this simple first-order scheme the half-life was obtained from the first-order plots. The half-lives of all the species in all samples are given in the Tables AI to AXXXV, together with a statement as to whether or not the species

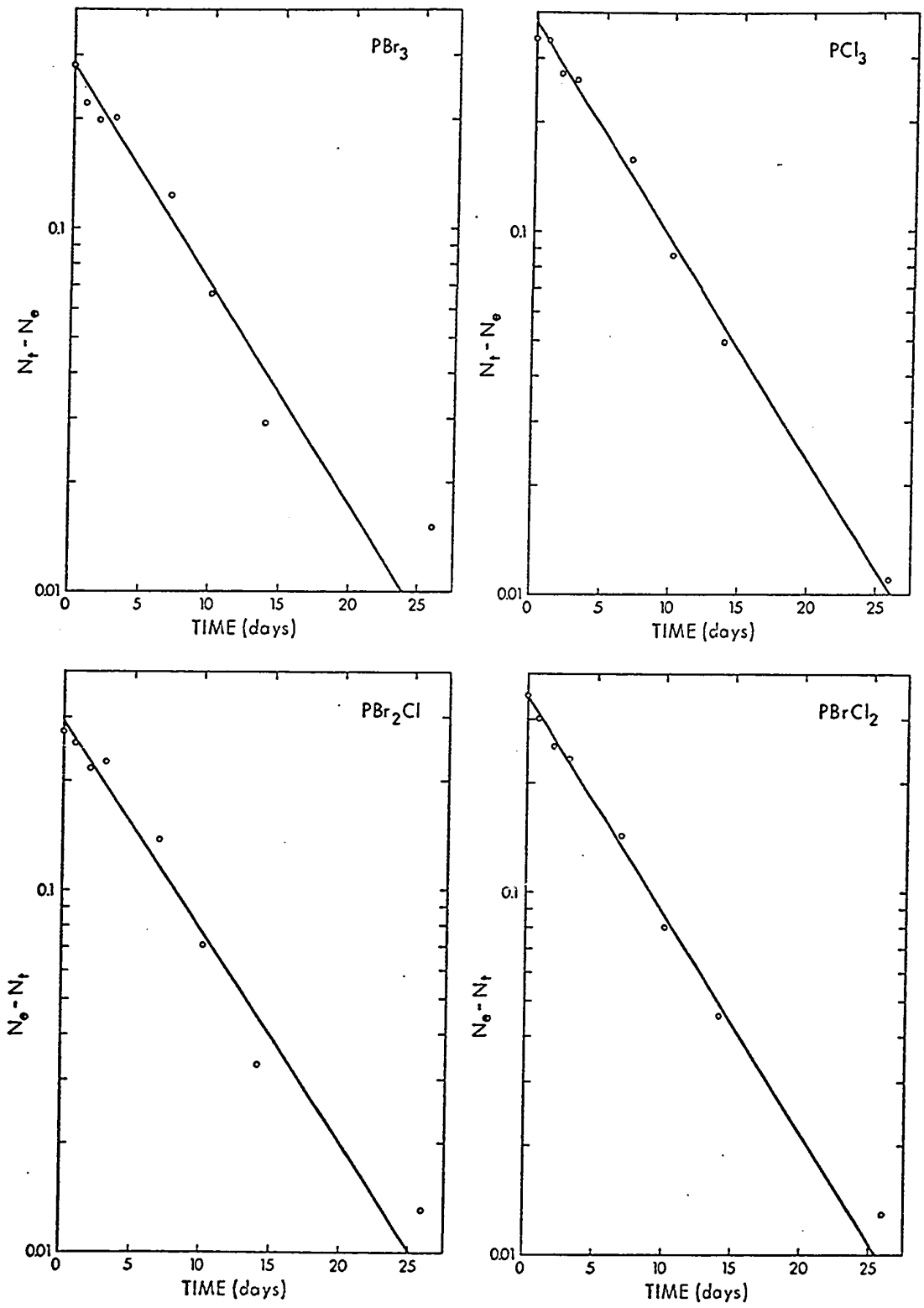


Figure 8: First-order plots for the PCl_3-PBr_3 reaction in sample 10 at 60°C.

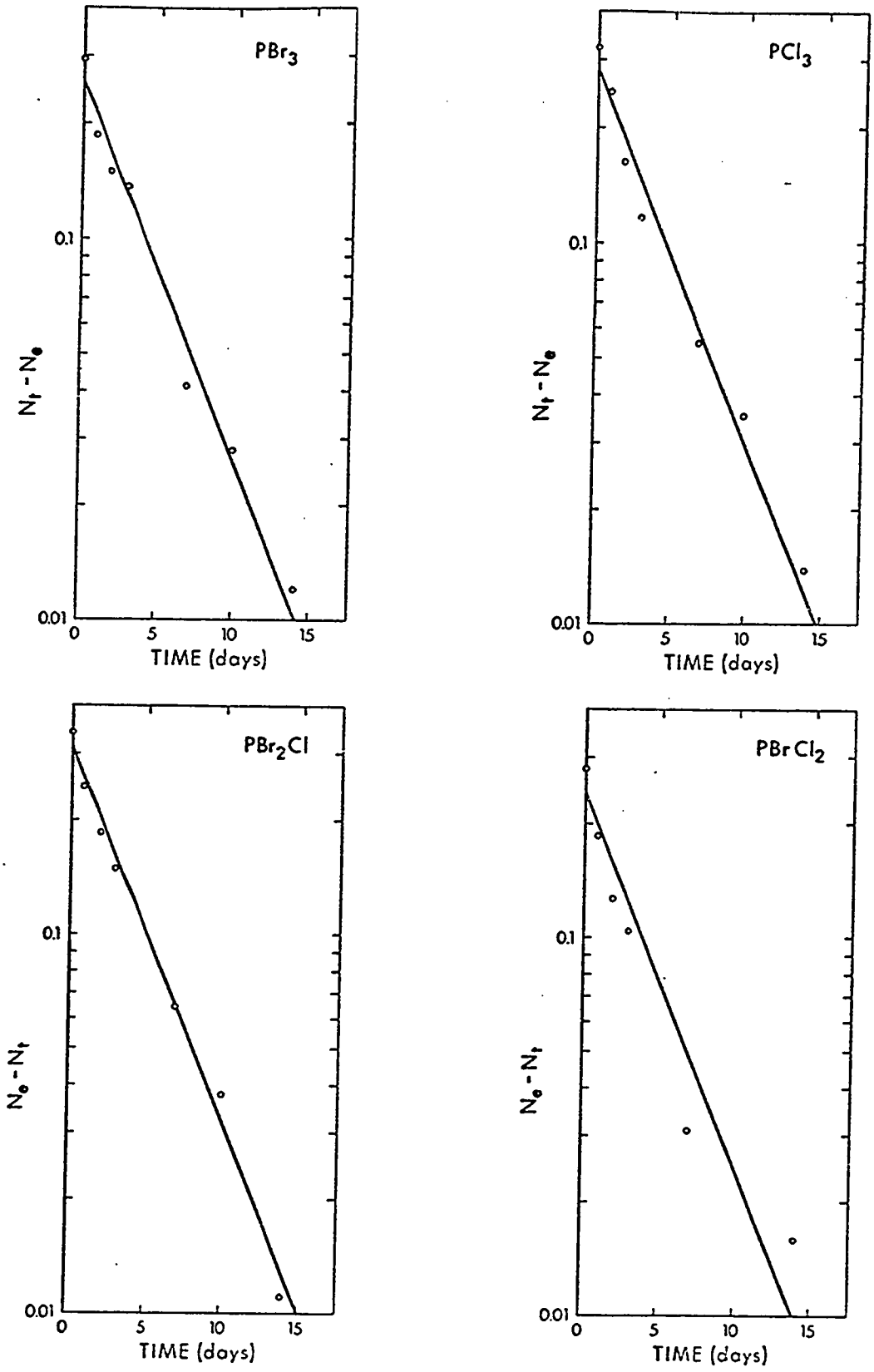


Figure 9: First-order plots for the PCl_3-PBr_3 reaction in sample 11 at 60°C.

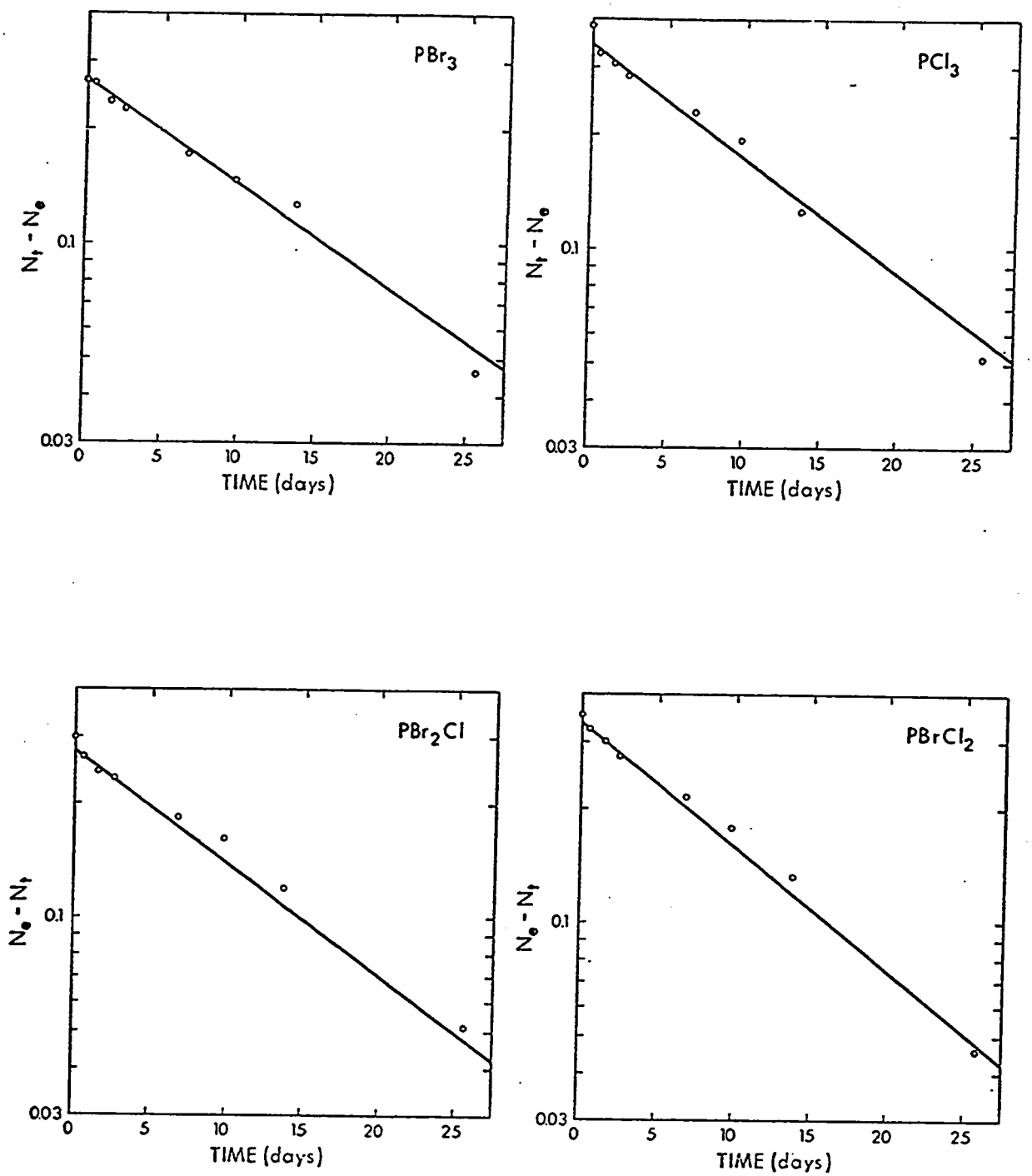


Figure 10: First-order plots for the PCl_3-PBr_3 reaction in sample 12 at 70°C.

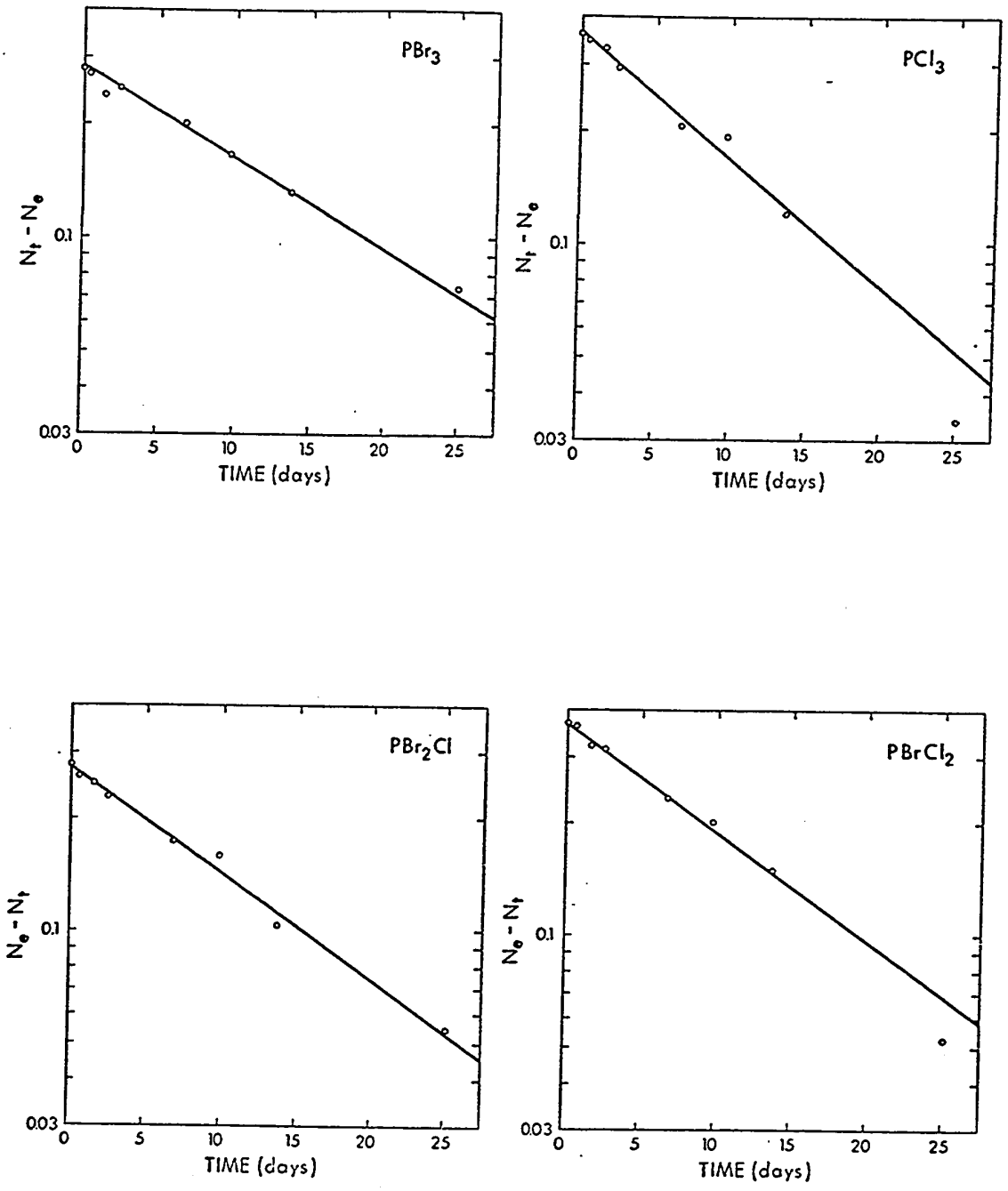


Figure 11: First-order plots for the PCl_3-PBr_3 reaction in sample 13 at 70°C.

concentration obeyed first-order kinetics.

A review of all the half-lives obtained indicates that for most samples the half-life of PBr_3 is the same as that of PBr_2Cl, while the half-life of $PBrCl_2$ is the same as that of PCl_3. In all of these samples, the two sets of half-lives are different by less than 20%, and for most of them by less than 10%.

The simplest kinetic scheme that can be written is one in which one molecule of one species reacts with the catalyst C, to yield one molecule of another species. The catalyst may not be the same for each reaction, but its total concentration is constant throughout the reaction. If only one halogen atom is exchanged, then there are three possible reactions:

$$PCl_3 + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PBrCl_2 + C \quad , \tag{III.17}$$

$$PBr_3 + C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} PBr_2Cl + C \quad , \tag{III.18}$$

$$PBrCl_2 + C \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} PBr_2Cl + C \quad . \tag{III.19}$$

Ideally all these equations should be written to indicate that the reactants form a reactive intermediate X, which then decomposes to the products. However, because the steady-state approximation can be applied to the formation of X, this step can be omitted. The rate law for each species, derived on the basis of equations (III.17) to (III.19), is given in (III.20) to (III.23):

$$-d[PCl_3]/dt = k_1[C][PCl_3] - k_{-1}[C][PBrCl_2] \quad , \qquad \text{(III.20)}$$

$$-d[PBr_3]/dt = k_2[C][PBr_3] - k_{-2}[C][PBr_2Cl] \quad , \qquad \text{(III.21)}$$

$$d[PBrCl_2]/dt = k_1[C][PCl_3] - k_{-1}[C][PBrCl_2] + k_{-3}[C][PBr_2Cl] - k_3[C][PBrCl_2] \quad , \qquad \text{(III.22)}$$

$$d[PBr_2Cl]/dt = k_2[C][PBr_3] - k_{-2}[C][PBr_2Cl] + k_3[C][PBrCl_2] - k_{-3}[C][PBr_2Cl] \quad . \qquad \text{(III.23)}$$

In order to maintain chemical balance the following relationships must hold:

$$[Cl]_T = 3[PCl_3] + 2[PBrCl_2] + [PBr_2Cl] \quad , \qquad \text{(III.24)}$$

$$[Br]_T = 3[PBr_3] + 2[PBr_2Cl] + [PBrCl_2] \quad . \qquad \text{(III.25)}$$

The terms $[Cl]_T$ and $[Br]_T$ denote the total concentration of chlorine and bromine atoms.

The integrated form of (III.20) is obtained by first substituting for $[PBrCl_2]$ from (III.24):

$$-d[PCl_3]/dt = k_1[C][PCl_3] - \tfrac{1}{2}k_{-1}[C][Cl]_T + \tfrac{3}{2}k_{-1}[C][PCl_3] + \tfrac{1}{2}k_{-1}[C][PBr_2Cl] \quad . \qquad \text{(III.26)}$$

By grouping terms together this can be simplified to:

$$-d[PCl_3]/dt = (k_1 + \frac{3}{2} k_{-1})[C][PCl_3] - \frac{1}{2} k_{-1}[C]([Cl]_T - [PBr_2Cl]) \quad . \qquad \text{(III.27)}$$

The second term in the rate law can be simplified further with the following approximation:

$$[Cl]_T - [PBr_2Cl] \simeq [Cl]_T \quad . \qquad \text{(III.28)}$$

However $[Cl]_T = 3[PCl_3]_o$, where $[PCl_3]_o$ is the initial concentration of PCl_3, hence equation (III.27) reduces to:

$$-d[PCl_3]/dt = (k_1 + \frac{3}{2} k_{-1})[C][PCl_3] - \frac{3}{2} k_{-1}[C][PCl_3]_o \quad . \qquad \text{(III.29)}$$

If the substitutions $k_1' = k_1[C]$ and $k_{-1}' = \frac{3}{2} k_{-1}[C]$ are made in the above equation, then:

$$-d[PCl_3]/dt = (k_1' + k_{-1}')[PCl_3] - k_{-1}'[PCl_3]_o \quad . \qquad \text{(III.30)}$$

Integration of (III.30) yields:

$$\ln \frac{k_1'[PCl_3]_o}{(k_1' + k_{-1}')[PCl_3] - k_{-1}'[PCl_3]_o} = (k_1' + k_{-1}')t \quad . \qquad \text{(III.31)}$$

This equation can be simplified by introducing the equilibrium concentration $[PCl_3]_e$ which is derived by setting $-d[PCl_3]/dt = 0$, a relationship which applies only at equilibrium. Thus, at equilibrium equation (III.30) states that:

$$(k_1' + k_{-1}')[PCl_3]_e = k_{-1}'[PCl_3]_o \quad . \qquad \text{(III.32)}$$

The expression for $[PCl_3]_e$ is then given by:

$$[PCl_3]_e = \frac{k_{-1}'}{k_1' + k_{-1}'} [PCl_3]_o \quad . \qquad \text{(III.33)}$$

Equation (III.31) can then be written as:

$$\ln \left(\frac{[PCl_3]_o - [PCl_3]_e}{[PCl_3] - [PCl_3]_e}\right) = (k_1' + k_{-1}')t \quad . \qquad \text{(III.34)}$$

This is the integrated form of a first-order process with an effective rate constant $(k_1' + k_{-1}')$, which can be obtained from a plot of $\ln([PCl_3]-[PCl_3]_e)$ against time.

The integrated form of the rate equation for PBr_3 is obtained analogously to that for PCl_3. In this case, substitution for $[PBr_2Cl]$ in (III.21) is made from (III.25). The second term in the rate law thus obtained is simplified by the approximation:

$$[Br]_T - [PBrCl_2] \simeq [Br]_T \quad . \qquad \text{(III.35)}$$

Proceeding in exactly the same way as for PCl_3, the first-order integrated rate equation is derived:

$$\ln \left(\frac{[PBr_3]_o - [PBr_3]_e}{[PBr_3] - [PBr_3]_e}\right) = (k_2' + k_{-2}')t \quad . \qquad \text{(III.36)}$$

The effective first-order rate constant, $(k_2' + k_{-2}')$, is obtained from a plot of $\ln([PBr_3]-[PBr_3]_e)$ against time.

The only approximations that were necessary in the above derivations were those in (III.28) and (III.35). Obviously this approx-

imation is very good at the beginning of the reaction and gets progressively worse as $[PBr_2Cl]$ and $[PBrCl_2]$ increase. Both approximations are equally good when the initial concentrations of PBr_3 and PCl_3 are the same. The majority of samples prepared contained initial concentrations of PBr_3 and PCl_3 in the ratio of 0.4 to 0.6. For these samples, the approximation that $[Cl]_T-[PBr_2Cl] \simeq [Cl]_T$ is much better than the approximation that $[Br]_T-[PBrCl_2] \simeq [Br]_T$, because $[Cl]_T$ is larger than $[Br]_T$, and $[PBr_2Cl]$ is smaller than $[PBrCl_2]$. Nevertheless, even for samples with the largest differences in the initial concentration of PBr_3 and PCl_3, the worse of the two approximations yields a value which is less than 30% different from the true value, after the reaction has proceeded to 90% completion.

There is no easy way to obtain the integrated forms of the rate equations for PBr_2Cl and $PBrCl_2$. However, the experimental evidence indicates that both the $PBrCl_2$ and PBr_2Cl obey first-order kinetics, and that in fact more often than not the half-life for the reaction of $PBrCl_2$ is the same as that for PCl_3, and the half-life for the reaction of PBr_2Cl is the same as that for PBr_3. If the terms containing k_3 and k_{-3} in equations (III.22) and (III.23), for the rate laws of $PBrCl_2$ and PBr_2Cl, are small compared to the terms containing k_1 and k_{-1}, or k_2 and k_{-2}, then equations (III.22) and (III.23) simplify to the equations (III.20) and (III.21) respectively. In other words the rate of formation of $PBrCl_2$ is equal to the rate of disappearance of PCl_3 and the rate of formation of PBr_2Cl is equal to the rate of disappearance of PBr_3:

$$d[PBrCl_2]/dt = -d[PCl_3]/dt; \quad d[PBr_2Cl]/dt = -d[PBr_3]/dt \quad . \qquad \text{(III.37)}$$

Another way of looking at this result is that reaction (III.19), which involves the interconversion of $PBrCl_2$ to PBr_2Cl, is insignificant compared to reactions (III.17) and (III.18). In any case, the above rationale explains the experimental observations satisfactorily.

Having attempted to elucidate the rate law of the catalyzed reorganization in the PCl_3-PBr_3 system with respect to all the species involved, some possibilities as to the nature of the catalyst should be investigated. Experiments indicated that there is a marked increase in the rate of the reaction on addition of minute amounts of water. It is estimated that a total concentration of approximately 10.7 M in reactants is catalyzed by a concentration of water of less than 0.03 M to such an extent as to cause the half-life of the reaction to decrease from nearly eleven days at 70°C to less than two hours at 35°C. Hence, the nature of the catalyst could be of major importance.

The catalyst could be the water itself or, since the trihalides are easily hydrolyzed, one of the products or intermediates of hydrolysis. Most of the work on the hydrolysis of PCl_3 and PBr_3 has been carried out with excess water, the products being the corresponding hydrohalic acid and phosphorous acid:

$$PX_3 + 3H_2O \rightarrow H_3PO_3 + 3HX \qquad (X = Cl, Br) \quad . \qquad \text{(III.38)}$$

However, Blaser[152] indicated that a more complicated acid $H_4P_2O_5$ (diphosphorous or pyrophosphorous acid), was also formed. Goubeau and Schulz[153] showed that in excess PCl_3 the products of hydrolysis

are HCl, H_3PO_3, and $H_4P_2O_5$, together with some $POCl_3$ and a compound which analyzed for P_4O, and was termed phosphorus suboxide. In order to explain the presence of $POCl_3$ and P_4O, the authors postulated the formation of PCl_2OH by the partial hydrolysis of PCl_3. The PCl_2OH can then disproportionate according to the equation:

$$9PCl_2OH \rightarrow 5POCl_3 + P_4O + 3HCl + 3H_2O \quad . \qquad \text{(III.39)}$$

In fact, the authors postulated that the H_3PO_3 was formed by rearrangement of $P(OH)_3$, which was in turn obtained from the reorganization of PCl_2OH, according to the equation:

$$3PCl_2OH \rightarrow P(OH)_3 + 2PCl_3 \quad . \qquad \text{(III.40)}$$

The stepwise hydrolysis of PCl_3 to give PCl_2OH, $PCl(OH)_2$, and finally H_3PO_3 had been postulated first by Voigt[154] to explain the three breaks obtained in a plot of the temperature elevation in ether solutions of PCl_3 as a function of the volume of water added. The breaks corresponded to the addition of 1, 2, and 3 moles of water per 1 mole of PCl_3. Care had been taken to saturate the PCl_3 solutions with HCl in order to exclude the possibility of the temperature elevations being caused by the dissolution of the HCl, formed during the hydrolysis. The postulate that halogenated intermediates are formed in the hydrolysis of PCl_3 is not unreasonable, in view of the fact that there is evidence for such intermediates in the hydrolysis of PF_3.[155] In a series of papers concerned with the study of condensed phosphorous acids, Hossenlopp and Ebel[156,157,158,159,160] elucidated the

nature of the formation of $H_4P_2O_5$ from the reaction of PCl_3 or PBr_3 with H_3PO_3. The authors established that this reaction occurs reversibly:

$$5H_3PO_3 + PX_3 \rightleftarrows 3H_4P_2O_5 + 3HX \quad (X = Cl, Br) \quad . \qquad (III.41)$$

Moreover, it was shown that the equilibrium is displaced to the left in the case of PBr_3, in contrast to the PCl_3 case, in which the equilibrium is displaced to the right. This difference is due in large part to the greater solubility of HBr than HCl in phosphorous acid. It is worth mentioning at this point that PCl_3 and PBr_3 are only slightly soluble in the H_3PO_3-$H_4P_2O_5$ mixture, and that two distinct phases are formed.

The hydrolysis of PCl_3 or PBr_3 is clearly complex, and more work in this field is needed in order to clarify it. No rates have been reported for these reactions, although it appears that PBr_3 hydrolyzes more rapidly than PCl_3. In two separate experiments in which a small amount of water was allowed to react with large amounts of PCl_3 or PBr_3 in a sealed tube, the reaction seemed to occur within a few minutes, and a distinct, oily liquid was formed as a separate phase. For this reason, it is unlikely that the catalyst for the reorganization of PCl_3 with PBr_3 would be the pure water. In fact, if water were the catalyst, the rate of the reaction would decrease with time as the water concentration diminishes, due to hydrolysis. This is not consistent with the experimental results, which indicate a uniform behaviour throughout the reaction. This narrows down the catalyst to one or more of the products of hydrolysis, still a rather

large choice. The HCl and HBr, however, can be eliminated on the basis of experiments in which these compounds were added to the reactants without causing a detectable increase in the rate of the reaction. Finally, unstable intermediates such as PCl_2OH and $PCl(OH)_2$ or PBr_2OH and $PBr(OH)_2$, as well as the phosphorous acids should also be considered as potential catalysts.

It is still not completely clear why reproducible samples could not be made. None of the experiments performed to answer this question were conclusive. It is possible that the minute quantities of water are not being added quantitatively. In addition, it is possible that the catalysis may be heterogeneous because the reactants are not miscible with some of their hydrolysis products.

An interesting case of catalyzed reorganization on phosphorus when coordinated to platinum has recently been reported.[161] The coordination complex, $cis[(CH_3)_2NPF_2]_2PtCl_2$ is formed from $(CH_3)_2NPF_2$ and $PtCl_2$ at 60°C. However, on prolonged heating with excess $(CH_3)_2NPF_2$, the phosphorus ligand on platinum undergoes reorganization, whereas the $(CH_3)_2NPF_2$ ligand does not reorganize under the same conditions in the absence of $PtCl_2$:

$$4(CH_3)_2NPF_2 + PtCl_2 \rightarrow cis\{[(CH_3)_2N]_2PF\}_2PtCl_2 + 2PF_3 \quad . \qquad (III.42)$$

This result is also obtained when the initial complex is allowed to react with excess $(CH_3)_2NPF_2$. The authors postulated a mechanism whereby a third molecule of $(CH_3)_2NPF_2$ coordinates to the $cis[(CH_3)_2NPF_2]_2PtCl_2$ to form a five-coordinate intermediate. This undergoes exchange of

substituents on phosphorus and subsequently loses PF_3. Although this reaction is not an exact analogue to the present case, it does indicate that exchange may be favoured by a catalyst which brings the ligands close together on a site.

3. Equilibrium Studies in the PCl_3-PBr_3 System

The equilibrium constant for the reaction of PCl_3 with PBr_3 to yield PBr_2Cl and $PBrCl_2$ is given by the expression:

$$K = [PBr_2Cl][PBrCl_2]/[PCl_3][PBr_3] \quad . \qquad \text{(III.43)}$$

A preliminary study indicated that the value of the equilibrium constant was 4.5 at 35°C. The value quoted by Fluck and co-workers[22] was 7.1 at 25°C. This discrepancy prompted a systematic study of the equilibrium constant, and its variation with temperature.

All the studies on the value of the equilibrium constant were carried out on samples that had been used for kinetic investigations. In fact, the infinite time measurements of kinetic runs provided a large number of data at 35°C. The results are given in Appendix B in Tables BI to BVI, which contain the data for the equilibrium constant at 35°C, 37°C, 40.5°C, 50°C, and 70°C respectively. The upper limit of the temperature used was determined by the fact that above 70°C the signal-to-noise ratio of the nmr spectrum became rather small, and the lower limit by the fact that the reactions took too long to equilibrate below 35°C.

As in the kinetic studies, the concentration of each species at equilibrium is given in units of mole fraction. Two or more scans at equilibrium were taken in order to obtain average mole fractions, from which the equilibrium constant was calculated. In Tables BI to BVI the range for the value of each equilibrium constant is indicated rather than the error for that value. This is given by the smallest

and largest value of the equilibrium constant, calculated from the individual scans.

The average equilibrium constants for each temperature, computed from all the values obtained, are given in Table XI. Again the range on each equilibrium constant is given by the smallest and largest value in the list. The variation of the equilibrium constant with temperature is quite small.

The relationship between the equilibrium constant and the thermodynamic paramaters for a reaction have already been given in the introduction:

$$\ln K = -\Delta H^{\circ}/RT + \Delta S^{\circ}/R \quad . \qquad \text{(III.44)}$$

A plot of lnK against 1/T, in $^{\circ}K^{-1}$, should yield a straight line, whose slope and intercept are given by $-\Delta H^{\circ}/R$ and $\Delta S^{\circ}/R$ respectively. Figure 12 is a semilogarithmic plot of K against $10^3/T$ for the values in Table XI. The vertical lines indicate the range for the equilibrium constant at each temperature. The data were fitted to equation (III.45) with a non-linear least-squares programme.[162]

$$K = \exp(-\Delta H^{\circ}/RT)\exp(\Delta S^{\circ}/R) \quad . \qquad \text{(III.45)}$$

The best-fit values of the equilibrium constant are given in Table XI. From the slope and intercept of the line, the values of ΔH° and ΔS° are 956 cal mol^{-1} and 5.93 eu respectively. By drawing lines of maximum positive and negative slope, encompassing the entire range of equilibrium constants, the lower and upper limits for the enthalpy change

TABLE XI

Variation of the Equilibrium Constant with Temperature for the PCl_3-PBr_3 System

T(°C)	$10^3/T(°K^{-1})$	Ave K_{obsd} [a]	K_{calcd} [b]
35.0	3.25	4.06^{25} (3.29 → 4.65)	4.14
37.0	3.22	4.09^{9} (3.42 → 4.80)	4.20
40.5	3.19	4.39^{11} (3.83 → 5.08)	4.27
50.0	3.10	4.71^{5} (4.17 → 5.17)	4.45
60.0	3.00	4.62^{5} (3.68 → 5.14)	4.67
70.0	2.92	4.78^{6} (3.78 → 5.34)	4.86

[a] This refers to the number of samples whose equilibrium constants were used to obtain the average value.

[b] From a least-squares fit analysis.

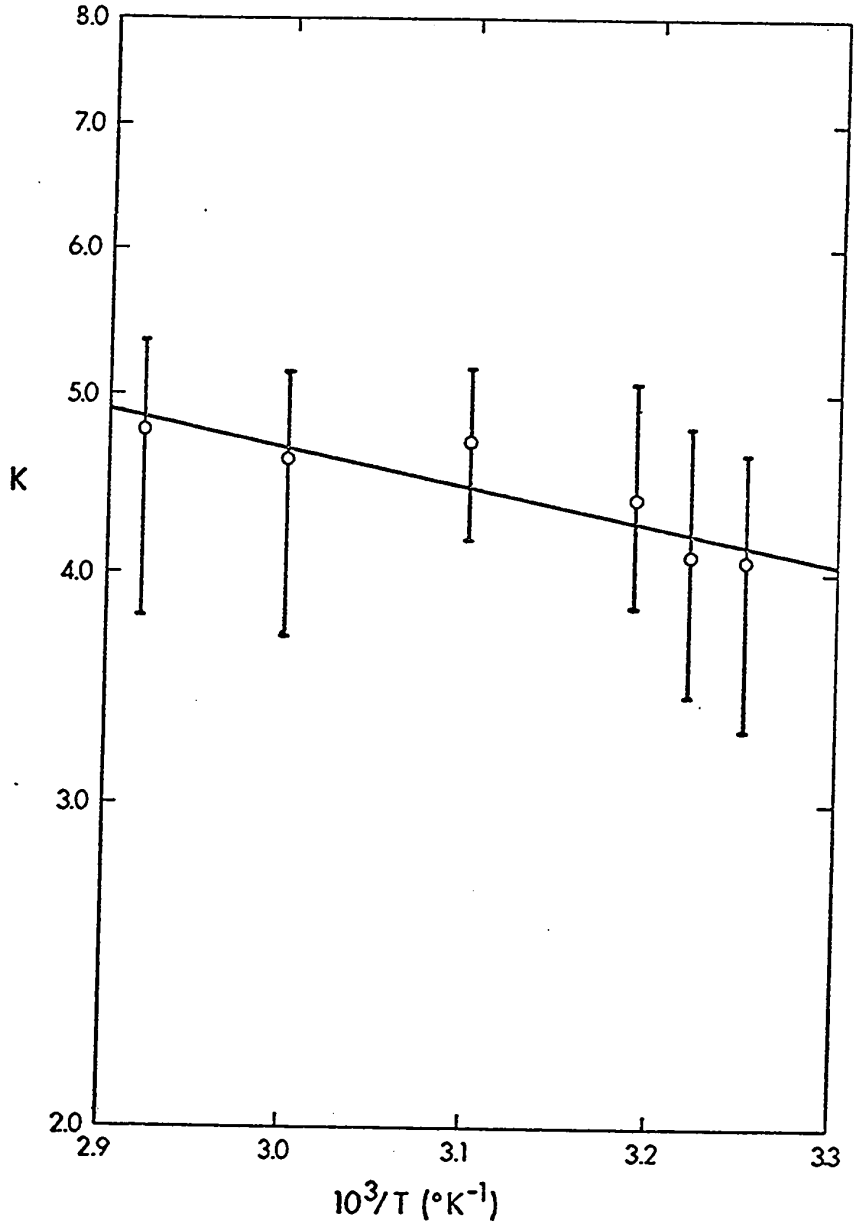


Figure 12: Temperature variation of logK for the PCl_3-PBr_3 system.

and the entropy change are obtained. Hence ΔH^{o} = 956(-1233 → 2445) cal mol^{-1} and ΔS^{o} = 5.93(-0.96 → 10.47) eu.

The results indicate that the reaction is only slightly endothermic and that, within the range of values obtained, it can be considered essentially thermoneutral. This reaction is therefore very close to being a random reorganization reaction. The equilibrium constant for the random reorganization of this system, calculated from the statistical distribution of all the species, is 9. The equilibrium constant of a random reorganization reaction is governed only by the $\Delta S^{o}/R$ term, hence ΔS^{o} = 4.37 eu for K = 9. The experimental value of 5.93 eu obtained for this system agrees quite well with the value calculated for random reorganization.

The thermodynamic functions in the temperature range 200-2000°K have been calculated[163] for PBr_3, PCl_3, PBr_2Cl, and $PBrCl_2$. The calculations have been made for the ideal gases at one atmosphere pressure, on the basis of a rigid rotator and harmonic oscillator model. At 300°K the enthalpy functions, $(H^{o}-H_{o}^{o})/T$, for PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 are 14.21, 13.81, 13.32, and 12.79 cal mol^{-1} deg^{-1} respectively. The corresponding entropies, S^{o}, are 83.02, 82.56, 79.74, and 74.44 eu respectively.

The enthalpy and entropy changes for the reaction of PBr_3 and PCl_3 to give PBr_2Cl and $PBrCl_2$ are calculated to be 39 cal mol^{-1} and 4.73 eu respectively. Again, these values are within the error range of the experimental values.

The reason for the discrepancy between the equilibrium constant

obtained in this study and that quoted by Fluck and co-workers[22] is probably due to the difference in the techniques used to determine the mole fractions of the species. It is believed that the figures quoted in this study are the more reliable ones, in view of the technique used and the number of determinations made.

4. Kinetic Studies of the CF_3PCl_2-CF_3PBr_2 System

The redistribution reaction of CF_3PBr_2 and CF_3PCl_2 has not been investigated previously. This project was originally undertaken in order to investigate the effect of substitution of one of the halogen positions in P(III) halides on the kinetics of the redistribution reaction. Preliminary experiments indicated that the reaction could be followed by the change in the ^{19}F nmr spectrum of the system with time. The preparation of samples, kinetic procedures, and technical aspects in this system are similar to those for the PCl_3-PBr_3 system, and have been discussed previously.

The reaction of CF_3PCl_2 and CF_3PBr_2 coming to equilibrium is simple in that only one product is formed:

$$CF_3PCl_2 + CF_3PBr_2 \rightleftarrows 2CF_3PBrCl \ . \qquad \text{(III.46)}$$

The (CF_3) groups do not exchange, as evidenced by the absence of $(CF_3)_2PCl$, $(CF_3)_2PBr$, and $(CF_3)_3P$. This was also proved by mixing equimolar quantities of $(CF_3)_2PCl$ and $(CF_3)_2PBr$ in a sealed nmr tube. After one year at room temperature no new products were detected.

The ^{19}F chemical shifts and P-F coupling constants for CF_3PBr_2 (ϕ = 67.8 ppm; J = 69.6 Hz) and CF_3PCl_2 (ϕ = 72.1 ppm; J = 79.9 Hz) in $CFCl_3$ solution have been reported.[164] The ^{19}F chemical shifts and P-F coupling constants were determined for CF_3PBr_2 (ϕ = 67.8 ppm; J = 69.5 Hz), CF_3PBrCl (ϕ = 70.0 ppm; J = 74.5 Hz) and CF_3PCl_2 (ϕ = 72.0 ppm; J = 80.5 Hz) in a mixture of these three compounds in the neat liquid. All values of chemical shifts are upfield relative to $CFCl_3$.

Because there is only one reaction leading to the exchange of substituents on phosphorus, as represented by equation (III.46), the kinetics of this system can be studied over all the reaction. Hence, the half-life of a reaction is truly the half-life of reaction (III.46). Therefore, the study of the exchange between CF_3PCl_2 and CF_3PBr_2 is much simpler than that between PCl_3 and PBr_3. Preliminary experiments on samples which had been prepared on a grease-lubricated system indicated that the reaction had reached equilibrium in a few hours. The systematic study of the reaction was started after it had been established that water was a catalyst for the exchange between PCl_3 and PBr_3, thus all the samples studied here were prepared on a grease-free system.

The concentration-time data for samples 1 to 6 are given in Appendix C in Tables CI to CVI respectively. Since the reactants cannot be weighed, their initial molar concentrations are unknown. However, these may be determined from the spectra of the sample after they have been recorded. Initial mole fractions can be estimated from the first spectrum scanned, but the results are not accurate if the reaction is fast. A much better method is to calculate the total chlorine content of the sample, Cl_T, from the mole fractions of the chlorine containing species in a spectrum of the sample at equilibrium, according to:

$$Cl_T = 2N_{CF_3PCl_2} + N_{CF_3PBr_2} \quad , \qquad \text{(III.47)}$$

where N denotes mole fractions.

The initial mole fraction of CF_3PCl_2, $iN_{CF_3PCl_2}$, is then given by:

$$iN_{CF_3PCl_2} = Cl_T/2 \quad . \qquad \text{(III.48)}$$

The initial mole fraction of CF_3PBr_2, $iN_{CF_3PBr_2}$, is obtained by subtraction of $iN_{CF_3PCl_2}$ from unity.

Molar concentrations of the reactants can be calculated from their initial mole fractions, their molecular weights, their densities, and the total volume of liquid. Since the densities of CF_3PCl_2 and CF_3PBr_2 have not been reported, they were determined from 20°C to 69°C in ten degree intervals. The variation of the density with temperature is given in Table XII, for CF_3PCl_2 and Table XIII, for CF_3PBr_2.

The first experiment performed on this system was designed to find out if water had the same catalytic effect on the CF_3PCl_2-CF_3PBr_2 exchange as it had on the PCl_3-PBr_3 exchange. Sample 1, containing equimolar quantities of CF_3PCl_2 and CF_3PBr_2, reacted with a half-life of 65 min at 40°C. Another sample, prepared on the same day as sample 1 and containing the same quantities of reactants and 0.01 ml water, reached equilibrium within 25 min at 40°C. This experiment indicated that water or the products of the hydrolysis of the compounds were catalyzing the reaction. Thus, the same problems that had been encountered for the PCl_3-PBr_3 system were probably present in the CF_3PCl_2-CF_3PBr_2 system.

Next, the reproducibility of results in the absence of added water was checked. Samples 2 and 3, each containing the same amounts of reactants, were prepared. However, the half-life of the reaction

TABLE XII

Variation of Density with Temperature for CF_3PCl_2

T(°C)	vp[a] (mm)	Height$_l$[b] (cm)	Volume$_l$[c] (ml)	Weight$_l$[d] (g)	Density (g ml^{-1})
20.15	369	4.697	0.1942	0.3055	1.573
29.90	520	4.760	0.1968	0.3052	1.551
39.40	757	4.841	0.2002	0.3047	1.522
51.00	1114	4.934	0.2040	0.3041	1.491
59.15	1445	4.994	0.2065	0.3035	1.470
69.35	2026	5.064	0.2094	0.3026	1.445

[a] $\log P = 4.229 + 1.75 \log T - 0.002743T - 1516/T$.[165]

[b] Height of tube is 10.60 cm.

[c] The volume occupied by 1 cm of liquid in the tube is 0.04135 ml.

[d] The original weight of the liquid, 0.3063 g, is corrected for the amount that goes into the vapour.

TABLE XIII

Variation of Density with Temperature for CF_3PBr_2

T(°C)	vp[a] (mm)	Height$_l$[b] (cm)	Volume$_l$[c] (ml)	Weight$_l$[d] (g)	Density (g ml^{-1})
20.85	64.4	1.736	0.0718	0.1607	2.238
30.00	96.2	1.753	0.0725	0.1606	2.215
39.40	143.0	1.768	0.0731	0.1604	2.194
48.90	208.2	1.784	0.0738	0.1602	2.171
59.20	305.2	1.795	0.0742	0.1598	2.154
69.00	429.0	1.818	0.0752	0.1594	2.120

[a] $\log P = 3.8579 - 0.00206T + 1.75 \log T - 1694.74/T$.[166]

[b] Height of tube is 8.92 cm.

[c] The volume occupied by 1 cm of liquid in the tube is 0.04135 ml.

[d] The original weight of the liquid, 0.1610 g, is corrected for the amount that goes into the vapour.

was approximately 11.5 hr for sample 2 and 104 min for sample 3 at 42°C. In another set of experiments three samples, containing the same quantities of reactants as samples 2 and 3, were prepared. Samples 4 and 5 reacted with a half-life of 43 hr and 48 hr respectively, but sample 6 attained equilibrium within a few minutes at 42°C.

No further attempts were made to obtain reproducible results. and the lower limit of the half-life of the reaction is quoted as 48 hr at 42°C. The reaction was not studied as a function of water concentration, nor was any attempt made to isolate the specific catalyst involved in the reaction.

An anomaly was noticed for the reaction in sample 4. The results indicate that the reaction had attained equilibrium in 1.5 days since no change was observed for 29.5 days after that period. However, the equilibrium constant for the reaction of CF_3PCl_2 with CF_3PBr_2 to yield CF_3PBrCl is considerably lower than the average value, obtained from other samples. The value obtained for sample 4 was 2.26, whereas other samples indicate that the value lies between 2.64 and 2.99 at 42°C. The same anomaly is indicated for sample 5, whose reaction seems to have reached equilibrium in 14.8 days. The concentration of the species remain the same after 31 days, but the equilibrium constant is 2.16. This is a large deviation, in view of the accuracy with which the equilibrium constant for this reaction can be determined. Because this discrepancy was only noticed for the slowest reactions studied, the most likely explanation that can be given is that the catalyst has been consumed by some other reaction.

Similar mechanistic arguments to those discussed for the PBr_3-PCl_3 exchange can be applied in an analogous manner to the CF_3PCl_2-CF_3PBr_2 exchange. However, the chemistry of these compounds is quite new and little evaluation of the possibilities of ionic, radical, or bridged mechanisms can be made.

In order to check for the possibility of the reaction being first-order with respect to each species, as was observed for the PCl_3-PBr_3 exchange, the analogous first-order plots were made for all the samples. Unlike the PCl_3-PBr_3 system, only one sample obeyed first-order kinetics. The integrated form of the rate equation for a reversible second-order reaction as written in equation (III.46) has been solved.[167] The necessary plot required to give a straight line, if this mechanism is obeyed, was performed for the data of two samples. Sample 3 gave a straight line, while sample 1 did not. Not much faith is placed in this plot, because it is extremely sensitive to very small changes in the value of the equilibrium constant.

Catalysts of a similar nature to those of the PCl_3-PBr_3 system could be involved in this system. The hydrolysis of CF_3PCl_2 and CF_3PBr_2 yield the corresponding hydrohalic acid and $CF_3P(OH)_2$:[168]

$$CF_3PX_2 + 2H_2O \rightarrow CF_3P(OH)_2 + 2HX \quad (X = Cl, Br) \; . \qquad (III.49)$$

Although the water is immiscible with the reactants, the hydrolysis proceeds to yield a homogeneous solution.

5. Equilibrium Studies in the CF_3PCl_2-CF_3PBr_2 System

The equilibrium constant for the reaction of CF_3PCl_2 with CF_3PBr_2 to yield CF_3PBrCl is given by the expression:

$$K = [CF_3PBrCl]^2/[CF_3PBr_2][CF_3PCl_2] \quad . \qquad \text{(III.50)}$$

No value for this equilibrium constant has been quoted to date.

The variation of the equilibrium constant with temperature was studied for a sample that had been prepared on the grease-lubricated system. The reaction in this sample had proceeded to completion in a few hours at 25°C. The equilibrium constant was determined for increasing temperatures and decreasing temperatures several times. The temperature ranged from 25°C to 60°C. Additional data was obtained from the infinite time measurements of kinetic runs at 42°C.

The results are given in Appendix D in Tables DI and DII. Two or more scans at equilibrium were taken in order to obtain average mole fractions, from which the equilibrium constant was calculated. The error on each value is indicated by the smallest and largest values, calculated from the individual scans.

The average equilibrium constant for each temperature, calculated from all the values obtained, are given in Table XIV. Again, the range of each equilibrium constant is given by the smallest and largest values in the list.

The semilogarithmic plot of K against $10^3/T$, from which the thermodynamic parameters ΔH° and ΔS° can be obtained, has been explained in detail for the PCl_3-PBr_3 system. This plot for the CF_3PCl_2-CF_3PBr_2

TABLE XIV

Variation of the Equilibrium Constant with Temperature for the CF_3PCl_2-CF_3PBr_2 System

T(°C)	$10^3/T(°K^{-1})$	Ave K_{obsd}[a]	K_{calcd}[b]
25.0	3.36	2.70 (2.58 → 2.79)	2.75
30.0	3.30	2.77 (2.76 → 2.78)	2.77
40.0	3.19	2.96 (2.76 → 3.29)	2.82
42.0	3.17	2.81 (2.64 → 2.99)	2.83
50.0	3.10	2.83 (2.70 → 3.08)	2.85
60.0	3.00	2.86 (2.54 → 3.06)	2.90

[a] The average over all values at a particular temperature.

[b] From a least-squares fit analysis.

system is given in Figure 13. The vertical lines indicate the range of the equilibrium constant at each temperature and the line drawn through the data is the least-squares best-fit line. The latter is computed in the same way as for the PCl_3-PBr_3 system, and the computed values of the equilibrium constants are given in Table XIV. The thermodynamic parameters were calculated for the best-fit line, and their lower and upper limits were calculated for the lines drawn with maximum positive and negative slopes through the entire range of equilibrium constants. Hence, $\Delta H^\circ = 286$ (-39 → 715) cal mol^{-1} and $\Delta S^\circ = 2.97$ (0.72 → 4.25) eu.

The results indicate that the reaction is thermoneutral, within the experimental error. The equilibrium constant for the random reorganization of this system, calculated from the statistical distribution of all the species, is 4. The entropy of mixing corresponding to this equilibrium constant is 2.76 eu. The experimental value of 2.97 eu is in good agreement with the value calculated for random reorganization.

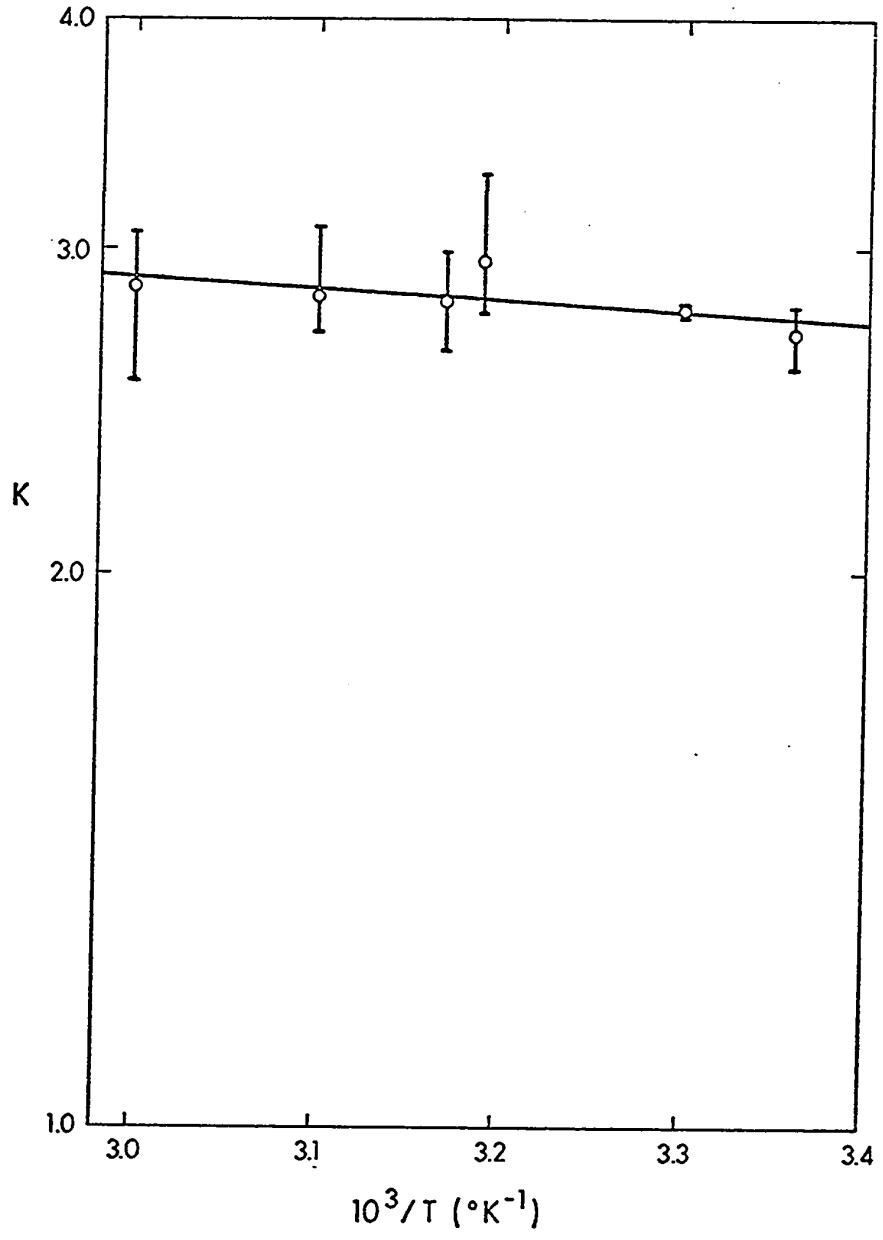


Figure 13: Temperature variation of logK for the CF_3PCl_2-CF_3PBr_2 system.

CHAPTER IV

RESULTS AND DISCUSSION OF NUCLEAR MAGNETIC RELAXATION STUDIES

In this chapter the results of the nuclear magnetic relaxation measurements on the series of compounds PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 will be presented and interpreted. The samples used were prepared in a grease-free vacuum system. The method for the preparation of the samples, together with the experimental procedure and the treatment of the raw data have been fully described in the chapter on experimental techniques.

The studies of the ^{31}P relaxation times were carried out for two samples which contained different concentrations of the four species. One sample, with initial mole fractions of 0.37 and 0.63 for PBr_3 and PCl_3 respectively, was allowed to reach equilibrium before being studied. The mole fractions of PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 at equilibrium were 0.10, 0.26, 0.33, and 0.31 respectively. The other sample, containing mole fractions of 0.31 and 0.69 for PBr_3 and PCl_3 respectively, was studied in the absence of PBr_2Cl and $PBrCl_2$. This sample was kept frozen in liquid nitrogen between measurements, and only trace amounts of PBr_2Cl and $PBrCl_2$ were detected on completion of the project. The same samples were used for the measurements of both the transverse and longitudinal relaxation times.

The studies of the ^{35}Cl relaxation time in PCl_3 were carried out for a sample containing mole fractions of 0.40 and 0.60 for PBr_3 and PCl_3 respectively, and for a sample containing only PCl_3.

1. ^{35}Cl Transverse Relaxation

There are two isotopes of chlorine, ^{35}Cl and ^{37}Cl, whose natural abundance is 75.4% and 24.6% respectively. Both chlorine isotopes have a nuclear spin of 3/2, therefore they possess a non-zero quadrupole moment. As has been pointed out in the introduction, relaxation of nuclei possessing a quadrupole moment occurs predominantly by a quadrupolar interaction mechanism. For covalently bonded nuclei, such as in PCl_3, this mechanism is especially effective and the values of $1/T_2$ are large. Because of the larger isotopic abundance and greater sensitivity of the ^{35}Cl over the ^{37}Cl nuclei, the chlorine relaxation rate in PCl_3 was measured for the ^{35}Cl nucleus.

The values of $1/T_2$ as a function of temperature for a sample containing neat PCl_3 are given in Table XV. Repetitive measurements indicated that the reproducibility of these values is approximately ±5%. The data are plotted as $\log(1/T_2)$ against $10^3/T$, in $°K^{-1}$, in Figure 14. The points lie on a straight line, whose slope yields an apparent activation energy for the relaxation process of 1.81 kcal mol^{-1}. The temperature dependence of $1/T_2$ is in agreement with the theory presented in the introduction; it was shown that for a quadrupolar interaction mechanism $1/T_2$ is proportional to τ_Q, which according to the Debye-BPP theory increases as the temperature decreases. The extrapolated value of $1/T_2$ at 25°C is $(22.7 \pm 1.1)\times10^3$ sec^{-1}. This value is slightly larger than the value of $(16.7 \pm 1.4)\times10^3$ sec^{-1} at 26°C obtained by Johnson, Hunt, and Dodgen.[169]

In order to obtain the ^{35}Cl relaxation rate in a medium of the

TABLE XV

Variation of $1/T_2$ with Temperature for ^{35}Cl in PCl_3

T(°C)	$10^3/T(°K^{-1})$	$1/T_2{}^a(sec^{-1})$	$1/T_2{}^b(sec^{-1})$
29.4	3.306	$20.9x10^3$	-
41.8	3.176	$19.7x10^3$	-
46.0	3.134	$18.1x10^3$	$20.0x10^3$
71.0	2.906	$15.3x10^3$	$17.2x10^3$

[a] Determined in neat PCl_3.

[b] Determined in a mixture of PCl_3 and PBr_3 of approximate mole fractions 0.4 and 0.6 respectively.

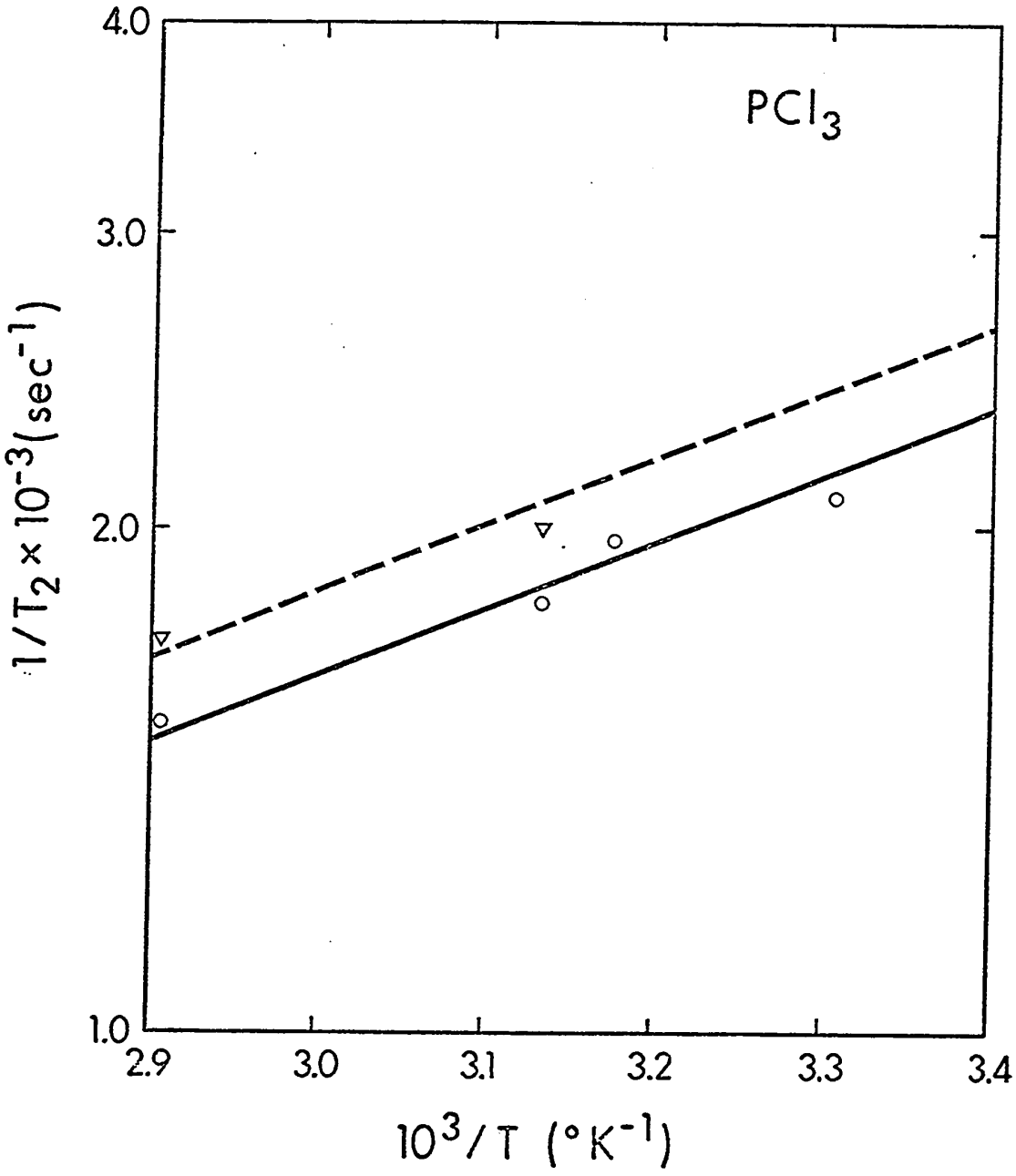


Figure 14: Temperature variation of $\log(1/T_2)$ for ^{35}Cl in PCl_3: in neat PCl_3, (O), and in a mixture of PCl_3 and PBr_3, (∇).

same viscosity as that in which the phosphorus relaxation rates were determined, the ^{35}Cl relaxation rate in PCl_3 was determined for a sample containing an appropriate mixture of PCl_3 and PBr_3. Due to the decrease in the signal intensity, only the higher temperature measurements could be made with reasonable accuracy. The values of $1/T_2$ are given in Table XV, and they are plotted as $\log(1/T_2)$ against $10^3/T$, in $°K^{-1}$, in Figure 14. Assuming that the ^{35}Cl relaxation process in the mixture of PCl_3 and PBr_3 occurs with the same activation energy as the relaxation process in pure PCl_3, a straight line may be drawn through the points. This assumption is justifiable in view of the close agreement of this activation energy with that obtained from the phosphorus relaxation rate measurements. The extrapolated value of $1/T_2$ at 25°C is $(25.3 \pm 1.3)\times10^3$ sec^{-1}.

From equation (I.24), the contribution to the relaxation rate due to a quadrupolar mechanism for a nucleus with a spin of 3/2, is given by:

$$\frac{1}{T_{2Q}} = \frac{1}{10}\left(1 + \frac{\tilde{\eta}^2}{3}\right)\left(\frac{e^2qQ}{\hbar}\right)^2 \tau_Q \quad . \qquad \text{(IV.1)}$$

The ^{35}Cl quadrupole coupling constant in solid PCl_3 is -52.3 MHz.[170] If it is assumed that this value applies for the liquid, and that the asymmetry parameter may be taken as zero, the value of τ_Q may be calculated. At 25°C, using the value of 25.3×10^3 sec^{-1} for $1/T_{2Q}$, the value of τ_Q is 2.34×10^{-12} sec.

Bromine also has two isotopes, ^{79}Br and ^{81}Br, with a natural abundance of 50.6% and 49.4% respectively. Each bromine isotope

has a nuclear spin of 3/2, thus a quadrupolar interaction mechanism dominates the relaxation of bromine nuclei. The value of $1/T_{2Q}$ for ^{79}Br in PBr_3 in the mixture of PBr_3 and PCl_3, which was used to obtain $1/T_{2Q}$ for ^{35}Cl in PCl_3, may be calculated from equation (IV.1). The ^{79}Br quadrupole coupling constant in solid PBr_3 is 439.2 MHz.[170] The same assumptions as before are made, and using the value of τ_Q calculated from the chlorine data, the value of $1/T_{2Q}$ for ^{79}Br in PBr_3 is 17.8×10^5 sec^{-1} at 25°C.

The assumption that τ_Q for PBr_3 is the same as τ_Q for PCl_3 is not strictly correct according to the Debye-BPP equation. Although the viscosity is uniform, the hydrodynamic radius of PBr_3 is somewhat different from that of PCl_3. However, in view of the fact that the Debye-BPP equation has not been particularly successful in predicting the reorientational correlation time in systems such as this[169], the correlation time for all the species may be assumed to be the same to a first approximation.

2. ^{31}P Transverse Relaxation

The results of the ^{31}P transverse relaxation rate in PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 as a function of temperature are given in Appendix E. The values of $1/T_2$ for PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 for the sample containing all four species are given in Tables EI to EIV respectively. The values of $1/T_2$ for PBr_3 and PCl_3 for the sample containing just these two species are given in Tables EV and EVI respectively. The errors in the values of $1/T_2$ are estimated as approximately ± 1.5 sec^{-1}, and are based on the error in measuring the linewidths.

In order to convert the measurements of the linewidths at half-maximum intensity into units of Hz, for the calculation of $1/T_2$, a calibration of the spectra in Hz per cm was necessary. The chemical shifts of PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 in a sample containing P_4O_6 in a capillary tube were determined from 30°C to 80°C. The results given in Table XVI indicate that although the absolute values of the chemical shifts vary with temperature, the chemical shift differences between the various species remain constant within the experimental error. Linewidth measurements for all species were taken directly from the observed spectra, using the average chemical shift difference of 158 Hz between PBr_3 and $PBrCl_2$ to calibrate the spectra. Similarly, spectra showing only PBr_3 and PCl_3 were calibrated for the purposes of linewidth calculations by the average chemical shift difference of 376 Hz between the latter two species.

The data for each species are presented in Figures 15 to 20 in

TABLE XVI

Variation of ^{31}P Chemical Shifts[a] with Temperature for PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3

T(°C)	δ_{PBr_3} (Hz)	δ_{PBr_2Cl} (Hz)	δ_{PBrCl_2} (Hz)	δ_{PCl_3} (Hz)
80.0	4685	4655	4528	4310
80.0	4684	4655	4529	4308
70.0	4682	4653	4526	4305
70.0	4682	4654	4526	4307
70.0	4680	4650	4521	4303
70.0	4681	4651	4651	4306
60.0	4677	4647	4519	4300
60.0	4676	4647	4519	4299
50.0	4675	4646	4517	4296
50.0	4674	4644	4516	4297
40.0	4671	4642	4513	4293
40.0	4672	4642	4513	4296
30.0	4670	4640	4511	4294
30.0	4670	4641	4511	4294

[a] Downfield from P_4O_6.

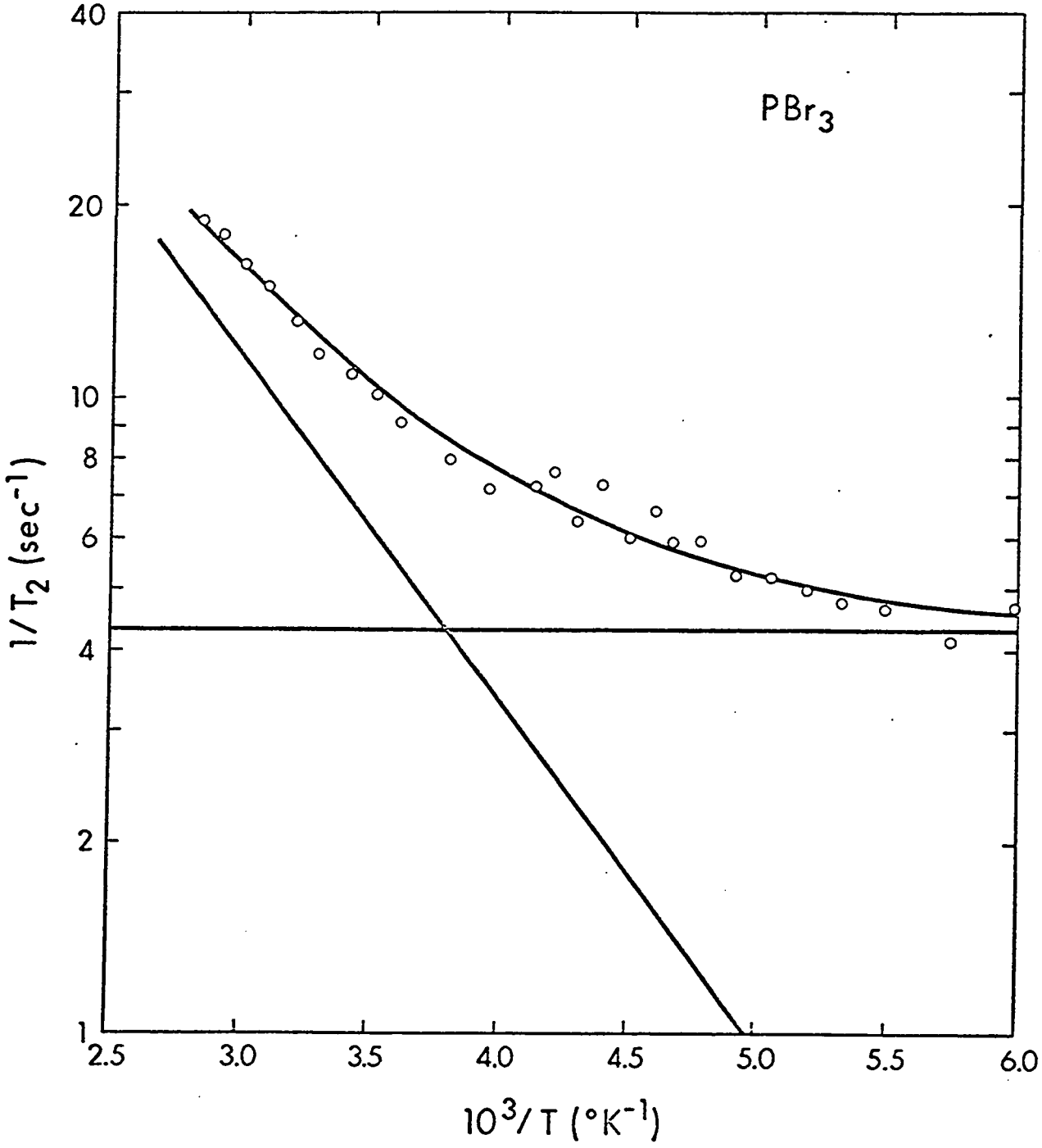


Figure 15: Temperature variation of $\log(1/T_2)$ for ^{31}P in PBr_3, in a sample containing PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3.

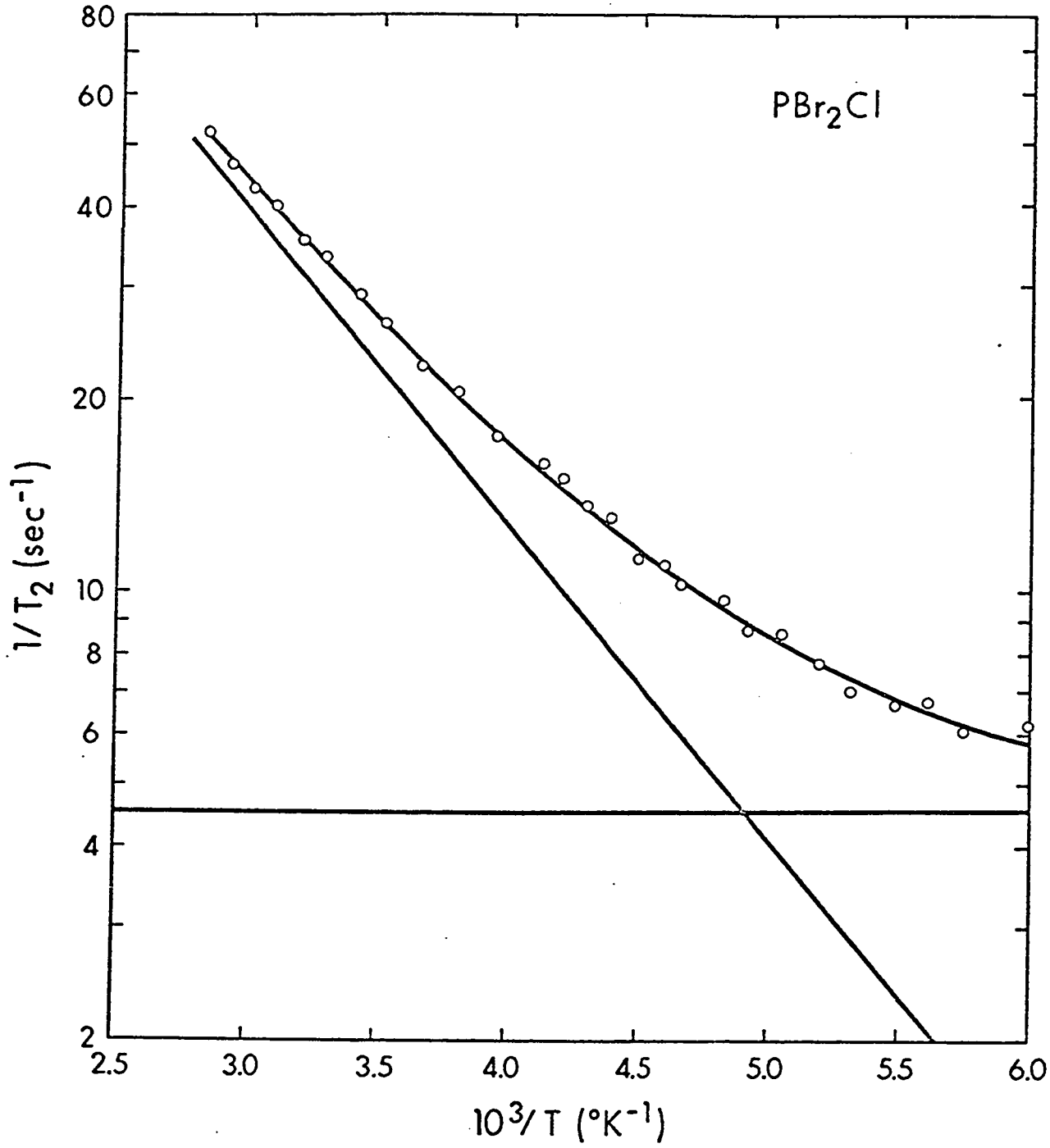


Figure 16: Temperature variation of $\log(1/T_2)$ for ^{31}P in PBr_2Cl, in a sample containing PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3.

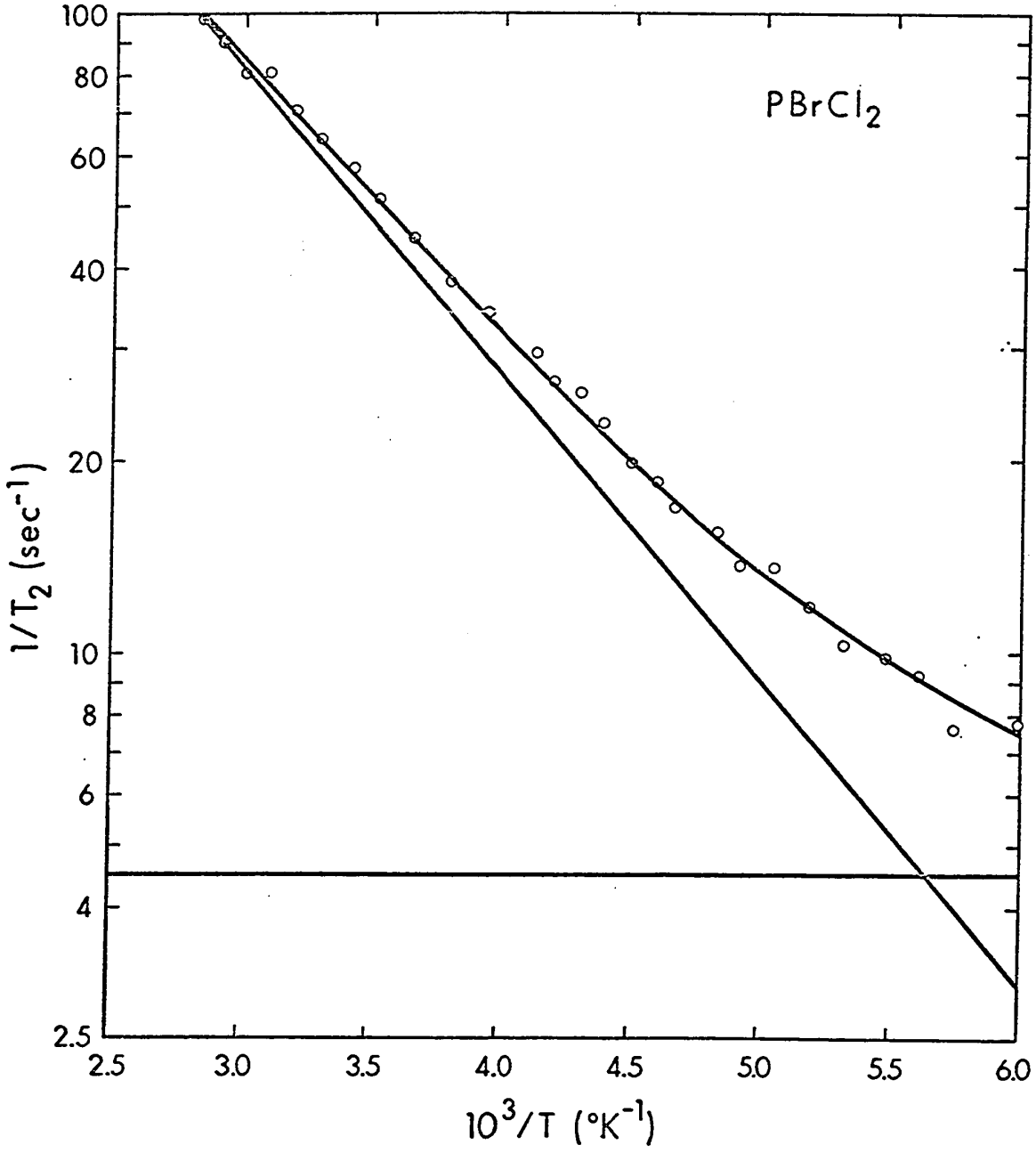


Figure 17: Temperature variation of $\log(1/T_2)$ for ^{31}P in $PBrCl_2$, in a sample containing PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3.

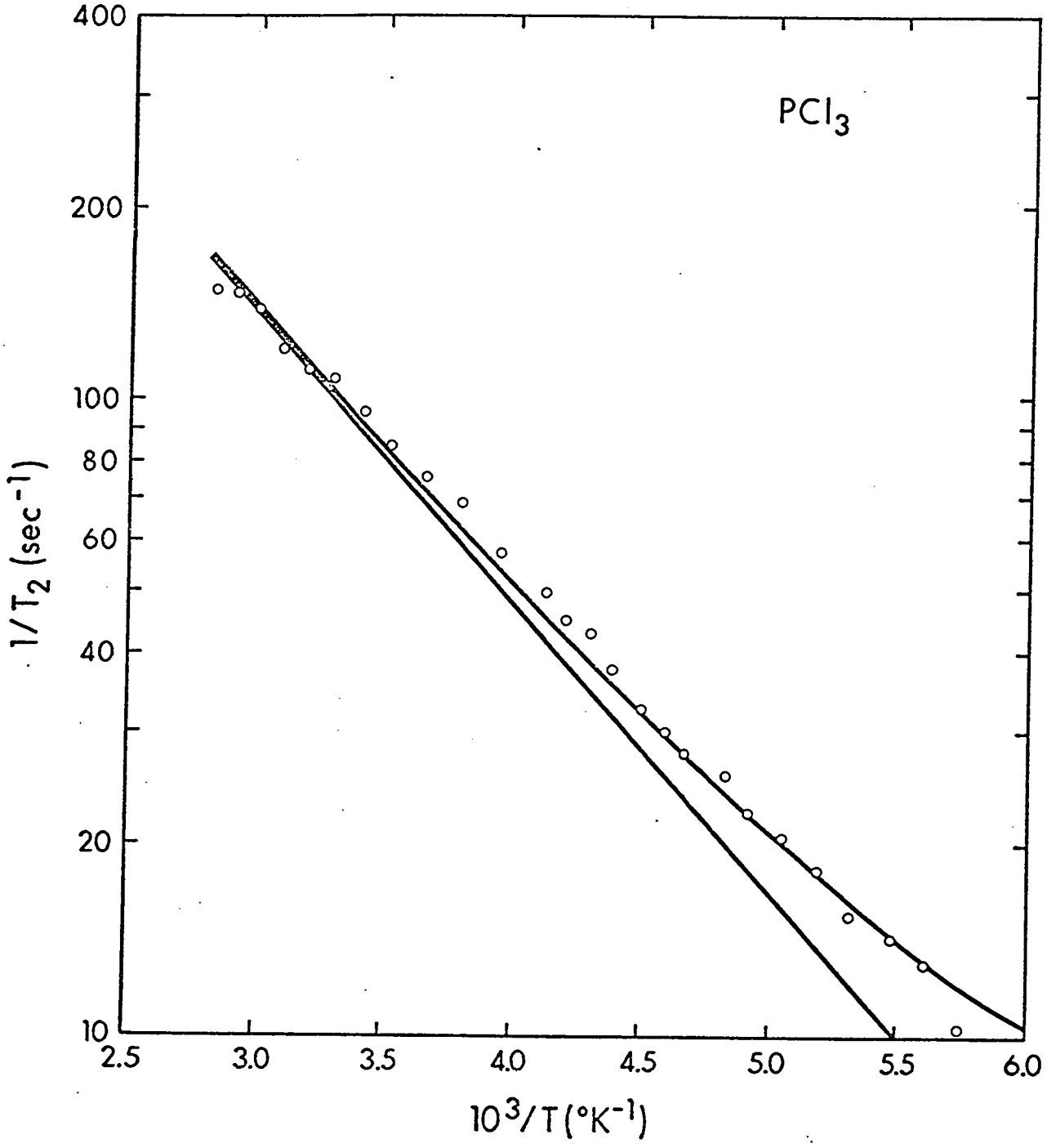


Figure 18: Temperature variation of $\log(1/T_2)$ for ^{31}P in PCl_3, in a sample containing PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3.

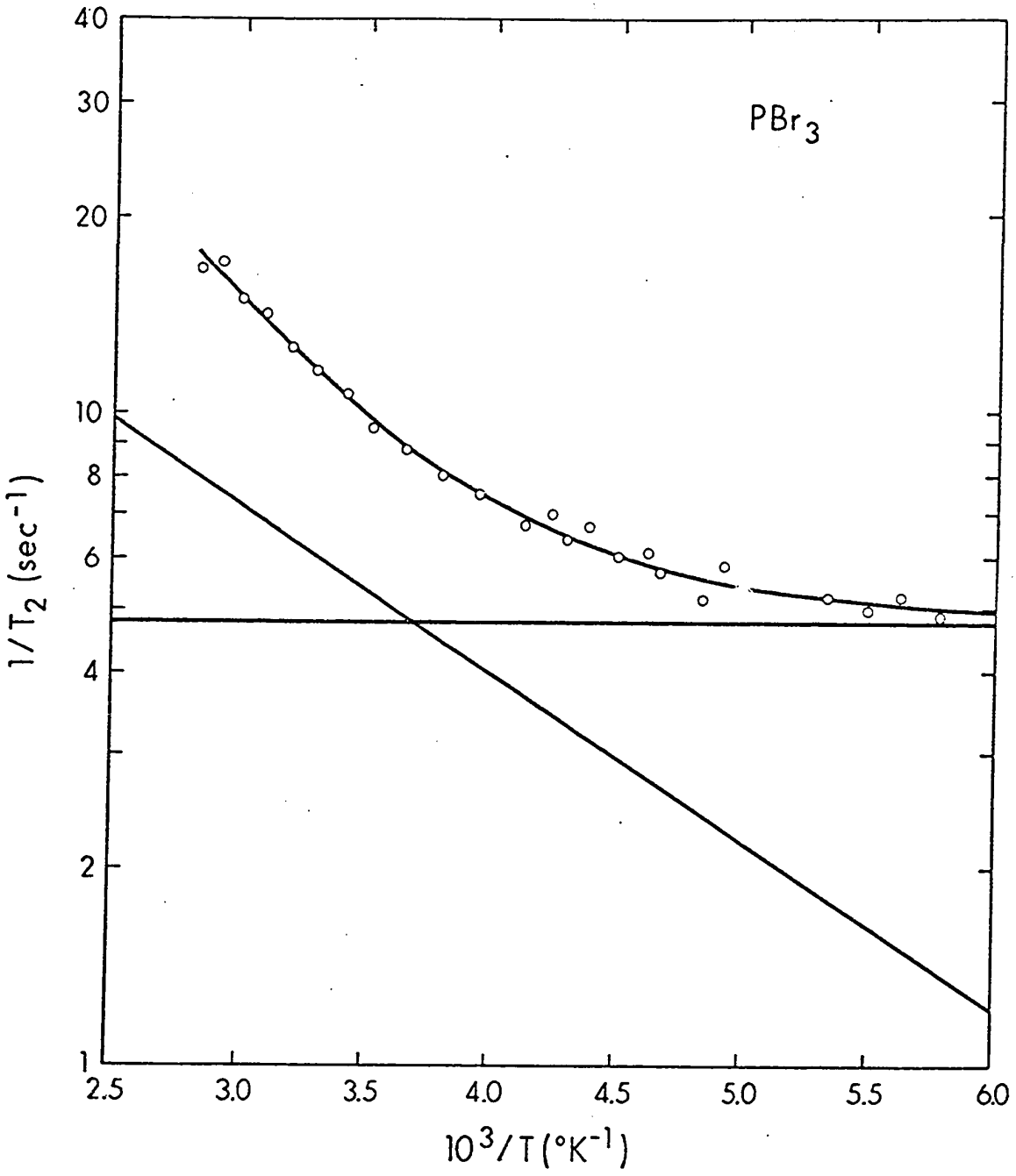


Figure 19: Temperature variation of $\log(1/T_2)$ for ^{31}P in PBr_3, in a sample containing PBr_3 and PCl_3.

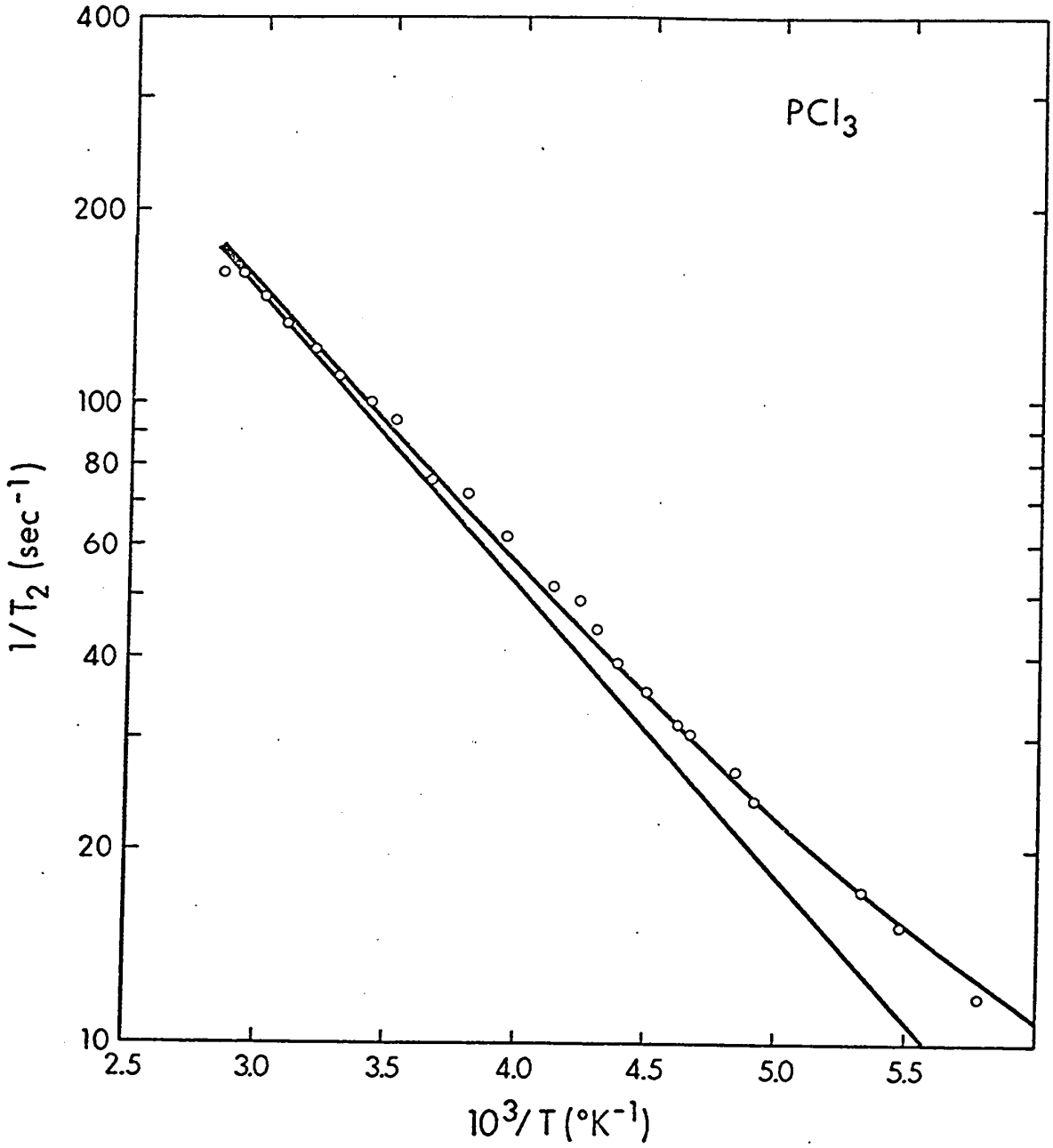


Figure 20: Temperature variation of $\log(1/T_2)$ for ^{31}P in PCl_3, in a sample containing PBr_3 and PCl_3.

the form of a plot of $\log(1/T_2)$ versus $10^3/T$, in $°K^{-1}$. The curves for PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 for the sample containing all the species are given in Figures 15 to 18, while those for PBr_3 and PCl_3 for the sample in which only those species are present are given in Figures 19 and 20. The data in Figures 15 and 19 for the $1/T_2$ in PBr_3 and the data in Figures 18 and 20 for the $1/T_2$ in PCl_3 are the same within experimental error. Thus, no distinction in the discussion of the ^{31}P relaxation rate in PBr_3 and PCl_3 for the two samples will be made.

Figures 15 to 20 indicate that the plots of $\log(1/T_2)$ versus $10^3/T$ are linear for values of $1/T_2$ greater than approximately 10 sec^{-1}, after which they slowly level off to a value of approximately 5 sec^{-1} for $1/T_2$. This is clearly shown in Figures 15 and 19 for the relaxation rate in PBr_3, which covers the range of 20 sec^{-1} to 5 sec^{-1} in the temperature region studied. The change in linearity might be attributed to a new relaxation mechanism with opposite temperature dependence. However, because the non-linearity is observed when the values of $1/T_2$ are very small, it is believed that the effect is due to the limits of the linewidth resolution of the nmr spectrometer.

The values of $1/T_2$ for each species were fitted with a non-linear least-squares programme[162] to the equation;

$$\frac{1}{T_2} = \frac{1}{T_{2_o}} + A\exp(-E_A/RT) \quad , \qquad \text{(IV.2)}$$

where $1/T_{2_o}$ is the contribution to $1/T_2$ which arises from machine broadening; and the second term represents the relaxation rate due

to a mechanism whose temperature dependence follows an exponential function, where A is the pre-exponential term, and E_A is the apparent activation energy for the mechanism. The best-fit values of $1/T_2$ are given in Tables EI to EVI, and the corresponding parameters, $1/T_{2_o}$, A, and E_A, are given in Table XVII. The errors given are the approximately 95% confidence limits calculated by the programme.

The values of $1/T_{2_o}$ obtained range from 4.79 sec^{-1} for PBr_3 to 0.86 sec^{-1} for PCl_3. Since the value of $1/T_{2_o}$ is a property of the spectrometer resolution, it should be a constant value for all the species. The values of $1/T_{2_o}$ obtained for PBr_3 and PBr_2Cl are believed to be the most realistic ones, since these species have the narrowest linewidths and therefore the $1/T_{2_o}$ contribution is more important. Thus the value of $1/T_{2_o}$ is taken as 4.5 sec^{-1}, an average of the values obtained for PBr_3 and PBr_2Cl. This value of $1/T_{2_o}$ was used to fit the observed values of $1/T_2$ for $PBrCl_2$ and PCl_3 to a modification of equation (IV.2), given by:

$$\frac{1}{T_2} = 4.5 + A\exp(-E_A/RT) \quad . \qquad \text{(IV.3)}$$

The best-fit values of $1/T_2$ for $PBrCl_2$ and PCl_3 are given in Table EIII and Tables EIV and EVI, respectively. The corresponding parameters, A and E_A, with their approximately 95% confidence limits as calculated by the programme, are given in Table XVIII. The errors in A and E_A are slightly larger for the fit to equation (IV.3) than for the fit to equation (IV.2). This might be expected since the former is a two

TABLE XVII

Best-fit Parameters for $1/T_2 = 1/T_{2_o} + A\exp(-E_A/RT)$

Species	$1/T_{2_o}$ $(sec^{-1})^c$	$A(Sec^{-1})^c$	$E_A(kcal\ mol^{-1})^c$
PBr_3 [a]	4.302 ± 0.281	$(4.792 \pm 0.456)x10^2$	2.470 ± 0.052
PBr_2Cl [a]	4.452 ± 0.194	$(1.136 \pm 0.030)x10^3$	2.231 ± 0.014
$PBrCl_2$ [a]	3.730 ± 0.401	$(1.921 \pm 0.058)x10^3$	2.096 ± 0.015
PCl_3 [a]	0.856 ± 0.642	$(2.253 \pm 0.065)x10^3$	1.863 ± 0.013
PBr_3 [b]	4.787 ± 0.167	$(6.377 \pm 0.378)x10^2$	2.738 ± 0.034
PCl_3 [b]	2.007 ± 0.543	$(2.552 \pm 0.058)x10^3$	1.906 ± 0.008

[a] For a sample containing all four species; the best-fit values of $1/T_2$ for PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 are given in Tables EI to EIV respectively.

[b] For a sample containing only PBr_3 and PCl_3; the best-fit values of $1/T_2$ for PBr_3 and PCl_3 are given in Tables EV and EVI respectively.

[c] Extra significant figures have been carried in order to avoid round-off errors in recalculating $1/T_2$ values.

TABLE XVIII

Best-fit Parameters for $1/T_2 = 4.5 + A\exp(-E_A/RT)$

Species	$A(sec^{-1})^c$	$E_A(kcal\ mol^{-1})^c$
$PBrCl_2$ [a]	$(2.211 \pm 0.062)\times10^3$	2.188 ± 0.014
PCl_3 [a]	$(3.210 \pm 0.125)\times10^3$	2.092 ± 0.019
PCl_3 [b]	$(3.236 \pm 0.091)\times10^3$	2.059 ± 0.014

[a] For a sample containing all four species; the best-fit values of $1/T_2$ for $PBrCl_2$ and PCl_3 are given in Tables EIII and EIV respectively.

[b] For a sample containing only PBr_3 and PCl_3; the best-fit values of $1/T_2$ for PCl_3 are given in Table EVI.

[c] Extra significant figures have been carried in order to avoid round-off errors in recalculating $1/T_2$ values.

parameter fit, while the latter is a three parameter fit. However, the values of $1/T_2$ calculated from the best fit to equation (IV.3) are well within the experimental error on the observed values of $1/T_2$.

The apparent activation energy, E_A, for the relaxation mechanism in the various species appears to decrease slightly in going from PBr_3 to PCl_3. In order to test whether this trend is meaningful, the observed values of $1/T_2$ for PBr_3 were fitted to a modification of equation (IV.2), given by:

$$\frac{1}{T_2} = \frac{1}{T_{2_o}} + A\exp(-2.183\times10^3/RT) \quad . \qquad \text{(IV.4)}$$

where 2.183 kcal mol^{-1} is the average of the values of E_A in Tables XVII and XVIII. The best-fit values for PBr_3 in the two samples are given in Tables EI and EV. The corresponding parameters, $1/T_{2_o}$ and A, with their approximately 95% confidence limits as calculated by the programme, are given in Table XIX. The best-fit values of $1/T_2$ are well within the experimental error of the observed values of $1/T_2$. Thus, the values of the activation energies of the relaxation mechanism in the various species are considered to be equal within the limits of the experimental error in the observed values of $1/T_2$.

The results of the manipulation of the data, as discussed above, are presented in Figures 15 to 20. The smooth curve through the observed values of $1/T_2$ for PBr_3 and PBr_2Cl, shown in Figures 15 and 19, and 16 respectively, is drawn from the best-fit values of $1/T_2$

TABLE XIX

Best-fit Parameters for $1/T_2 = 1/T_{2_o} + A\exp(-2.183\times10^3/RT)$

Species	$1/T_{2_o}$ $(sec^{-1})^c$	$A(sec^{-1})^c$
PBr_3 [a]	4.006 ± 0.235	$(3.097 \pm 0.232)\times10^2$
PBr_3 [b]	4.303 ± 0.193	$(2.733 \pm 0.169)\times10^2$

[a] For a sample containing all four species; the best-fit values of $1/T_2$ for PBr_3 are given in Table EI.

[b] For a sample containing only PBr_3 and PCl_3; the best-fit values of $1/T_2$ for PBr_3 are given in Table EV.

[c] Extra significant figures have been carried in order to avoid round-off errors in recalculating $1/T_2$ values.

to equation (IV.2). The two terms in the equation are given by the straight lines, whose parameters are given In Table XVII. The smooth curve through the observed values of $1/T_2$ for $PBrCl_2$ and PCl_3, shown in Figures 17, and 18 and 20 respectively, is drawn from the best-fit values of $1/T_2$ to equation (IV.3). The two terms in the equation are given by the straight lines, whose parameters are given in Table XVIII. In Figures 18 and 20, the straight line through 4.5 sec^{-1} is off scale.

The temperature dependence of $1/T_2$ is in agreement with that due to a spin-rotation mechanism or a scalar interaction mechanism of the second kind. It will be seen in the following section that the values of $1/T_{1SR}$ are less than 0.4 sec^{-1} for all the species, over the entire temperature range studied. Since the relaxation measurements are made under conditions of extreme narrowing, the spin-rotation contribution to $1/T_2$ is the same as its contribution to $1/T_1$. Clearly this mechanism does not account for the large values of $1/T_2$ which range from approximately 5 sec^{-1} to 150 sec^{-1}. The relaxation is therefore attributed to a scalar interaction mechanism of the second kind.

The contribution of the scalar interaction mechanism to $1/T_2$ is given by equation (I.26), which may be simplified to equation (I.27) if the condition $(\omega_I - \omega_S)\tau_2 >> 1$ applies. The latter may be rewritten as $(\omega_P - \omega_X)T_{2X} >> 1$, where $(\omega_P - \omega_X)$ is the difference between the Larmor frequency of the phosphorus nucleus and the halogen nucleus X, and T_{2X} is the corresponding transverse relaxation time for the halogen nucleus. Using the values of $1/T_2$ for ^{35}Cl in PCl_3 and ^{79}Br in PBr_3 at 25°C, given in the previous section, it can be shown that at the

operating frequency of 40.5 MHz for the ^{31}P nucleus, the value of $(\omega_P - \omega_X)T_{2X}$ is 7.62×10^3 and 54.5 for $P^{35}Cl_3$ and $P^{79}Br_3$ respectively. These values satisfy the condition under which equation (I.27) applies.

The transverse relaxation rate of the phosphorus nuclei in PCl_3 due to a scalar interaction with the spin 3/2 chlorine nuclei is given by:

$$\frac{1}{T_{2Sc}} = \frac{5}{4} N_{Cl} A^2_{P-Cl} T_{2Cl} \quad , \qquad \text{(IV.5)}$$

where T_{2Cl} has been substituted for T_1, the longitudinal relaxation of the quadrupolar nucleus, in equation (I.27). Since the values of $1/T_{2Cl}$ were obtained under conditions of extreme narrowing, the substitution of T_{2Cl} for T_{1Cl} is valid. The existence of two chlorine isotopes, ^{35}Cl and ^{37}Cl, gives rise to four different PCl_3 species, therefore the straightforward substitutions of $N_{Cl} = 3$ in equation (IV.5) is invalid. Rather, the specific contributions to $1/T_{2Sc}$ for PCl_3 from $P^{35}Cl_3$, $P^{35}Cl_2{}^{37}Cl$, $P^{35}Cl^{37}Cl_2$, and $P^{37}Cl_3$ which occur with relative abundance f_1, f_2, f_3, and f_4 respectively, are given by the four terms in the following equation:

$$\frac{1}{T_{2Sc}} = \frac{5}{4}\left[(3A^2_{P-35}T_{2-35})f_1 + (2A^2_{P-35}T_{2-35} + A^2_{P-37}T_{2-37})f_2 + (A^2_{P-35}T_{2-35} + 2A^2_{P-37}T_{2-37})f_3 + (3A^2_{P-37}T_{2-37})f_4\right] \quad , \qquad \text{(IV.6)}$$

where A_{P-35} and A_{P-37} are the P-^{35}Cl and P-^{37}Cl scalar coupling constants

in PCl_3 respectively; T_{2-35} and T_{2-37} are the corresponding transverse relaxation times for the ^{35}Cl and ^{37}Cl nuclei; and the values of f_1, f_2, f_3, and f_4 are normalized to unity.

The scalar coupling constant is proportional to the product of the magnetogyric ratios of the two nuclei being coupled:

$$A_{P-35} \propto \gamma_P\gamma_{35} \; ; \quad A_{P-37} \propto \gamma_P\gamma_{37} \; . \tag{IV.7}$$

Thus A_{P-37} may be expressed in terms of A_{P-35} by:

$$A_{P-37} = A_{P-35}\gamma_{37}/\gamma_{35} \; , \tag{IV.8}$$

where γ_{35} and γ_{37} are the magnetogyric ratios of ^{35}Cl and ^{37}Cl respectively. Similarly, from equation (IV.1), the transverse relaxation rate for the chlorine nucleus is proportional to the quadrupole coupling constant:

$$\frac{1}{T_{2-35}} \propto (e^2qQ/\hbar)^2_{35} \; ; \quad \frac{1}{T_{2-37}} \propto (e^2qQ/\hbar)^2_{37} \; . \tag{IV.9}$$

Thus T_{2-37} may be expressed in terms of T_{2-35} by:

$$T_{2-37} = T_{2-35} \frac{(e^2qQ/\hbar)^2_{35}}{(e^2qQ/\hbar)^2_{37}} \; , \tag{IV.10}$$

which may be simplified to:

$$T_{2-37} = T_{2-35}Q^2_{35}/Q^2_{37} \; , \tag{IV.11}$$

where Q_{35} and Q_{37} are the quadrupole moments of the ^{35}Cl and ^{37}Cl nuclei respectively in PCl_3.

Equation (IV.6) may be simplified by expressing it in terms of only the ^{35}Cl parameters, using the relationships developed above. Thus,

$$\frac{1}{T_{2Sc}} = \frac{5}{4} A^2_{P-35} T_{2-35} [3f_1 + (2 + \gamma^2_{37} Q^2_{35} / \gamma^2_{35} Q^2_{37}) f_2 + (1 + 2\gamma^2_{37} Q^2_{35} / \gamma^2_{35} Q^2_{37}) f_3 + (3\gamma^2_{37} Q^2_{35} / \gamma^2_{35} Q^2_{37}) f_4] \quad . \tag{IV.12}$$

The values of γ_{35} and γ_{37} are 2.6214×10^3 and 2.1815×10^3 rad sec^{-1} $gauss^{-1}$ respectively,[86] thus γ_{37}/γ_{35} is 0.8322. The value of Q_{35}/Q_{37} has not been determined for PCl_3. However, it has been shown[171] that the value of Q_{35}/Q_{37} is 1.2687(8) in $SOCl_2$, $POCl_3$, and only the last figure is different for each molecule; therefore Q_{35}/Q_{37} for PCl_3 is taken as 1.2687. Thus, the term $\gamma^2_{37} Q^2_{35} / \gamma^2_{35} Q^2_{37}$ is equal to 1.115. The value of $1/T_{2-35}$ at 25°C, calculated in the previous section, is 25.3×10^3 sec^{-1}. The corresponding experimental value of $1/T_{2Sc}$ at 25°C may be calculated from equation (IV.3) and the appropriate parameters; the average value of $1/T_{2Sc}$ from the two samples studied is 96.92 sec^{-1}. If the values of $1/T_{2Sc}$, $1/T_{2-35}$, $\gamma^2_{37} Q^2_{35} / \gamma^2_{35} Q^2_{37}$, together with the relative abundance of the different PCl_3 species given by[172] f_1; 0.4287, f_2; 0.4196, f_3; 0.1369, and f_4; 0.0149, are substituted into equation (IV.12), a value for A_{P-35} of 797.4 sec^{-1} or 128.9 Hz is obtained.

Similarly, the two isotopes of bromine, ^{79}Br and ^{81}Br, give rise to four specific PBr_3 molecules with different isotopic composition and relative abundance. The contributions to $1/T_{2Sc}$ for PBr_3 from $P^{79}Br_3$, $P^{79}Br_2{}^{81}Br$, $P^{79}Br^{81}Br_2$, and $P^{81}Br_3$ may be developed in the same manner

as for PCl_3 from equations (IV.5) to (IV.12) with the substitution of the various terms for ^{35}Cl and ^{37}Cl by the corresponding terms for ^{79}Br and ^{81}Br. The values of γ_{79} and γ_{81} are 6.7023×10^3 7.2244×10^3 rad sec^{-1} $gauss^{-1}$ respectively, thus γ_{81}/γ_{79} is 1.0779. The value of Q_{79}/Q_{81} for PBr_3 is 1.19711.[170] Thus, the term $\gamma_{81}^2 Q_{79}^2/\gamma_{79}^2 Q_{81}^2$ is equal to 1.665. The value of $1/T_{2-79}$ at 25°C, calculated in the previous section, is 17.8×10^5 sec^{-1}. The corresponding experimental value of $1/T_{2Sc}$ at 25°C may be calculated from equation (IV.2) and the appropriate parameters; the average value of $1/T_{2Sc}$ from the two samples studied is 6.83 sec^{-1}. Substitution of the values of $1/T_{2Sc}$, $1/T_{2-79}$, $\gamma_{81}^2 Q_{79}^2/\gamma_{79}^2 Q_{81}^2$, together with the relative abundance of the different PBr_3 species given by[172] f_1; 0.1293, f_2; 0.3792, f_3; 0.3707, and f_4; 0.1208 into equation (IV.12) appropriately modified for PBr_3, yields a value of A_{P-79} of 1562 sec^{-1} or 248.6 Hz.

The transverse relaxation rate of the phosphorus nuclei in PCl_2Br due to a scalar interaction with the chlorine and bromine nuclei, each of spin 3/2, is given by an obvious extension of (IV.5) to take into account the existence of two types of quadrupolar nuclei:

$$\frac{1}{T_{2Sc}} = \frac{5}{4} N_{Cl} (A_{P-Cl}^2)' (T_{2-Cl})' + \frac{5}{4} N_{Br} (A_{P-Br}^2)' (T_{2-Br})' \quad , \quad \text{(IV.13)}$$

where $(A_{P-Cl})'$ and $(A_{P-Br})'$ are the P-Cl and P-Br coupling constants in $PBrCl_2$, as opposed to A_{P-Cl} and A_{P-Br} which refer to the corresponding coupling constants in PCl_3 and PBr_3 respectively. Similarly, $(T_{2-Cl})'$

and $(T_{2-Br})'$ are the chlorine and bromine transverse relaxation times in the PCl_2Br. To a first approximation, it may be assumed that the P-Cl and P-Br coupling constants in PCl_2Br are the same as the P-Cl coupling constant in PCl_3 and the P-Br coupling constant in PBr_3. Similarly, the transverse relaxation times of the Cl and Br nuclei in PCl_2Br, may be taken to be the same as those for the Cl nucleus in PCl_3 and the Br nucleus in PBr_3 respectively. Thus, the primes in equation (IV.13) are removed, and this approximation is tested by calculating the value of $1/T_{2Sc}$ for PCl_2Br and comparing it to the experimentally obtained value. The contributions to $1/T_{2Sc}$ for PCl_2Br from $P^{35}Cl_2{}^{79}Br$, $P^{35}Cl_2{}^{81}Br$, $P^{35}Cl^{37}Cl^{79}Br$, $P^{35}Cl^{37}Cl^{81}Br$, $P^{37}Cl_2{}^{79}Br$, and $P^{37}Cl_2{}^{81}Br$ which occur with relative abundance f_1, f_2, f_3, f_4, f_5, and f_6 respectively, are given by:

$$\frac{1}{T_{2Sc}} = \frac{5}{4}\,[(2A^2_{P-35}T_{2-35} + A^2_{P-79}T_{2-79})f_1 + (2A^2_{P-35}T_{2-35} + A^2_{P-81}T_{2-81})f_2 +$$

$$(A^2_{P-35}T_{2-35} + A^2_{P-37}T_{2-37} + A^2_{P-79}T_{2-79})f_3 +$$

$$(A^2_{P-35}T_{2-35} + A^2_{P-37}T_{2-37} + A^2_{P-81}T_{2-81})f_4 +$$

$$(2A^2_{P-37}T_{2-37} + A^2_{P-79}T_{2-79})f_5 + (2A^2_{P-37}T_{2-37} + A^2_{P-81}T_{2-81})f_6]\ , \qquad \text{(IV.14)}$$

where all the terms have already been defined, and the values of f_1, f_2, f_3, f_4, f_5, and f_6 are normalized to unity.

As before, the values of A_{P-37}, T_{2-37}, A_{P-81}, and T_{2-81} are

expressed in terms of A_{P-35}, T_{2-35}, A_{P-79} and T_{2-79}. Thus equation (IV.14) may be simplified by expressing it only in terms of the ^{35}Cl and ^{79}Br parameters:

$$\frac{1}{T_{2Sc}} = \frac{5}{4}\,[(2A^2_{P-35}T_{2-35} + A^2_{P-79}T_{2-79})f_1 +$$

$$(2A^2_{P-35}T_{2-35} + A^2_{P-79}T_{2-79}\gamma^2_{81}Q^2_{79}/\gamma^2_{79}Q^2_{81})f_2 +$$

$$(A^2_{P-35}T_{2-35} + A^2_{P-35}T_{2-35}\gamma^2_{37}Q^2_{35}/\gamma^2_{35}Q^2_{37} + A^2_{P-79}T_{2-79})f_3 +$$

$$(A^2_{P-35}T_{2-35} + A^2_{P-35}T_{2-35}\gamma^2_{37}Q^2_{35}/\gamma^2_{35}Q^2_{37} +$$

$$A^2_{P-79}T_{2-79}\gamma^2_{81}Q^2_{79}/\gamma^2_{79}Q^2_{81})f_4 +$$

$$(2A^2_{P-35}T_{2-35}\gamma^2_{37}Q^2_{35}/\gamma^2_{35}Q^2_{37} + A^2_{P-79}T_{2-79})f_5 +$$

$$(2A^2_{P-35}T_{2-35}\gamma^2_{37}Q^2_{35}/\gamma^2_{35}Q^2_{37} + A^2_{P-79}T_{2-79}\gamma^2_{81}Q^2_{79}/\gamma^2_{79}Q^2_{81})f_6] \quad . \tag{IV.15}$$

The terms $\gamma^2_{37}Q^2_{35}/\gamma^2_{35}Q^2_{37}$ and $\gamma^2_{81}Q^2_{79}/\gamma^2_{79}Q^2_{81}$ are 1.116 and 1.665 respectively; the values of $1/T_{2-35}$ and $1/T_{2-79}$ are 25.3×10^3 sec^{-1} and 17.8×10^5 sec^{-1} respectively at 25°C; the values of A_{P-35} and A_{P-79}, calculated from the PCl_3 and PBr_3 data, are 797.4 sec^{-1} and 1562 sec^{-1} respectively; and the relative abundance of the different PCl_2Br species is given by[172] f_1; 0.2875, f_2; 0.2810, f_3; 0.1876, f_4; 0.1834, f_5; 0.0306, and f_6; 0.0299. Substitution of these values into equation (IV.15) yields a calculated value of 66.80 sec^{-1} for

$1/T_{2Sc}$ at 25°C. The experimental value of $1/T_{2Sc}$ for PCl_2Br, calculated from equation (IV.3) with the appropriate parameters, is 54.90 sec^{-1} at 25°C.

It can be shown by an analogous development that the contributions to $1/T_{2Sc}$ for $PClBr_2$ from $P^{35}Cl^{79}Br_2$, $P^{37}Cl^{79}Br_2$, $P^{35}Cl^{79}Br^{81}Br$, $P^{37}Cl^{79}Br^{81}Br$, $P^{35}Cl^{81}Br_2$ and $P^{37}Cl^{81}Br_2$ may be given by equation (IV.15) with the substitution of the various terms for ^{35}Cl and ^{37}Cl by the corresponding terms for ^{79}Br and ^{81}Br, and the various terms for ^{79}Br and ^{81}Br by the corresponding terms for ^{35}Cl and ^{37}Cl. The relative abundance of the different $PClBr_2$ species is given by[172] f_1; 0.1928, f_2; 0.0629, f_3; 0.3770, f_4; 0.1230, f_5; 0.1842, and f_6; 0.0601, and the other terms have been given before. Substitution into equation (IV.15), appropriately modified for $PClBr_2$, yields a calculated value of 36.86 sec^{-1} for $1/T_{2Sc}$ at 25°C. The experimental value of $1/T_{2Sc}$ for $PClBr_2$, calculated from equation (IV.2) with the appropriate parameters, is 26.26 sec^{-1} at 25°C.

A comparison between the calculated and observed values of $1/T_{2Sc}$ indicates that the agreement is much better for PCl_2Br than for $PClBr_2$. Nevertheless, the agreement is quite good in view of the approximations made. Since the value of $A^2_{P-35}T_{2-35}$ is 25.13 sec^{-1}, while the value of $A^2_{P-79}T_{2-79}$ is 1.37 sec^{-1} at 25°C, the contribution to $1/T_{2Sc}$ from the ^{35}Cl terms is going to be much larger than the contribution from the ^{79}Br terms. It can be shown that the ^{79}Br contribution to $1/T_{2Sc}$ for PCl_2Br is 3.4%, while its contribution to $1/T_{2Sc}$ for $PClBr_2$ is 12.4%. If the contribution of the $A^2_{P-79}T_{2-79}$ terms to the $1/T_{2Sc}$ for

PCl_2Br and $PClBr_2$ are neglected, the calculated values of $1/T_{2Sc}$ can be brought into agreement with the observed values, if it is assumed that the value of $A^2_{P-35}T_{2-35}$ varies by approximately 10% from its value in PCl_3 for each substitution of a chlorine atom by a bromine atom. Since $T_{2-35} \propto (e^2qQ/\hbar)^{-2}_{35}$, then $A^2_{P-35}T_{2-35} \propto A^2_{P-35}(e^2qQ/\hbar)^{-2}_{35}$. It is not possible to determine whether the 10% change in $A^2_{P-35}T_{2-35}$ for a change of one chlorine atom is due to a variation in the scalar coupling constant, A_{P-35}, or in the quadrupole coupling constant, $(e^2qQ/\hbar)$.

3. ^{31}P Longitudinal Relaxation

The results of the ^{31}P longitudinal relaxation rate in PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 as a function of temperature are given in Appendix F. The values of $1/T_1$ for PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 for the sample containing all four species are given in Tables FI to FIV respectively. The values of $1/T_1$ for PBr_3 and PCl_3 for the sample containing just these two species are given in Tables FV and FVI respectively. The errors in the values of $1/T_1$ are estimated as approximately ±5% of the observed value.

The data for each species are presented in Figures 21 to 26 in the form of a plot of $\log(1/T_1)$ versus $10^3/T$, in $°K^{-1}$. The curves for PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 for the sample containing all the species are given in Figures 21 to 24, while those for PBr_3 and PCl_3 for the sample in which only those species are present are given in Figures 25 and 26. The $1/T_2$ data for each species corresponding to the $1/T_1$ data presented in Figures 21 to 26 are given in Figures 15 to 20 respectively. The data in Figures 24 and 26 for the $1/T_1$ in PCl_3 are the same within the experimental error throughout the entire temperature range studied. However, the data in Figures 21 and 25 for the $1/T_1$ in PBr_3 are the same below approximately -40°C, while they differ by nearly 20% above that temperature.

Figures 20 to 26 suggest that two mechanisms with opposite temperature dependence are contributing to the $1/T_1$. The values of $1/T_1$ for each species were therefore fitted with a non-linear least-squares programme[162] to the equation:

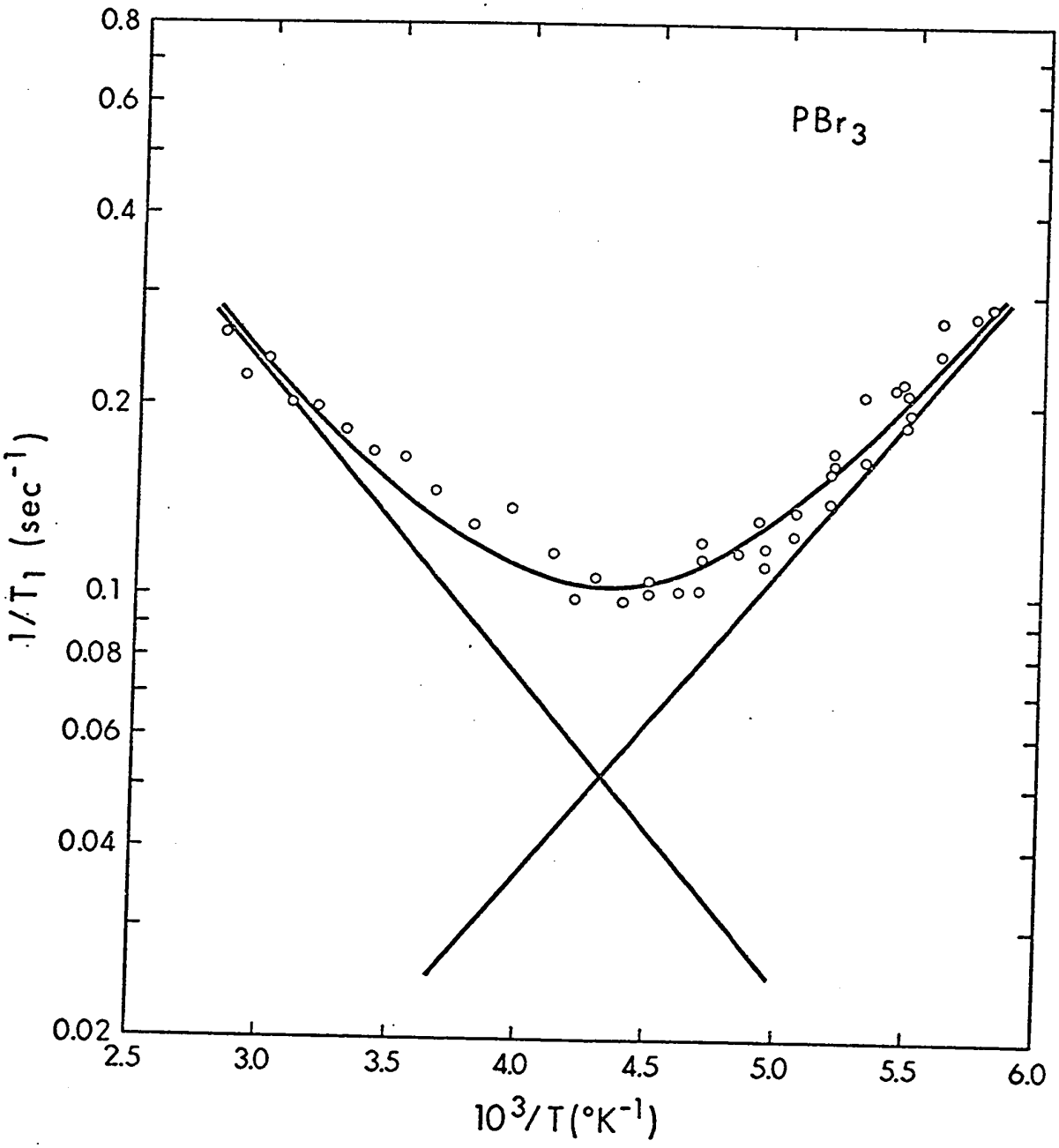


Figure 21: Temperature variation of $\log(1/T_1)$ for ^{31}P in PBr_3, in a sample containing PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3.

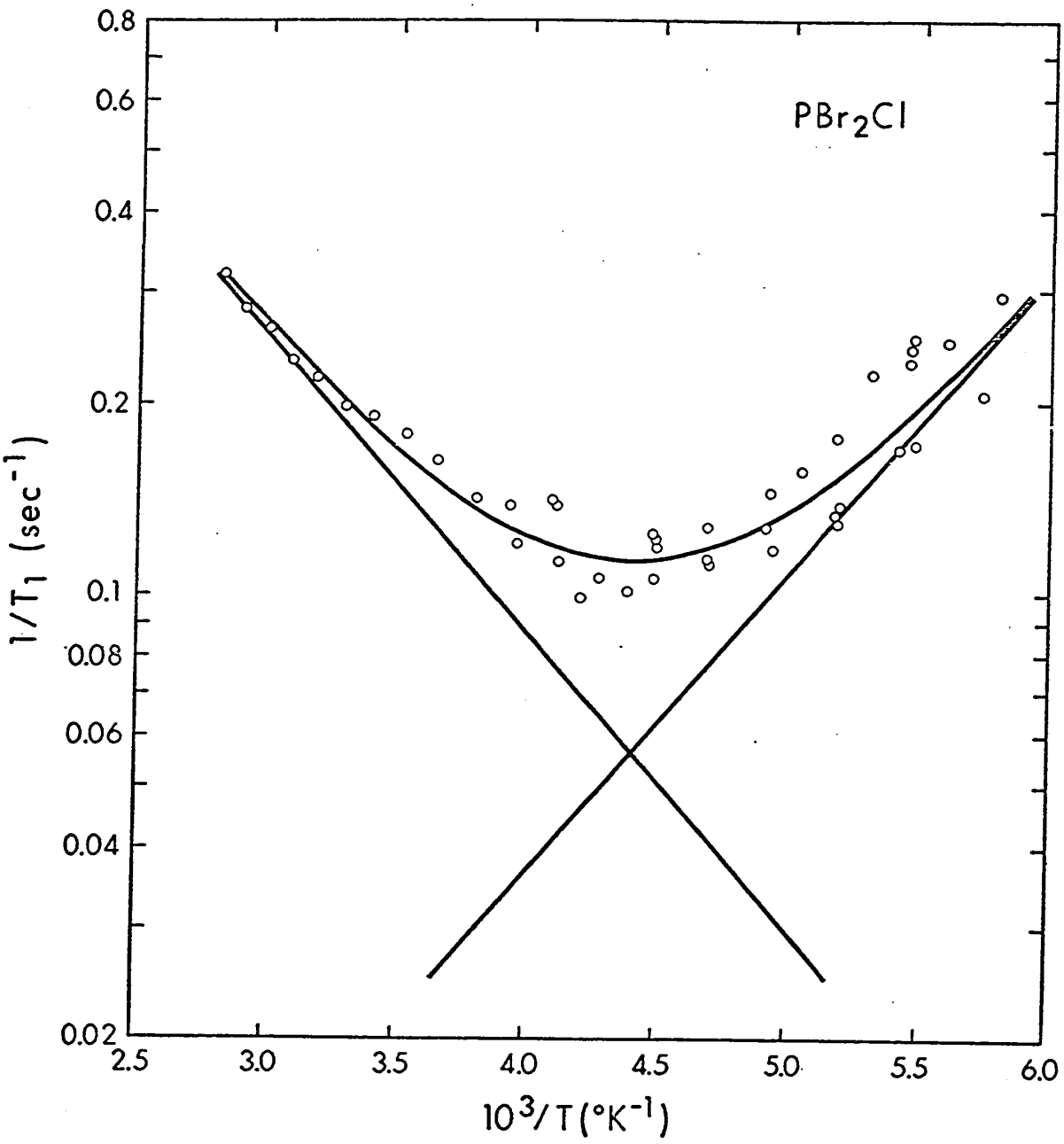


Figure 22: Temperature variation of $\log(1/T_1)$ for ^{31}P in PBr_2Cl, in a sample containing PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3.

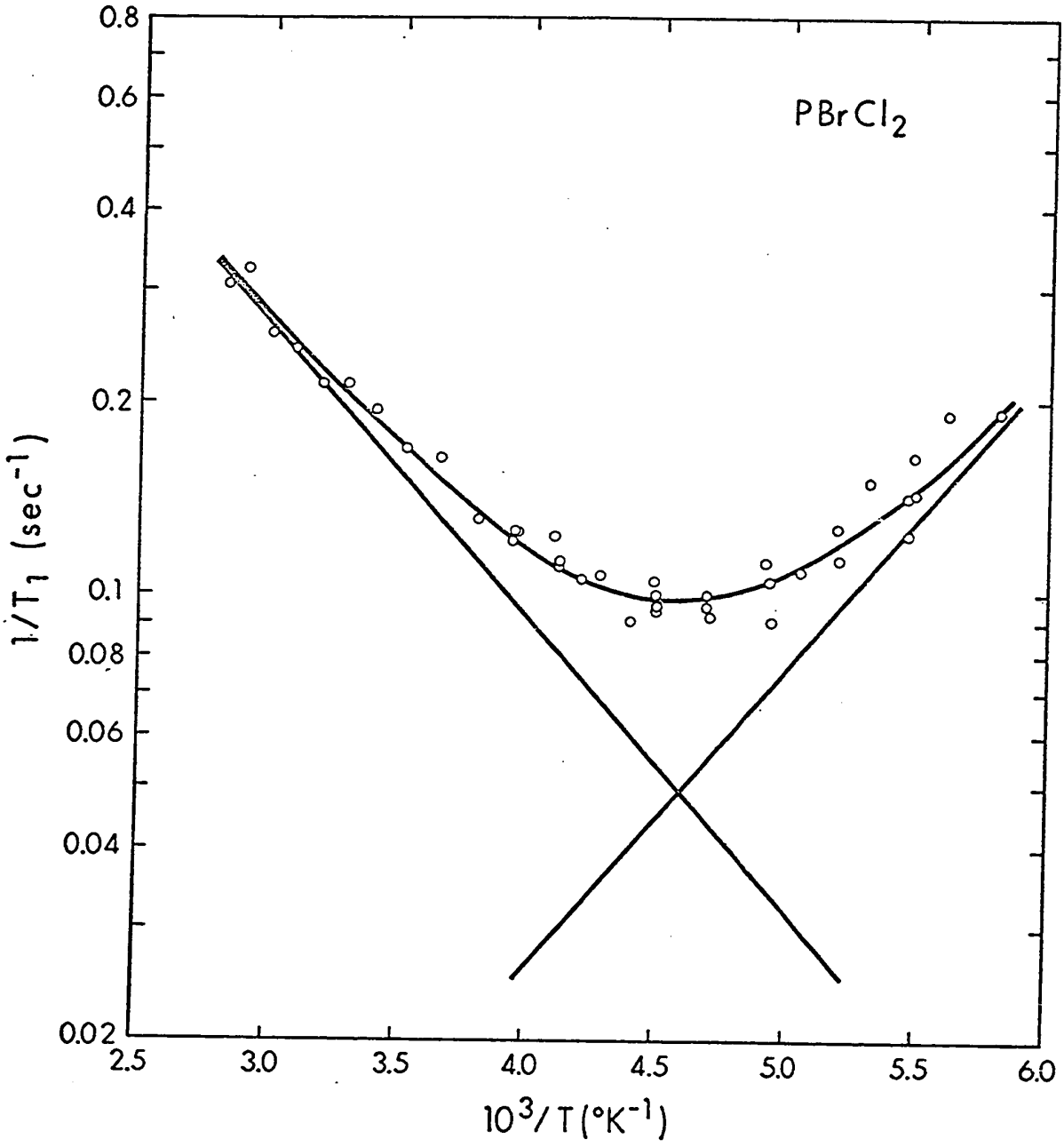


Figure 23: Temperature variation of $\log(1/T_1)$ for ^{31}P in $PBrCl_2$, in a sample containing PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3.

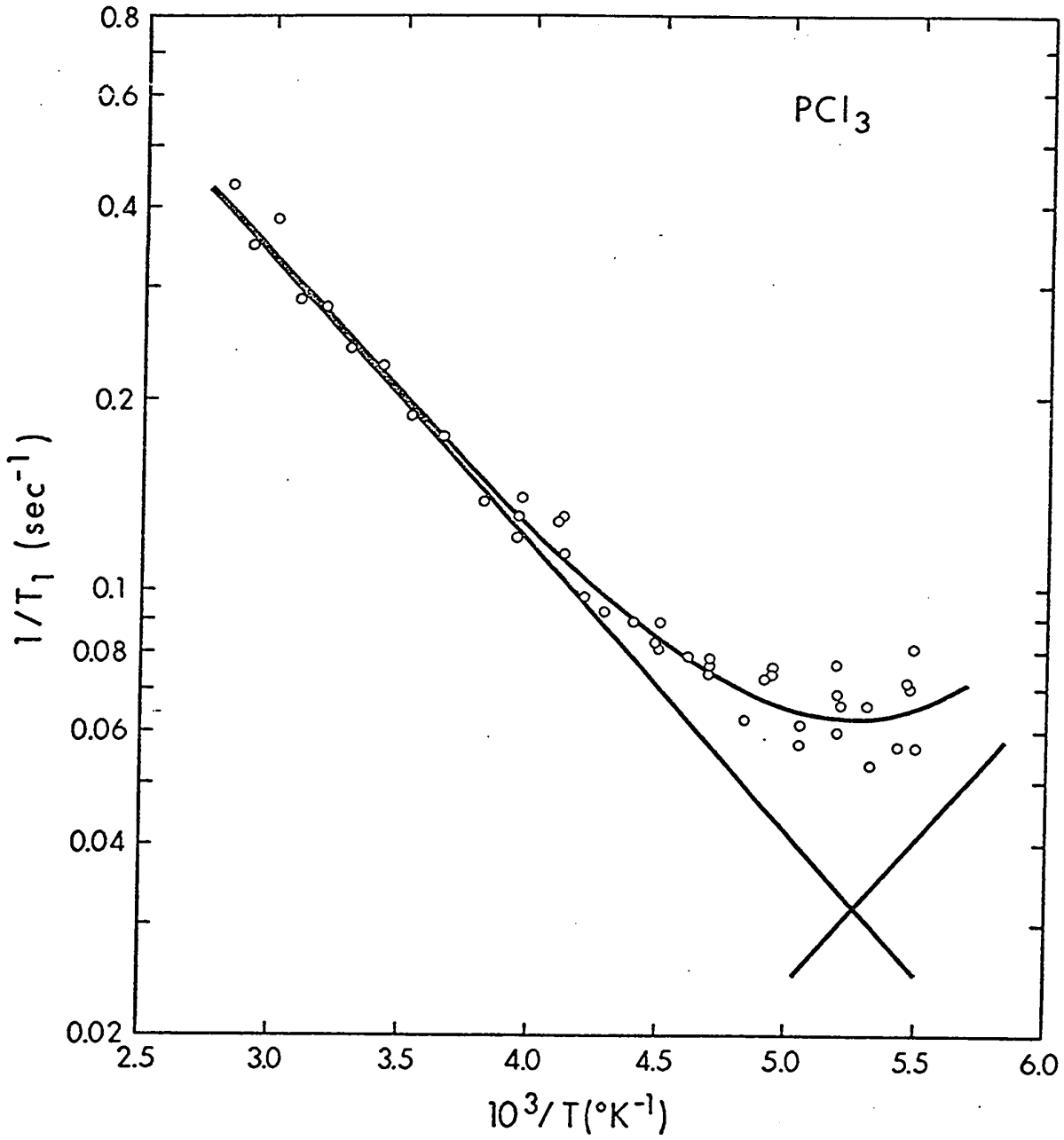


Figure 24: Temperature variation of $\log(1/T_1)$ for ^{31}P in PCl_3, in a sample containing PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3.

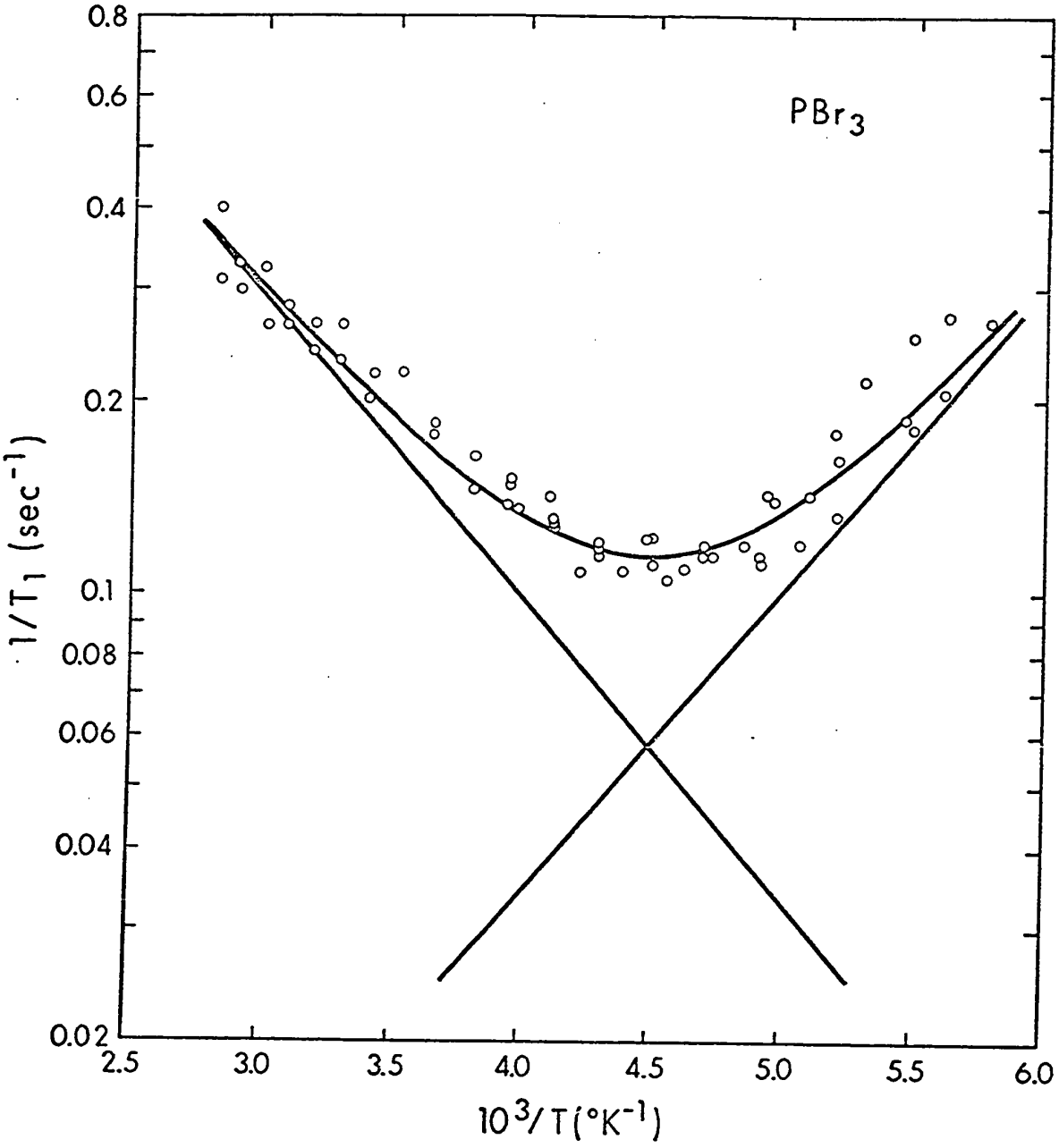


Figure 25: Temperature variation of $\log(1/T_1)$ for ^{31}P in PBr_3, in a sample containing PBr_3 and PCl_3.

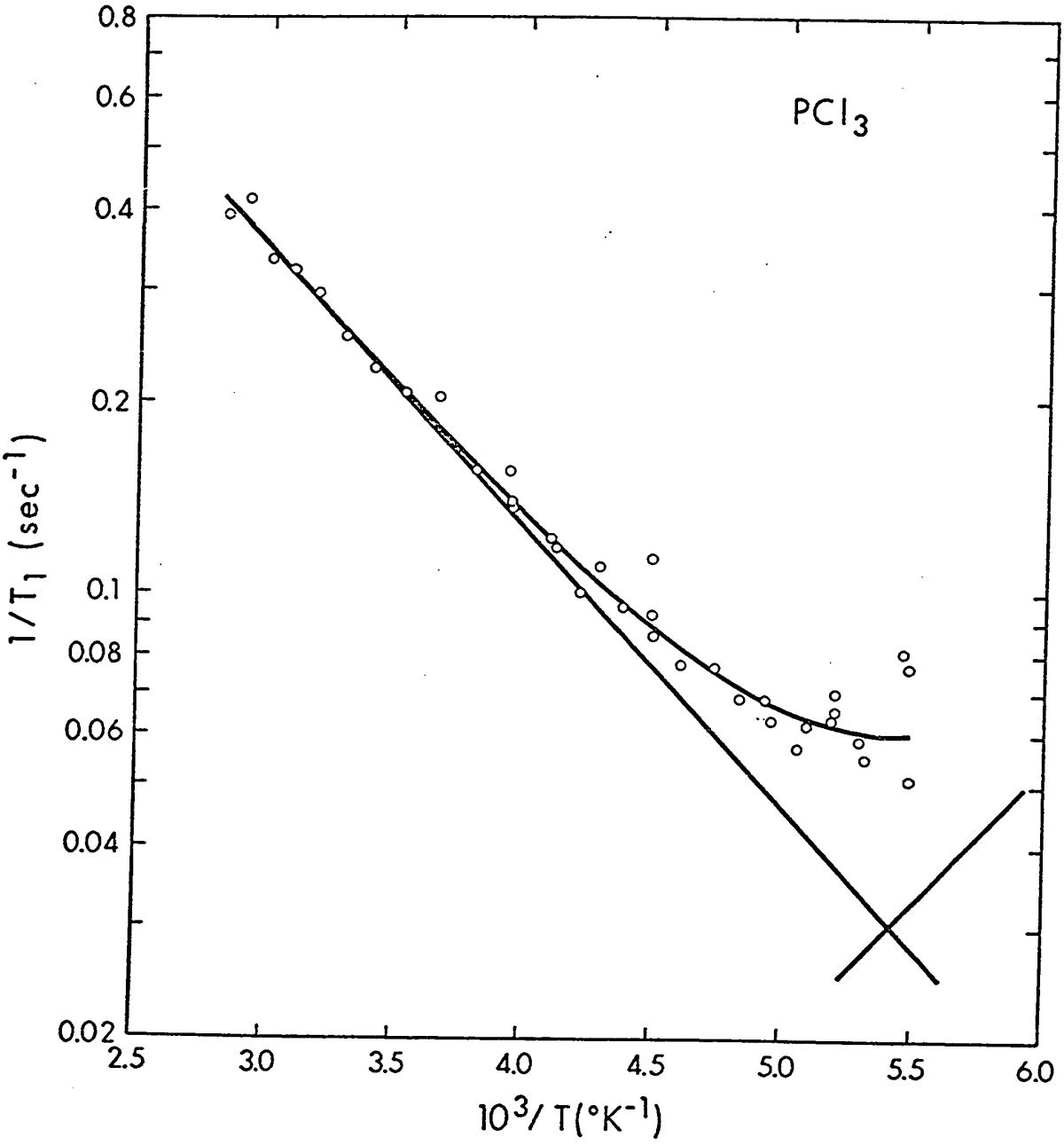


Figure 26: Temperature variation of $\log(1/T_1)$ for ^{31}P in PCl_3, in a sample containing PBr_3 and PCl_3.

$$\frac{1}{T_1} = B\exp(E_B/RT) + C\exp(-E_C/RT) \quad , \qquad \text{(IV.16)}$$

where each term represents the relaxation rate due to a mechanism whose temperature dependence follows an exponential function; B and C are the pre-exponential terms and E_B and E_C are the corresponding apparent activation energies of the two mechanisms respectively. The best-fit values of $1/T_1$ are given in Tables FI to FVI, and the corresponding parameters, B, E_B, C, and E_C, are given in Table XX. The errors given are the approximately 95% confidence limits calculated by the programme.

The discussion of the various relaxation mechanisms in the introduction, led to the conclusion that for a molecule undergoing isotropic reorientational Brownian motion, the correlation times for all the mechanisms can ultimately be related to the bulk viscosity of the medium. On the basis of this assumption, the values of the activation energies, E_B and E_C, for the two mechanisms should be the same. In order to test whether this assumption may be justified for this system, the values of $1/T_1$ for each species were fitted to a modification of equation (IV.16), by setting E_B equal to E_C;

$$\frac{1}{T_1} = B\exp(E_B/RT) + C\exp(-E_B/RT) \quad . \qquad \text{(IV.17)}$$

The best-fit values of $1/T_1$ are given in Tables FI to FVI. The corresponding parameters, B, E_B, and C, with their approximately 95% confidence limits as calculated by the programme, are given in Table XXI.

TABLE XX

Best-fit Parameters for $1/T_1 = B\exp(E_B/RT) + C\exp(-E_C/RT)$

Species	$B(sec^{-1})$ [c]	$E_B(kcal\ mol^{-1})$ [c]	$C(sec^{-1})$ [c]	$E_C(kcal\ mol^{-1})$ [c]
PBr_3 [a]	$(4.409 \pm 0.351)\times10^{-5}$	3.008 ± 0.038	2.543 ± 0.197	1.616 ± 0.037
PBr_2Cl [a]	$(2.581 \pm 0.337)\times10^{-4}$	2.361 ± 0.070	4.860 ± 0.621	1.947 ± 0.045
$PBrCl_2$ [a]	$(1.033 \pm 0.102)\times10^{-4}$	2.561 ± 0.050	4.508 ± 0.303	1.879 ± 0.032
PCl_3 [a]	$(6.080 \pm 0.940)\times10^{-4}$	1.538 ± 0.151	8.904 ± 0.668	2.178 ± 0.079
PBr_3 [b]	$(4.210 \pm 0.148)\times10^{-5}$	3.002 ± 0.058	4.334 ± 0.288	1.781 ± 0.023
PCl_3 [b]	$(8.185 \pm 2.714)\times10^{-7}$	3.801 ± 0.552	5.675 ± 0.400	1.857 ± 0.032

[a] For a sample containing all four species; the best-fit values of $1/T_1$ for PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 are given in Tables FI to FIV respectively.

[b] For a sample containing only PBr_3 and PCl_3; the best-fit values of $1/T_1$ for PBr_3 and PCl_3 are given in Tables FV and FVI respectively.

[c] Extra significant figures have been carried in order to avoid round-off errors in recalculating $1/T_1$ values.

TABLE XXI

Best-fit Parameters for $1/T_1 = B\exp(E_B/RT) + C\exp(-E_B/RT)$

Species	$B(sec^{-1})^c$	$E_B(kcal\ mol^{-1})^c$	$C(sec^{-1})^c$
PBr_3 [a]	$(4.239 \pm 0.289)\times10^{-4}$	2.212 ± 0.030	6.274 ± 0.590
PBr_2Cl [a]	$(5.022 \pm 0.532)\times10^{-4}$	2.126 ± 0.047	6.376 ± 0.744
$PBrCl_2$ [a]	$(3.767 \pm 0.296)\times10^{-4}$	2.106 ± 0.032	6.374 ± 0.413
PCl_3 [a]	$(1.322 \pm 0.200)\times10^{-4}$	2.070 ± 0.037	7.568 ± 0.461
PBr_3 [b]	$(4.303 \pm 0.380)\times10^{-4}$	2.172 ± 0.036	7.839 ± 0.551
PCl_3 [b]	$(1.299 \pm 0.283)\times10^{-4}$	1.997 ± 0.038	7.072 ± 0.464

[a] For a sample containing all four species; the best-fit values of $1/T_1$ for PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 are given in Tables FI to FIV respectively.

[b] For a sample containing only PBr_3 and PCl_3; the best-fit values of $1/T_1$ are given in Tables FV and FVI respectively.

[c] Extra significant figures have been carried in order to avoid round-off errors in recalculating $1/T_1$ values.

The agreement of the calculated values of $1/T_1$ with the observed values of $1/T_1$ is the same for the three parameter fit as for the four parameter fit. Thus the three parameter fit, for which the activation energies of the two mechanisms are assumed to be the same, can be used to fit the data satisfactorily. The smooth curve through the observed values of $1/T_1$ for all the species, shown in Figures 20 to 26, is drawn from the best-fit values of $1/T_1$ to equation (IV.17). The two terms in the equation are given by the straight lines, whose parameters are given in Table XXI. It is worth mentioning that the average value of E_B, 2.11 kcal mol^{-1}, obtained from fitting the observed $1/T_1$ data, agrees quite well with the average value of E_A, 2.30 kcal mol^{-1}, obtained from fitting the observed $1/T_2$ data, and is well within the range of the activation energies obtained for the individual species.

In the high temperature region, the temperature dependence of $1/T_1$ is consistent with that due to a spin-rotation mechanism. In the low temperature region, the temperature dependence of $1/T_1$ is consistent with that due to a dipolar mechanism, an anisotropic chemical shift mechanism, or a scalar interaction mechanism of the second kind. The temperature dependence of $1/T_1$ in the high and low temperature regions is given by the negative and positive exponential terms respectively in equation (IV.17). The mechanisms contributing to each of these terms will be discussed separately.

The high-temperature region of $1/T_1$ is controlled only by a spin-rotation mechanism. Since the extreme narrowing condition

applies, the contribution to $1/T_1$ from a spin-rotation mechanism is given by equation (I.30). This equation may be used to evaluate the spin-rotation coupling constant for each species provided that the moment of inertia and the spin-rotation correlation time for each species is known.

The moments of inertia in the x, y, and z direction were calculated for PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3.[173] The bond distances and bond angles in PCl_3 are[174] 2.043 ± 0.003Å and 100.1 ± 1.3° respectively. The bond distances and bond angles in PBr_3 are[175] 2.23 ± 0.1Å and 100 ± 0.2° respectively. No data on the structural parameters of PBr_2Cl and $PBrCl_2$ are available. Since the bond angles do not change in going from PBr_3 to PCl_3, it is assumed that they are the same in PBr_2Cl and $PBrCl_2$, and a value of 100° is assigned to all bond angles. Furthermore, it is assumed that the P-Cl and P-Br bond lengths in PBr_2Cl and $PBrCl_2$ are the same as in PCl_3 and PBr_3, namely 2.04Å and 2.23Å respectively. The values of I_x, I_y and I_z, together with an average moment of inertia, I, are given in Table XXII for all the species.

The values of τ_{SR} at 25°C, calculated from equation (I.31) with τ_D equal to the value of τ_Q at 25°C, 2.34×10^{-12} sec, assumed to be the same for all species, are given in Table XXII. Since the values of τ_{SR} are at least a factor of twelve smaller than the value of τ_D, the condition under which equation (I.31) applies is fulfilled.

The values of $1/T_{1SR}$ at 25°C, calculated from the second term in equation (IV.17) and the appropriate parameters are given in

TABLE XXII

Parameters for the Spin-Rotation Contributions to $1/T_1$ at 25°C [a]

	PBr_3	PBr_2Cl	$PBrCl_2$	PCl_3
$I_x \times 10^{40}$ (g cm^2)	830.05	823.55	329.15	325.99
$I_y \times 10^{40}$ (g cm^2)	829.65	435.34	579.20	325.99
$I_z \times 10^{40}$ (g cm^2)	1559.36	1170.65	829.25	579.21
$I^b \times 10^{40}$ (g cm^2)	1073.0	809.9	579.2	410.4
$\tau_{SR} \times 10^{-14}$ (sec)	18.58	14.02	10.03	7.11
$1/T_{1SR}{}^c$ (sec^{-1})	0.150[d] 0.200[e]	0.176	0.182	0.230[d] 0.243[e]
$(C_{xx}{}^2+C_{yy}{}^2+C_{zz}{}^2)^{\frac{1}{2}}$ (kHz)	2.78[d] 3.21[e]	3.99	5.67	9.00[d] 9.25[e]

[a] The value of τ_D at 25°C is 2.34×10^{-12} sec.

[b] $I = (I_x + I_y + I_z)/3$.

[c] $1/T_{1SR} = C\exp(-E_B/RT)$, from equation (IV.17).

[d] For a sample containing PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3.

[e] For a sample containing PBr_3 and PCl_3.

Table XXII, together with the values for the spin-rotation coupling constant. The latter value is denoted by $(C_{xx}^2 + C_{yy}^2 + C_{zz}^2)^{\frac{1}{2}}$, which for the PBr_3 and PCl_3 simplifies to $(2C_{\perp}^2 + C_{\parallel}^2)^{\frac{1}{2}}$ because of the symmetry of these molecules. Although the spin-rotation coupling constants for both PBr_3 and PCl_3 are slightly larger for the sample which does not contain the PBr_2Cl and $PBrCl_2$ species, it is not believed that this discrepancy is significant.

The relative importance of the dipolar, scalar interaction, and anisotropic chemical shift mechanisms to the low temperature region of $1/T_1$ may be determined by comparing the contribution due to each mechanism to the experimentally observed value, given by $(1/T_1 - 1/T_{1SR})$. The values of $(1/T_1 - 1/T_{1SR})$, which may be calculated from the first term in equation (IV.17) and the appropriate parameters, are given in Table XXIII at 25°C.

The intramolecular dipolar contribution to $1/T_1$ for the molecules studied here may be obtained from equation (I.8) as:

$$\frac{1}{T_{1D}} = \frac{4}{3}\hbar^2\gamma_P^2\left[\sum_X \gamma_X^2 I_X(I_X + 1)(r_{P-X})^{-6}\right]\tau_D \quad , \qquad \text{(IV.18)}$$

where P refers to the phosphorus atom and X to the halogen. Since both the chlorine and bromine nuclei possess a spin of 3/2, equation (IV.18) may be rewritten as:

$$\frac{1}{T_{1D}} = 5\hbar^2\gamma_P^2\left[\sum_X \gamma_X^2 (r_{P-X})^{-6}\right]\tau_D \quad . \qquad \text{(IV.19)}$$

In order to take into account the two isotopes of chlorine and bromine,

the values γ^2_{Cl} and γ^2_{Br} are substituted by $(0.754\ \gamma^2_{35} + 0.246\ \gamma^2_{37})$ and $(0.506\ \gamma^2_{79} + 0.494\ \gamma^2_{81})$ respectively, where all the terms have been defined elsewhere. The P-Cl and P-Br internuclear distances are taken as 2.04Å and 2.23Å for all the molecules, γ_P is 10.8291×10^3 rad gauss^{-1} sec^{-1}, and τ_D is 2.34×10^{-12} sec at 25°C. The values of $1/T_{1D}$ at 25°C are given in Table XXIII. The values of $1/T_{1D}$ are at most only 10% of the values of $(1/T_1 - 1/T_{1SR})$, thus the intramolecular dipolar mechanism alone cannot explain the experimental observations. The value of the intermolecular dipolar contribution, $1/T_{1D}'$, is not estimated here because it has been shown that for pure PCl_3[118] and PBr_3,[119] the intermolecular contribution is approximately 10% and 6% respectively of the intramolecular contribution. Thus the $1/T_{1D}'$ contribution is quite insignificant.

The scalar interaction contribution of the second kind to $1/T_1$ may be calculated from equation (I.25). The values of $1/T_{1Sc}$ are calculated taking into consideration the isotopic population of the nuclear species, in a analogous manner as in the treatment of the $1/T_{2Sc}$ data in the previous section. The values of $1/T_{1Sc}$ at 25°C are given in Table XXIII. The contribution of $1/T_{1Sc}$ is negligible for PCl_3, but quite significant for the bromine compounds. This is mainly due to the fact that the bromine transverse relaxation time in PBr_3 is much shorter than the chlorine transverse relaxation time in PCl_3.

The anisotropic chemical shift contribution to $1/T_1$ may be calculated from equation (I.22) if the anisotropy of the chemical

TABLE XXIII

Contributions to $1/T_1$ other than $1/T_{1SR}$ at 25°C[a]

	PBr_3	PBr_2Cl	$PBrCl_2$	PCl_3
$(1/T_1-1/T_{1SR})^b(sec^{-1})$	1.78×10^{-2}[c] 1.68×10^{-2}[d]	1.82×10^{-2}	1.33×10^{-2}	4.36×10^{-3}[c] 3.79×10^{-3}[d]
$1/T_{1D}(sec^{-1})$	1.81×10^{-3}	1.34×10^{-3}	8.70×10^{-4}	4.03×10^{-4}
$1/T_{1Sc}(sec^{-1})$	3.57×10^{-3}	2.38×10^{-3}	1.19×10^{-3}	2.76×10^{-6}
$1/T_{1A}(sec^{-1})$	1.01×10^{-3}	-	-	1.54×10^{-3}

[a] The value of τ_D at 25°C is 2.34×10^{-12} sec.

[b] $1/T_1-1/T_{1SR} = Bexp(E_B/RT)$ from equation (IV.17).

[c] For a sample containing PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3.

[d] For a sample containing PBr_3 and PCl_3.

shift, $\delta_{z'}$, and the asymmetry parameter, η, are known. For a symmetric top molecule, such as PCl_3 or PBr_3, η is zero, and $\delta_{z'}$ may be expressed as:

$$\delta_{z'} = \frac{2}{3}(\delta_{\perp'} - \delta_{\parallel'}) \quad , \tag{IV.20}$$

where $\delta_{\parallel'}$ and $\delta_{\perp'}$ are the paramagnetic chemical shifts along the major axis of the molecule and perpendicular to it respectively. The corresponding diamagnetic terms are assumed to be isotropic. Thus equation (I.22) reduces to:

$$\frac{1}{T_{1A}} = \frac{2}{15}\gamma^2 H_o^2 (\delta_{\perp'} - \delta_{\parallel'})^2 \tau_A \quad . \tag{IV.21}$$

The values of $(\delta_{\perp'}-\delta_{\parallel'})$ for PCl_3 and PBr_3, obtained by Deverell[122] from values calculated by Gutowsky and Larmann,[176] are 276×10^{-6} and 224×10^{-6} respectively. Using the value of τ_A equal to τ_Q at 25°C, 2.34×10^{-12} sec, the values of $1/T_{1A}$ for PCl_3 and PBr_3 at 40.5 MHz are calculated and given in Table XXIII. Since $\delta_{z'}$ values are not available, the anistropic chemical shift contribution to PBr_2Cl and $PBrCl_2$ cannot be calculated.

The sum of $1/T_{1D}$, $1/T_{1Sc}$, and $1/T_{1A}$ for PBr_3 and PCl_3 at 25°C are 6.39×10^{-3} sec^{-1} and 1.94×10^{-3} sec^{-1} respectively. This discrepancy between these values and the average experimentally obtained values, $(1/T_1-1/T_{1SR})$ in Table XXIII, may be due in large part to the long extrapolation necessary to obtain the latter value at 25°C. It is important to notice, however, that the anisotropic chemical shift

makes a significant contribution, and in the case of PCl_3 is the dominant factor. This effect has generally been neglected, and in the case of previous work on PCl_3[118] this omission has resulted in a misinterpretation of the results. This will be discussed in more detail in the following section.

4. Discussion of Nuclear Relaxation Results

The results obtained in the previous sections of this chapter may be compared to those of other workers in a number of cases.

As has already been mentioned, the value of $1/T_2$ for ^{35}Cl in a neat sample of PCl_3 at 25°C, reported in this thesis is slightly larger than that measured by Johnson, Hunt, and Dodgen[169] at 26°C. The measured value of $1/T_2$ for ^{35}Cl in PCl_3 in a mixture with PBr_3, which is about 10% higher than the value in the neat PCl_3, and the known quadrupole coupling constant in PCl_3 have been used to obtain a value of τ_Q, the reorientational correlation time. It may be noted that the value of τ_Q is approximately an order of magnitude smaller[169] than that calculated by the Debye-BPP hard-sphere approximation.

The value of τ_Q obtained and the known quadrupole coupling constant in PBr_3 were then used to calculate the value of $1/T_2$ for ^{79}Br in PBr_3 in the mixture of PCl_3 and PBr_3. On the basis of the results of $1/T_1$ for ^{35}Cl in PCl_3, it is expected that the value of $1/T_1$ for ^{79}Br in neat PBr_3 would be about 10% higher than in the mixture.

From the measurement of the $1/T_2$ values for ^{31}P in PCl_3 and PBr_3, in a mixture of these compounds and in a mixture with PBr_2Cl and $PBrCl_2$, and the $1/T_2$ values for ^{35}Cl and ^{79}Br, the P-^{35}Cl and P-^{79}Br scalar coupling constants were calculated. The value of 129 Hz obtained here for the P-^{35}Cl scalar coupling constant is in good agreement with that of 120 Hz determined by Strange and Morgan[130] from measurements of $1/T_1$ in the rotating frame as a function of field strength, for ^{31}P in PCl_3.

However, the value of 249 Hz obtained for the P-^{79}Br coupling constant does not agree with that of 350 Hz determined by Rhodes, Aksnes, and Strange[119]. The value of the product $T_{2Br}A_{P-Br}$ obtained in this work predicts the rotating frame $1/T_1$ values of Rhodes *et al*[119] correctly, thus the discrepancy must be due to the methods of separating T_{2Br} and A_{P-Br}. Rhodes *et al*[119] attributed the difference in the measured $1/T_1$ at 9 MHz and 18 MHz to the scalar interaction mechanism, and obtained values of A_{P-Br}/T_{2Br}, which when combined with the rotating frame $1/T_1$ values permit calculation of T_{2Br} and A_{P-Br}. It may be noted that the rotating frame measurements do not agree with the low temperature 9 MHz data. Moreover, the 9 MHz and 18 MHz data differ at high temperatures in a region where no frequency dependence should exist.

It is not possible to determine the P-^{35}Cl and P-^{79}Br scalar coupling constant, and the ^{35}Cl and ^{35}Br quadrupole coupling constants in PBr_2Cl and $PBrCl_2$. However, calculations based on the assumption that these values are the same as in PCl_3 and PBr_3, yield values of $1/T_2$ for ^{31}P in PBr_2Cl and $PBrCl_2$ which are in reasonable agreement with the observed values. The discrepancy can be explained by small changes in the quadrupole coupling constants or in the scalar coupling constants from those assumed.

Measurements of $1/T_1$ for ^{31}P in PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 as a function of temperature have shown that in the high temperature region, the spin-rotation contribution is the controlling mechanism. From the known value of τ_D, equal to τ_Q, it is possible to calculate the spin-rotation coupling constant, $(C_{xx}^2 + C_{yy}^2 + C_{zz}^2)^{\frac{1}{2}}$. For

the symmetric top molecules PCl_3 and PBr_3 this parameter may be written as $(2C_\perp^2 + C_{||}^2)^{\frac{1}{2}}$. The theoretical values of $C_\perp$ and $C_{||}$ for PCl_3 and PBr_3 have been calculated by Deverell.[122] For PCl_3, $C_{||}$ and $C_\perp$ are -2.59 kHz and -6.43 kHz respectively, thus $(2C_\perp^2 + C_{||}^2)^{\frac{1}{2}}$ is equal to 9.46 kHz. This is in excellent agreement with the average value of 9.13 kHz obtained in this work. Similarly, the values of $C_{||}$ and $C_\perp$ for PBr_3 are -1.02 kHz and -2.46 kHz respectively, yielding a value of 3.63 kHz for $(2C_\perp^2 + C_{||}^2)^{\frac{1}{2}}$. This is somewhat larger than the average value of 3.00 kHz obtained here. It should be pointed out that the theoretical value of $(2C_\perp + C_{||})/3$ for ^{19}F in CHF_3 agrees well with that obtained from molecular beam measurements.[122] The values of $(2C_\perp^2 + C_{||}^2)^{\frac{1}{2}}$ obtained previously for PCl_3[118] and PBr_3[119] are 14.0 kHz and 7.6 kHz respectively. These values are in error because they were calculated using an incorrect value for τ_D, as will be explained in the following paragraph. Calculated values for the spin-rotation coupling constant parameters for PBr_2Cl and $PBrCl_2$ are not available, and therefore no comparison can be made with the experimental values.

Measurements of $1/T_1$ for ^{31}P in PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3 as a function of temperature have also shown that the low temperature region is consistent with contributions due to dipolar, scalar interaction, and anisotropic chemical shift mechanisms. In the previous work on PCl_3 by Aksnes, Rhodes, and Powles[118] at 9 MHz, only the dipolar term was considered. However, the τ_D value obtained here indicates a 25% contribution from the scalar interaction and aniso-

tropic chemical shift mechanisms at 9 MHz. In addition, the resolution of the dipolar contribution in the previous work could be considerably in error since it derives from a bending in the $1/T_1$ versus $10^3/T$ curve at a temperature approximately 30°C below the freezing point of PCl_3. This bending could simply be due to a non-exponential temperature dependence of the viscosity in the supercooled liquid. Strange and Morgan[130] have obtained a value of 25×10^3 sec^{-1} for $1/T_1$ for ^{35}Cl in PCl_3 at room temperature, which is in excellent agreement with the value quoted in this work. However, use of the value of τ_D from the results of Aksnes and co-workers[118] for the calculation of the ^{35}Cl quadrupole coupling constant yields a value of 25 MHz, which is much smaller than the experimentally obtained value of 52.1 MHz.[170] In the case if PBr_3, previous work[119] has given a value of τ_D larger than it should be, as is demonstrated by the fact that the ^{79}Br quadrupole coupling constant is 230 MHz, in comparison to the experimental value of 439 MHz.[170] Rhodes and co-workers[119] have noted that their τ_D values are in error because of the small dipolar contribution from which it is derived.

CHAPTER V

CONCLUSIONS

The studies of redistribution reactions in phosphorus trihalides indicated that reproducible kinetic results could not be obtained. The non-reproducibility was found to be associated with very effective catalysis by traces of water. Extensive efforts to eliminate this catalysis appear to have failed, although the reaction half-time has been increased from about one hour at 40°C to about 10.5 days at 70°C. The results obtained here indicate that even the qualitative reaction times quoted by previous workers for reactions involving halogen ligand redistributions on phosphorus may be grossly in error. This may also apply to similar redistribution reactions on other Group VA central atoms. It may be generally concluded that redistribution reactions involving halogens may be more susceptible to catalysis by moisture since the halogens hydrolyze more rapidly.

On the basis of the kinetic results obtained here, it would seem that two approaches to determining the kinetics of redistribution reactions may be profitable. Since it seems unlikely that the catalytic effects can be completely removed, studies on systems not involving halogen atoms might yield meaningful kinetic results. Alternatively, the catalytic process itself might be investigated by preparing possible catalysts and studying their effects on redistribution reactions. It appears that the hydrolysis products of the phosphorus halides are the catalysts, but in the case of PCl_3 and PBr_3 these have not been properly characterized. A compound such as OPF_2H, which has been characterized,[141]

is an analogue of a likely intermediate arising from the hydrolysis of PCl_3 and PBr_3; this and similar compounds could be tested for their catalytic effect. The understanding of the catalytic reaction might be useful in future preparative work on mixed ligand phosphorus compounds.

The study of the ^{31}P longitudinal relaxation rate in PCl_3 and PBr_3, and the ^{35}Cl transverse relaxation rate in PCl_3 as a function of temperature have yielded values for the spin-rotation coupling constants for these compounds in excellent agreement with the theoretical values calculated by Deverell.[122] These studies have also pointed out the importance of the anisotropic chemical shift mechanism to the ^{31}P longitudinal relaxation rate of these compounds at 40.5 MHz. This mechanism has generally been neglected by previous workers in this field. The anisotropic chemical shift contribution to the relaxation rates of both the ^{31}P and ^{19}F nuclei may therefore be quite significant especially at high frequencies.

In the present work, the reorientational correlation time, τ_D, was determined from an experimental value of the ^{35}Cl transverse relaxation rate in PCl_3 and the known ^{35}Cl quadrupole coupling constant in this compound. This value of τ_D is about one order of magnitude smaller than the value calculated from the Debye-BPP equation.[81,169] This indicates that results from studies whose interpretation is based on a τ_D calculated from the Debye-BPP equation may be significantly in error. For example, in the studies by Hubbard and co-workers[97,98] on CF_4 and SF_6, the spin-rotation constants which have been obtained

are about a factor of three larger than expected from molecular-beam experiments.[122] This discrepancy may be due to the use of too large a value of τ_D, which was calculated from the Debye-BPP equation. If the discrepancy between the real and calculated values of τ_D is the same in CF_4 and SF_6 as it is in the PCl_3-PBr_3 system then, the spin-rotation coupling constants calculated by Hubbard and co-workers[97,98] would be smaller by $(10)^{\frac{1}{2}}$ and would then be in excellent agreement with the values calculated by Deverell.[122] Therefore, it can be concluded that it is crucial to have a value of τ_D based on experimental measurements, in order to interpret properly nuclear magnetic relaxation results.

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APPENDIX A

Appendix A consists of Tables AI to AXXXV which contain the concentration-time data for samples 1 to 35 respectively, for the kinetics in the PCl_3-PBr_3 system. All concentrations are in mole fractions. For samples 1 to 8, the initial mole fractions of the reactants were calculated from the weight measurements of PCl_3 and PBr_3. For samples 9 to 35, the initial mole fractions of the reactants were calculated from the mole fractions of all the species at equilibrium, as has been explained in the text. The half-lives of the reactions were obtained from the usual first-order semi-logarithmic plot, for those reactions that obey first-order kinetics. For those reactions not obeying first-order kinetics, the half-lives were estimated from the time-concentration plots. In the samples containing water, the water was distilled into the nmr tubes after the PCl_3 and PBr_3, unless otherwise stated.

TABLE AI

Kinetic Data[a] at 41°C for Sample 1[b] with

$iN_{PBr_3} = 0.51$, $iN_{PCl_3} = 0.49$

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
1.1	0.498	0.012	0.024	0.465
11.1	0.397	0.061	0.085	0.458
15.9	0.403	0.081	0.097	0.418
22.2	0.399	0.196	0.121	0.384
29.2	0.380	0.120	0.154	0.346
33.8	0.346	0.139	0.162	0.353
38.8	0.344	0.150	0.172	0.333
45.3	0.327	0.161	0.179	0.333
51.8	0.311	0.165	0.213	0.312
56.8	0.306	0.174	0.205	0.315
62.9	0.292	0.188	0.221	0.299
69.8	0.279	0.196	0.236	0.289
75.0	0.272	0.193	0.253	0.283
81.6	0.284	0.201	0.260	0.255
87.4	0.259	0.226	0.248	0.268
93.7	0.247	0.224	0.267	0.263
99.2	0.264	0.231	0.267	0.238
105.9	0.254	0.226	0.279	0.241
111.6	0.259	0.226	0.282	0.233
119.3	0.244	0.235	0.289	0.232
124.6	0.240	0.270	0.279	0.211
131.6	0.228	0.251	0.310	0.210
137.0	0.215	0.260	0.289	0.236
142.6	0.221	0.260	0.304	0.226

TABLE AI (Cont'd)

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
149.2	0.221	0.249	0.305	0.225
158.3	0.217	0.273	0.316	0.194
185.2	0.185	0.299	0.314	0.201
191.7	0.198	0.281	0.318	0.202
196.9	0.173	0.282	0.335	0.210
203.3	0.210	0.280	0.324	0.186
209.4	0.190	0.285	0.330	0.195
215.3	0.181	0.299	0.340	0.180
221.1	0.175	0.290	0.347	0.188
227.4	0.181	0.329	0.336	0.154
233.3	0.181	0.309	0.325	0.185
239.5	0.198	0.302	0.325	0.175
244.8	0.182	0.318	0.333	0.167
261.9	0.190	0.305	0.337	0.168
312.8	0.199	0.291	0.352	0.159
321.3	0.185	0.300	0.353	0.162
339.4	0.183	0.312	0.345	0.160
346.4	0.168	0.341	0.335	0.156
356.9	0.178	0.327	0.338	0.157
369.2	0.173	0.322	0.354	0.151
401.8	0.175	0.315	0.337	0.173
420.3	0.163	0.307	0.352	0.178
8 days	0.177	0.321	0.343	0.160
8 days	0.173	0.296	0.355	0.175

[a] $t_{1/2}PBr_3$ = 56 min, $t_{1/2}PBr_2Cl$ = 59 min, $t_{1/2}PBrCl_2$ = 52 min, $t_{1/2}PCl_3$ = 52 min. Data obeys first-order kinetics.

[b] Sample, prepared by weighing, contained 5.3 M PCl_3 and 5.5 M PBr_3.

TABLE AII

Kinetic Data[a] at 41°C for Sample 2[b] with

$iN_{PBr_3} = 0.35$, $iN_{PCl_3} = 0.65$

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
5.2	0.280	0.035	0.075	0.610
12.6	0.196	0.115	0.124	0.565
18.1	0.180	0.144	0.184	0.492
24.2	0.135	0.158	0.212	0.495
35.0	0.115	0.185	0.295	0.405
40.2	0.105	0.195	0.295	0.405
45.4	0.100	0.195	0.315	0.390
50.6	0.100	0.205	0.330	0.365
55.7	0.095	0.215	0.360	0.330
60.9	0.085	0.220	0.360	0.335
66.3	0.078	0.203	0.362	0.357
72.2	0.080	0.210	0.375	0.335
80.9	0.080	0.195	0.380	0.345
86.9	0.075	0.215	0.400	0.310
92.4	0.075	0.210	0.390	0.325
98.4	0.080	0.215	0.380	0.325
104.0	0.070	0.220	0.385	0.325
118.7	0.070	0.220	0.385	0.325
126.2	0.065	0.215	0.375	0.355
132.8	0.070	0.220	0.340	0.370
142.1	0.075	0.210	0.375	0.340
149.2	0.075	0.245	0.385	0.295
156.4	0.060	0.215	0.405	0.320

TABLE AII (Cont'd)

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
165.5	0.065	0.225	0.400	0.310
196.6	0.065	0.235	0.390	0.310
227.6	0.065	0.225	0.385	0.325
24 hr	0.065	0.225	0.395	0.315
24 hr	0.060	0.225	0.385	0.330

[a] $t_{1/2}PBr_3$ = 16.5 min, $t_{1/2}PBr_2Cl$ = 16 min, $t_{1/2}PBrCl_2$ = 17 min, $t_{1/2}PCl_3$ = 18 min. Data obeys first-order kinetics.

[b] Sample, prepared by weighing, contained 7.1 M PCl_3 and 3.8 M PBr_3.

TABLE AIII

Kinetic Data[a] at 41°C for Sample 3[b] with

$iN_{PBr_3} = 0.66$, $iN_{PCl_3} = 0.34$

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
4.7	0.544	0.115	0.132	0.209
9.8	0.386	0.280	0.193	0.141
14.3	0.374	0.329	0.207	0.090
19.0	0.329	0.348	0.244	0.079
24.0	0.334	0.374	0.230	0.063
29.5	0.317	0.364	0.240	0.079
34.0	0.326	0.360	0.240	0.074
38.5	0.305	0.389	0.238	0.068
43.6	0.319	0.399	0.222	0.061
48.7	0.327	0.382	0.225	0.066
53.3	0.311	0.379	0.239	0.071
58.5	0.314	0.377	0.232	0.077

[a] $t_{½}PBr_3 = 5$ min, $t_{½}PBr_2Cl = 4.8$ min, $t_{½}PBrCl_2 = 4.7$ min, $t_{½}PCl_3 = 4.0$ min. Data obeys first-order kinetics.

[b] Sample, prepared by weighing, contained 3.7 M PCl_3 and 7.0 M PBr_3.

TABLE AIV

Kinetic Data[a] at 41°C for Sample 4[b] with

$iN_{PBr_3} = 0.64$, $iN_{PCl_3} = 0.36$

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
5.5	0.609	0.008	0.020	0.362
9.2	0.577	0.021	0.033	0.370
14.3	0.601	0.027	0.045	0.328
21.3	0.552	0.041	0.065	0.341
27.8	0.561	0.048	0.071	0.321
33.5	0.557	0.061	0.061	0.321
38.8	0.550	0.068	0.069	0.313
44.8	0.523	0.075	0.072	0.329
52.5	0.516	0.082	0.096	0.305
58.7	0.501	0.103	0.095	0.301
67.5	0.520	0.108	0.104	0.269
73.3	0.492	0.115	0.094	0.297
87.5	0.494	0.134	0.106	0.267
97.8	0.535	0.124	0.117	0.224
103.9	0.480	0.140	0.127	0.253
116.9	0.483	0.152	0.125	0.240
129.1	0.462	0.163	0.144	0.230
134.6	0.467	0.173	0.156	0.204
147.2	0.445	0.185	0.146	0.224
161.1	0.451	0.195	0.159	0.196
172.8	0.432	0.221	0.160	0.187
187.2	0.441	0.225	0.176	0.158
197.5	0.413	0.243	0.177	0.167

TABLE AIV (Cont'd)

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
212.5	0.413	0.240	0.174	0.174
228.8	0.391	0.246	0.195	0.167
242.9	0.409	0.243	0.188	0.160
257.7	0.387	0.270	0.190	0.154
272.5	0.399	0.263	0.197	0.141
287.9	0.367	0.299	0.204	0.130
302.6	0.361	0.295	0.199	0.145
317.8	0.356	0.286	0.230	0.129
332.8	0.389	0.297	0.212	0.102
347.7	0.366	0.319	0.207	0.108
362.5	0.370	0.306	0.215	0.112
378.0	0.336	0.316	0.223	0.125
24 hr	0.284	0.402	0.238	0.077
24 hr	0.284	0.387	0.231	0.098

[a] $t_{1/2}PBr_3$ = 170 min, $t_{1/2}PBr_2Cl$ = 162 min, $t_{1/2}PBrCl_2$ = 106 min, $t_{1/2}PCl_3$ = 120 min. Data obeys first-order kinetics.

[b] Sample, prepared by weighing, contained 3.9 M PCl_3 and 6.9 M PBr_3.

TABLE AV

Kinetic Data[a] at 41°C for Sample 5[b] with

$iN_{PBr_3} = 0.63$, $iN_{PCl_3} = 0.37$

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.0	0.589	0.029	0.020	0.362
9.5	0.597	0.039	0.038	0.326
15.0	0.574	0.071	0.069	0.286
22.5	0.548	0.092	0.082	0.278
28.1	0.519	0.106	0.105	0.270
34.6	0.498	0.122	0.132	0.249
40.0	0.470	0.134	0.145	0.252
47.0	0.466	0.158	0.134	0.241
52.2	0.463	0.173	0.130	0.234
59.4	0.462	0.173	0.153	0.212
72.5	0.419	0.200	0.173	0.208
82.5	0.391	0.214	0.193	0.203
92.1	0.419	0.212	0.182	0.187
102.4	0.373	0.247	0.204	0.177
112.3	0.387	0.243	0.202	0.168
122.3	0.380	0.255	0.212	0.153
133.5	0.353	0.277	0.213	0.157
142.5	0.362	0.274	0.207	0.156
152.3	0.352	0.296	0.215	0.136
164.9	0.352	0.309	0.205	0.134
172.2	0.333	0.319	0.205	0.143
182.8	0.340	0.312	0.233	0.114
197.9	0.317	0.321	0.232	0.130

TABLE AV (Cont'd)

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
212.8	0.318	0.304	0.254	0.125
228.1	0.307	0.335	0.236	0.122
243.0	0.308	0.340	0.225	0.126
257.2	0.298	0.349	0.237	0.116
273.1	0.310	0.333	0.246	0.111
287.1	0.293	0.364	0.249	0.094
302.8	0.283	0.351	0.270	0.096
519.4	0.264	0.386	0.253	0.097
530.2	0.278	0.375	0.256	0.091
591.8	0.274	0.392	0.258	0.076
602.8	0.272	0.389	0.258	0.080
23 hr	0.270	0.403	0.255	0.072
23 hr	0.278	0.391	0.260	0.072

[a] $t_{1/2}PBr_3$ = 72 min, $t_{1/2}PBr_2Cl$ = 86 min, $t_{1/2}PBrCl_2$ = 74 min, $t_{1/2}PCl_3$ = 82 min. Data obeys first-order kinetics.

[b] Sample, prepared by weighing, contained 4.0 M PCl_3 and 6.7 M PBr_3.

TABLE AVI

Kinetic Data[a] at 35°C for Sample 6[b] with

$iN_{PBr_3} = 0.41$, $iN_{PCl_3} = 0.59$

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.6	0.381	0.025	0.047	0.548
7.2	0.369	0.030	0.024	0.576
12.1	0.402	0.042	0.059	0.497
18.1	0.372	0.047	0.079	0.502
23.0	0.357	0.072	0.081	0.491
29.9	0.320	0.085	0.101	0.494
34.9	0.309	0.091	0.109	0.491
40.6	0.300	0.100	0.138	0.462
46.2	0.306	0.113	0.130	0.451
51.7	0.278	0.131	0.142	0.449
57.0	0.306	0.133	0.142	0.419
62.7	0.281	0.143	0.158	0.418
71.8	0.250	0.159	0.193	0.398
78.6	0.252	0.173	0.174	0.402
84.5	0.265	0.175	0.189	0.372
90.6	0.241	0.189	0.196	0.374
96.2	0.253	0.152	0.204	0.391
104.7	0.237	0.177	0.212	0.374
110.1	0.254	0.200	0.217	0.329
116.6	0.230	0.179	0.229	0.361
122.1	0.244	0.171	0.241	0.344
132.7	0.223	0.172	0.232	0.373
141.9	0.218	0.181	0.228	0.373

TABLE AVI (Cont'd)

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
152.8	0.218	0.182	0.218	0.382
161.8	0.220	0.209	0.225	0.346
173.4	0.215	0.174	0.243	0.368
187.1	0.226	0.178	0.242	0.354
202.6	0.218	0.187	0.258	0.338
330.0	0.199	0.205	0.280	0.316
335.0	0.185	0.210	0.266	0.340
32 hr	0.099	0.265	0.379	0.257
32 hr	0.096	0.249	0.389	0.265

[a] $t_{1/2}PBr_3$ = 70 min, $t_{1/2}PBr_2Cl$ = 54 min, $t_{1/2}PBrCl_2$ = 87 min, $t_{1/2}PCl_3$ = 57 min. Data does not obey first-order kinetics.

[b] Sample, prepared by weighing, contained 6.5 M PCl_3 and 4.5 M PBr_3.

TABLE AVII

Kinetic Data[a] at 35°C for Sample 7[b] with

$iN_{PBr_3} = 0.42$, $iN_{PCl_3} = 0.58$

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.4	0.389	0.018	0.115	0.478
8.4	0.303	0.095	0.131	0.472
14.2	0.276	0.167	0.183	0.374
20.6	0.186	0.197	0.265	0.352
26.1	0.167	0.220	0.295	0.318
32.4	0.140	0.252	0.323	0.285
38.3	0.125	0.282	0.340	0.253
44.3	0.110	0.278	0.354	0.258
50.0	0.105	0.290	0.358	0.247
56.3	0.107	0.261	0.372	0.259
62.3	0.112	0.290	0.368	0.230
114.3	0.118	0.334	0.338	0.210
8 hr	0.103	0.279	0.387	0.230
8 hr	0.095	0.273	0.390	0.241

[a] $t_{½}PBr_3 = 10.5$ min, $t_{½}PBr_2Cl = 10.3$ min, $t_{½}PBrCl_2 = 12.5$ min, $t_{½}PCl_3 = 10.8$ min. Data obeys first-order kinetics.

[b] Sample, prepared by weighing, contained 6.4 M PCl_3 and 4.6 M PBr_3.

TABLE AVIII

Kinetic Data[a] at 35°C for Sample 8[b] with

$iN_{PBr_3} = 0.42$, $iN_{PCl_3} = 0.58$

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
3.0	0.439	0.000	0.000	0.561
8.3	0.373	0.047	0.048	0.533
14.4	0.358	0.052	0.079	0.511
20.3	0.335	0.094	0.095	0.475
26.3	0.336	0.098	0.134	0.432
32.7	0.283	0.121	0.162	0.433
39.5	0.273	0.136	0.197	0.394
45.4	0.263	0.131	0.208	0.398
51.3	0.255	0.170	0.247	0.328
57.6	0.215	0.165	0.223	0.397
63.3	0.226	0.189	0.244	0.342
72.4	0.195	0.195	0.265	0.345
82.5	0.188	0.208	0.281	0.323
92.5	0.174	0.235	0.256	0.339
102.5	0.184	0.231	0.269	0.317
112.4	0.174	0.234	0.286	0.305
122.0	0.167	0.267	0.311	0.255
132.7	0.166	0.223	0.315	0.296
142.3	0.143	0.246	0.349	0.262
152.5	0.135	0.245	0.335	0.285
177.4	0.130	0.245	0.356	0.269
184.6	0.125	0.254	0.346	0.275
192.1	0.147	0.256	0.321	0.276

TABLE AVIII (Cont'd)

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
197.3	0.115	0.260	0.344	0.281
212.4	0.127	0.248	0.366	0.259
227.3	0.122	0.258	0.338	0.282
27 hr	0.095	0.274	0.379	0.253
27 hr	0.091	0.277	0.373	0.258

[a] $t_{1/2}PBr_3$ = 53 min, $t_{1/2}PBr_2Cl$ = 48 min, $t_{1/2}PBrCl_2$ = 48 min, $t_{1/2}PCl_3$ = 45 min. Data obeys first-order kinetics.

[b] Sample, prepared by weighing, contained 6.3 M PCl_3 and 4.6 M PBr_3.

TABLE AIX

Kinetic Data[a] at 33°C for Sample 9[b] with

$iN_{PBr_3} = 0.39$, $iN_{PCl_3} = 0.61$

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
3.8	0.334	0.039	0.042	0.585
12.2	0.319	0.068	0.091	0.522
20.7	0.291	0.091	0.124	0.494
28.5	0.288	0.099	0.161	0.451
36.5	0.268	0.119	0.181	0.431
45.6	0.264	0.137	0.192	0.406
54.5	0.234	0.153	0.218	0.395
63.3	0.226	0.171	0.224	0.379
71.6	0.226	0.171	0.235	0.368
80.2	0.214	0.173	0.250	0.362
90.1	0.210	0.182	0.255	0.353
226.0	0.170	0.218	0.304	0.309
235.0	0.149	0.224	0.319	0.308
7.8 hr	0.130	0.243	0.341	0.287
8.0 hr	0.124	0.244	0.332	0.300
17.6 hr	0.108	0.241	0.350	0.301
17.7 hr	0.112	0.242	0.342	0.304

[a] $t_{½}PBr_3 = 50$ min, $t_{½}PBr_2Cl = 40$ min, $t_{½}PBrCl_2 = 38$ min, $t_{½}PCl_3 = 31$ min. Data does not obey first-order kinetics.

[b] Sample was prepared on a grease-free system.

TABLE AX

Kinetic Data[a] at 60°C for Sample 10[b] with

$iN_{PBr_3} = 0.59$, $iN_{PCl_3} = 0.41$

time(days)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
0.0	0.388	0.000	0.000	0.612
0.0	0.414	0.000	0.000	0.586
0.8	0.332	0.032	0.046	0.590
0.8	0.323	0.027	0.043	0.607
1.9	0.303	0.074	0.091	0.532
1.9	0.302	0.065	0.097	0.536
1.9	0.308	0.064	0.095	0.533
3.0	0.304	0.060	0.115	0.521
3.0	0.308	0.060	0.110	0.522
6.9	0.224	0.148	0.201	0.427
6.9	0.231	0.150	0.211	0.407
10.0	0.177	0.215	0.265	0.344
10.0	0.166	0.216	0.271	0.347
14.0	0.138	0.258	0.299	0.305
14.0	0.131	0.250	0.307	0.312
26.0	0.117	0.282	0.340	0.261
26.0	0.122	0.266	0.332	0.279
42.0	0.106	0.264	0.353	0.278
42.0	0.107	0.263	0.373	0.257
63.0	0.099	0.281	0.351	0.268
63.0	0.097	0.269	0.353	0.282

TABLE AX (Cont'd)

time(days)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
150.0	0.104	0.285	0.342	0.269
150.0	0.109	0.281	0.352	0.258
150.0	0.105	0.292	0.349	0.254
150.0	0.103	0.290	0.352	0.255

[a] $t_{1/2}PBr_3$ = 4.9 days, $t_{1/2}PBr_2Cl$ = 5.1 days, $t_{1/2}PBrCl_2$ = 4.9 days, $t_{1/2}PCl_3$ = 5.0 days. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

TABLE AXI

Kinetic Data[a] at 60°C for Sample 11[b] with

$iN_{PBr_3} = 0.51$, $iN_{PCl_3} = 0.49$

time(days)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
0.0	0.520	0.000	0.000	0.480
0.0	0.459	0.000	0.000	0.541
0.0	0.483	0.000	0.000	0.518
0.0	0.495	0.000	0.000	0.505
0.8	0.384	0.095	0.098	0.423
0.8	0.377	0.091	0.089	0.443
1.9	0.358	0.158	0.148	0.336
1.9	0.356	0.161	0.143	0.341
1.9	0.327	0.156	0.156	0.361
1.9	0.334	0.144	0.168	0.354
3.0	0.330	0.189	0.180	0.300
3.0	0.332	0.193	0.173	0.303
6.9	0.238	0.277	0.247	0.238
6.9	0.232	0.274	0.254	0.240
9.9	0.230	0.290	0.254	0.226
9.9	0.215	0.316	0.257	0.212
14.1	0.207	0.336	0.262	0.195
14.1	0.206	0.326	0.268	0.200
26.0	0.196	0.346	0.271	0.186
26.0	0.197	0.355	0.257	0.191
42.0	0.196	0.332	0.273	0.199
42.0	0.188	0.329	0.271	0.212

TABLE AXI (Cont'd)

time(days)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
63.0	0.203	0.335	0.278	0.183
63.0	0.200	0.342	0.272	0.186
150.0	0.194	0.339	0.279	0.189
150.0	0.191	0.343	0.283	0.184
150.0	0.196	0.340	0.281	0.183
150.0	0.197	0.340	0.281	0.181

[a] $t_{1/2}PBr_3$ = 3.0 days, $t_{1/2}PBr_2Cl$ = 3.0 days, $t_{1/2}PBrCl_2$ = 3.0 days, $t_{1/2}PCl_3$ = 3.1 days. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

TABLE AXII

Kinetic Data[a] at 70°C for Sample 12[b] with

$iN_{PBr_3} = 0.45$, $iN_{PCl_3} = 0.55$[c]

time(days)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
0.0	0.400	0.000	0.000	0.600
0.0	0.417	0.000	0.000	0.583
0.0	0.402	0.000	0.000	0.598
0.0	0.400	0.004	0.000	0.596
0.5	0.399	0.034	0.030	0.536
0.5	0.399	0.034	0.030	0.536
1.5	0.379	0.058	0.056	0.507
1.5	0.368	0.059	0.053	0.521
2.5	0.361	0.066	0.078	0.495
2.5	0.365	0.066	0.078	0.490
6.8	0.315	0.121	0.133	0.431
6.8	0.299	0.113	0.146	0.443
9.8	0.287	0.139	0.179	0.395
9.8	0.279	0.138	0.175	0.409
13.7	0.267	0.184	0.223	0.326
13.7	0.259	0.177	0.222	0.342
25.6	0.179	0.244	0.311	0.266
25.6	0.185	0.255	0.307	0.253
41.6	0.124	0.307	0.389	0.180
41.6	0.133	0.291	0.362	0.215
62.7	0.130	0.301	0.358	0.211
62.7	0.130	0.300	0.358	0.212

TABLE AXII (Cont'd)

time(days)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
149.5	0.140	0.315	0.343	0.203
149.5	0.135	0.308	0.350	0.207
149.5	0.132	0.289	0.368	0.211
149.5	0.137	0.293	0.356	0.213

[a] $t_{1/2}PBr_3$ = 11.0 days, $t_{1/2}PBr_2Cl$ = 11.2 days, $t_{1/2}PBrCl_2$ = 10.2 days, $t_{1/2}PCl_3$ = 10.2 days. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] However, the average value at 0 day yields iN_{PCl_3} = 0.41, iN_{PBr_3} = 0.59.

TABLE AXIII

Kinetic Data[a] at 70°C for Sample 13[b] with

$iN_{PBr_3} = 0.41$, $iN_{PCl_3} = 0.59$[c]

time(days)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
0.0	0.376	0.000	0.000	0.624
0.0	0.385	0.000	0.000	0.615
0.0	0.386	0.000	0.000	0.614
0.0	0.380	0.000	0.000	0.620
0.5	0.372	0.019	0.007	0.601
0.5	0.368	0.019	0.007	0.605
1.5	0.339	0.028	0.048	0.584
1.5	0.335	0.032	0.048	0.585
2.5	0.341	0.051	0.053	0.555
2.5	0.353	0.049	0.054	0.544
6.7	0.295	0.107	0.136	0.462
6.7	0.303	0.104	0.135	0.458
9.7	0.261	0.116	0.171	0.452
9.7	0.268	0.123	0.169	0.439
13.7	0.234	0.181	0.218	0.367
13.7	0.226	0.169	0.225	0.380
25.1	0.163	0.224	0.318	0.295
25.1	0.179	0.227	0.320	0.274
41.6	0.096	0.290	0.376	0.239
41.6	0.096	0.285	0.385	0.234
62.7	0.084	0.302	0.377	0.237
62.7	0.088	0.276	0.383	0.254

TABLE AXIII (Cont'd)

time (days)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
149.5	0.103	0.287	0.363	0.246
149.5	0.092	0.286	0.370	0.252
149.5	0.097	0.269	0.380	0.255
149.5	0.094	0.279	0.375	0.253

[a] $t_{1/2}PBr_3$ = 12.4 days, $t_{1/2}PBr_2Cl$ = 10.5 days, $t_{1/2}PBrCl_2$ = 10.2 days, $t_{1/2}PCl_3$ = 8.8 days. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] However, the average value at 0 day yields iN_{PBr_3} = 0.38, iN_{PBr_3} = 0.62.

TABLE AXIV

Kinetic Data[a] at 35°C for Sample 14[b] with

iN_{PBr_3} = 0.42, iN_{PCl_3} = 0.58 and 0.0303 mmol H_2O[c]

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.6	0.379	0.039	0.041	0.541
10.2	0.293	0.089	0.105	0.513
17.0	0.309	0.113	0.146	0.432
24.2	0.253	0.139	0.181	0.427
29.5	0.255	0.149	0.211	0.384
36.9	0.226	0.174	0.238	0.362
43.8	0.220	0.187	0.260	0.333
49.9	0.200	0.197	0.268	0.335
55.7	0.197	0.210	0.283	0.310
63.1	0.169	0.223	0.298	0.310
69.6	0.160	0.237	0.307	0.296
76.8	0.144	0.238	0.321	0.297
86.8	0.147	0.245	0.332	0.276
94.2	0.135	0.251	0.338	0.276
100.7	0.139	0.264	0.341	0.257
108.0	0.133	0.263	0.347	0.257
113.6	0.129	0.258	0.359	0.255
123.3	0.127	0.265	0.355	0.254
7.0 hr	0.109	0.271	0.379	0.240
7.2 hr	0.105	0.276	0.382	0.236

TABLE AXIV (Cont'd)

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
20.0 hr	0.105	0.293	0.380	0.222
20.2 hr	0.104	0.283	0.382	0.231

[a] $t_{\frac{1}{2}}PBr_3$ = 33 min, $t_{\frac{1}{2}}PBr_2Cl$ = 33 min, $t_{\frac{1}{2}}PBrCl_2$ = 32 min, $t_{\frac{1}{2}}PCl_3$ = 33 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the volume of its vapour.

TABLE AXV

Kinetic Data[a] at 35°C for Sample 15[b] with

iN_{PBr_3} = 0.41, iN_{PCl_3} = 0.59 and 0.0132 mmol H_2O[c]

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
3.2	0.373	0.028	0.014	0.585
9.6	0.355	0.036	0.021	0.587
15.6	0.345	0.056	0.048	0.551
22.8	0.319	0.067	0.076	0.538
28.7	0.304	0.083	0.089	0.524
35.9	0.300	0.087	0.103	0.510
46.6	0.292	0.099	0.130	0.479
63.0	0.246	0.136	0.158	0.460
78.1	0.238	0.148	0.184	0.430
93.3	0.210	0.167	0.208	0.415
107.4	0.203	0.183	0.211	0.402
211.8	0.155	0.217	0.286	0.342
222.4	0.163	0.223	0.295	0.319
235.0	0.153	0.238	0.298	0.311
251.0	0.150	0.236	0.304	0.310
263.0	0.147	0.240	0.316	0.297
322.7	0.135	0.246	0.321	0.297
333.4	0.129	0.248	0.327	0.296
342.6	0.135	0.245	0.334	0.286
363.2	0.131	0.235	0.334	0.300
427.1	0.117	0.254	0.353	0.277
438.4	0.117	0.244	0.351	0.289
489.1	0.113	0.252	0.351	0.284

TABLE AXV (Cont'd)

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
498.2	0.112	0.253	0.357	0.278
17.7 hr	0.100	0.265	0.359	0.276
17.8 hr	0.099	0.261	0.371	0.269
5.0 days	0.095	0.278	0.385	0.242
5.0 days	0.096	0.277	0.388	0.239

[a] $t_{\frac{1}{2}}PBr_3$ = 70 min, $t_{\frac{1}{2}}PBr_2Cl$ = 70 min, $t_{\frac{1}{2}}PBrCl_2$ = 84 min, $t_{\frac{1}{2}}PCl_3$ = 86 min. Data does not obey first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the volume of its vapour.

TABLE AXVI

Kinetic Data[a] at 35°C for Sample 16[b] with

iN_{PBr_3} = 0.41, iN_{PCl_3} = 0.59 and 0.0193 mmol H_2O[c]

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
3.1	0.364	0.032	0.034	0.569
10.0	0.316	0.081	0.084	0.519
16.8	0.287	0.130	0.143	0.441
24.0	0.244	0.152	0.178	0.426
30.8	0.233	0.144	0.215	0.408
37.9	0.209	0.173	0.236	0.382
44.7	0.211	0.175	0.271	0.342
52.0	0.171	0.211	0.288	0.330
58.8	0.173	0.213	0.301	0.313
67.2	0.156	0.216	0.317	0.311
77.8	0.153	0.238	0.317	0.292
108.0	0.121	0.252	0.350	0.277
113.7	0.118	0.259	0.365	0.258
124.5	0.117	0.270	0.355	0.258
137.8	0.112	0.276	0.371	0.242
153.1	0.106	0.277	0.372	0.246
226.6	0.106	0.277	0.372	0.246
233.9	0.104	0.273	0.377	0.246
242.7	0.105	0.263	0.385	0.248
253.4	0.106	0.273	0.374	0.247

TABLE AXVI (Cont'd)

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
4.2 days	0.104	0.274	0.376	0.246
4.2 days	0.102	0.276	0.374	0.248

[a] $t_{\frac{1}{2}}PBr_3$ = 27 min, $t_{\frac{1}{2}}PBr_2Cl$ = 29 min, $t_{\frac{1}{2}}PBrCl_2$ = 26 min, $t_{\frac{1}{2}}PCl_3$ = 26 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the volume of its vapour.

TABLE AXVII

Kinetic Data[a] at 35°C for Sample 17[b] with

iN_{PBr_3} = 0.38, iN_{PCl_3} = 0.62 and 0.0258 mmol H_2O[c]

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
3.1	0.349	0.033	0.059	0.558
9.7	0.263	0.086	0.136	0.515
15.8	0.244	0.116	0.218	0.423
23.0	0.164	0.168	0.280	0.389
29.7	0.152	0.193	0.322	0.332
37.4	0.116	0.209	0.349	0.325
44.8	0.108	0.237	0.368	0.287
53.0	0.098	0.244	0.371	0.283
60.1	0.096	0.238	0.385	0.281
68.5	0.091	0.239	0.386	0.284
74.9	0.090	0.239	0.388	0.282
83.4	0.091	0.254	0.384	0.270
106.0	0.091	0.249	0.385	0.274
122.9	0.084	0.251	0.390	0.275
4.0 days	0.088	0.258	0.388	0.266
4.0 days	0.086	0.250	0.381	0.283

[a] $t_{½}PBr_3$ = 11.5 min, $t_{½}PBr_2Cl$ = 12.5 min, $t_{½}PBrCl_2$ = 10.5 min, $t_{½}PCl_3$ = 11.0 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the volume of its vapour.

TABLE AXVIII

Kinetic Data[a] at 35°C for Sample 18[b] with

iN_{PBr_3} = 0.41, iN_{PCl_3} = 0.59 and 0.0064 mmol H_2O[c]

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.7	0.407	0.000	0.000	0.593
10.4	0.378	0.019	0.014	0.589
16.8	0.356	0.032	0.028	0.584
24.0	0.355	0.037	0.043	0.565
30.8	0.350	0.041	0.058	0.551
37.8	0.341	0.046	0.058	0.554
44.6	0.332	0.051	0.073	0.545
51.8	0.339	0.063	0.082	0.516
59.7	0.321	0.071	0.095	0.513
68.2	0.292	0.080	0.098	0.529
77.7	0.297	0.090	0.118	0.495
94.0	0.277	0.105	0.136	0.482
109.8	0.282	0.124	0.157	0.436
123.2	0.270	0.137	0.159	0.434
240.3	0.218	0.184	0.225	0.373
247.0	0.203	0.184	0.230	0.383
263.7	0.200	0.196	0.244	0.359
288.2	0.189	0.204	0.251	0.356
393.0	0.173	0.214	0.286	0.326
400.0	0.171	0.212	0.291	0.326
458.0	0.167	0.220	0.302	0.311
466.0	0.155	0.217	0.309	0.319

TABLE AXVIII (Cont'd)

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
17.7 hr	0.122	0.270	0.349	0.259
17.8 hr	0.120	0.262	0.348	0.270
22.9 hr	0.108	0.269	0.369	0.254
23.0 hr	0.109	0.268	0.362	0.261
47.0 hr	0.104	0.267	0.371	0.257
47.0 hr	0.109	0.268	0.377	0.246

[a] $t_{\frac{1}{2}}PBr_3$ = 132 min, $t_{\frac{1}{2}}PBr_2Cl$ = 150 min, $t_{\frac{1}{2}}PBrCl_2$ = 162 min, $t_{\frac{1}{2}}PCl_3$ = 156 min. Data does not obey first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the volume of its vapour.

TABLE AXIX

Kinetic Data[a] at 35°C for Sample 19[b] with

iN_{PBr_3} = 0.40, iN_{PCl_3} = 0.60 and 0.0130 mmol H_2O[c]

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
4.8	0.328	0.054	0.069	0.549
12.2	0.292	0.090	0.135	0.483
18.6	0.272	0.115	0.174	0.439
25.2	0.228	0.146	0.211	0.416
31.8	0.202	0.172	0.247	0.380
39.1	0.173	0.200	0.268	0.359
45.9	0.166	0.196	0.298	0.339
53.2	0.153	0.215	0.314	0.319
59.7	0.143	0.209	0.334	0.313
68.6	0.133	0.240	0.339	0.288
77.7	0.118	0.250	0.350	0.283
93.3	0.112	0.255	0.355	0.278
107.7	0.102	0.251	0.375	0.272
122.9	0.099	0.258	0.383	0.260
226.5	0.095	0.258	0.382	0.265
234.3	0.095	0.258	0.377	0.270
28.6 hr	0.094	0.254	0.385	0.267
28.7 hr	0.097	0.271	0.375	0.257

[a] $t_{½}PBr_3$ = 23 min, $t_{½}PBr_2Cl$ = 23 min, $t_{½}PBrCl_2$ = 22 min, $t_{½}PCl_3$ = 20 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the volume of its vapour.

TABLE AXX

Kinetic Data[a] at 35°C for Sample 20[b] with

iN_{PBr_3} = 0.39, iN_{PCl_3} = 0.61 and 0.0193 mmol H_2O[c]

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.8	0.300	0.068	0.101	0.531
9.0	0.234	0.122	0.195	0.451
20.1	0.186	0.182	0.284	0.347
27.2	0.139	0.200	0.320	0.341
33.7	0.140	0.232	0.337	0.290
40.4	0.121	0.237	0.358	0.284
45.5	0.118	0.240	0.363	0.279
53.1	0.102	0.242	0.378	0.278
59.7	0.101	0.252	0.373	0.273
67.2	0.098	0.255	0.379	0.268
76.8	0.102	0.260	0.378	0.259
84.3	0.093	0.250	0.397	0.259
107.8	0.094	0.259	0.391	0.256
116.3	0.093	0.261	0.387	0.259
129.8	0.095	0.268	0.384	0.253
137.1	0.090	0.268	0.379	0.263
13.2 hr	0.089	0.260	0.392	0.259

[a] $t_{½}PBr_3$ = 13.5 min, $t_{½}PBr_2Cl$ = 13.0 min, $t_{½}PBrCl_2$ = 12.0 min, $t_{½}PCl_3$ = 12.0 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the volume of its vapour.

TABLE AXXI

Kinetic Data[a] at 35°C for Sample 21[b] with

iN_{PBr_3} = 0.37, iN_{PCl_3} = 0.63 and 0.0126 mmol H_2O[c]

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.9	0.335	0.042	0.033	0.589
9.9	0.277	0.064	0.084	0.575
16.8	0.284	0.084	0.117	0.514
25.1	0.236	0.114	0.146	0.504
31.8	0.230	0.125	0.182	0.463
39.1	0.218	0.136	0.195	0.450
45.7	0.189	0.161	0.219	0.431
54.2	0.183	0.167	0.230	0.420
72.3	0.155	0.195	0.277	0.373
79.9	0.147	0.199	0.282	0.373
92.8	0.149	0.205	0.298	0.348
108.4	0.127	0.209	0.310	0.354
122.4	0.125	0.215	0.316	0.344
153.5	0.119	0.226	0.336	0.319
354 days	0.080	0.247	0.381	0.292
354 days	0.078	0.249	0.384	0.289
354 days	0.083	0.248	0.376	0.294
354 days	0.077	0.250	0.381	0.292

[a] $t_{½}PBr_3$ = 46 min, $t_{½}PBr_2Cl$ = 41 min, $t_{½}PBrCl_2$ = 45 min, $t_{½}PCl_3$ = 42 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the volume of its vapour, and allowed to react for 2 hr with PBr_3 prior to addition of PCl_3.

TABLE AXXII

Kinetic Data[a] at 35°C for Sample 22[b] with

iN_{PBr_3} = 0.39, iN_{PCl_3} = 0.61 and 0.0126 mmol H_2O[c]

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.6	0.327	0.045	0.113	0.516
10.1	0.234	0.125	0.195	0.446
16.7	0.210	0.163	0.256	0.371
23.9	0.171	0.203	0.281	0.345
31.0	0.154	0.215	0.306	0.325
38.0	0.132	0.227	0.327	0.314
44.7	0.126	0.233	0.336	0.305
53.1	0.118	0.255	0.342	0.285
62.9	0.116	0.261	0.348	0.275
70.8	0.108	0.265	0.356	0.271
82.8	0.097	0.262	0.368	0.274
93.3	0.091	0.267	0.371	0.271
354 days	0.081	0.264	0.387	0.268
354 days	0.080	0.276	0.374	0.270
354 days	0.082	0.258	0.385	0.276
354 days	0.084	0.261	0.385	0.269

[a] $t_{½}PBr_3$ = 12.5 min, $t_{½}PBr_2Cl$ = 13.0 min, $t_{½}PBrCl_2$ = 11.0 min, $t_{½}PCl_3$ = 10.5 min. Data does not obey first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the volume of its vapour, and allowed to react for 2 hr with PBr_3 prior to addition of PCl_3.

TABLE AXXIII

Kinetic Data[a] at 35°C for Sample 23[b] with

iN_{PBr_3} = 0.36, iN_{PCl_3} = 0.64 and 0.0127 mmol H_2O[c]

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
3.0	0.336	0.013	0.022	0.629
10.0	0.303	0.041	0.053	0.603
16.8	0.289	0.052	0.072	0.587
24.1	0.281	0.062	0.089	0.563
30.7	0.279	0.071	0.103	0.548
40.2	0.257	0.084	0.122	0.537
47.6	0.257	0.093	0.146	0.504
63.1	0.235	0.110	0.171	0.483
77.6	0.205	0.136	0.200	0.459
93.3	0.183	0.149	0.227	0.441
250.6	0.119	0.213	0.334	0.334
258.2	0.115	0.217	0.334	0.334
368.0	0.099	0.221	0.361	0.319
374.0	0.097	0.223	0.364	0.315
354 days	0.076	0.234	0.396	0.295
354 days	0.067	0.222	0.402	0.309
354 days	0.076	0.238	0.398	0.288
354 days	0.076	0.234	0.391	0.300

[a] $t_{½}PBr_3$ = 100 min, $t_{½}PBr_2Cl$ = 76 min, $t_{½}PBrCl_2$ = 96 min, $t_{½}PCl_3$ = 82 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the volume of its vapour, and allowed to react for 2 hr with PCl_3 prior to addition of PBr_3.

TABLE AXXIV

Kinetic Data[a] at 35°C for Sample 24[b] with

iN_{PBr_3} = 0.35, iN_{PCl_3} = 0.65 and 0.0124 mmol H_2O[c]

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.5	0.318	0.026	0.037	0.619
9.0	0.283	0.061	0.059	0.597
15.6	0.263	0.086	0.101	0.550
21.7	0.231	0.104	0.134	0.531
28.8	0.218	0.119	0.161	0.502
36.2	0.192	0.131	0.187	0.490
45.1	0.183	0.158	0.219	0.440
52.6	0.150	0.164	0.252	0.434
63.7	0.146	0.191	0.268	0.395
72.7	0.120	0.190	0.292	0.398
80.5	0.119	0.200	0.297	0.384
354 days	0.070	0.228	0.394	0.308
354 days	0.068	0.230	0.387	0.314
354 days	0.064	0.225	0.392	0.320
354 days	0.069	0.224	0.392	0.315

[a] $t_{½}PBr_3$ = 33 min, $t_{½}PBr_2Cl$ = 29 min, $t_{½}PBrCl_2$ = 38 min, $t_{½}PCl_3$ = 37 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the volume of its vapour, and allowed to react for 2 hr with PCl_3 prior to addition of PBr_3.

TABLE AXXV

Kinetic Data[a] at 35°C for Sample 25[b] with

iN_{PBr_3} = 0.38, iN_{PCl_3} = 0.62 and 0.00759 mmol H_2O[c]

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
3.5	0.332	0.027	0.014	0.627
9.6	0.304	0.050	0.044	0.602
15.7	0.279	0.071	0.084	0.567
28.3	0.253	0.096	0.123	0.528
40.7	0.229	0.120	0.183	0.468
55.1	0.184	0.165	0.232	0.419
62.7	0.177	0.183	0.249	0.392
81.3	0.144	0.191	0.292	0.373
93.3	0.139	0.205	0.309	0.347
110.2	0.123	0.212	0.327	0.338
126.2	0.121	0.219	0.347	0.314
159.1	0.102	0.229	0.365	0.305
19.0 hr	0.092	0.243	0.376	0.288
19.1 hr	0.088	0.247	0.371	0.294

[a] $t_{1/2}PBr_3$ = 38 min, $t_{1/2}PBr_2Cl$ = 37 min, $t_{1/2}PBrCl_2$ = 34 min, $t_{1/2}PCl_3$ = 34 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the weight of the cobalt complex.

TABLE AXXVI

Kinetic Data[a] at 35°C for Sample 26[b] with

iN_{PBr_3} = 0.38, iN_{PCl_3} = 0.62 and 0.0145 mmol H_2O[c]

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.5	0.302	0.074	0.108	0.517
8.6	0.165	0.183	0.239	0.412
14.8	0.146	0.208	0.307	0.339
20.8	0.102	0.242	0.341	0.314
26.7	0.096	0.257	0.361	0.286
32.9	0.084	0.256	0.374	0.286
38.5	0.090	0.250	0.376	0.284
46.9	0.080	0.255	0.379	0.286
62.7	0.086	0.249	0.374	0.291

[a] $t_{½}PBr_3$ = 6 min, $t_{½}PBr_2Cl$ = 6 min, $t_{½}PBrCl_2$ = 6 min, $t_{½}PCl_3$ = 6 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the weight of the cobalt complex.

TABLE AXXVII

Kinetic Data[a] at 35°C for Sample 27[b] with

iN_{PBr_3} = 0.38, iN_{PCl_3} = 0.62 and 0.0148 mmol H_2O[c]

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
3.1	0.342	0.025	0.041	0.592
8.6	0.259	0.085	0.118	0.538
14.7	0.252	0.116	0.181	0.451
20.9	0.202	0.143	0.217	0.439
26.7	0.191	0.153	0.240	0.415
34.3	0.162	0.178	0.265	0.395
42.6	0.157	0.192	0.293	0.358
54.0	0.131	0.204	0.321	0.343
62.6	0.126	0.223	0.342	0.309
78.0	0.103	0.232	0.362	0.303
5.9 hr	0.085	0.246	0.389	0.280
6.0 hr	0.086	0.249	0.389	0.277

[a] $t_{½}PBr_3$ = 20.5 min, $t_{½}PBr_2Cl$ = 20.0 min, $t_{½}PBrCl_2$ = 20.8 min, $t_{½}PCl_3$ = 20.6 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the weight of the cobalt complex.

TABLE AXXVIII

Kinetic Data[a] at 35°C for Sample 28[b] with

iN_{PBr_3} = 0.39, iN_{PCl_3} = 0.61 and 0.0215 mmol H_2O[c]

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.8	0.326	0.051	0.082	0.541
9.9	0.243	0.126	0.167	0.465
15.7	0.205	0.168	0.217	0.411
23.2	0.171	0.188	0.254	0.386
30.0	0.161	0.203	0.288	0.348
36.9	0.145	0.224	0.313	0.319
42.6	0.134	0.225	0.329	0.312
54.1	0.123	0.241	0.342	0.294
62.7	0.104	0.245	0.363	0.288
16.4 hr	0.094	0.265	0.364	0.277
16.5 hr	0.096	0.263	0.368	0.273

[a] $t_{½}PBr_3$ = 16.7 min, $t_{½}PBr_2Cl$ = 16.0 min, $t_{½}PBrCl_2$ = 14.5 min, $t_{½}PCl_3$ = 14.7 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the weight of the cobalt complex.

TABLE AXXIX

Kinetic Data[a] at 35°C for Sample 29[b] with

iN_{PBr_3} = 0.39, iN_{PCl_3} = 0.61 and 0.00796 mmol H_2O[c]

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.2	0.317	0.046	0.054	0.583
9.8	0.225	0.139	0.135	0.501
15.3	0.209	0.145	0.221	0.425
23.1	0.149	0.164	0.253	0.434
39.0	0.135	0.219	0.326	0.320
47.0	0.104	0.231	0.348	0.316
51.6	0.108	0.237	0.350	0.306
59.1	0.094	0.215	0.380	0.311
70.4	0.097	0.238	0.367	0.298
78.8	0.089	0.251	0.378	0.282
349.1	0.088	0.257	0.385	0.270
357.5	0.087	0.258	0.382	0.274
335 days	0.090	0.250	0.386	0.275
335 days	0.082	0.253	0.384	0.282
335 days	0.086	0.259	0.390	0.265
335 days	0.085	0.260	0.382	0.274

[a] $t_{½}PBr_3$ = 14.0 min, $t_{½}PBr_2Cl$ = 15.0 min, $t_{½}PBrCl_2$ = 14.5 min, $t_{½}PCl_3$ = 15.0 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the weight of the cobalt complex.

TABLE AXXX

Kinetic Data[a] at 35°C for Sample 30[b] with

iN_{PBr_3} = 0.37, iN_{PCl_3} = 0.63 and 0.0147 mmol H_2O[c]

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.8	0.277	0.096	0.113	0.515
11.4	0.144	0.174	0.239	0.443
17.8	0.137	0.190	0.300	0.373
25.1	0.105	0.213	0.338	0.344
33.0	0.101	0.217	0.352	0.330
41.1	0.083	0.235	0.367	0.315
334 days	0.072	0.240	0.396	0.291
334 days	0.072	0.240	0.391	0.296
334 days	0.078	0.249	0.394	0.279
334 days	0.071	0.242	0.397	0.290

[a] $t_{½}PBr_3$ = 10.5 min, $t_{½}PBr_2Cl$ = 11.0 min, $t_{½}PBrCl_2$ = 11.5 min, $t_{½}PCl_3$ = 12.0 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the weight of the cobalt complex.

TABLE AXXXI

Kinetic Data[a] at 35°C for Sample 31[b] with

iN_{PBr_3} = 0.36, iN_{PCl_3} = 0.64 and 0.0213 mmol H_2O[c]

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.5	0.282	0.048	0.060	0.610
9.1	0.199	0.110	0.148	0.544
14.7	0.205	0.131	0.208	0.456
22.3	0.146	0.171	0.258	0.425
28.6	0.138	0.183	0.302	0.376
35.1	0.108	0.200	0.331	0.360
42.9	0.108	0.219	0.354	0.320
50.0	0.094	0.215	0.363	0.329
56.8	0.090	0.214	0.385	0.311
62.9	0.081	0.232	0.381	0.306
234 days	0.073	0.236	0.395	0.295
234 days	0.074	0.236	0.398	0.292
234 days	0.076	0.234	0.403	0.287
234 days	0.075	0.236	0.401	0.289

[a] $t_{1/2}PBr_3$ = 14.5 min, $t_{1/2}PBr_2Cl$ = 14.0 min, $t_{1/2}PBrCl_2$ = 14.5 min, $t_{1/2}PCl_3$ = 14.0 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the weight of the cobalt complex.

TABLE AXXXII

Kinetic Data[a] at 35°C for Sample 32[b] with

iN_{PBr_3} = 0.38, iN_{PCl_3} = 0.62 and 0.0148 mmol H_2O[c]

time (min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.3	0.340	0.011	0.009	0.640
9.1	0.325	0.034	0.028	0.613
15.6	0.317	0.047	0.049	0.588
22.9	0.279	0.071	0.084	0.566
38.8	0.266	0.089	0.127	0.519
47.8	0.244	0.101	0.135	0.520
60.1	0.237	0.122	0.153	0.489
72.9	0.202	0.143	0.178	0.477
96.9	0.188	0.159	0.210	0.443
195.7	0.147	0.202	0.291	0.360
203.0	0.130	0.200	0.300	0.370
16.6 hr	0.092	0.238	0.373	0.297
16.7 hr	0.090	0.245	0.366	0.299

[a] $t_{1/2}PBr_3$ = 75 min, $t_{1/2}PBr_2Cl$ = 67 min, $t_{1/2}PBrCl_2$ = 79 min, $t_{1/2}PCl_3$ = 78 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the weight of the cobalt complex, and allowed to react for 2 hr with PCl_3 prior to addition of PBr_3.

TABLE AXXXIII

Kinetic Data[a] at 35°C for Sample 33[b] with

iN_{PBr_3} = 0.37, iN_{PCl_3} = 0.63 and 0.0145 mmol H_2O[c]

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
3.2	0.333	0.017	0.009	0.641
9.9	0.318	0.031	0.037	0.614
15.7	0.306	0.038	0.065	0.590
25.1	0.296	0.044	0.074	0.586
38.7	0.290	0.055	0.100	0.555
47.7	0.274	0.065	0.104	0.557
59.8	0.264	0.076	0.122	0.539
73.0	0.251	0.088	0.136	0.525
107.0	0.226	0.113	0.177	0.484
122.8	0.210	0.115	0.191	0.484
138.8	0.208	0.127	0.195	0.470
170.9	0.177	0.139	0.246	0.437
187.5	0.182	0.158	0.252	0.408
14.9 hr	0.086	0.245	0.375	0.295
15.0 hr	0.081	0.227	0.379	0.312

[a] $t_{½}PBr_3$ = 128 min, $t_{½}PBr_2Cl$ = 132 min, $t_{½}PBrCl_2$ = 122 min, $t_{½}PCl_3$ = 128 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the weight of the cobalt complex, and allowed to react for 2 hr with PCl_3 prior to addition of PBr_3.

TABLE AXXXIV

Kinetic Data[a] at 35°C for Sample 34[b] with

iN_{PBr_3} = 0.39, iN_{PCl_3} = 0.61 and 0.0147 mmol H_2O[c]

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
3.5	0.324	0.053	0.070	0.553
9.8	0.238	0.106	0.157	0.499
17.5	0.214	0.134	0.232	0.420
23.8	0.182	0.172	0.270	0.377
29.5	0.170	0.170	0.295	0.365
37.5	0.144	0.200	0.311	0.344
59.9	0.114	0.235	0.358	0.294
66.6	0.111	0.238	0.358	0.294
82.3	0.113	0.235	0.365	0.286
98.4	0.107	0.238	0.373	0.282
344.3	0.096	0.248	0.379	0.276
363.2	0.091	0.254	0.377	0.278
21.8 hr	0.099	0.264	0.377	0.260
21.9 hr	0.096	0.258	0.375	0.271

[a] $t_{½}PBr_3$ = 16.0 min, $t_{½}PBr_2Cl$ = 17.5 min, $t_{½}PBrCl_2$ = 14.7 min, $t_{½}PCl_3$ = 16.0 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the weight of the cobalt complex, and allowed to react for 2 hr with PBr_3 prior to addition of PCl_3.

TABLE AXXXV

Kinetic Data[a] at 35°C for Sample 35[b] with

iN_{PBr_3} = 0.38, iN_{PCl_3} = 0.62 and 0.0144 mmol H_2O[c]

time(min)	N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}
2.8	0.310	0.039	0.052	0.599
8.9	0.258	0.091	0.112	0.538
15.7	0.247	0.112	0.170	0.471
24.6	0.200	0.149	0.204	0.447
31.6	0.183	0.157	0.231	0.429
40.2	0.158	0.172	0.256	0.413
48.7	0.161	0.184	0.278	0.377
66.7	0.134	0.206	0.302	0.358
91.0	0.119	0.212	0.340	0.329
15.2 hr	0.086	0.249	0.380	0.285
15.3 hr	0.085	0.251	0.386	0.278

[a] $t_{½}PBr_3$ = 29.0 min, $t_{½}PBr_2Cl$ = 29.5 min, $t_{½}PBrCl_2$ = 30.5 min, $t_{½}PCl_3$ = 31.0 min. Data obeys first-order kinetics.

[b] Sample was prepared on a grease-free system.

[c] Determined from the weight of the cobalt complex, and allowed to react for 2 hr with PBr_3 prior to addition of PCl_3.

APPENDIX B

Appendix B consists of Tables BI to BVI which contain the equilibrium mole fractions and equilibrium constants for the PCl_3-PBr_3 system at 35°C, 37°C, 40.5°C, 50°C, 60°C, and 70°C respectively. The equilibrium constants are of the form

$$K = (N_{PBr_2Cl})(N_{PBrCl_2})/(N_{PBr_3})(N_{PCl_3})$$

Each entry in a table corresponds to a different sample. The equilibrium constants are calculated from mole fractions, which are given as the average of two or more scans. The range for each equilibrium constant, which is obtained from the calculation of the individual scans, is placed in brackets next to the equilibrium constant calculated from the average mole fractions.

TABLE BI

Equilibrium Mole Fractions and Equilibrium Constants at 35°C

N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}	K[a]
0.092	0.270	0.384	0.254	4.44^4 (4.25 → 4.62)
0.105	0.288	0.381	0.226	4.62^2 (4.50 → 4.78)
0.086	0.251	0.389	0.274	4.14^4 (4.00 → 4.29)
0.096	0.275	0.375	0.254	4.23^4 (4.06 → 4.31)
0.096	0.277	0.387	0.240	4.65^2 (4.65 → 4.68)
0.104	0.273	0.376	0.247	4.00^7 (3.89 → 4.08)
0.087	0.254	0.385	0.274	4.10^2 (3.91 → 4.27)
0.108	0.268	0.370	0.254	3.61^4 (3.41 → 3.77)
0.095	0.260	0.380	0.265	3.92^4 (3.79 → 4.07)
0.092	0.263	0.387	0.258	4.29^5 (4.19 → 4.42)
0.080	0.248	0.380	0.292	4.03^4 (3.82 → 4.24)
0.082	0.265	0.382	0.271	4.55^4 (4.39 → 4.78)
0.076	0.235	0.395	0.294	4.15^3 (4.01 → 4.33)
0.068	0.227	0.391	0.314	4.16^4 (4.04 → 4.31)
0.090	0.245	0.374	0.291	3.50^2 (3.45 → 3.54)
0.085	0.252	0.376	0.287	3.88^4 (3.68 → 4.22)
0.086	0.247	0.389	0.278	4.02^2 (4.02 → 4.07)
0.095	0.264	0.366	0.275	3.70^2 (3.69 → 3.70)
0.091	0.241	0.370	0.298	3.29^2 (3.25 → 3.33)
0.084	0.236	0.377	0.303	3.50^2 (3.40 → 3.62)
0.096	0.256	0.377	0.271	3.71^4 (3.55 → 3.87)
0.086	0.250	0.383	0.281	3.96^2 (3.86 → 4.10)
0.086	0.256	0.385	0.273	4.20^6 (3.90 → 4.43)
0.074	0.236	0.399	0.291	4.37^4 (4.33 → 4.37)
0.073	0.243	0.395	0.289	4.55^4 (4.40 → 4.65)

[a] The superscript refers to the number of scans used to obtain the average mole fractions and equilibrium constant.

TABLE BII

Equilibrium Mole Fractions and Equilibrium Constants at 37°C

N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}	K^a
0.174	0.305	0.361	0.160	3.95^2 (3.88 → 4.06)
0.064	0.216	0.388	0.332	3.95^2 (3.87 → 4.13)
0.296	0.384	0.245	0.075	4.24^2 (4.04 → 4.48)
0.275	0.393	0.238	0.094	3.62^2 (3.24 → 4.06)
0.286	0.364	0.255	0.095	3.42^2 (3.08 → 3.76)
0.098	0.257	0.384	0.261	3.82^2 (3.81 → 3.95)
0.099	0.276	0.389	0.236	4.60^2 (4.56 → 4.65)
0.093	0.275	0.376	0.256	4.34^2 (4.32 → 4.40)
0.106	0.296	0.378	0.220	4.80^2 (4.72 → 4.88)

[a] The superscript refers to the number of scans used to obtain the average mole fractions and equilibrium constant.

TABLE BIII

Equilibrium Mole Fractions and Equilibrium Constants at 40.5°C

N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}	K^a
0.172	0.316	0.346	0.166	3.83^9 (3.03 → 4.39)
0.064	0.225	0.393	0.318	4.34^6 (4.10 → 4.54)
0.319	0.378	0.233	0.070	3.94^8 (3.49 → 4.55)
0.284	0.395	0.234	0.087	3.70^2 (3.21 → 4.38)
0.259	0.370	0.276	0.095	4.15^2 (3.91 → 4.28)
0.080	0.262	0.400	0.258	5.08^2 (5.02 → 5.20)
0.082	0.265	0.391	0.262	4.82^2 (4.69 → 5.04)
0.083	0.260	0.399	0.258	4.84^2 (4.79 → 4.96)
0.216	0.365	0.302	0.117	4.36^2 (4.09 → 4.67)
0.103	0.274	0.390	0.233	4.45^2 (4.39 → 4.57)
0.117	0.310	0.369	0.204	4.79^4 (4.19 → 5.30)

[a] The superscript refers to the number of scans used to obtain the average mole fractions and equilibrium constant.

TABLE BIV

Equilibrium Mole Fractions and Equilibrium Constants at 50°C

N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}	K^a
0.261	0.364	0.281	0.094	4.17^4 (3.80 → 4.52)
0.074	0.253	0.405	0.268	5.17^2 (5.02 → 5.35)
0.084	0.260	0.390	0.266	4.54^2 (4.45 → 4.65)
0.205	0.369	0.312	0.114	4.93^4 (4.27 → 5.75)
0.123	0.310	0.370	0.197	4.73^2 (4.58 → 4.86)

[a] The superscript refers to the number of scans used to obtain the average mole fractions and equilibrium constant.

TABLE BV

Equilibrium Mole Fractions and Equilibrium Constants at 60°C

N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}	K^a
0.105	0.287	0.349	0.259	3.68^2 (3.51 → 3.87)
0.258	0.371	0.280	0.091	4.42^4 (4.03 → 4.98)
0.079	0.258	0.396	0.267	4.84^2 (4.76 → 4.94)
0.077	0.259	0.398	0.266	5.03^2 (4.91 → 5.23)
0.205	0.380	0.305	0.110	5.14 (5.05 → 5.21)

[a] The superscript refers to the number of scans used to obtain the average mole fractions and equilibrium constant.

TABLE BVI

Equilibrium Mole Fractions and Equilibrium Constants at 70°C

N_{PBr_3}	N_{PBr_2Cl}	N_{PBrCl_2}	N_{PCl_3}	K^a
0.136	0.301	0.355	0.208	3.78^2 (3.68 → 3.84)
0.097	0.280	0.372	0.251	4.28^2 (4.28 → 4.30)
0.250	0.380	0.280	0.090	4.73^4 (4.06 → 5.54)
0.076	0.274	0.384	0.266	5.20^2 (5.18 → 5.22)
0.078	0.267	0.399	0.256	5.34^2 (5.21 → 5.47)
0.211	0.384	0.302	0.103	5.34^2 (5.27 → 5.45)

[a] The superscript refers to the number of scans used to obtain the average mole fractions and equilibrium constant.

APPENDIX C

Appendix C consists of Tables CI to CVI which contain the concentration-time data for samples 1 to 6 respectively, for the kinetics of the CF_3PCl_2-CF_3PBr_2 system. All concentrations are in mole fractions. For all the samples the initial mole fractions of the reactants were calculated from the mole fractions of all the species at equilibrium, as has been explained in the text. The half-lives of the reactions were estimated from the concentration versus time plots.

TABLE CI

Kinetic Data[a] at 40°C for Sample 1 with

$iN_{CF_3PBr_2} = 0.49$, $iN_{CF_3PCl_2} = 0.51$

time (min)	$N_{CF_3PBr_2}$	N_{CF_3PBrCl}	$N_{CF_3PCl_2}$
5.6	0.481	0.048	0.471
12.6	0.462	0.082	0.456
15.6	0.452	0.095	0.452
20.6	0.443	0.117	0.441
25.6	0.433	0.135	0.431
30.6	0.423	0.150	0.427
36.6	0.415	0.168	0.417
42.7	0.408	0.184	0.408
50.9	0.394	0.202	0.404
60.9	0.387	0.224	0.389
75.9	0.374	0.246	0.380
90.9	0.362	0.266	0.372
106.9	0.353	0.283	0.364
120.9	0.342	0.300	0.357
145.9	0.335	0.316	0.348
168.9	0.321	0.335	0.344
181.9	0.320	0.343	0.337
301.9	0.288	0.397	0.315
24.0 hr	0.257	0.459	0.284
48.0 hr	0.255	0.464	0.281

[a] $t_{1/2}CF_3PBr_2 = 64$ min, $t_{1/2}CF_3PBrCl = 67$ min, $t_{1/2}CF_3PCl_2 = 63$ min.

Data does not obey either first-order or second-order kinetics.

TABLE CII

Kinetic Data[a] at 42°C for Sample 2 with

$iN_{CF_3PBr_2} = 0.46$, $iN_{CF_3PCl_2} = 0.54$

time (min)	$N_{CF_3PBr_2}$	N_{CF_3PBrCl}	$N_{CF_3PCl_2}$
5.9	0.484	0.000	0.516
9.9	0.489	0.002	0.509
15.9	0.484	0.005	0.511
22.9	0.457	0.007	0.536
30.9	0.454	0.008	0.539
45.9	0.450	0.010	0.540
60.9	0.444	0.015	0.540
145.9	0.446	0.031	0.525
278.0	0.442	0.055	0.504
336.0	0.440	0.065	0.495
416.0	0.442	0.077	0.481
471.0	0.445	0.086	0.469
17.9 hr	0.324	0.288	0.388
23.8 hr	0.274	0.377	0.349
28.3 hr	0.267	0.391	0.341
32.2 hr	0.264	0.402	0.333
49.9 hr	0.243	0.436	0.321
49.9 hr	0.240	0.433	0.327
10.1 days	0.231	0.461	0.308
10.1 days	0.231	0.460	0.309

[a] $t_{1/2}CF_3PBr_2 = 8.0$ hr, $t_{1/2}CF_3PBrCl = 14.2$ hr, $t_{1/2}CF_3PCl_2 = 12.7$ hr. Data does not obey first-order kinetics.

TABLE CIII

Kinetic Data[a] at 42°C for Sample 3 with

$iN_{CF_3PBr_2} = 0.47$, $iN_{CF_3PCl_2} = 0.53$

time (min)	$N_{CF_3PBr_2}$	N_{CF_3PBrCl}	$N_{CF_3PCl_2}$
5.9	0.473	0.010	0.517
9.9	0.467	0.020	0.514
14.9	0.456	0.030	0.514
20.9	0.451	0.045	0.504
26.9	0.443	0.055	0.503
35.9	0.435	0.082	0.484
45.9	0.420	0.104	0.476
60.9	0.401	0.150	0.449
198.9	0.304	0.343	0.353
255.9	0.287	0.375	0.338
326.9	0.275	0.399	0.326
390.9	0.273	0.409	0.318
16.7 hr	0.247	0.448	0.305
23.5 hr	0.247	0.448	0.304
27.9 hr	0.247	0.457	0.297
27.9 hr	0.247	0.455	0.298
30.8 hr	0.251	0.453	0.296
48.7 hr	0.246	0.452	0.302
48.7 hr	0.248	0.447	0.305
10.2 days	0.248	0.451	0.302
10.2 days	0.245	0.457	0.298

[a] $t_{1/2}CF_3PBr_2 = 105$ min, $t_{1/2}CF_3PBrCl = 103$ min, $t_{1/2}CF_3PCl_2 = 104$ min.

Data obeys both first-order and second-order kinetics.

TABLE CIV

Kinetic Data[a] at 42°C for Sample 4 with

$iN_{CF_3PBr_2} = 0.48$, $iN_{CF_3PCl_2} = 0.52$

time(hr)	$N_{CF_3PBr_2}$	N_{CF_3PBrCl}	$N_{CF_3PCl_2}$
0.1	0.489	0.000	0.511
0.2	0.487	0.000	0.513
0.4	0.487	0.000	0.513
0.5	0.484	0.000	0.516
1.6	0.478	0.013	0.509
4.5	0.467	0.027	0.506
11.3	0.450	0.059	0.491
11.3	0.449	0.059	0.493
17.9	0.429	0.097	0.474
17.9	0.433	0.096	0.471
25.8	0.400	0.144	0.457
25.8	0.405	0.143	0.451
36.0	0.385	0.189	0.426
36.0	0.385	0.189	0.427
43.2	0.371	0.213	0.416
43.2	0.369	0.210	0.420
49.8	0.359	0.238	0.404
49.8	0.355	0.240	0.406
59.8	0.343	0.262	0.395
59.8	0.342	0.264	0.394
67.5	0.333	0.282	0.386
67.5	0.330	0.285	0.385
74.8	0.330	0.291	0.379
74.8	0.330	0.291	0.379

TABLE CIV (Cont'd)

time(hr)	$N_{CF_3PBr_2}$	N_{CF_3PBrCl}	$N_{CF_3PCl_2}$
83.7	0.320	0.310	0.370
83.7	0.319	0.308	0.373
91.4	0.313	0.320	0.367
91.4	0.313	0.321	0.366
98.1	0.311	0.324	0.364
98.1	0.309	0.326	0.364
107.8	0.305	0.332	0.363
107.8	0.306	0.333	0.360
115.4	0.302	0.350	0.348
115.4	0.300	0.348	0.352
122.7	0.301	0.350	0.350
122.7	0.302	0.348	0.350
140.1	0.294	0.367	0.340
140.1	0.296	0.366	0.339
156.4	0.288	0.378	0.334
156.4	0.289	0.376	0.335
356.5	0.263	0.429	0.308
356.5	0.259	0.428	0.313
21.7 days	0.264	0.431	0.305
21.7 days	0.266	0.429	0.305
21.7 days	0.266	0.426	0.308
31.0 days	0.262	0.425	0.312
31.0 days	0.262	0.422	0.316
31.0 days	0.261	0.428	0.311

[a] $t_{1/2}CF_3PBr_2$ = 40 hr, $t_{1/2}CF_3PBrCl$ = 43 hr, $t_{1/2}CF_3PCl_2$ = 47 hr.

Data does not obey first-order kinetics.

TABLE CV

Kinetic Data[a] at 42°C for Sample 5 with

$iN_{CF_3PBr_2} = 0.48$, $iN_{CF_3PCl_2} = 0.52$

time(hr)	$N_{CF_3PBr_2}$	N_{CF_3PBrCl}	$N_{CF_3PCl_2}$
0.1	0.496	0.000	0.504
0.2	0.494	0.000	0.506
0.3	0.477	0.000	0.523
0.5	0.475	0.000	0.525
1.8	0.477	0.008	0.515
2.0	0.474	0.013	0.514
3.9	0.475	0.020	0.505
11.9	0.450	0.063	0.488
11.9	0.451	0.062	0.487
18.5	0.428	0.094	0.478
18.5	0.433	0.095	0.472
25.4	0.408	0.135	0.456
25.4	0.412	0.135	0.454
35.1	0.393	0.168	0.440
35.1	0.395	0.168	0.437
42.7	0.381	0.193	0.426
42.7	0.383	0.193	0.424
49.5	0.378	0.203	0.418
49.5	0.376	0.204	0.420
59.3	0.369	0.223	0.408
59.3	0.367	0.223	0.410

TABLE CV (Cont'd)

time(hr)	$N_{CF_3PBr_2}$	N_{CF_3PBrCl}	$N_{CF_3PCl_2}$
66.9	0.358	0.240	0.402
66.9	0.356	0.241	0.403
74.3	0.357	0.252	0.391
74.3	0.355	0.254	0.392
83.2	0.348	0.258	0.394
83.2	0.342	0.263	0.395
90.0	0.337	0.279	0.385
90.0	0.339	0.274	0.387
97.8	0.330	0.284	0.380
97.8	0.337	0.282	0.381
107.3	0.327	0.294	0.379
107.3	0.325	0.299	0.378
115.0	0.327	0.302	0.371
115.0	0.324	0.300	0.376
122.3	0.321	0.313	0.366
122.3	0.322	0.312	0.365
139.6	0.318	0.324	0.357
139.6	0.315	0.326	0.359
156.1	0.304	0.342	0.354
156.1	0.309	0.342	0.349
156.1	0.311	0.340	0.349
14.8 days	0.263	0.422	0.315
14.8 days	0.272	0.415	0.313
14.8 days	0.269	0.422	0.309

TABLE CV (Cont'd)

time(hr)	$N_{CF_3PBr_2}$	N_{CF_3PBrCl}	$N_{CF_3PCl_2}$
21.7 days	0.271	0.422	0.307
21.7 days	0.268	0.418	0.313
21.7 days	0.269	0.419	0.312
31.0 days	0.261	0.434	0.305
31.0 days	0.262	0.428	0.310
31.0 days	0.259	0.428	0.314

[a] $t_{1/2}CF_3PBr_2$ = 44 hr, $t_{1/2}CF_3PBrCl$ = 51 hr, $t_{1/2}CF_3PCl_2$ = 50 hr.

Data does not obey first-order kinetics.

TABLE CVI

Kinetic Data[a] at 42°C for Sample 6 with

$iN_{CF_3PBr_2} = 0.49$, $iN_{CF_3PCl_2} = 0.51$

time(min)	$N_{CF_3PBr_2}$	N_{CF_3PBrCl}	$N_{CF_3PCl_2}$
8.0	0.284	0.462	0.255
12.0	0.281	0.466	0.252
15.0	0.277	0.462	0.261
20.7 days	0.267	0.454	0.279
20.7 days	0.266	0.456	0.278
20.7 days	0.268	0.455	0.277
30.0 days	0.263	0.459	0.278
30.0 days	0.262	0.456	0.282
30.0 days	0.269	0.448	0.283

[a] $t_{1/2}$ for all species is a few minutes.

APPENDIX D

Appendix D consists of Tables DI and DII which contain the equilibrium mole fractions and equilibrium constants for the CF_3PCl_2-CF_3PBr_2 system from 25°C to 60°C. The equilibrium constants are of the form

$$K = (N_{CF_3PClBr})^2/(N_{CF_3PBr_2})(N_{CF_3PCl_2})$$

All the equilibrium constants in Table DI pertain to one sample, whereas every entry in Table DII corresponds to a different sample. The equilibrium constants are calculated from mole fractions which are given as the average of two or more scans. The range for each equilibrium constant, which is obtained from the calculation of the individual scans, is placed in brackets next to the equilibrium constant calculated from the average mole fractions.

TABLE DI

Equilibrium Mole Fractions and Equilibrium Constants

at Various Temperatures

$N_{CF_3PBr_2}$	N_{CF_3PBrCl}	$N_{CF_3PCl_2}$	K	T(°C)
0.232	0.448	0.320	2.70 (2.58 → 2.79)	25.0
0.232	0.451	0.317	2.77 (2.76 → 2.79)	30.0
0.228	0.455	0.317	2.84 (2.83 → 2.85)	40.0
0.223	0.469	0.308	3.20 (3.17 → 3.29)	40.0
0.227	0.459	0.314	2.96 (2.89 → 3.03)	40.0
0.227	0.453	0.320	2.83 (2.76 → 2.92)	40.0
0.231	0.456	0.313	2.88 (2.84 → 2.90)	50.0
0.225	0.450	0.325	2.77 (2.70 → 2.85)	50.0
0.227	0.453	0.320	2.83 (2.77 → 3.08)	50.0
0.230	0.461	0.309	2.98 (2.91 → 3.06)	60.0
0.228	0.457	0.315	2.91 (2.90 → 2.96)	60.0
0.232	0.447	0.321	2.68 (2.54 → 2.79)	60.0
0.256	0.462	0.282	2.96 (2.89 → 3.00)	40.0[a]

[a] Different sample from the rest of the table.

TABLE DII

Equilibrium Mole Fractions and Equilibrium Constants at 42°C

$N_{CF_3PBr_2}$	N_{CF_3PBrCl}	$N_{CF_3PCl_2}$	K
0.247	0.450	0.303	2.71 (2.64 → 2.74)
0.246	0.454	0.300	2.79 (2.72 → 2.86)
0.231	0.461	0.308	2.99 (2.96 → 2.99)
0.267	0.455	0.278	2.79 (2.77 → 2.82)
0.265	0.454	0.281	2.77 (2.64 → 2.88)

APPENDIX E

Appendix E consists of Tables EI to EVI which contain the data for the variation of $1/T_2$ with temperature for ^{31}P in PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3. The data for Tables EI to EIV were collected for a sample in which all the species were present at their equilibrium concentrations. A sample containing just PBr_3 and PCl_3 was used to obtain the data in Tables EV and EVI. The experimental values of $1/T_2$ are compared to the values obtained from a least-squares fit of the data. The equations to which the data were fitted are given in footnotes to the tables.

TABLE EI

Variation of $1/T_2$ with Temperature for ^{31}P in PBr_3 [a]

T(°C)	$10^3/T(°K^{-1})$	$(1/T_2)_{obsd}$	$(1/T_2)_{calcd}$ [b]	$(1/T_2)_{calcd}$ [c]
80.0	2.83	19.00	18.53	17.78
69.2	2.92	18.05	17.03	16.48
59.8	3.00	16.20	15.82	15.43
50.3	3.09	14.90	14.60	14.35
39.5	3.20	13.20	13.29	13.17
30.7	3.29	11.60	12.34	12.31
19.0	3.42	10.80	11.14	11.20
11.0	3.52	10.13	10.34	10.45
0.0	3.66	9.07	9.38	9.53
- 9.6	3.80	7.97	8.57	8.74
- 20.1	3.95	7.20	7.84	8.02
- 31.0	4.13	7.27	7.13	7.30
- 35.4	4.21	7.70	6.86	7.02
- 40.2	4.30	6.40	6.59	6.74
- 45.3	4.39	7.33	6.35	6.48
- 50.8	4.50	5.97	6.09	6.20
- 56.0	4.60	6.60	5.88	5.97
- 59.4	4.67	5.93	5.75	5.83
- 65.8	4.83	5.93	5.49	5.53
- 69.8	4.92	5.27	5.36	5.39
- 74.8	5.05	5.23	5.20	5.20
- 80.4	5.19	4.97	5.06	5.03
- 85.0	5.32	4.77	4.95	4.90
- 90.4	5.48	4.67	4.83	4.75
- 94.9	5.61	5.10	4.75	4.65

TABLE EI (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_2)_{obsd}$	$(1/T_2)_{calcd}$ [b]	$(1/T_2)_{calcd}$ [c]
- 98.8	5.74	4.17	4.68	4.56
-106.0	5.99	4.70	4.58	4.43

[a] For a sample containing a mixture of PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3; values of $1/T_2$ in sec^{-1}.

[b] From a least-squares fit of the data to the equation

$$1/T_2 = 1/T_{2_o} + A\exp(-E_A/RT).$$

[c] From a least-squares fit of the data to the equation

$$1/T_2 = 1/T_{2_o} + A\exp(-2.183\times10^3/T).$$

TABLE EII

Variation of $1/T_2$ with Temperature for ^{31}P in PBr_2Cl[a]

T(°C)	$10^3/T(°K^{-1})$	$(1/T_2)_{obsd}$	$(1/T_2)_{calcd}$[b]
80.0	2.83	52.5	51.78
69.2	2.92	46.90	47.23
59.8	3.00	42.60	43.55
50.3	3.09	40.05	39.80
39.5	3.20	35.55	35.69
30.7	3.29	32.75	32.69
19.0	3.42	29.10	28.85
11.0	3.52	26.37	26.26
0.0	3.66	22.43	23.09
- 9.6	3.80	20.50	20.38
- 20.1	3.95	17.67	17.91
- 31.0	4.13	15.90	15.44
- 35.4	4.21	15.03	14.50
- 40.2	4.30	13.63	13.53
- 45.3	4.39	13.07	12.66
- 50.8	4.50	11.33	11.71
- 56.0	4.60	11.03	10.94
- 59.4	4.67	10.33	10.45
- 65.8	4.83	9.70	9.46
- 69.8	4.92	8.67	8.98
- 74.8	5.05	8.60	8.36
- 8.04	5.19	7.73	7.79
- 85.0	5.32	7.00	7.34
- 90.4	5.48	6.67	6.87
- 94.9	5.61	6.73	6.54

TABLE EII (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_2)_{obsd}$	$(1/T_2)_{calcd}$ [b]
- 98.8	5.74	6.07	6.25
-106.0	5.99	6.17	5.81

[a] For a sample containing a mixture of PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3; values of $1/T_2$ in sec^{-1}.

[b] From a least-squares fit of the data to the equation

$$1/T_2 = 1/T_{2_o} + Aexp(-E_A/RT).$$

TABLE EIII

Variation of $1/T_2$ with Temperature for ^{31}P in $PBrCl_2$ [a]

T(°C)	$10^3/T(°K^{-1})$	$(1/T_2)_{obsd}$	$(1/T_2)_{calcd}$ [b]	$(1/T_2)_{calcd}$ [c]
80.0	2.83	98.70	100.79	102.61
69.2	2.92	90.20	92.00	93.35
59.8	3.00	80.80	84.85	85.86
50.3	3.09	80.10	77.51	78.19
39.5	3.20	70.50	69.42	69.79
30.7	3.29	63.70	63.47	63.63
19.0	3.42	57.30	55.82	55.75
11.0	3.52	51.30	50.60	50.40
0.0	3.66	44.55	44.17	43.85
- 9.6	3.80	38.10	38.61	38.23
- 20.1	3.95	34.00	33.51	33.09
- 31.0	4.13	29.50	28.36	27.96
- 35.4	4.21	26.55	26.37	25.98
- 40.2	4.30	25.55	24.31	23.95
- 45.3	4.39	22.90	22.45	22.12
- 50.8	4.50	19.90	20.40	20.11
- 56.0	4.60	18.55	18.73	18.48
- 59.4	4.67	16.90	17.66	17.44
- 65.8	4.83	15.50	15.50	15.35
- 69.8	4.92	13.70	14.43	14.33
- 74.8	5.05	13.60	13.06	13.02
- 80.4	5.19	11.80	11.78	11.80
- 85.0	5.32	10.30	10.75	10.83
- 90.4	5.48	9.80	9.66	9.81
- 94.9	5.61	9.25	8.90	9.10

TABLE EIII (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_2)_{obsd}$	$(1/T_2)_{calcd}$ [b]	$(1/T_2)_{calcd}$ [c]
- 98.8	5.74	7.60	8.24	8.49
-106.0	5.99	7.80	7.19	7.53

[a] For a sample containing a mixture of PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3; values of $1/T_2$ in sec^{-1}.

[b] From a least-squares fit of the data to the equation $1/T_2 = 1/T_{2_o} + Aexp(-E_A/RT)$.

[c] From a least-squares fit of the data to the equation $1/T_2 = 4.5 + Aexp(-E_A/RT)$.

TABLE EIV

Variation of $1/T_2$ with Temperature for ^{31}P in PCl_3[a]

T(°C)	$10^3/T(°K^{-1})$	$(1/T_2)_{obsd}$	$(1/T_2)_{calcd}$[b]	$(1/T_2)_{calcd}$[c]
80.0	2.83	148.80	159.49	167.39
69.2	2.92	147.80	146.65	152.66
59.8	3.00	138.30	136.12	140.69
50.3	3.09	119.70	125.17	128.37
39.5	3.20	111.80	112.99	114.82
30.7	3.29	107.20	103.92	104.84
19.0	3.42	95.00	92.09	92.00
11.0	3.52	84.20	83.93	83.25
0.0	3.66	75.00	73.71	72.46
- 9.6	3.80	68.60	64.75	63.14
- 20.1	3.95	57.30	56.36	54.57
- 31.0	4.13	49.80	47.74	45.92
- 35.4	4.21	44.90	44.36	42.57
- 40.2	4.30	42.90	40.84	39.13
- 45.3	4.39	37.50	37.60	36.00
- 50.8	4.50	32.70	34.00	32.55
- 56.0	4.60	31.10	31.03	29.75
- 59.4	4.67	27.90	29.12	27.95
- 65.8	4.83	25.70	25.18	24.32
- 69.8	4.92	22.40	23.21	22.52
- 74.8	5.05	20.50	20.65	20.22
- 80.4	5.19	18.20	18.21	18.06
- 85.0	5.32	15.50	16.22	16.33
- 90.4	5.48	14.30	14.08	14.49
- 94.9	5.61	13.00	12.56	13.21

TABLE EIV (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_2)_{obsd}$	$(1/T_2)_{calcd}$ [b]	$(1/T_2)_{calcd}$ [c]
- 98.8	5.74	10.30	11.22	12.10
-106.0	5.99	9.90	9.05	10.34

[a] For a sample containing a mixture of PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3; values of $1/T_2$ in sec^{-1}.

[b] From a least-squares fit of the data to the equation

$$1/T_2 = 1/T_{2_o} + A\exp(-E_A/RT).$$

[c] From a least-squares fit of the data to the equation

$$1/T_2 = 4.5 + A\exp(-E_A/RT).$$

TABLE EV

Variation of $1/T_2$ with Temperature for ^{31}P in PBr_3 [a]

T(°C)	$10^3/T(°K^{-1})$	$(1/T_2)_{obsd}$	$(1/T_2)_{calcd}$ [b]	$(1/T_2)_{calcd}$ [c]
79.6	2.84	16.70	17.51	16.32
69.2	2.92	17.00	16.18	15.31
59.8	3.00	15.05	14.99	14.38
50.3	3.09	14.15	13.80	13.43
39.5	3.20	12.60	12.53	12.39
30.7	3.29	11.50	11.63	11.63
19.0	3.42	10.73	10.51	10.65
11.0	3.52	9.50	9.77	9.99
0.0	3.66	8.80	8.90	9.18
- 9.6	3.80	8.00	8.17	8.48
- 20.1	3.95	7.47	7.54	7.84
- 31.0	4.13	6.77	6.94	7.21
- 36.4	4.23	7.00	6.66	6.91
- 40.2	4.30	6.40	6.49	6.72
- 44.7	4.38	6.70	6.31	6.51
- 50.8	4.50	6.03	6.08	6.24
- 56.4	4.62	6.10	5.88	6.00
- 59.4	4.67	5.70	5.81	5.91
- 66.4	4.84	5.20	5.59	5.63
- 69.8	4.92	5.87	5.51	5.52
- 85.4	5.33	5.20	5.20	5.08
- 90.5	5.48	5.00	5.12	4.96
- 95.0	5.62	5.20	5.06	4.87

TABLE EV (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_2)_{obsd}$	$(1/T_2)_{calcd}$ [b]	$(1/T_2)_{calcd}$ [c]
- 99.9	5.78	4.90	5.01	4.78
-106.8	6.02	5.00	4.95	4.67

[a] For a sample containing only PBr_3 and PCl_3; values of $1/T_2$ in sec^{-1}.

[b] From a least-squares fit of the data to the equation

$$1/T_2 = 1/T_{2_o} + A\exp(-E_A/RT).$$

[c] From a least-squares fit of the data to the equation

$$1/T_2 = 1/T_{2_o} + A\exp(-2.183\times10^3/T).$$

TABLE EVI

Variation of $1/T_2$ with Temperature for ^{31}P in PCl_3 [a]

T(°C)	$10^3/T(°K^{-1})$	$(1/T_2)_{obsd}$	$(1/T_2)_{calcd}$ [b]	$(1/T_2)_{calcd}$ [c]
79.6	2.84	158.70	169.51	175.14
69.2	2.92	158.50	157.14	161.57
59.8	3.00	146.10	145.68	149.07
50.3	3.09	133.70	133.80	136.20
39.5	3.20	121.00	120.61	122.02
30.7	3.29	110.30	110.80	111.55
19.0	3.42	99.60	98.05	98.06
11.0	3.52	93.40	89.27	88.85
0.0	3.66	75.80	78.30	77.46
- 9.6	3.80	72.00	68.72	67.61
- 20.1	3.95	61.80	59.78	58.53
- 31.0	4.13	51.50	50.62	49.33
- 36.4	4.23	49.00	46.17	44.92
- 40.2	4.30	44.40	43.31	42.09
- 44.7	4.38	39.40	40.26	39.10
- 50.8	4.50	35.40	36.10	35.06
- 56.4	4.62	31.40	32.39	31.49
- 59.4	4.67	30.20	30.97	30.12
- 66.4	4.84	26.70	26.61	25.98
- 69.8	4.92	23.90	24.80	24.28
- 85.4	5.33	17.30	17.39	17.43
- 90.5	5.48	15.20	15.33	15.60
- 95.0	5.62	13.70	13.65	14.08

TABLE EVI (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_2)_{obsd}$	$(1/T_2)_{calcd}$ [b]	$(1/T_2)_{calcd}$ [c]
- 99.9	5.78	11.80	11.99	12.61
-106.8	6.02	10.30	9.94	10.83

[a] For a sample containing only PBr_3 and PCl_3; values of $1/T_2$ in sec^{-1}.

[b] From a least-squares fit of the data to the equation

$$1/T_2 = 1/T_{2_o} + A\exp(-E_A/RT).$$

[c] From a least-squares fit of the data to the equation

$$1/T_2 = 4.5 + A\exp(-E_A/RT).$$

APPENDIX F

Appendix F consists of Tables FI to FVI which contain the data for the variation of $1/T_1$ with temperature for ^{31}P in PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3. The data for Tables FI to FIV were collected for a sample in which all the species were present at their equilibrium concentrations. A sample containing just PBr_3 and PCl_3 was used to obtain the data in Tables FV and FVI. The experimental values of $1/T_1$ are compared to the values obtained from a least-squares fit of the data. The equations to which the data were fitted are given in footnotes to the tables.

TABLE FI

Variation of $1/T_1$ with Temperature for ^{31}P in PBr_3 [a]

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$ [b]	$(1/T_1)_{calcd}$ [c]
80.0	2.83	0.259	0.258	0.279
70.1	2.91	0.221	0.242	0.257
59.8	3.00	0.237	0.226	0.235
50.3	3.09	0.201	0.211	0.215
40.3	3.19	0.199	0.195	0.195
30.4	3.30	0.182	0.180	0.176
19.9	3.41	0.168	0.166	0.160
10.2	3.53	0.165	0.153	0.145
0.3	3.66	0.147	0.141	0.132
- 10.6	3.81	0.129	0.129	0.120
- 20.2	3.96	0.137	0.119	0.111
- 30.4	4.12	0.117	0.112	0.106
- 35.4	4.21	0.985	0.109	0.104
- 39.6	4.28	0.107	0.107	0.103
- 45.3	4.39	0.977	0.105	0.104
- 50.3	4.49	0.101	0.105	0.105
- 50.4	4.49	0.106	0.105	0.105
- 56.0	4.61	0.102	0.107	0.109
- 59.7	4.69	0.122	0.109	0.112
- 59.8	4.69	0.102	0.109	0.112
- 60.3	4.70	0.114	0.110	0.113
- 65.8	4.83	0.117	0.116	0.121
- 69.5	4.91	0.132	0.121	0.127
- 70.3	4.93	0.113	0.123	0.128
- 70.5	4.94	0.119	0.124	0.129

TABLE FI (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$ [b]	$(1/T_1)_{calcd}$ [c]
- 74.8	5.05	0.125	0.134	0.140
- 75.0	5.05	0.136	0.134	0.140
- 80.2	5.19	0.170	0.151	0.156
- 80.3	5.19	0.158	0.151	0.156
- 80.4	5.19	0.142	0.151	0.156
- 80.6	5.20	0.161	0.153	0.158
- 84.5	5.31	0.209	0.170	0.173
- 85.0	5.32	0.164	0.172	0.175
- 88.9	5.43	0.214	0.194	0.194
- 89.9	5.46	0.219	0.201	0.199
- 90.4	5.48	0.185	0.206	0.203
- 9.04	5.48	0.210	0.206	0.203
- 91.0	5.49	0.196	0.209	0.205
- 94.9	5.61	0.241	0.242	0.230
- 94.9	5.61	0.275	0.242	0.230
- 98.8	5.74	0.278	0.286	0.263
-102.0	5.81	0.287	0.314	0.282

[a] For a sample containing a mixture of PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3; values of $1/T_1$ in sec^{-1}.

[b] From a least-squares fit of the data to the equation

$$1/T_1 = B\exp(E_B/RT) + C\exp(-E_C/RT).$$

[c] From a least-squares fit of the data to the equation

$$1/T_1 = B\exp(E_B/RT) + C\exp(-E_B/RT).$$

TABLE FII

Variation of $1/T_1$ with Temperature for ^{31}P in PBr_2Cl[a]

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$[b]	$(1/T_1)_{calcd}$[c]
80.0	2.83	0.321	0.311	0.319
70.1	2.91	0.284	0.289	0.294
59.8	3.00	0.263	0.266	0.270
50.3	3.09	0.236	0.245	0.247
40.3	3.19	0.220	0.225	0.225
30.4	3.30	0.199	0.205	0.204
19.9	3.41	0.191	0.187	0.185
10.2	3.53	0.181	0.170	0.168
0.3	3.66	0.163	0.155	0.152
- 10.6	3.81	0.143	0.140	0.138
- 19.5	3.94	0.139	0.130	0.128
- 20.2	3.96	0.121	0.129	0.127
- 29.1	4.10	0.142	0.121	0.120
- 30.2	4.12	0.142	0.120	0.119
- 30.4	4.12	0.114	0.120	0.119
- 35.4	4.20	0.990	0.117	0.116
- 39.6	4.28	0.107	0.115	0.114
- 45.3	4.39	0.102	0.113	0.113
- 50.0	4.48	0.125	0.113	0.113
- 50.3	4.49	0.124	0.113	0.114
- 50.4	4.49	0.107	0.113	0.114
- 51.0	4.50	0.120	0.113	0.114
- 59.7	4.69	0.114	0.117	0.118
- 59.8	4.69	0.129	0.117	0.118
- 60.3	4.70	0.112	0.117	0.119

TABLE FII (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$ [b]	$(1/T_1)_{calcd}$ [c]
- 69.5	4.91	0.128	0.128	0.129
- 70.3	4.93	0.146	0.129	0.131
- 70.5	4.94	0.118	0.130	0.132
- 75.0	5.05	0.157	0.139	0.140
- 80.2	5.19	0.130	0.153	0.154
- 80.3	5.19	0.134	0.153	0.154
- 80.4	5.19	0.178	0.153	0.154
- 80.6	5.20	0.138	0.154	0.156
- 84.5	5.31	0.227	0.168	0.169
- 88.9	5.43	0.170	0.187	0.187
- 89.9	5.46	0.232	0.192	0.192
- 90.1	5.47	0.246	0.194	0.193
- 90.4	5.48	0.256	0.196	0.195
- 91.0	5.49	0.172	0.198	0.197
- 94.9	5.61	0.250	0.222	0.219
- 98.8	5.74	0.206	0.254	0.248
-100.9	5.81	0.298	0.273	0.265

[a] For a sample containing a mixture of PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3; values of $1/T_1$ in sec^{-1}.

[b] From a least-squares fit of the data to the equation

$$1/T_1 = B\exp(E_B/RT) + C\exp(-E_C/RT).$$

[c] From a least-squares fit of the data to the equation

$$1/T_1 = B\exp(E_B/RT) + C\exp(-E_B/RT).$$

TABLE FIII

Variation of $1/T_1$ with Temperature for ^{31}P in $PBrCl_2$[a]

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$[b]	$(1/T_1)_{calcd}$[c]
80.0	2.83	0.306	0.314	0.325
70.1	2.91	0.323	0.292	0.300
59.8	3.00	0.256	0.269	0.274
50.3	3.09	0.242	0.248	0.251
40.3	3.19	0.214	0.227	0.228
30.4	3.300	0.213	0.206	0.205
19.9	3.41	0.194	0.188	0.186
10.2	3.53	0.169	0.170	0.167
0.3	3.66	0.163	0.153	0.150
- 10.6	3.81	0.131	0.137	0.134
- 19.5	3.94	0.122	0.125	0.122
- 20.1	3.95	0.127	0.124	0.122
- 20.2	3.96	0.126	0.124	0.121
- 29.1	4.10	0.123	0.114	0.112
- 30.2	4.12	0.116	0.112	0.111
- 30.4	4.12	0.113	0.112	0.111
- 35.4	4.21	0.106	0.108	0.106
- 39.6	4.28	0.107	0.104	0.103
- 45.3	4.39	0.0903	0.101	0.100
- 50.0	4.48	0.105	0.984	0.0987
- 50.3	4.49	0.100	0.0982	0.0986
- 50.4	4.49	0.0949	0.0982	0.0986
- 51.0	4.50	0.0957	0.0980	0.0985
- 59.7	4.69	0.0956	0.0969	0.0985
- 59.8	4.69	0.0998	0.0969	0.0985

TABLE FIII (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$ [b]	$(1/T_1)_{calcd}$ [c]
- 60.3	4.70	0.0918	0.0970	0.0986
- 69.5	4.91	0.112	0.101	0.104
- 70.3	4.93	0.104	0.102	0.104
- 70.5	4.94	0.0902	0.102	0.105
- 75.0	5.05	0.108	0.107	0.110
- 80.3	5.19	0.127	0.116	0.118
- 80.6	5.20	0.113	0.117	0.119
- 84.5	5.31	0.150	0.126	0.128
- 89.9	5.46	0.141	0.143	0.142
- 90.1	5.47	0.123	0.144	0.143
- 90.4	5.48	0.164	0.146	0.144
- 91.0	5.49	0.143	0.147	0.146
- 94.9	5.61	0.191	0.165	0.161
-100.9	5.81	0.191	0.203	0.191

[a] For a sample containing a mixture of PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3; values of $1/T_1$ in sec^{-1}.

[b] From a least-squares fit of the data to the equation

$$1/T_1 = B\exp(E_B/RT) + C\exp(-E_C/RT).$$

[c] From a least-squares fit of the data to the equation

$$1/T_1 = B\exp(E_B/RT) + C\exp(-E_B/RT).$$

TABLE FIV

Variation of $1/T_1$ with Temperature for ^{31}P in PCl_3 [a]

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$ [b]	$(1/T_1)_{calcd}$ [c]
80.0	2.83	0.432	0.406	0.399
70.1	2.91	0.350	0.372	0.367
59.8	3.00	0.383	0.338	0.335
50.3	3.09	0.287	0.308	0.306
40.3	3.19	0.278	0.277	0.276
30.4	3.30	0.239	0.247	0.247
19.9	3.41	0.226	0.220	0.221
10.2	3.53	0.189	0.195	0.196
0.3	3.66	0.174	0.171	0.173
- 10.6	3.81	0.138	0.148	0.150
- 19.5	3.94	0.121	0.131	0.133
- 20.1	3.95	0.132	0.130	0.132
- 20.2	3.96	0.140	0.129	0.130
- 29.1	4.10	0.129	0.114	0.115
- 30.2	4.12	0.130	0.112	0.113
- 30.4	4.12	0.115	0.112	0.113
- 35.4	4.21	0.0987	0.104	0.105
- 39.6	4.28	0.0920	0.0984	0.0989
- 45.3	4.39	0.0896	0.0906	0.0908
- 50.0	4.48	0.0833	0.0851	0.0851
- 50.3	4.48	0.0814	0.0845	0.0845
- 50.4	4.48	0.0814	0.0845	0.0845
- 51.0	4.50	0.0894	0.0840	0.0839
- 56.0	4.61	0.0790	0.0784	0.0782
- 59.7	4.69	0.0744	0.0750	0.0746

TABLE FIV (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$ [b]	$(1/T_1)_{calcd}$ [c]
- 59.8	4.69	0.0770	0.0750	0.0746
- 60.3	4.70	0.0781	0.0746	0.0742
- 65.8	4.83	0.0631	0.0702	0.0696
- 69.5	4.91	0.0734	0.0681	0.0674
- 70.3	4.93	0.0739	0.0676	0.0669
- 70.5	4.94	0.0758	0.0674	0.0667
- 74.8	5.05	0.0571	0.0654	0.0647
- 75.0	5.05	0.0623	0.0654	0.0647
- 80.2	5.19	0.0602	0.0639	0.0634
- 80.3	5.19	0.0694	0.0639	0.0634
- 80.4	5.19	0.0770	0.0639	0.0634
- 80.6	5.20	0.0664	0.0638	0.0634
- 84.5	5.31	0.0661	0.0634	0.0633
- 85.0	5.32	0.0536	0.0634	0.0634
- 88.9	5.43	0.0567	0.0638	0.0643
- 89.9	5.46	0.0722	0.0640	0.0647
- 90.1	5.47	0.0710	0.0641	0.0648
- 90.4	5.48	0.0817	0.0642	0.0650
- 91.0	5.49	0.0566	0.0642	0.0651

[a] For a sample containing a mixture of PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3; values of $1/T_1$ in sec^{-1}.

[b] From a least-squares fit of the data to the equation

$$1/T_1 = B\exp(E_B/RT) + C\exp(-E_C/RT).$$

[c] From a least-squares fit of the data to the equation

$$1/T_1 = B\exp(E_B/RT) + C\exp(-E_B/RT).$$

TABLE FV

Variation of $1/T_1$ with Temperature for ^{31}P in PBr_3 [a]

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$ [b]	$(1/T_1)_{calcd}$ [c]
80.5	2.82	0.310	0.349	0.368
80.0	2.83	0.405	0.346	0.365
71.2	2.91	0.300	0.323	0.336
70.1	2.91	0.333	0.323	0.336
59.8	3.00	0.322	0.298	0.306
59.4	3.01	0.264	0.296	0.303
50.2	3.09	0.264	0.276	0.280
50.3	3.09	0.284	0.276	0.280
40.8	3.19	0.240	0.254	0.254
40.3	3.19	0.266	0.254	0.254
30.8	3.29	0.233	0.233	0.230
30.4	3.30	0.264	0.231	0.228
19.9	3.41	0.201	0.211	0.206
19.5	3.42	0.221	0.210	0.204
9.9	3.53	0.222	0.192	0.186
1.3	3.65	0.178	0.175	0.168
0.3	3.66	0.185	0.174	0.167
- 10.4	3.81	0.165	0.156	0.149
- 10.6	3.81	0.146	0.156	0.149
- 19.5	3.94	0.138	0.143	0.137
- 19.9	3.95	0.152	0.142	0.137
- 20.1	3.95	0.149	0.142	0.137
- 21.7	3.98	0.136	0.140	0.134
- 29.2	4.10	0.142	0.131	0.127
- 30.1	4.12	0.129	0.129	0.126

TABLE FV (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$ [b]	$(1/T_1)_{calcd}$ [c]
- 30.2	4.12	0.131	0.129	0.126
- 30.2	4.12	0.128	0.129	0.126
- 36.0	4.22	0.109	0.123	0.121
- 39.7	4.29	0.115	0.120	0.119
- 39.7	4.29	0.121	0.120	0.119
- 40.0	4.29	0.121	0.120	0.119
- 44.7	4.38	0.109	0.117	0.117
- 49.7	4.48	0.123	0.115	0.116
- 50.5	4.49	0.123	0.115	0.116
- 50.8	4.50	0.111	0.115	0.116
- 53.0	4.55	0.107	0.114	0.116
- 56.4	4.62	0.110	0.114	0.117
- 59.5	4.69	0.115	0.115	0.119
- 60.2	4.70	0.119	0.115	0.119
- 61.5	4.73	0.115	0.116	0.120
- 66.4	4.84	0.120	0.120	0.125
- 69.0	4.90	0.112	0.123	0.128
- 69.4	4.91	0.114	0.123	0.129
- 70.3	4.93	0.144	0.125	0.130
- 71.4	4.96	0.140	0.127	0.132
- 75.4	5.06	0.119	0.135	0.140
- 76.5	5.09	0.142	0.137	0.142
- 80.5	5.19	0.179	0.149	0.152
- 80.7	5.20	0.132	0.150	0.153
- 80.7	5.20	0.162	0.150	0.153
- 84.2	5.30	0.217	0.164	0.165

TABLE FV (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$ [b]	$(1/T_1)_{calcd}$ [c]
- 89.9	5.46	0.187	0.194	0.189
- 90.4	5.48	0.180	0.198	0.192
- 90.5	5.48	0.251	0.198	0.192
- 95.0	5.62	0.206	0.233	0.218
- 95.0	5.62	0.272	0.233	0.218
- 99.9	5.78	0.266	0.286	0.253

[a] For a sample containing only PBr_3 and PCl_3; values of $1/T_1$ in sec^{-1}.

[b] From a least-squares fit of the data to the equation

$$1/T_1 = B\exp(E_B/RT) + C\exp(-E_C/RT).$$

[c] From a least-squares fit of the data to the equation

$$1/T_1 = B\exp(E_B/RT) + C\exp(-E_B/RT).$$

TABLE FVI

Variation of $1/T_1$ with Temperature for ^{31}P in PCl_3 [a]

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$ [b]	$(1/T_1)_{calcd}$ [c]
80.0	2.83	0.391	0.403	0.414
70.1	2.91	0.415	0.374	0.382
59.8	3.00	0.332	0.344	0.349
50.3	3.09	0.320	0.316	0.320
40.3	3.19	0.295	0.288	0.290
30.4	3.30	0.251	0.260	0.260
19.9	3.41	0.227	0.235	0.234
10.2	3.53	0.207	0.210	0.208
0.3	3.66	0.204	0.186	0.184
- 10.6	3.81	0.155	0.162	0.160
- 19.5	3.94	0.156	0.144	0.142
- 19.9	3.95	0.139	0.143	0.140
- 20.1	3.95	0.137	0.143	0.140
- 29.2	4.10	0.122	0.125	0.123
- 30.2	4.12	0.118	0.123	0.121
- 40.0	4.29	0.110	0.106	0.105
- 44.7	4.38	0.0952	0.0982	0.0972
- 49.7	4.48	0.114	0.0905	0.0901
- 50.5	4.49	0.0928	0.0898	0.0894
- 50.8	4.50	0.0861	0.0891	0.0888
- 56.4	4.62	0.0788	0.0813	0.0816
- 61.5	4.73	0.0762	0.0752	0.0760
- 66.4	4.84	0.0686	0.0702	0.0714
- 70.3	4.93	0.0684	0.0668	0.0683
- 71.4	4.96	0.0628	0.0658	0.0674

TABLE FVI (Cont'd)

T(°C)	$10^3/T(°K^{-1})$	$(1/T_1)_{obsd}$	$(1/T_1)_{calcd}$ [b]	$(1/T_1)_{calcd}$ [c]
- 74.8	5.05	0.0571	0.0634	0.0650
- 76.5	5.09	0.0628	0.0626	0.0641
- 79.8	5.18	0.0637	0.0613	0.0625
- 80.7	5.20	0.0655	0.0611	0.0622
- 80.7	5.20	0.0700	0.0611	0.0622
- 84.2	5.30	0.0590	0.0607	0.0611
- 85.4	5.33	0.0553	0.0609	0.0609
- 89.9	5.46	0.0813	0.0626	0.0607
- 90.4	5.48	0.0762	0.0630	0.0607
- 90.5	5.48	0.0515	0.0630	0.0607

[a] For a sample containing only PBr_3 and PCl_3; values of $1/T_1$ in sec^{-1}.

[b] From a least-squares fit of the data to the equation

$$1/T_1 = B\exp(E_B/RT) + C\exp(-E_C/RT).$$

[c] From a least-squares fit of the data to the equation

$$1/T_1 = B\exp(E_B/RT) + C\exp(-E_B/RT).$$