13442

NATIONAL LIBRARY
OTTAWA

CANADA

BIBLIOTHÈQUE NATIONALE
OTTAWA

NAME OF AUTHOR.. RICHARD.. DONALD.. KRAUSE.....

TITLE OF THESIS. ANALYTICAL.. BROMINATION.. AND.....
OXIDATION-REDUCTION.. REACTIONS.....
IN.. PROPYLENE.. CARBONATE.....

UNIVERSITY. UNIVERSITY.. OF.. ALBERTA.....

DEGREE FOR WHICH THESIS WAS PRESENTED... Ph.D.....

YEAR THIS DEGREE GRANTED.... 1972.....

Permission is hereby granted to THE NATIONAL LIBRARY OF CANADA to microfilm this thesis and to lend or sell copies of the film.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

(Signed) Richard D. Krause

PERMANENT ADDRESS:

Dept. of Pathology, Ohio State University
333 West 10th Ave., Columbus, Ohio 43210

.....

DATED.. June 14..... 1972

NL-91 (10-68)

THE UNIVERSITY OF ALBERTA

ANALYTICAL BROMINATION AND OXIDATION-REDUCTION REACTIONS IN PROPYLENE CARBONATE

by

© RICHARD DONALD KRAUSE, M.Sc.

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL, 1972

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled ANALYTICAL BROMINATION AND OXIDATION-REDUCTION REACTIONS IN PROPYLENE CARBONATE submitted by RICHARD DONALD KRAUSE in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Byron Kratochvil
B. Kratochvil, Supervisor

D.L. Rabenstein

Gary Horlick
G. Horlick

M.J. Robins

L.G. Chatten

A.I. Popov, External Examiner

Date June 14, 1972

ABSTRACT

A study of analytical bromination and oxidation-reduction reactions in propylene carbonate has been undertaken. Reagents investigated were bromine, ammonium hexanitratocerate(IV), iron(III) perchlorate, lead(IV) acetate, iodine, and potassium permanganate.

A method has been developed for the quantitative determination of phenols and aromatic amines in propylene carbonate by potentiometric titration with bromine. An excess of pyridine was added to accept the protons released in the substitution reactions. Phenols, including phenol, p-nitrophenol, p-cresol, and resorcinol, and aromatic amines such as aniline, m-phenylenediamine, and p-toluidine can be determined with a precision of several parts per thousand in the presence of pyridine, while anthranilic acid, aniline, m-phenylenediamine, and 8-hydroxyquinoline can be determined without the addition of pyridine because they have basic sites available for protonation.

Bromine in propylene carbonate was also investigated for the quantitative determination of olefinic compounds. Cyclohexene, octene, vinyl butyrate, oleic acid, and linoleic acid react stoichiometrically at room temperature, but at reduced temperatures consume excessive amounts of bromine with the formation of hydrogen bromide. High recoveries were obtained for allyl amine, allyl alcohol,

and allyl ether at room temperature. A direct titration with bromine in propylene carbonate can be used to determine the degree of unsaturation of castor, olive, corn, peanut, cottonseed, and linseed oils. Advantages of this method over those presently used include a reduction in the time required for each determination and a more accurate measure of the degree of unsaturation of oils containing conjugated double bonds.

Solutions of bromine in propylene carbonate decrease in strength by less than 0.3% per day when stored in a closed system and protected from light. The formation constant of the tribromide ion in propylene carbonate was measured by potentiometric titration of bromide with bromine and a log K value of 7.23 ± 0.01 was found at 25°C. The bromine—bromide reaction is therefore convenient for standardization of solutions of bromine. The log of the formation constant of the 1:1 complex formed between pyridine and bromine in propylene carbonate was determined to be 2.74 ± 0.03 at 25°C.

The titer of propylene carbonate solutions of ammonium hexanitratocerate(IV) decrease rapidly with time owing to apparent formation of a series of cerium(IV)-hydroxy species by reaction with traces of water in the solvent. The strength of these solutions is dependent upon the ease of oxidation of the compound being titrated.

Iron(III) perchlorate is a more powerful oxidant

than cerium(IV) in propylene carbonate but its solutions are unstable due to slow oxidation of the solvent to carbon dioxide and other products. Neither lead(IV) acetate nor potassium permanganate are suitable oxidizing titrants in propylene carbonate; lead(IV) acetate is rapidly hydrolyzed by traces of water in the solvent, and potassium permanganate is not a sufficiently strong oxidant in the absence of acid.

ACKNOWLEDGEMENTS

The author would like to express his appreciation to Dr. B. Kratochvil for his guidance and encouragement throughout this project.

Financial assistance from the National Research Council of Canada and the University of Alberta is gratefully acknowledged.

This thesis is dedicated to my wife, Sherry, without whose help and understanding this presentation would not have been possible.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Part I. INTRODUCTION

Nonaqueous solvents as reaction media in analytical chemistry have received considerable attention over the past 25 years. The bulk of the research in this area has been devoted to the study of acid-base reactions, and many titrimetric methods have been developed for the determination of compounds that are too weakly acidic or basic to be titrated in aqueous solution. In recent years, however, considerable interest has also been focussed on electron-transfer reactions in nonaqueous solvents and their analytical applications. Studies in this area would make available methods for the analysis of compounds that are insoluble in water or react with water through hydrolysis or oxidation.

To be useful as an analytical oxidation-reduction medium, a solvent should be resistant to oxidation or reduction and should be readily purified. The solvent also should be capable of keeping ionic reactants and products in solution since, with few exceptions, one or more of the products or reactants in an electron-transfer reaction will carry a charge. Solubilization of ionic compounds occurs primarily through solvation of individual ions, though if the dielectric constant of the solvent is low, the solvated species may be primarily ion pairs or higher aggregates. If ion-pairing is appreciable, reaction rates are likely to be slow; in general the logarithm of the rate constant of

an ion-ion reaction is related to the reciprocal of the solvent dielectric constant according to the expression

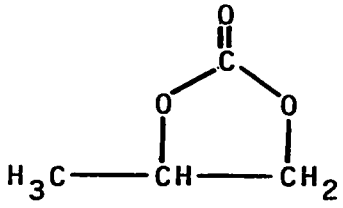
$$\ln \frac{k_1}{k_2} = \frac{Z_A Z_B e^2}{rkT} \left[\frac{1}{D_2} - \frac{1}{D_1}\right]$$

where k_1 and k_2 are rate constants for reactions in solvents of dielectric constants D_1 and D_2, Z_A and Z_B are the charges on the reactants A and B, r is the radius of the A-B species at the time of reaction (usually taken to be $r_A + r_B$), k is the Boltzmann constant, e is the electronic charge, and T is the absolute temperature[1]. This equation predicts that a change in dielectric constant from, for example, 78 (water) to 36 (acetonitrile, nitrobenzene) should decrease the reaction rate between singly charged ions by a factor of 10^7. Similar considerations apply to reactions between ions and dipolar solute molecules.

A recent review[2] of analytical oxidation-reduction reactions in organic solvents summarizes the solvents and titrants that have been used. Although acetic acid has a very low dielectric constant (D = 6.4), it was the first nonaqueous solvent to be used extensively in analytical electron-transfer reactions, probably because it had earlier become established as a solvent for acid-base titrations. At the present time acetonitrile has been found to be one of the most useful solvents for electron-transfer reactions. It has a moderately high dielectric constant (D = 36), a

convenient liquid range, a wide electrochemical range, and is not toxic. However, the purification of acetonitrile is difficult and time-consuming. Other solvents which have been used to a lesser extent include dimethylformamide, dimethylsulfoxide, the lower aliphatic alcohols, nitromethane, nitrobenzene, tetrahydrofuran, and dioxane.

In recent years, propylene carbonate (propanediol-1,2-carbonate, PC) has been receiving increasing attention as an electrochemical solvent.



Propylene Carbonate (PC)

Research, especially by United States government agencies, has centered largely on the possible applications of this solvent to the development of electrolytes for high energy density batteries. The properties of PC (Table I) that make it of interest in electrochemistry suggest its possible usefulness as a solvent for analytical oxidation-reduction reactions.

Table I. - Physical Properties of Propylene Carbonate

		Reference
Freezing point	-49.2°C	3
Boiling point	241.7°C	3
Dielectric constant, 25°C	64.4	4
	65.01	5
Density, 25°C	1.198 g/cm^3	4
	1.1998 g/cm^3	6
	1.19965 g/cm^3	7
Viscosity, 25°C	2.530 cP	4
	2.470 cP	6
	2.514 cP	7
Coefficient of cubic expansion	0.001	4
Specific heat, 20°C	0.615 cal/g/°C	3
Refractive index, n_D^{20}	1.4209	3

Harris[4] found that PC is a good solvent for many inorganic salts. Low-melting covalent salts such as $MgBr_2$ and $AlCl_3$ tend to be quite soluble, but solubilities decrease as the ionic character of the salt is increased. Because of the nature of the solvent dipole, PC solvates cations more effectively than it does anions. The negative charge is concentrated on the carbonyl oxygen and is exposed to solute molecules, but the positive charge of the dipole is spread over several atoms. As a result of its relatively poor solvating power for anions, PC does not dissolve ionic

salts to the extent predicted on the basis of its high dielectric constant. PC also dissolves a large variety of organic compounds and is miscible with many of the more common solvents. At 25°C the solubility of water in PC is 8.3 g in 100 g [3]; at temperatures above 73°C water and PC are miscible[8].

PC is stable under ordinary conditions of storage, but appreciable decomposition occu above 200°C. In the presence of acids or bases PC hydrolyzes fairly rapidly, even at room temperature. Although it is not hygroscopic to any great extent, PC gradually takes up moisture if exposed to a humid atmosphere[9].

Impurities commonly present in commercial PC are carbon dioxide, water, propylene oxide, allyl alcohol, and propylene glycol. A gas chromatographic method using a column of Poropak Q has been developed by Jasinski and Kirkland[10] for the analysis of water and volatile organic impurities. Carbon dioxide and water were detected by thermal conductivity cells, while a flame ionization detector was used for the organic components. For a 40-µl sample the lower limits of detection with this system are 1.5 ppm for water, 0.05 ppm for propylene oxide, and 0.5 ppm for propylene glycol.

Pure PC shows little or no absorption in the ultraviolet region between 240 nm and 340 nm, but impure PC does absorb in this area. Therefore the measurement of absorbance

in this range is a convenient test of the purity of PC, though the impurity (or impurities) that give rise to the absorption have not yet been identified.

Purification is generally accomplished by fractional distillation under reduced pressure. Because the presence of trace impurities produces marked effects on the performance of this solvent for high energy batteries, detailed studies have been carried out for the preparation of highly pure solvent[10,11].

PC is colorless, odorless, and essentially non-toxic. While moderately irritating to the eyes and mucous membranes of the respiratory tract, it is reported to present no serious hazard to health in its handling[3].

Courtot-Coupez and L'Her[12] determined the useful electrochemical potential range of PC with several electrode materials and supporting electrolytes. The limit of the anodic range in every case was determined by oxidation of the anion of the supporting electrolyte. The most positive potential (+3.2 V vs. a silver—0.01M silver perchlorate in PC reference electrode) was obtained in 0.1M potassium hexafluorophosphate in anhydrous PC at a platinum electrode. PC is equally stable to reduction; no evidence of limitation of the cathodic range because of reduction of the solvent was noted. A potential of -4.1 V vs. a silver—0.01M silver perchlorate in PC reference electrode was attained in 0.1M tetrabutylammonium bromide. The solvent is not reduced by

metallic lithium, sodium, or potassium[13]; in fact, the investigation of PC as a solvent for high energy density battery electrolytes was sparked by the successful electrodeposition of lithium metal from it by Harris[4]. However, Dey and Sullivan[14] reported that PC can be electrochemically reduced on a graphite cathode to propylene gas and carbonate ion with almost 100% coulombic efficiency.

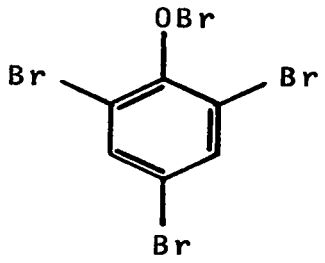
To the present time the only reference to appear in the literature regarding oxidation-reduction titrations in PC has been in the paper by Courtot-Coupez and L'Her mentioned earlier[12]. They titrated ferrocene with silver perchlorate to study the reversibility of the ferrocene—ferricenium couple in assessing the suitability of this couple for use as a reference electrode. Analytical applications of the method were not explored.

The high dielectric constant, favorable handling characteristics, wide liquid and electrochemical ranges, and good dissolving power of PC are advantages of this solvent over other nonaqueous solvents which have been used as titration media. The analytical utility of several electron-transfer systems in PC was studied in this work, with the goal of developing oxidation-reduction methods for compounds that cannot be determined in water.

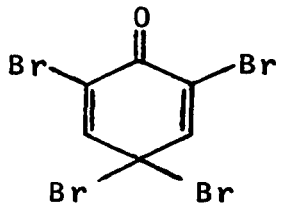
Part II. AROMATIC SUBSTITUTION REACTIONS OF BROMINE IN PROPYLENE CARBONATE

BACKGROUND

Bromine substitution reactions have been extensively used for the quantitative determination of phenols and aromatic amines. As a result of the strong activating effect of hydroxyl and amino groups on the hydrogen atoms of benzene, many aromatic compounds containing these groups react with bromine rapidly and stoichiometrically. Bromination of aniline in aqueous solution is so rapid, in fact, that the only product readily isolated is 2,4,6-tribromoaniline[15]. Addition of bromine water to an aqueous solution of phenol results in the precipitation of a tetrabromo derivative which is easily reduced to produce 2,4,6-tribromophenol[16]. Two structures have been proposed for the tetrabromo derivative. Since it is readily reduced to tribromophenol, Benedikt[17] concluded that the fourth bromine atom was not directly attached to the aromatic nucleus. Accordingly, he assigned the following structural formula:

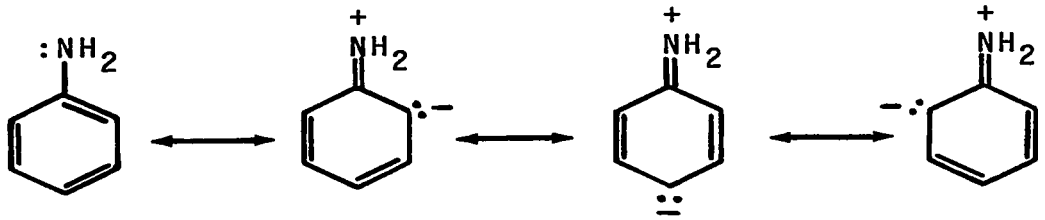


In view of the strong oxidizing properties of this compound Thiele and Eichwede[18] subsequently proposed a different structure:



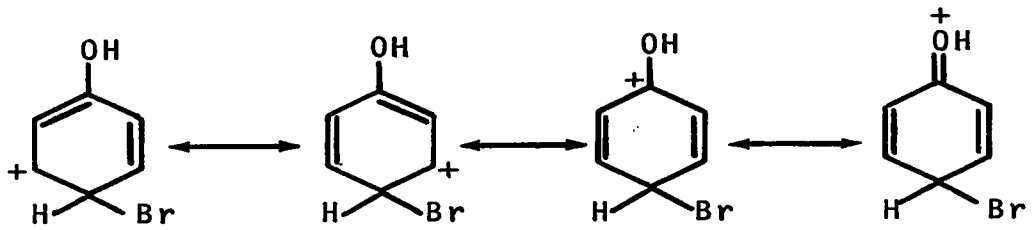
Lauer[19] was later able to show that this quinoid structure is highly improbable.

An amino or hydroxyl substituent on an aromatic nucleus increases the electron density of the ring and thereby activates other positions on the ring toward electrophilic attack by positive species. Both of these functional groups have unshared pairs of electrons which can interact with π electrons of the benzene ring. This effect may be represented by resonance among valence-bond structures, using aniline as an example:



An analogous set of resonating structures can be written for phenol. Amino or hydroxyl substituents on an aromatic

ring direct electrophilic substitution to open ortho or para positions. This is due to increased resonance stabilization of the intermediate carbonium ion resulting from attack by a positive species at one of these positions. For example, the following resonance structures can be written for the intermediate carbonium ion resulting from para attack of phenol by a positive bromonium ion:



Similar resonance structures can be written for the intermediate resulting from attack at the ortho position. A resonance structure in which the positive charge is delocalized into the hydroxyl group is not possible when attack occurs in the meta position.

The high vapor pressure of bromine makes aqueous bromine solutions unsatisfactory for use as titrants. Solutions of bromate and bromide are stable and behave as an equivalent solution of bromine upon acidification:

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

Solutions of bromate—bromide have often been utilized for the determination of organic aromatic compounds by

substitution reactions[20]. Two methods of performing such an analysis are available: the acidified test solution may be titrated directly with bromate-bromide mixture to a permanent yellow color, or a known amount of bromate-bromide solution may be added to the test solution, which is then acidified and the excess bromine determined. The second procedure has been the most popular; the time period between addition of reagent and back-titration can be varied to allow slower reactions to go to completion. Excess bromine is usually determined by addition of iodide followed by titration of the released iodine with thiosulfate using the starch-iodine endpoint.

The presence of certain groups other than hydrogen in the ortho or para positions can introduce errors in analytical bromine reactions. Bromination of salicylic acid for example, is accompanied by partial cleavage of the carboxyl group, resulting in the formation of carbon dioxide and tribromophenol[21]. Callan and Henderson[22] found that the sulfonic acid group is eliminated in the bromination of sulfanilic acid with the formation of tribromoaniline. Francis[24] observed that when saligenin (o-hydroxybenzyl alcohol) is brominated the hydroxymethyl group is displaced and formaldehyde is produced. Sprung[25] reported that phenols which contain primary alkyl groups at the ortho or para positions produce results which may be 10% to 150% high as a consequence of bromination of the alkyl group.

These and subsequent investigators attempted, with some success, to vary the bromination conditions to either make the side reactions quantitative or to inhibit them completely.

Sweetser and Bricker[26] applied spectrophotometric endpoint detection to direct titrations with bromate–bromide solutions. They were able to determine phenol, aniline, and o-cresol with an average error of less than 1%. Addition of 40% of methanol to the solvent was necessary to prevent precipitation of the brominated products.

The bromate–bromide method requires the use of aqueous systems, which limits its applicability for less soluble phenols and amines. Ingberman[27] investigated the use of glacial acetic acid as a solvent for substitution reactions. Complete bromination of phenol in this solvent was found to require 45 minutes at 80°C. The addition of pyridine as a catalyst greatly increased the reaction rate; it is probable that the active brominating agent under these conditions is a pyridine–bromine molecular complex. Ingberman determined several phenolic compounds in glacial acetic acid by adding an excess of bromine in the presence of pyridine, allowing several minutes for the reaction to occur, and then determining the excess bromine by adding an aqueous iodide solution and titrating the liberated iodine with thiosulfate. Huber and Gilbert[28] directly titrated phenols in glacial acetic acid with 0.15M bromine in glacial acetic acid by utilizing high concentrations of pyridine.

The endpoint was detected by constant current potentiometry. Williams, Krudener and McFarland[29] introduced the use of pyridinium bromide perbromide ($PyH^+Br_3^-$) in glacial acetic acid as a titrant. With 1,1,3,3-tetramethylguanidine as a catalyst, several phenolic compounds were determinable by direct titration in glacial acetic acid.

The use of PC as a solvent for analytical bromine substitution reactions is discussed in this chapter. PC has been reported to be resistant to chemical attack by halogens[3]. Phenols and aromatic amines, as well as their bromination products, are soluble in PC. Due to the high dielectric constant of PC, bromine substitution reactions occurring in this solvent may be rapid enough to allow direct titration without the addition of a catalyst.

EXPERIMENTAL

Solvent Purification

The PC used was purified by fractional distillation in the apparatus shown in Figure 1. It consisted of a 3-liter Pyrex flask, a 48" x 1" vacuum-jacketed column packed with nichrome size C Heli-Pak (Podbielniak), and a distillation head designed to use a solenoid-operated glass plunger for control of the reflux ratio. A set of stopcocks were incorporated into the collection section in order to make it possible to collect a sample for analysis in a quartz spectrophotometer cell, and to change receiving flasks without breaking the vacuum in the column. The vacuum system consisted of a Welch Duo-Seal vacuum pump connected to the still head via a dry ice—acetonitrile vapor trap. The pressure within the system was monitored with a McLeod gauge measuring down to 0.001 mm of mercury. The solenoid which operated the plunger in the distillation head was controlled by an electronic switching device in which the "off" and "on" times were independently variable from 0 to 180 seconds.

In a typical distillation, 2 liters of technical grade PC (Jefferson Chemical Co.) were placed in the still pot, the system was evacuated and held under total reflux for several hours before the switching device was activated and collection begun. Figure 2 illustrates the ultraviolet spectra of PC samples collected during a representative

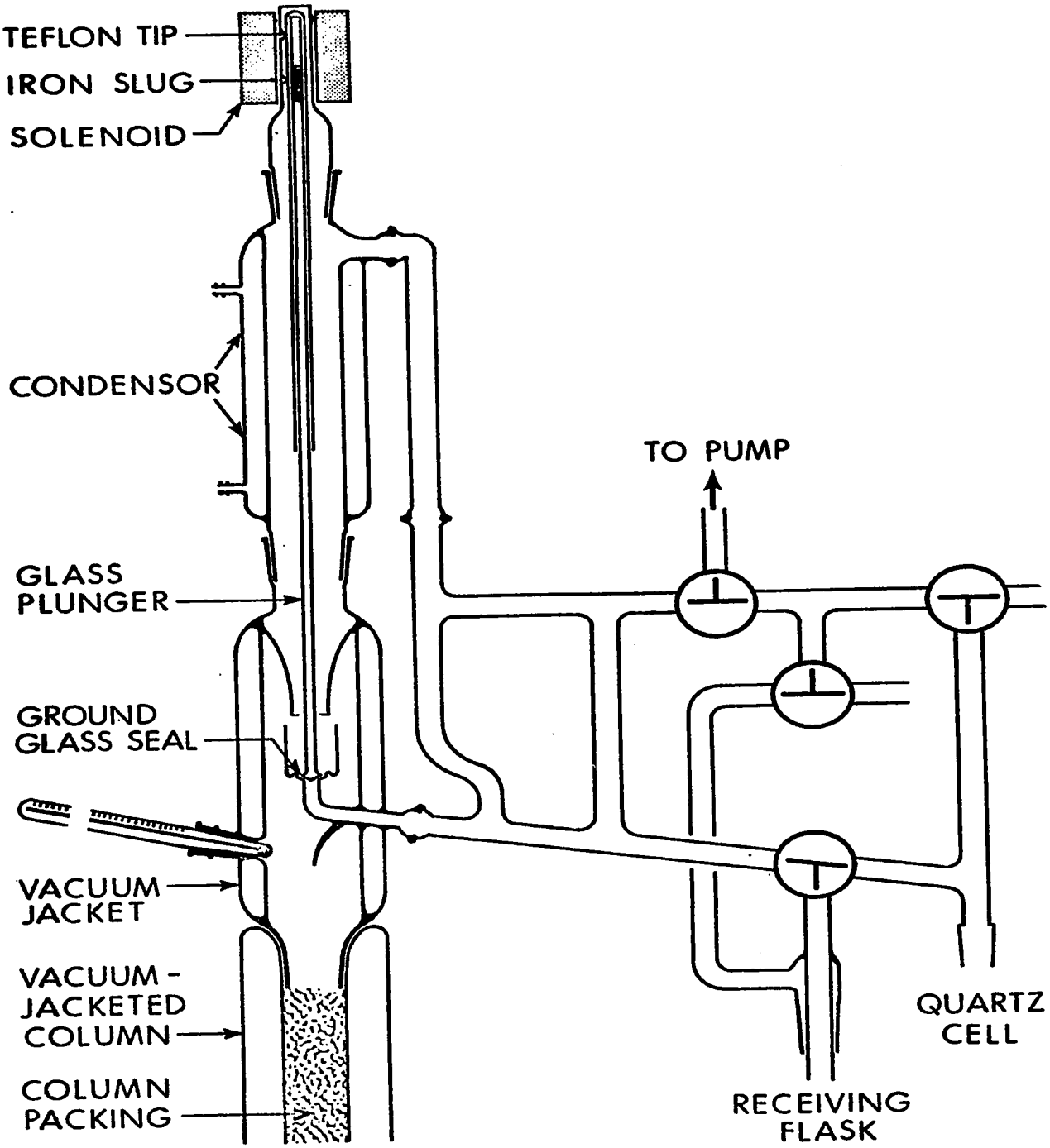


Figure 1. Apparatus Employed for Distillation of Propylene Carbonate

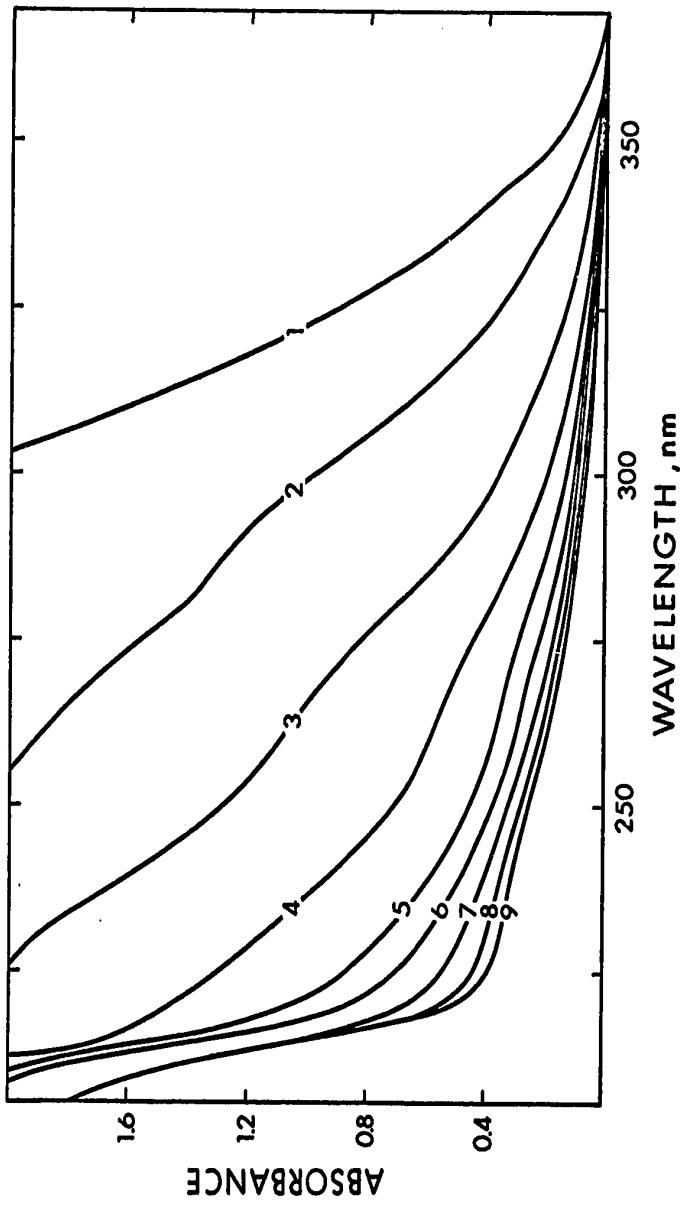


Figure 2. Spectra of Fractions in Propylene Carbonate Distillation (Curves 1 to 9 at Cumulative Volumes of 100, 200, 300, 450, 600, 750, 1000, 1500, and 1800 ml)

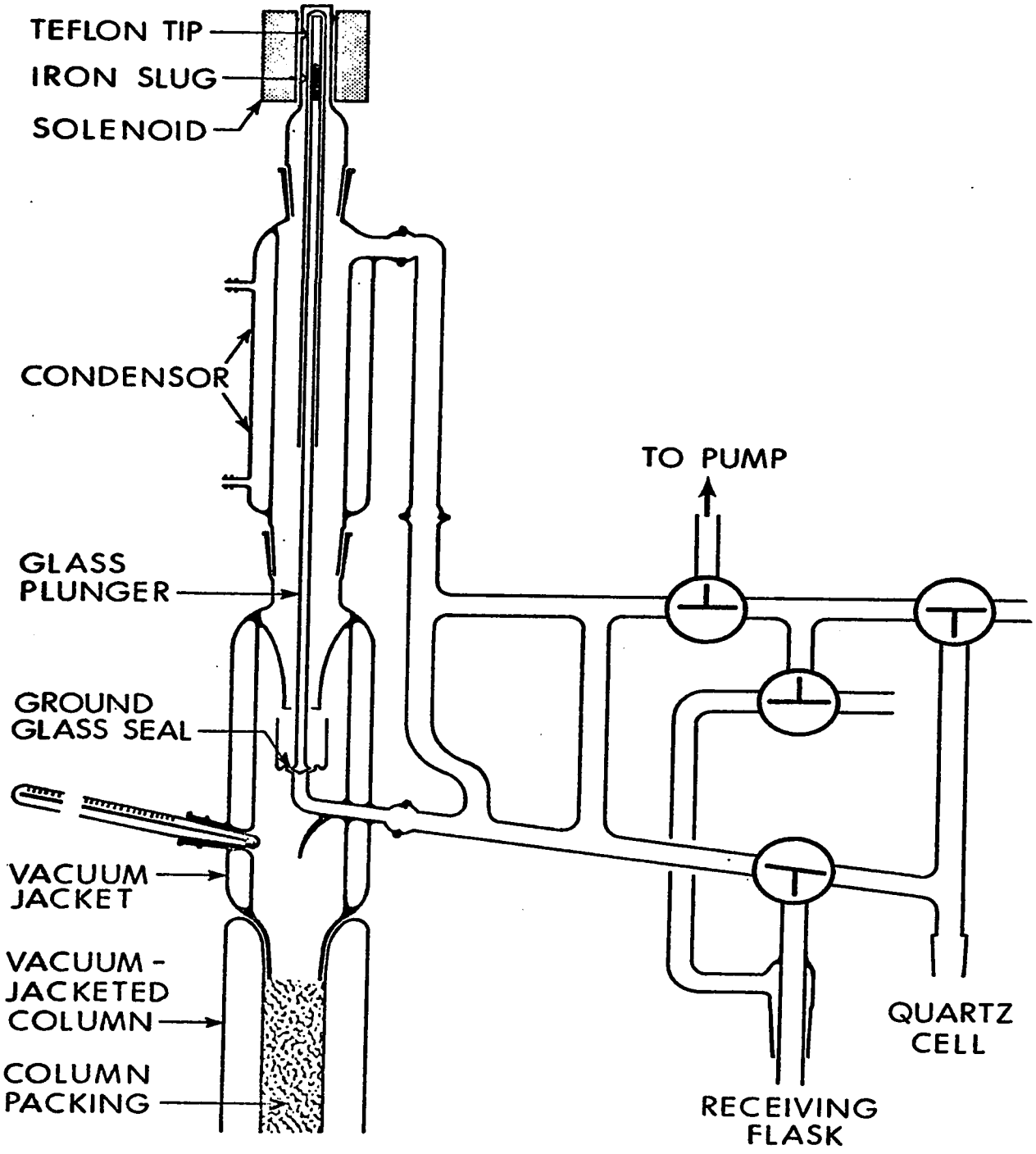


Figure 1. Apparatus Employed for Distillation of Propylene Carbonate

distillation. During the distillation the pressure varied within the range 0.003 to 0.011 mm of mercury and the temperature at the head of the column varied from 59.5°C to 61°C. The pot temperature varied somewhat with the voltage applied to the heating mantle, but remained in the area of 110°C throughout the distillation. When the plunger was timed to be down 20 seconds and up 2 seconds (10:1 reflux ratio), distillate accumulated at a rate of about 17 ml per hour. The first 800 ml and last 200 ml of a 2-liter charge were discarded. Distilled PC was stored in glass-stoppered borosilicate bottles until use.

Reagents and Apparatus

The solid phenols and aromatic amines used were all sublimed once at reduced pressure and stored in a desiccator until use. Aniline and p-phenetidine were distilled on a 30-cm Vigreux column at atmospheric pressure; the products were colorless.

A 0.05M solution of tetraethylammonium bromide in PC was prepared from tetraethylammonium bromide that had been recrystallized from ethanol and dried at 90°C under vacuum for 12 hours. This solution was standardized gravimetrically by mixing 25 ml of the PC solution with 250 ml of 0.01M nitric acid in deionized water and adding an excess of aqueous silver nitrate solution to precipitate silver bromide. After digestion for several hours at 80°C,

the precipitate was collected on a glass fiber mat, washed, and dried at 110°C for two hours before weighing. The tetraethylammonium bromide solution standardized in this way was subsequently used to standardize the bromine titrant.

All titrations were performed on a Metrohm Model E436 automatic titrator equipped with a 5-ml buret. The buret and all glass connections were covered with black tape to exclude light. Titrant solutions were stored in low-actinic glass flasks fitted with Teflon stoppers. A Teflon stopcock on top of the titrant reservoir was opened to admit air only when titrant was being transferred from the reservoir to the buret to prevent evaporation of bromine from the titrant.

The titration cells were 4 cm x 10 cm cylindrical glass weighing bottles with machined Teflon covers. A 1-cm^2 platinum flag was used as the indicating electrode. The reference electrode employed was similar to one described in the literature for use in PC solutions[30]. It consisted of a silver wire dipping into a 0.01M solution of silver perchlorate in PC in a glass tube sealed to a short length of porous Vycor glass rod. The Vycor rod was immersed in a bridge solution of 0.1M lithium perchlorate in PC which was separated from the solution being titrated by a 0.9-1.4 μ glass frit. The solution was stirred during titration by a 1-inch Teflon-coated magnetic stirring bar. Approximately 25 ml of solvent was used for each titration.

Standardization and Stability of Titrant

Due to the stability of the tribromide ion in PC, a sharp potential break occurs after the addition of one equivalent of bromine in a potentiometric titration of bromide in PC (Figure 3). Since this reaction is rapid and stoichiometric, and because a solution of tetraethylammonium bromide in PC is stable and can be accurately assayed gravimetrically, titration of bromide was chosen as the method of standardizing the bromine titrant. The strength of the titrant, a 0.5M solution of bromine in PC, was determined daily by titration of 25-ml aliquots of 0.05M tetraethylammonium bromide. The precision of these titrations when performed using the automatic titrator was 2 parts per thousand or better. The titrant was found to decrease in strength by about 0.25% per day if protected from light and stored in a closed system. This decrease is probably due primarily to evaporation of bromine, and not to chemical reaction. Addition of an equivalent amount of pyridine to a solution of bromine in PC to stabilize the bromine as a complex caused the titer of the solution to decrease too rapidly for it to be of use as a titrant.

Determination of Tribromide Ion Formation Constant in Propylene Carbonate

The formation of tribromide ion in the standardization reaction, and, as will be shown later, in most bromine substitution reactions, makes it of interest to determine

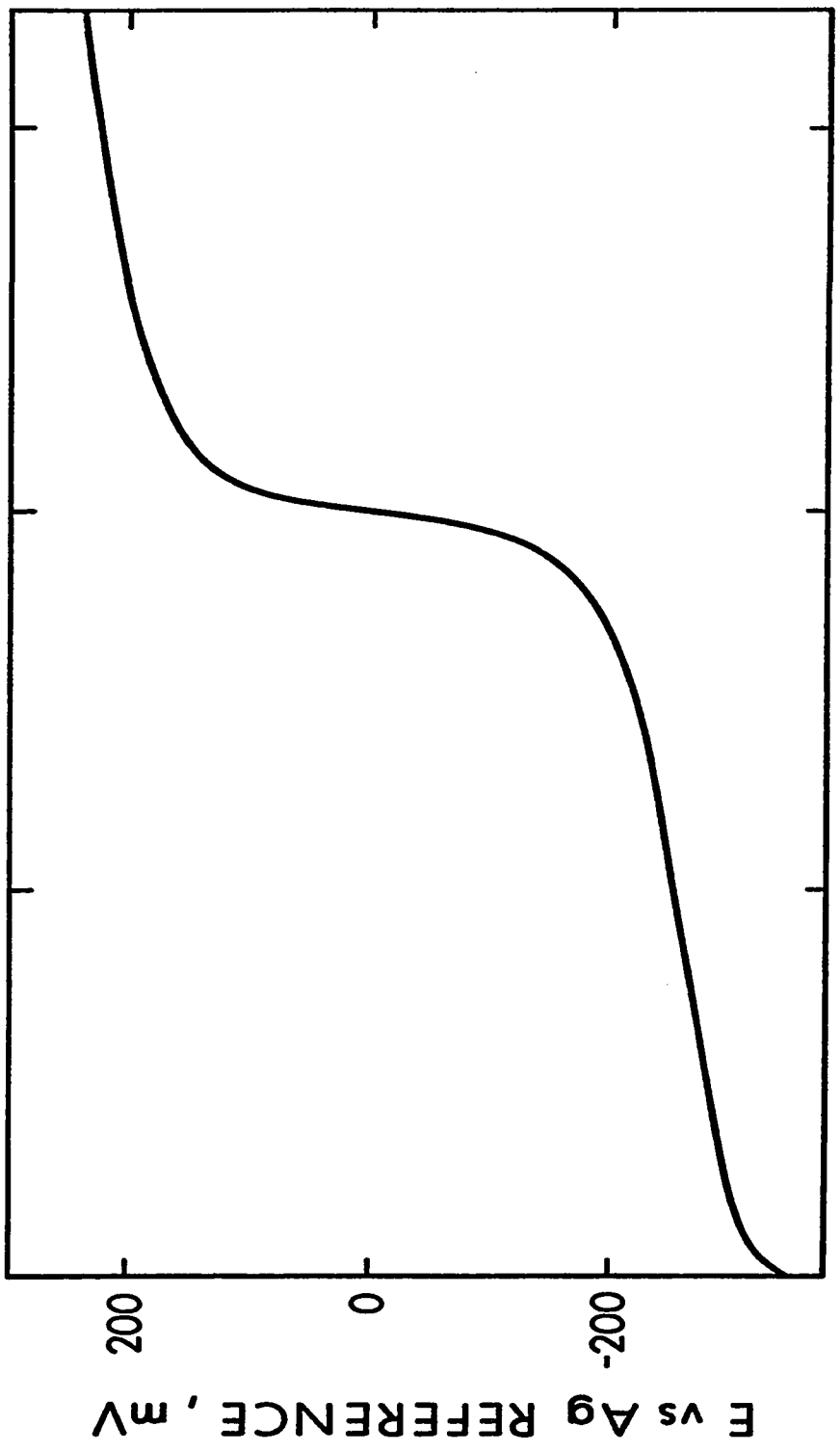


Figure 3. Potentiometric Titration of Bromide with Bromine in Propylene Carbonate

the stability of this ion in PC. Tribromide ion is produced by a reaction of bromine with bromide ion:

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$

The equilibrium constant of this reaction is the formation constant of the tribromide ion:

$$K_f = \frac{[Br_3^-]}{[Br_2][Br^-]}$$

Two independent potentiometric methods were devised to determine the value of K_f: analysis of the plot for the titration of an equimolar mixture of bromine and bromide with silver perchlorate, and analysis of a plot for the titration of bromide with bromine.

Titration of a solution of bromide with silver perchlorate in PC results in a titration curve such as curve a) in Figure 4, where the indicating electrode is a silver wire. During addition of the first one-half equivalent of silver ion no precipitate is produced because the soluble anionic species, $AgBr_2^-$, is formed. In this portion of the titration, the potential is determined by the equation:

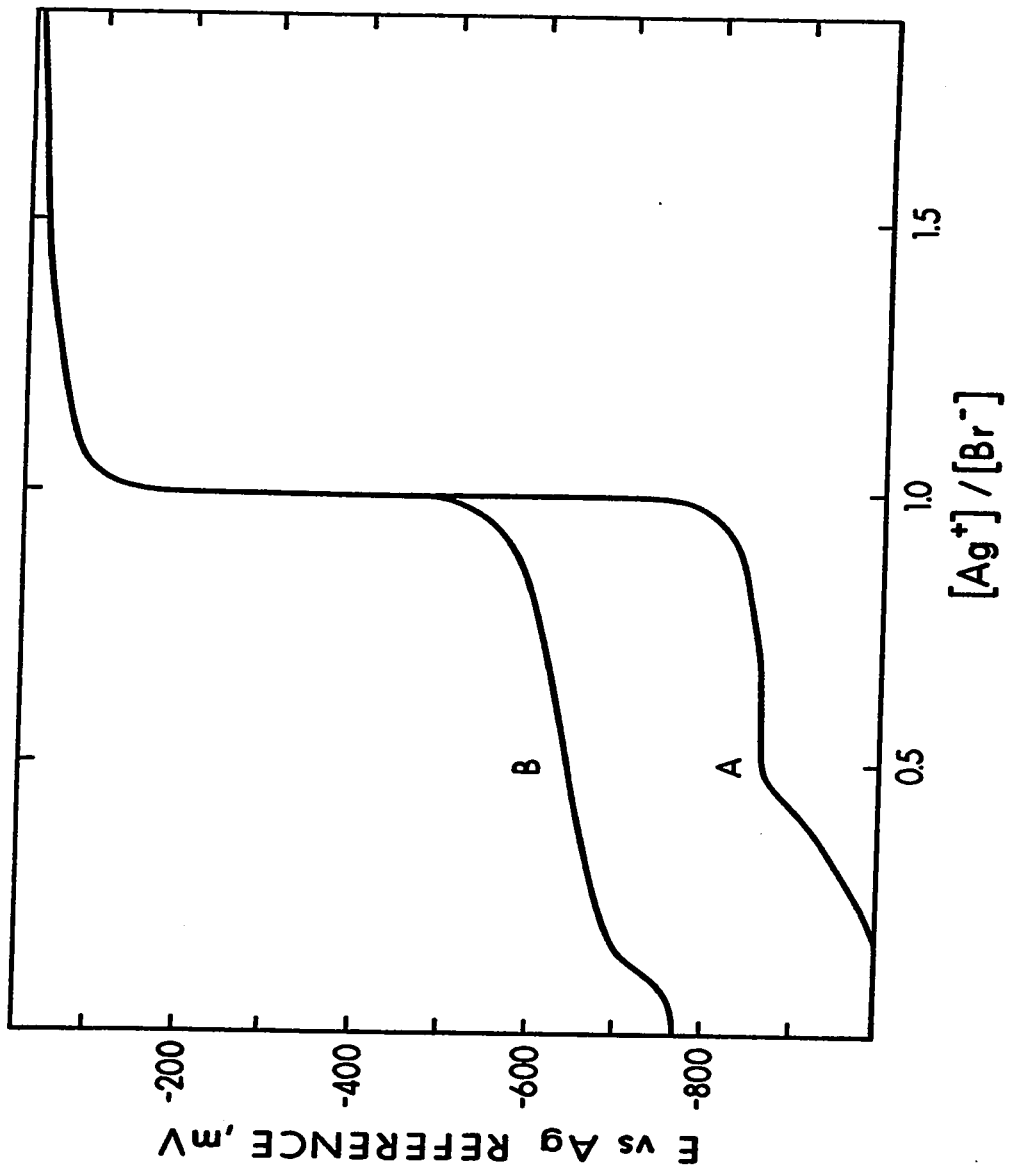


Figure 4. Potentiometric Titration of Bromide (a) and an Equimolar Mixture of Bromide and Bromine (b) with Silver Perchlorate in Propylene Carbonate

$$E = E^{\circ'}_{Ag/Ag^+} - 0.0591 \log C_{Br^-} - 0.0591[2 \log(1-2x)-\log(x)] - 0.0591 \log \beta_2$$

where $E^{\circ'}_{Ag/Ag^+}$ is the formal potential of the silver–silver(I) couple, C_{Br^-} is the initial molar concentration of bromide ion and x is the fraction titrated. The derivation of this equation is outlined in Appendix A, along with subsequent similar equations. β_2 is the equilibrium constant for the reaction

$$2Br^- + Ag^+ \rightleftharpoons AgBr_2^-$$

and is defined by the expression

$$\beta_2 = \frac{[AgBr_2^-]}{[Ag^+][Br^-]^2}$$

A graph of the function [2 log(1-2x)-log(x)] *vs.* potential in this region for a titration of a 5×10^{-3} M solution of bromide with 0.1M silver perchlorate is linear (data from a typical titration presented in Appendix B). The value of β_2 calculated from the intercept of this graph is $10^{20.9 \pm 0.2}$ (average of three titrations). A value of $10^{21.2 \pm 0.1}$ for this constant has been reported by Courtot-Coupez and L'Her[31].

During the addition of the second half-equivalent of silver perchlorate, a precipitate of silver bromide is produced:

$$AgBr_2^- + Ag^+ \rightleftharpoons 2AgBr$$

The potential at the silver electrode in this portion of the titration is given by the expression

$$E = E^{\circ'}_{Ag/Ag^+} - 0.0591 \log C_{Br^-} - 0.0591 \log(1-x) + 0.0591 \log K_p$$

where K_p, the equilibrium constant of the precipitation reaction occurring in this portion of the titration, is defined by the expression

$$K_p = [AgBr_2^-][Ag^+]$$

A plot of log(1-x) *vs.* the measured potential results in a straight line with a slope of -61.4 mV (see Appendix B for data from typical titration). The value calculated for K_p is $10^{-19.5\pm0.2}$ (average of three titrations); a value of $10^{-19.9\pm0.1}$ is reported in the literature[31].

The solubility product of silver bromide in PC (K_{sp}) is equal to the square root of the quantity K_p divided by β_2; the value calculated is $10^{-20.2\pm0.2}$. A value of $10^{-20.5\pm0.1}$ is reported by Courtot-Coupez and L'Her[31].

Since a silver electrode responds to the activity of silver ion in solution, which is in turn related to the activity of bromide ions through the solubility product of silver bromide, it is possible to determine the formation constant of the tribromide ion in PC by measuring the potential of a silver electrode immersed in a PC solution to which has been added known amounts of silver perchlorate,

bromide, and bromine. It can be shown that the potential seen at a silver electrode in the titration of an equimolar mixture of bromine and bromide with silver perchlorate (curve b, Figure 4) is determined by the equation

$$E = E^{\circ'}_{Ag/Ag^+} + 0.0591 \log K_{sp} + 0.0591 \log K_f - 0.0591[\log(1-x) - \log x]$$

The derivation of this equation, which includes several simplifying assumptions, is given in Appendix A. A graph of the potential before the endpoint in such a titration *vs.* the function [log(1-x) - log x] is linear (see Appendix B). The value of the formation constant calculated by this method is $10^{7.18\pm0.04}$ (average of three titrations).

The stability of the tribromide ion in PC is directly related to the size of the potential break in a titration of bromide with bromine. Therefore it is also possible to determine the value of K_f by analysis of such a titration curve. The formation constant is related to the formal potentials of the tribromide-bromide and bromine-tribromide couples according to the expression (at 25°C)

$$\log K_f = 11.30 \left[E^{\circ'}_{Br_2/Br_3^-} - E^{\circ'}_{Br_3/Br^-}\right]$$

Before the endpoint in a titration of bromide with bromine, the potential at a platinum electrode is determined by the

equation

$$E = E^{\circ'}_{Br_3^-/Br^-} - 0.0591 \log C_{Br^-} + \frac{0.0591}{2}\left[\log x - 3 \log(1-x)\right]$$

Thus a value of $E^{\circ'}_{Br_3^-/Br^-}$ can be calculated from the intercept of a graph of the function [log x - 3 log(1-x)] vs. the potential.

After the endpoint is reached in such a titration, the potential is determined by the equation

$$E = E^{\circ'}_{Br_2/Br_3^-} + \frac{0.0591}{2} \log C_{Br^-} + 3\left(\frac{0.0591}{2}\right) \log(x-1)$$

and a value of $E^{\circ'}_{Br_2/Br_3^-}$ can be calculated from the intercept of a graph of the function log(x-1) vs. the potential.

Values for the two formal potentials and for the formation constant determined by this method at three temperatures are shown in Table II. Data used in obtaining these values are presented in Appendix B. The value obtained for K_f at 25°C by this method, $10^{7.23\pm0.02}$, agrees well with the value obtained by the method described previously, $10^{7.18\pm0.04}$.

Table II. - Values of Constants Determined by Analysis of Bromine–Bromide Potentiometric Titration Curves in Propylene Carbonate

Temperature (°C)	$E^{o'}_{Br_3^-/Br_2}$ [a]	$E^{o'}_{Br_2/Br_3^-}$ [a]	log K_f
0	-0.3448	0.3093	7.39
25	-0.3398	0.3001	7.23
50	-0.3386	0.2889	7.09

[a] Formal potentials are reported in V vs. a silver–0.01M silver perchlorate in PC reference electrode.

The effect of temperature on K, the equilibrium constant of a reaction, can be predicted by integration of the Gibbs-Helmholtz equation, which leads to the expression

$$\log K = \frac{-\Delta H}{2.303RT} + C$$

where ΔH is the enthalpy of the reaction, R is the universal gas constant, T is the absolute temperature, and C is a constant of integration. Thus a plot of log K versus 1/T should result in a straight line with slope equal to $-\Delta H/2.303R$, allowing calculation of ΔH. Such a plot of the data in Table II is shown in Figure 5. The value of ΔH calculated from the slope of the plot is -2.42 Kcal/mole.

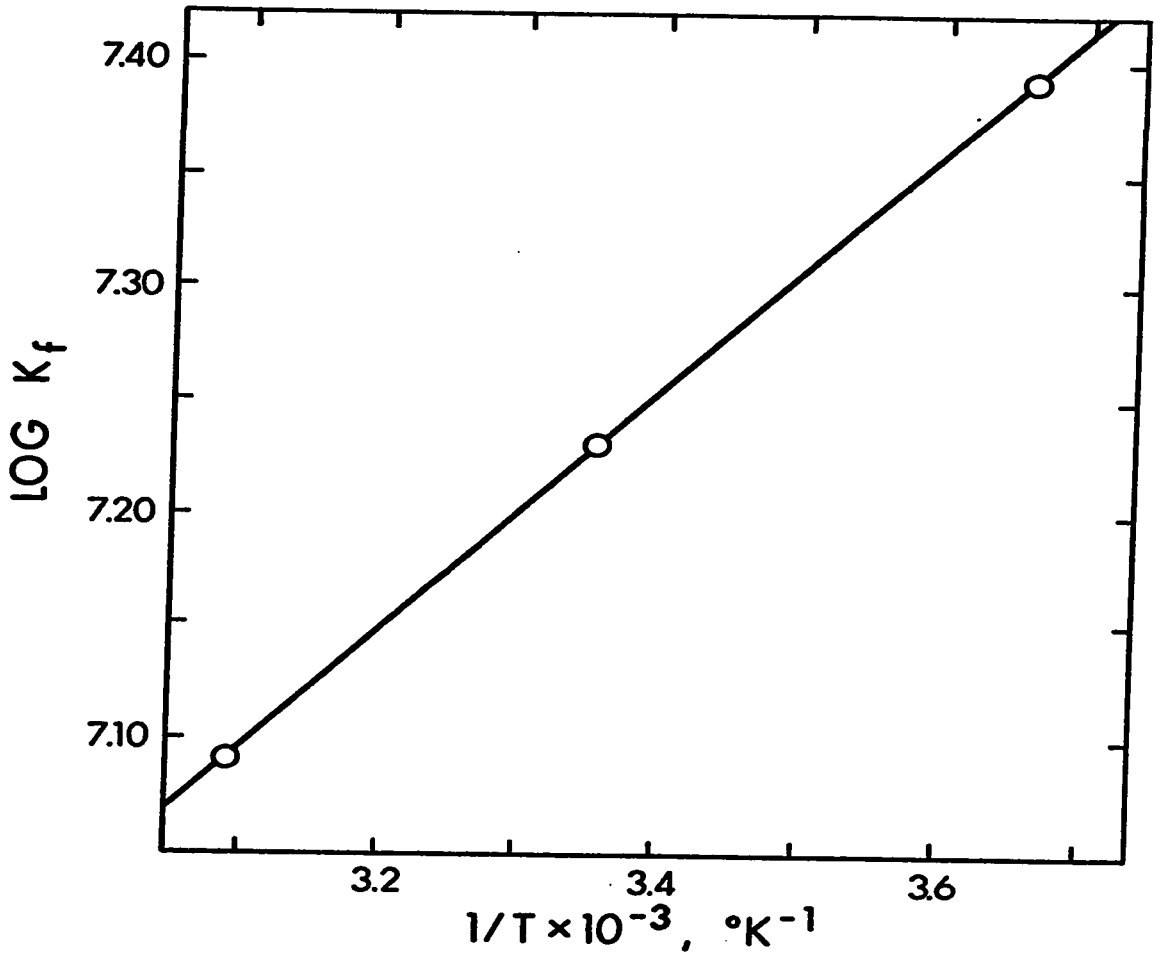
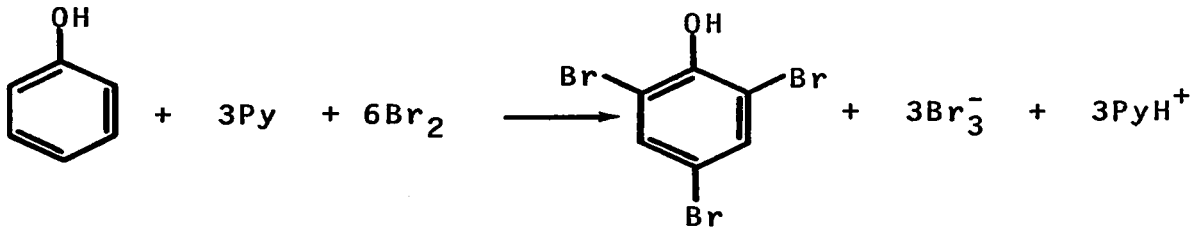


Figure 5. Plot for Determination of ΔH of Formation of Tribromide Ion in Propylene Carbonate

RESULTS AND DISCUSSION

Reaction with Phenols

Addition of bromine to a solution of phenol in PC does not result in discharge of the bromine color. Bromine substitution does not occur under these conditions since PC itself is not a sufficiently strong base to accept the protons released in the reaction. Upon addition of three or more equivalents of a base such as pyridine to each equivalent of phenol in the solution, however, the reaction goes quickly to complete formation of tribromophenol. As a result of the stability of the tribromide ion in PC, an additional bromine molecule combines with each bromide ion produced. Therefore, the bromination of phenol in the presence of excess pyridine proceeds according to the equation



where Py is pyridine and PyH^+ is pyridinium ion.

The effect on the stoichiometry of varying the amount of pyridine added in the titration of a variety of phenolic compounds is illustrated in Table III. The effect on potentiometric titration curves of two representative phenols as pyridine is added is illustrated in Figures 6

Table III. - Effect of Added Pyridine in Titration of Phenols with Bromine in Propylene Carbonate[a]

[Pyridine]/[Phenol] Ratio	1:1	2:1	3:1	4:1	6:1	8:1	10:1
Phenol	1.961	3.861	5.849	5.972	5.990	5.990	5.924
2-Naphthol	1.988	3.933	4.003	3.975	3.981	3.999	3.983
p-Nitrophenol	1.943	3.771	3.964	3.987	3.996	3.962	3.989
Salicylic Acid	2.026	4.044	4.610	4.670	4.542	4.487	4.427
Methyl Salicylate	1.910	3.730	4.130	4.050		4.020	
p-Cresol	1.983	3.788	5.780	5.966	5.975	5.987	6.013
Thymol	1.937	3.841	5.737	5.966	5.985	5.987	5.985
Resorcinol	1.797	4.188	4.856	7.679	9.958	10.014	10.022

[a] Numbers given are moles of bromine per mole of phenol added at the endpoint.

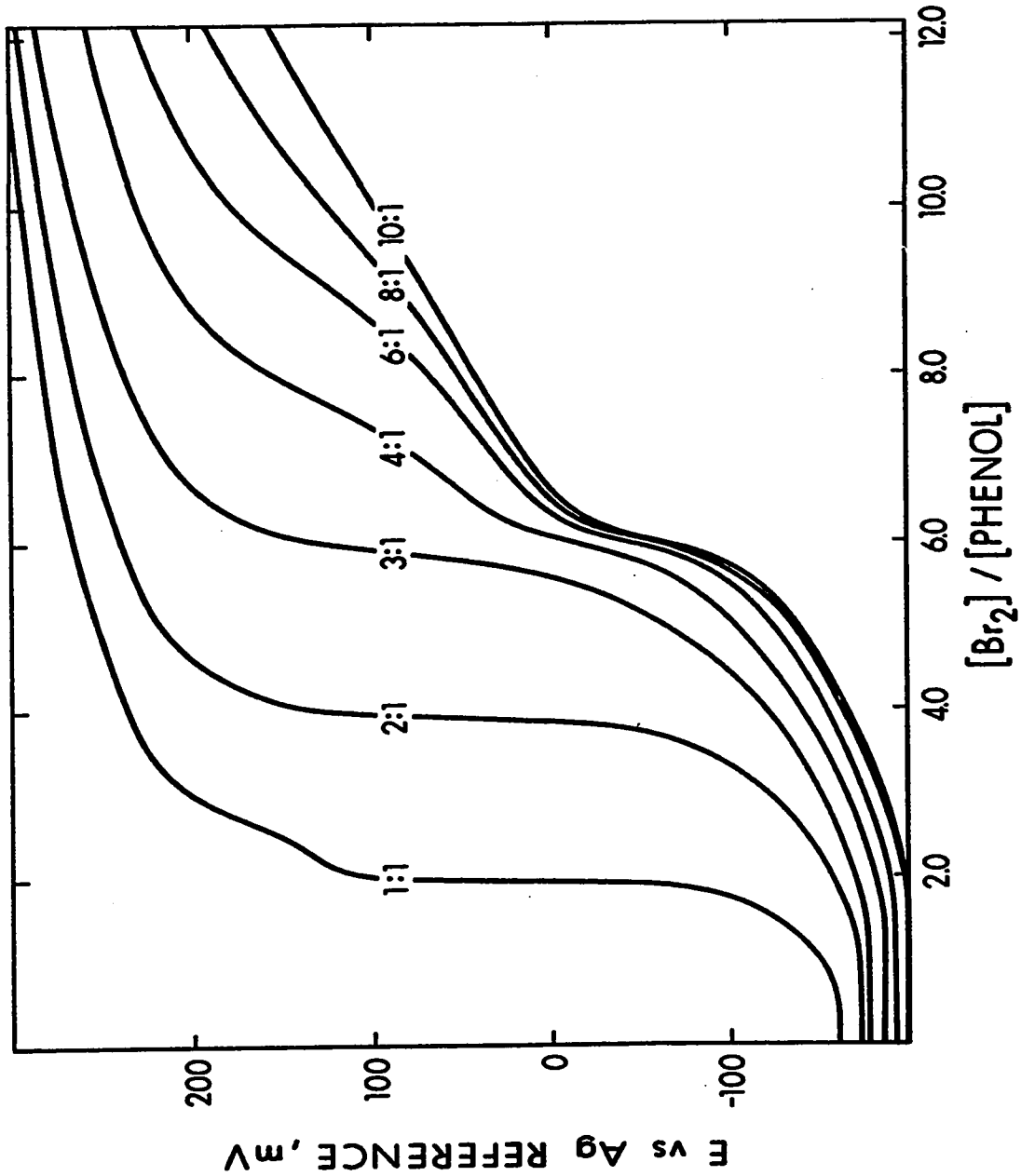


Figure 6. Effect of Varying the [Pyridine]/[Phenol] Ratio in Potentiometric Titration of Phenol with Bromine in Propylene Carbonate

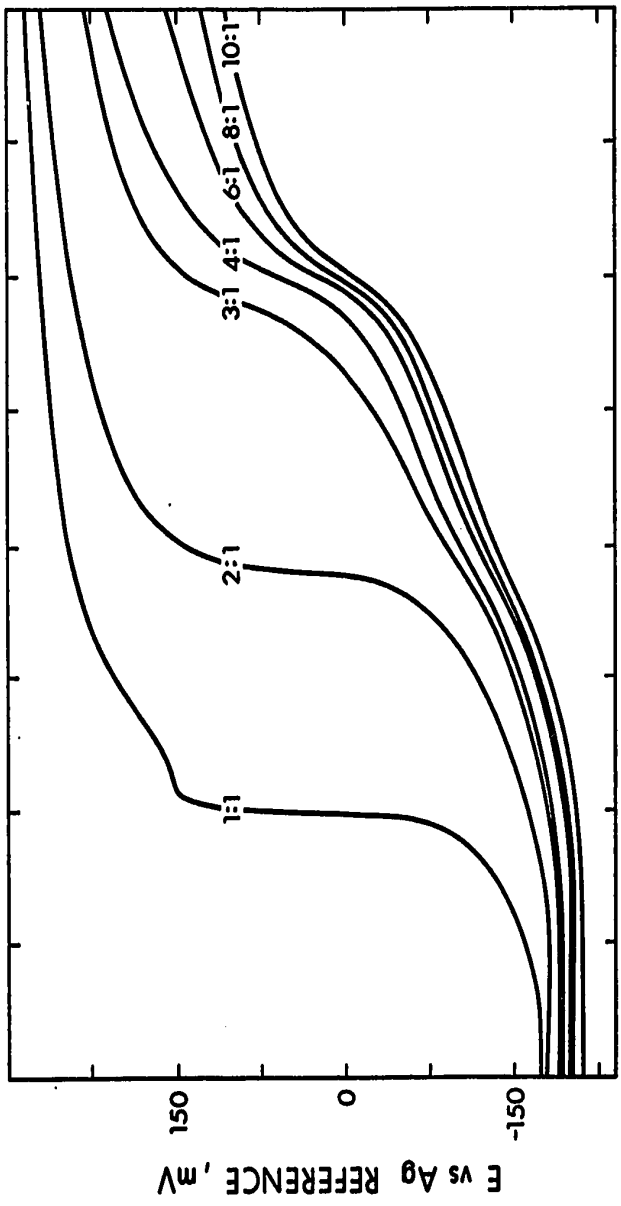


Figure 7. Effect of Varying the [Pyridine]/[p-Cresol] Ratio in Potentiometric Titration of p-Cresol with Bromine in Propylene Carbonate

and 7. The decrease in potential after the endpoint as increasing amounts of pyridine are added is due to the formation of a pyridine–bromine complex. The value of the formation constant of this complex in PC has been found to be $10^{2.74\pm0.03}$ by measurement of the potential at a platinum electrode immersed in solutions containing pyridine, bromine and tribromide ion (Appendix C).

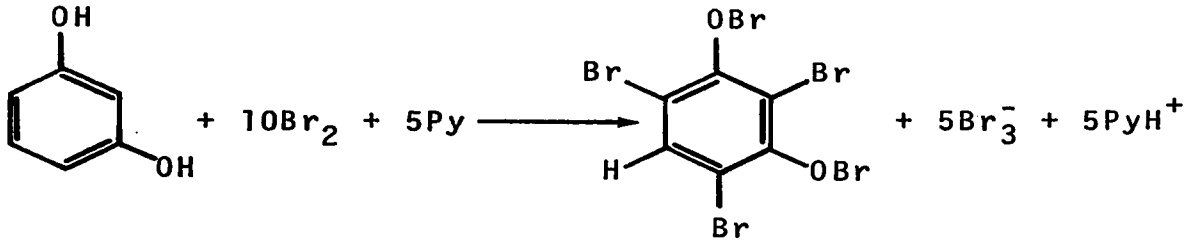
When less pyridine is added than is required to combine with each replaceable proton of the compound being brominated, the endpoint in the titration occurs after the addition of two moles of bromine per mole of pyridine. Under these conditions bromination can only proceed until all of the pyridine present has been protonated. This results in the substitution of one bromine atom and the formation of one tribromide ion for each molecule of pyridine present.

The results obtained for phenol, 2-naphthol, p-nitrophenol, and methyl salicylate were as expected. In the presence of an excess of pyridine, phenol consumes six moles and the remainder of the compounds consume four moles of bromine, with the formation of the tribrominated and dibrominated products respectively. Thus all free ortho and para positions are being brominated stoichiometrically with the comsumption of two moles of bromine for each position being brominated.

Salicylic acid consumes about 15% more than the

expected four equivalents of bromine. This may be due to partial substitution of the carboxylic acid group by bromine, a commonly occurring side reaction in the bromination of hydroxybenzoic acids[20]. Reduction of the temperature to -20°C reduced the error to about 8% but did not eliminate it entirely.

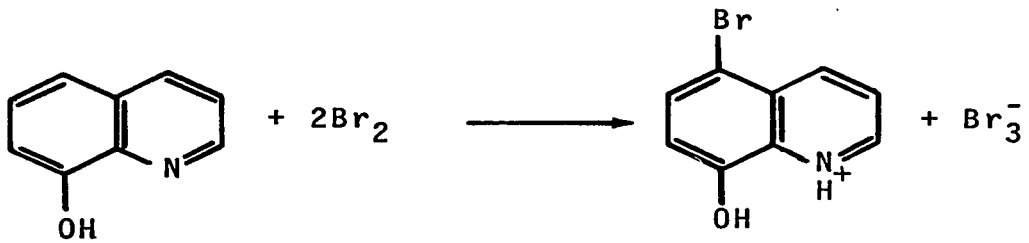
If the unoccupied ortho and para positions are the only positions being brominated in the titration of p-cresol, thymol, and resorcinol, the first two compounds should consume four moles of bromine instead of six, and resorcinol should consume six moles instead of ten. The additional bromine uptake can be explained by assuming replacement of the hydroxyl group protons of these compounds by bromine, as in the reaction



The products formed are analogous to tribromophenol bromide ($C_6H_2Br_3OBr$) which is formed in aqueous phenol solutions with an excess of bromine[19]. Only compounds which have electron-releasing substituents on the aromatic nucleus in addition to the first hydroxyl group were found to undergo substitution of the hydroxyl proton.

Support for the postulated tribromoresorcinol dibromide reaction product was obtained by comparison of the infrared spectra of a solution of resorcinol in PC before and after addition of an excess of both pyridine and bromine. The O—H stretching band seen at 3380 cm^{-1} in the spectrum of resorcinol disappears when more than five equivalents of pyridine and ten equivalents of bromine are added to the solution. One possible explanation for this is that the hydroxyl hydrogen is being replaced by bromine.

The presence of a basic site in the molecule of a phenolic compound allows its titration without the addition of pyridine. Oxine (8-hydroxyquinoline) consumes exactly two equivalents of bromine in the reaction



In a series of seven titrations of oxine in PC, an average recovery of 99.80% with a standard deviation of 0.1% was obtained. In the equation above, the bromine is shown in the 5-position. However, this has not been verified.

Reaction with Aromatic Amines

The amino group, like the hydroxyl group, acts as a powerful activator and ortho-, para-director in electrophilic aromatic substitution reactions. Aniline and substituted anilines can therefore be brominated as readily as phenols. Since these compounds contain a proton-accepting site in the amino nitrogen atom, some bromination should be possible in PC without the addition of a separate base as was necessary for phenols. Results of titrations of a variety of aromatic amines, both with and without the addition of excess pyridine as a proton acceptor, are summarized in Table IV. A qualitative description of the sharpness of each potential break is included in the table. Several of the potentiometric titration curves are shown in Figures 8 to 10.

In the titration of p-phenetidine, p-toluidine, and aniline, the potential remains below about -400 mV (vs. the silver–0.01M silver perchlorate in PC reference electrode) until the addition of one-half equivalent of bromine if no pyridine has been added to the solution, or until the addition of one equivalent of bromine if an excess of pyridine is present. An estimate of the ratio of bromide to tribromide before the first break is possible through use of the Nernst equation,

$$E = E^{\circ'}_{Br_3^-/Br^-} + \frac{0.0591}{2} \log \frac{[Br_3^-]}{[Br^-]^3}$$

Table IV. - Results Obtained by Titration of Aromatic Amines with Bromine in Propylene Carbonate

Compound	p-Nitroaniline	Anthranilic Acid	Anthranilic Acid (Py Added)
First Endpoint			
$[Br_2]$/[Amine] Ratio	1.07	2.00[c]	1.4 - 1.6
Size of Break (mV)	50	60	150
Sharpness[a]	ms	ms	g
Potential[b]	+150	+110	-150
Second Endpoint			
$[Br_2]$/[Amine] Ratio	none	none	4.1
Size of Break (mV)			60
Sharpness[a]			ms
Potential[b]			+10

Table IV. - Continued

Compound	Aniline	Aniline (Py Added)	m-Phenylenediamine	m-Phenylenediamine (Py Added)
First Endpoint				
$[Br_2]$/[Amine] Ratio	0.6 - 0.8	1.0 - 1.1	1.14	2.6
Size of Break (mV)	50	150	500	300
Sharpness[a]	g	vs	vs	vs
Potential[b]	-250	-325	-300	-400
Second Endpoint				
$[Br_2]$/[Amine] Ratio	2.00[c]	4.00[c]	3.00[c]	6.00[c]
Size of Break (mV)	250	100	50	50
Sharpness[a]	s	s	s	s
Potential[b]	+50	-30	+100	0

Table IV. - Continued

Compound	p-Toluidine	p-Toluidine (Py Added)	p-Phenetidine	p-Phenetidine (Py Added)
First Endpoint				
$[Br_2]$/[Amine] Ratio	0.47 - 0.52	0.9 - 1.1	0.46 - 0.47	1.00[c]
Size of Break (mV)	150	100	200	200
Sharpness[a]	s	g	s	vs
Potential[b]	-300	-275	-350	-350
Second Endpoint				
$[Br_2]$/[Amine] Ratio	1.7 - 1.8	4.00[c]	1.8	none
Size of Break (mV)	300	150	200	
Sharpness[a]	s	s	s	
Potential[b]	0	0	+50	

[a] vs: very sharp, s: sharp, ms: moderately sharp, g: gradual

[b] expressed as mV vs. silver-0.01M silver perchlorate in PC reference electrode

[c] endpoint appears to be suitable for analytical application

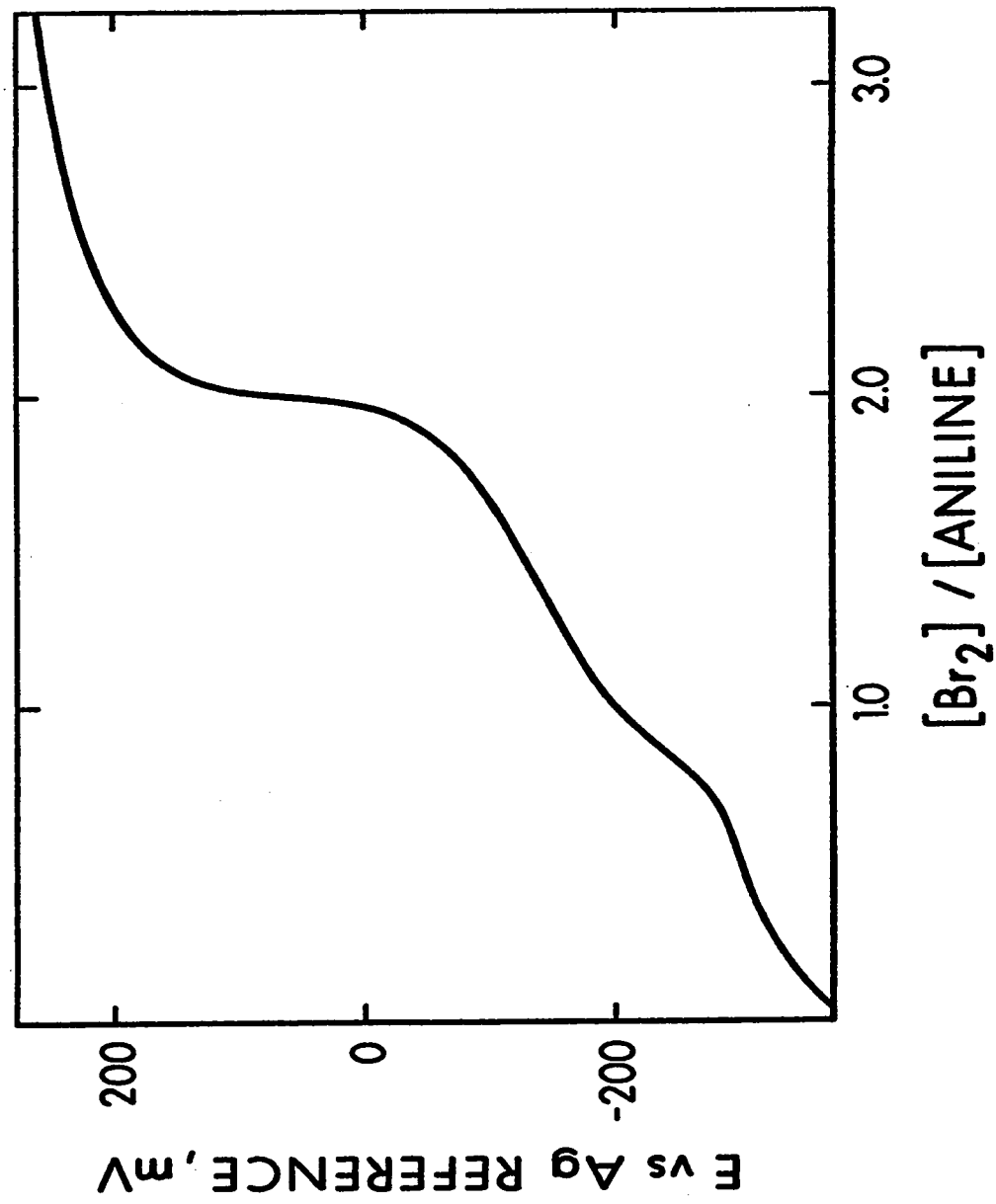


Figure 8. Potentiometric Titration of Aniline with Bromine in Propylene Carbonate

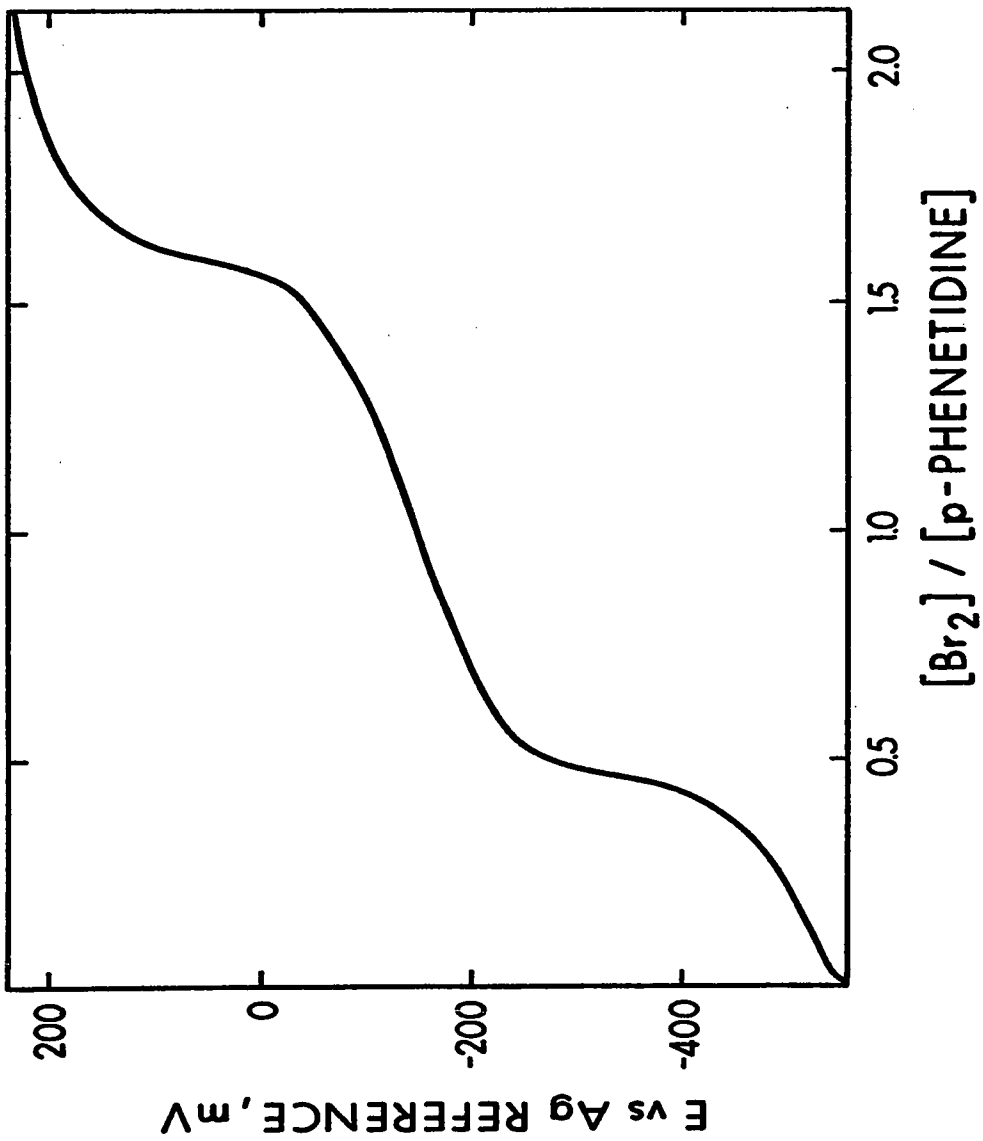


Figure 9. Potentiometric Titration of p-Phenetidine with Bromine in Propylene Carbonate

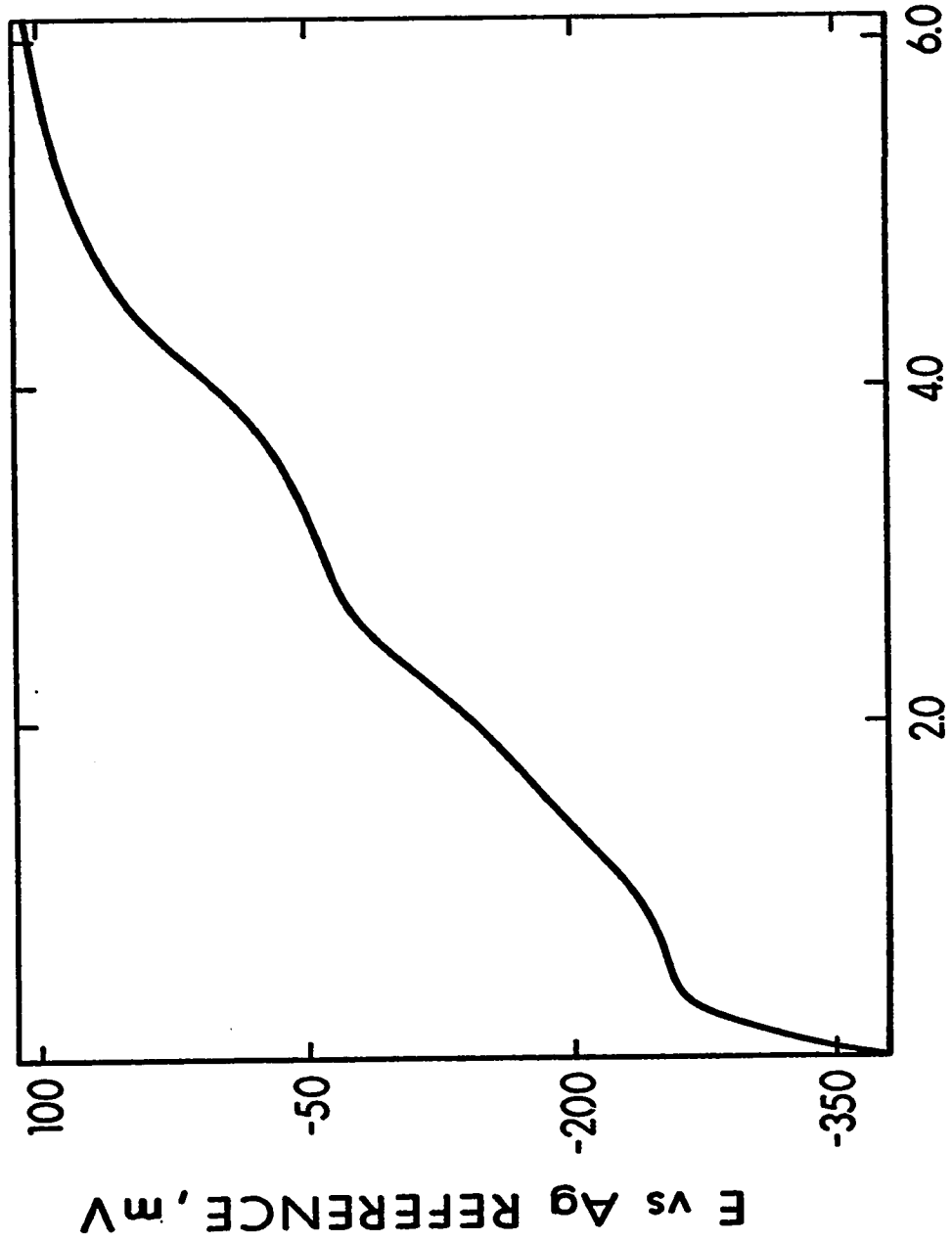
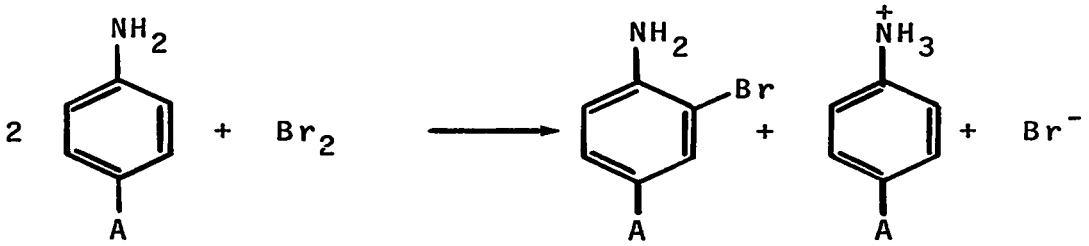


Figure 10. Potentiometric Titration of Anthranilic Acid with Bromine in Propylene Carbonate

if it is assumed that the potential in this region is controlled by the bromide–tribromide couple. The results of such calculations indicate that essentially no tribromide ion is being produced in the initial part of the reaction. For example, using values of -0.340 V for $E^{\circ'}_{Br_3^-/Br^-}$ and 10^{-2}M for the concentration of bromide ion, a ratio of bromide to tribromide of 10^6 is obtained at -400 mV. A bromide ion concentration of 10^{-2}M is approximately equal to that of the aromatic amine during the early part of the titration.

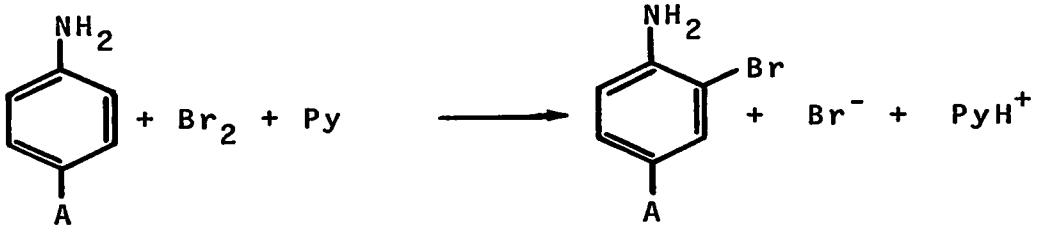
The absence of tribromide ion is also indicated by the observation that the solution remains colorless until the first potential break, whereupon a yellow color appears and increases in intensity during the remainder of the titration.

The occurrence of a potential break for these compounds after the addition of one-half equivalent of bromine in the absence of pyridine may be explained by the reaction



Since the electron-withdrawing effect of bromine makes the monobrominated aromatic amine a weaker base than the non-brominated compound, protons produced in the substitution step should be preferentially accepted by the non-brominated species. In addition, further bromination of the protonated amine would not be expected to occur readily because protonation of the amino group converts it from a strongly activating to a deactivating group toward electrophilic substitution.

In the presence of an excess of pyridine, however, the first potential break does not occur until after the addition of one equivalent of bromine since, under these conditions, none of the amine is deactivated by protonation. Pyridine, being a stronger base than the aromatic amines under study, preferentially accepts the protons released upon bromine substitution. The reaction occurring in these cases is



The appearance of free bromide ion rather than tribromide ion as a product of these reactions was somewhat

unexpected in view of the stability of the tribromide ion in PC. Apparently introduction of the first bromine atom onto the aromatic ring of these compounds proceeds so readily that the amine successfully competes with bromide ion for bromine. Only after all of the aromatic amine has been either monobrominated or protonated does the bromine react with bromide to produce tribromide ions. The introduction of an electron-withdrawing bromine atom onto the aromatic nucleus renders further bromination difficult, enabling the formation of tribromide ion to compete successfully with further bromine substitution.

The competition between bromide ion and amine for the bromine added in the early stages of the titration of an aromatic amine in PC allows an assessment of the ease of bromination of the amine being titrated. Highly reactive amines are brominated in preference to the formation of tribromide. The ratio of bromide to tribromide will thus be high, and the potential measured will be correspondingly low. On the other hand, a much higher potential is seen in the titration of less reactive aromatic amines since the concurrent formation of tribromide ion is more favored.

The ease of bromination of substituted anilines is related to the electron-withdrawing or electron-releasing properties of substituents directly attached to the aromatic nucleus. Groups which increase the electron density of the

aromatic ring are activating whereas electron-withdrawing groups are deactivating. The magnitude and direction of the electric dipole moment of benzene derivatives (C_6H_5-A) is related to the electron-releasing or electron-withdrawing power of the substituent, A. Listings of experimentally determined dipole moments of a variety of substituted benzene derivatives are available[32]. These values may be used to predict the relative ease of bromination of aniline and substituted anilines.

Values of the potential measured at a point midway between the start of titration and the first potential break for a variety of aromatic amines (midpoint potential) are shown in Table V. Also included in this table are values of the dipole moment contribution of the substituent, aside from the first amino group, present in that compound. Substituents which donate electrons to the ring are assigned a positive value; those which withdraw electrons are assigned a negative value. Hydrogen is assigned a value of zero. A plot of these values versus the midpoint potential measured in the titration of the amines is shown in Figure 11. The linear correlation between these two parameters suggests that both are a measure of the same parameter, that is, the ease of bromination of substituted aromatic amines.

Table V. - Dipole Moments and Midpoint Potentials of Selected Aromatic Amines

Compound	Substituent (A)	Dipole Moment[32] of C_6H_5-A	Midpoint Potential[a]
m-Phenylene-diamine	$-NH_2$	+1.5	-560
p-Phenetidine	$-OC_2H_5$	+1.4[b]	-540
p-Toluidine	$-CH_3$	+0.4	-410
Aniline	-H	0.0	-380
Anthranilic Acid	-COOH	-1.6	-220
p-Nitroaniline	$-NO_2$	-4.3	+ 80

[a] Potentials reported in mV vs. a silver-0.01M silver perchlorate in PC reference electrode.

[b] No value for the dipole moment of $C_6H_5-OC_2H_5$ was available; the value for $C_6H_5-OCH_3$ was used.

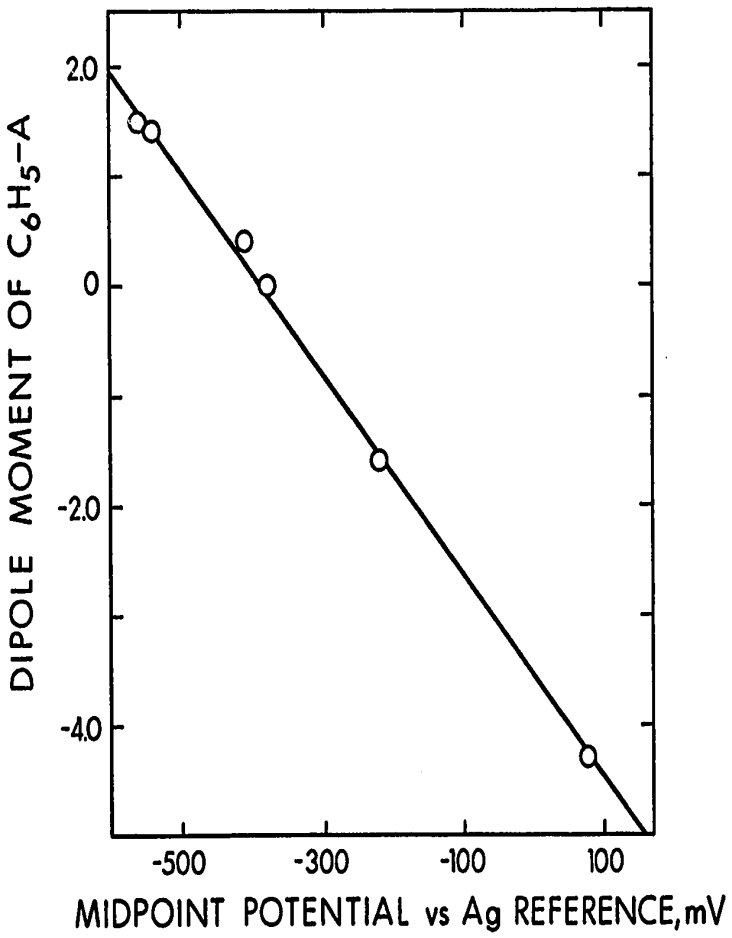


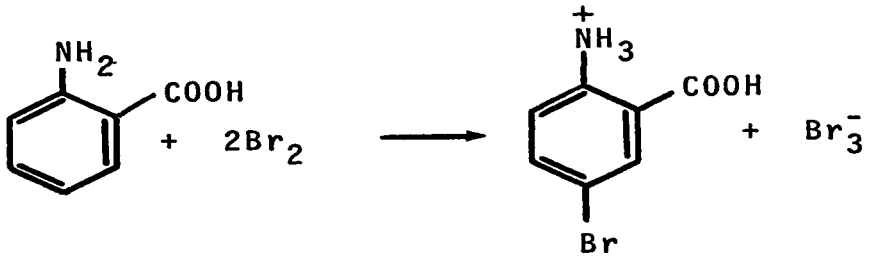
Figure 11. Relationship Between Dipole Moments of Selected Aromatic Amines and Midpoint Potentials Obtained in Titrations with Bromine in Propylene Carbonate

The correlation between electric dipole moment and reactivity can be carried one step further. In the titration of p-toluidine with bromine, a sharp increase in potential from about -400 mV to about -250 mV occurs after the addition of one-half equivalent of bromine. This potential break marks the completion of adding one bromine to p-toluidine to form 2-bromo-4-methyl aniline. Addition of the dipole moment values for a methyl substituent, +0.4, and for a bromine substituent, -1.8, results in an effective total contribution of -1.4. According to the graph in Figure 11 this should result in a midpoint potential of -240 mV for the second bromine substitution; this agrees very well with the potential actually observed. The potential after the first break in the titration of aniline and p-phenetidine can be predicted by a similar calculation.

As indicated in Table IV, the only potential break marking the onset of formation of tribromide ion which appears to be suitable for analytical use is that occurring in the titration of p-phenetidine in the presence of an excess of pyridine. The first break in the titration of aniline, m-phenylenediamine, and p-toluidine with and without the addition of pyridine either does not occur after the addition of exactly one-half or one equivalent of bromine, or is too gradual to be useful.

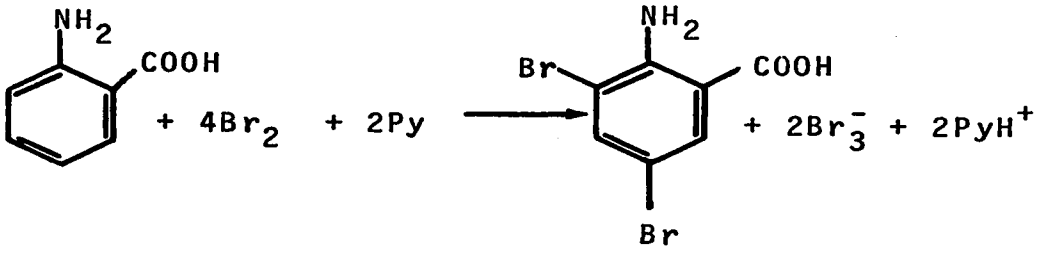
A potential break occurs after the addition of two equivalents of bromine in the titration of anthranilic acid.

The reaction occurring is postulated to be



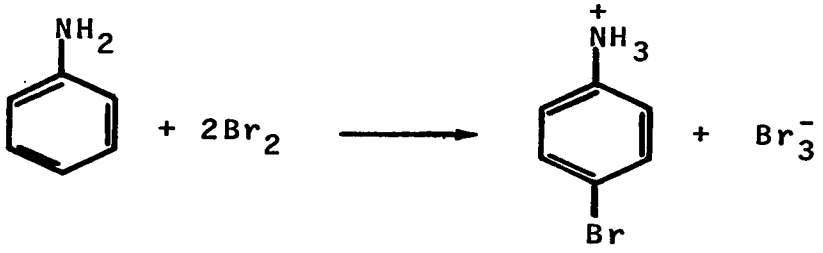
The actual position of bromination has not been established. Bromine substitution stops after all of the anthranilic acid has been protonated since no base is then available to accept protons which would be released if the remaining open ortho position were also brominated. This reaction can be used for the analysis of anthranilic acid; in a series of four titrations an average recovery of 99.4% with a standard deviation of 0.8% was obtained.

Addition of pyridine prior to titration of anthranilic acid results in a very gradual potential break after the addition of about two equivalents of bromine and a sharper break after the addition of somewhat more than four equivalents. Neither of these breaks can be used analytically, the first because it is too gradual, and the second because it is not stoichiometric. The reaction at the second break corresponds to the following equation:



In a series of five titrations of anthranilic acid in the presence of an excess of pyridine, an average recovery of 103.9% with a standard deviation of 0.6% was obtained. The high results are probably caused by partial replacement of the carboxyl group by bromine.

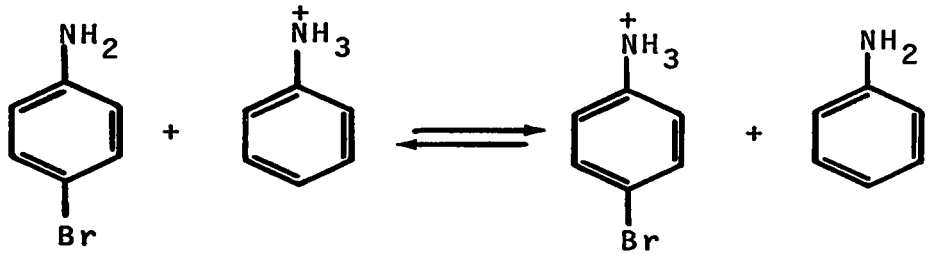
Aniline can be determined by titration with bromine in PC without the addition of pyridine. The potential break occurring at a [bromine] to [aniline] ratio of 2:1 is sharp and quite large. An average aniline recovery of 99.0% with a standard deviation of 0.1% was obtained in a series of such titrations. The reaction occurring can be written as



The NMR spectrum of a 2:1 mixture of bromine and aniline in PC was found to be identical to that of a PC solution

of p-bromoanilinium bromide.

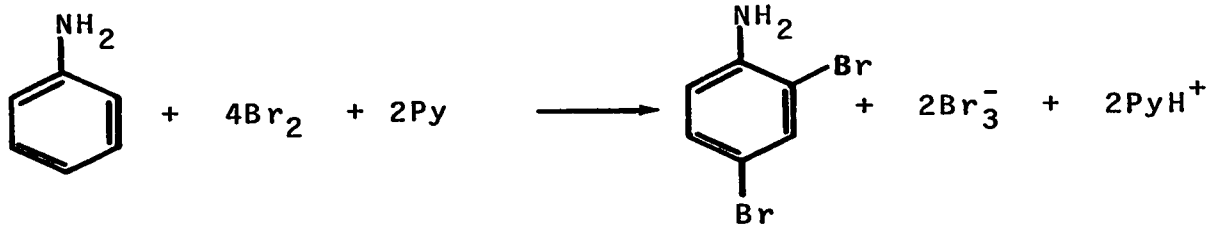
After the addition of one equivalent of bromine to aniline, one-half equivalent of p-bromoaniline and one-half equivalent of anilinium tribromide will have been produced. Further bromination of the protonated aniline appears to be possible only after proton exchange with the more weakly basic p-bromoaniline:



The aqueous pK_b's of aniline and p-bromoaniline are 9.34 and 10.06, respectively[33]. It thus appears that sufficient proton exchange occurs to allow stoichiometric formation of p-bromoanilinium tribromide. However, p-phenetidine and p-toluidine consume only 1.7 to 1.8 equivalents of bromine in a similar reaction, probably as a result of a less favorable equilibrium.

Aniline can also be quantitatively titrated with bromine in PC after the addition of an excess of pyridine. The second potential break occurs after the addition of exactly four equivalents of bromine. In a series of titrations in which the ratio of pyridine to aniline was varied from 4:1 to 12:1, an average recovery of 99.5% with a

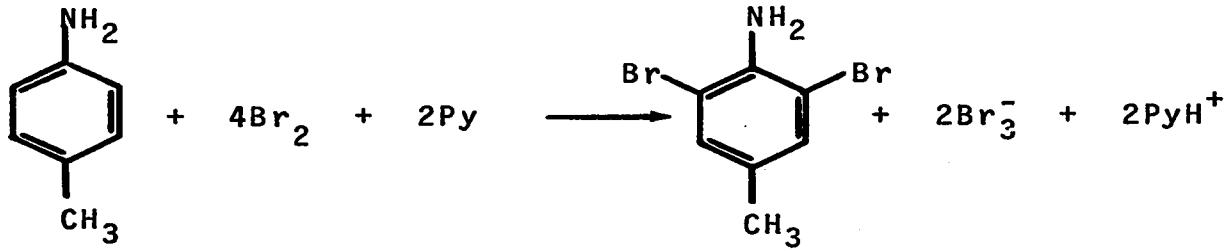
standard deviation of 0.6% was obtained. The reaction occurring under these conditions corresponds to the equation



Introduction of a third bromine atom into the remaining open ortho position appears to be too difficult to be achieved by direct titration because of the presence of two deactivating bromine atoms. From the sum of the dipole moments for two bromine substituents, -3.8, and Figure 11 it is predicted that the third bromine should add only with difficulty. After the addition of six equivalents of bromine, an amount sufficient to produce tribrominated aniline plus three equivalents of tribromide ion, a very small and gradual potential break is seen in the experimental titration curve. The size and sharpness of this potential break are enhanced to some extent by reducing the speed of the titration. This indicates that substitution of the third bromine atom is too slow and incomplete to be analytically useful.

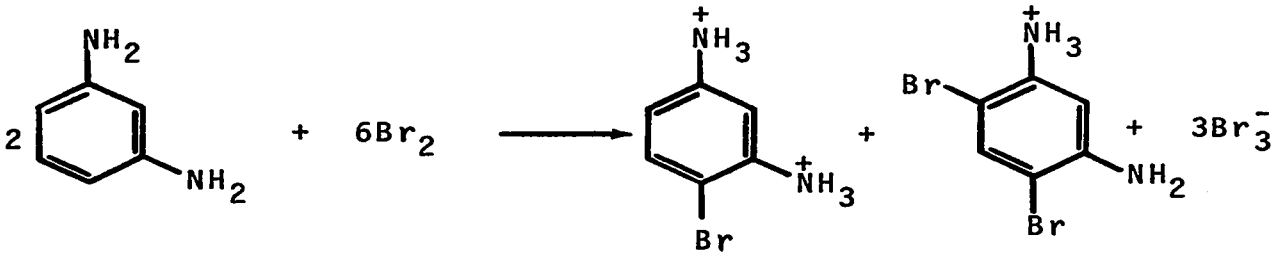
Quantitative titration of p-toluidine is possible in the presence of an excess of pyridine. A sharp potential

break occurs after the addition of exactly four equivalents of bromine. The reaction corresponds to

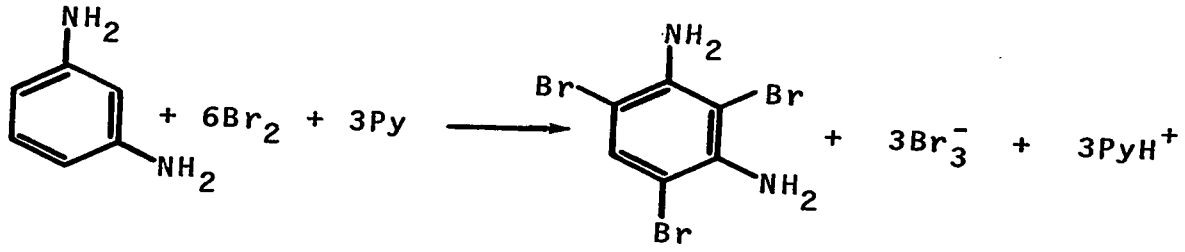


The presence of excess pyridine has no effect on the position of the endpoint; an average recovery of 99.5% with a standard deviation of 0.4% was obtained in a series of titrations in which the ratio of pyridine to p-toluidine was varied from 3:1 to 10:1.

Analysis of m-phenylenediamine by titration with bromine is possible with or without pyridine being present. In the absence of pyridine a potential break occurs after the addition of three equivalents of bromine. The reaction taking place is postulated to be



When an excess of pyridine is added to the solution before titration, m-phenylenediamine consumes six equivalents of bromine:

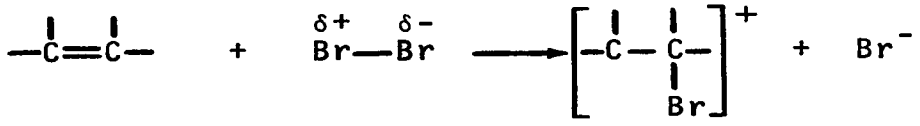


Part III. BROMINE ADDITION REACTIONS IN PROPYLENE CARBONATE

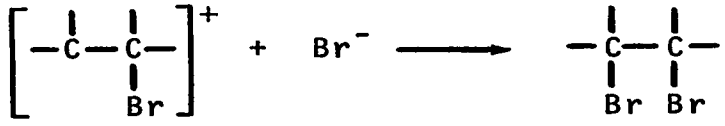
BACKGROUND

Most of the classical chemical methods for the determination of olefinic unsaturation involve halogenation. Bromine is the most useful of the halogens for this purpose, and so has enjoyed widespread application in analytical procedures. Chlorine is so reactive that its use is often accompanied by extensive substitution, while iodine adds rather reluctantly and only to a few ethylenic compounds. Two interhalogen compounds, iodine monochloride and iodine monobromide, have also been utilized with some success[34].

The mechanism of bromine addition to a carbon–carbon double bond involves two steps. The first is the electrophilic attack by the positive end of a polarized bromine molecule on the π electrons of the double bond to produce a positive carbonium ion intermediate:



The reaction is completed by attack of a bromide ion on the positive intermediate to produce a 1,2-dibromide:



The intermediate carbonium ion, once formed, may also react with other anions in solution. Thus a significant amount of ethylene bromohydrin (2-bromoethanol) is produced on addition of bromine to ethylene in the presence of water; if the reaction occurs in glacial acetic acid, 2-bromoethyl acetate is one of the products.

The number and nature of substituents on the olefinic carbon atoms influence the rate of addition of bromine. Electron-donating substituents (-OH, $-NH_2$, $-CH_3$) facilitate bromine addition while electron-withdrawing substituents (-COOH, $-NO_2$) reduce the rate of the reaction. The influence of substituents on the ease of the addition reaction is due to stabilization or destabilization of the intermediate carbonium ion.

Most halogenation methods for the determination of unsaturation are titrimetric, and with few exceptions the quantity of halogen reagent consumed is determined by back-titration of the excess added to the reaction mixture. Excess iodine is titrated directly with standard thiosulfate solution, but reagents containing the more volatile inter-halogen compounds or bromine are first treated with excess iodide to liberate an equivalent amount of iodine.

Traditionally, bromine has been the preferred reagent for use in the petroleum industry whereas iodine monochloride and iodine monobromide have been more widely used by the pharmaceutical industry for the determination of

unsaturation in oils and fats of animal and vegetable origin. Either iodine monochloride or pyridinium sulfate perbromide in a mixture of glacial acetic acid and carbon tetrachloride are employed in the official methods of the British Pharmacopoeia for the determination of the iodine value of fixed oils or fats[35]. A method has been described for the determination of the degree of unsaturation of these substances by the addition of an excess of bromine to the sample in a solvent consisting of chloroform and dioxane[36].

A wide variety of methods involving bromine have been proposed for the determination of unsaturation in petroleum products. Reagents that have been utilized include bromine in acetic acid[37] and in carbon tetrachloride[38], aqueous bromate–bromide[39], tribromide ion in methanol[40], coulometrically generated bromine[41], and pyridinium bromide perbromide[29]. Procedures involving back-titration of excess reagent have been chosen for most applications, but direct titration with a brominating reagent has also been investigated. The endpoint in direct titration techniques may be determined visually by the appearance of an excess of bromine[37], amperometrically[42], by the 'dead-stop' electrometric method[43], spectrophotometrically[26], and by constant current potentiometry[44].

It is generally necessary to add a mercuric salt as a catalyst to facilitate the direct titration of olefins in

non-polar solvents. Owing to the high dielectric constant of PC, the possibility that bromine addition reactions occurring in this solvent may be rapid enough to allow direct titration without the addition of a catalyst was considered feasible. Therefore an investigation of the analytical utility of such reactions in PC was undertaken.

EXPERIMENTAL

Propylene carbonate was purified as described previously in Part II. The apparatus employed for potentiometric titrations, and the preparation, storage, and standardization of the titrant have already been described in Part II. For titrations at reduced temperatures, the titration cells were packed in ice (0°C) or in a dry ice—methanol—water slush before and during the titration. A 30% solution of methanol in water was used to control the temperature at -20°C, a 50% solution was used at -45°C. The temperature was controlled at 50°C with a heat lamp adjacent to the titration cell. The power input of the heat lamp was controlled by a Variac. By this method the temperature could be controlled to ±1°C during the titrations.

Chloroform and all of the olefins listed in Table VI were reagent grade and were used as received. The fixed oils were all of the highest purity commercially available and were used without prior treatment.

A 0.125M solution of silver perchlorate was prepared by dissolving silver perchlorate which had been dried under vacuum at 80°C for several hours in distilled PC. The solution was standardized by titration of an aliquot of a gravimetrically standardized solution of tetraethylammonium bromide in PC (Part II).

A 0.05M solution of tetraethylammonium hydroxide in a mixture of PC and water was prepared by addition of a 10% aqueous solution of tetraethylammonium hydroxide to distilled PC. The solution was standardized by potentiometric titration of p-toluenesulfonic acid in PC using a platinum indicating electrode.

RESULTS AND DISCUSSION

The results obtained by titration of several olefinic compounds in PC at various temperatures are shown in Table VI. A potentiometric titration curve of cyclohexene is shown in Figure 12. Bromine consumption in excess of the theoretical quantity was noted in all instances except in the titration of cyclohexene and vinyl butyrate at room temperature and at 50°C and in the titration of linoleic acid at room temperature.

Bromine substitution reactions occurring at the double bond or at other sites in the olefinic molecule are a frequent source of positive error in analytical bromine addition reactions:

$$-CH{=}CH- + Br_2 \longrightarrow -CH{=}CBr- + HBr$$

$$-CH{=}CH-CH_2- + Br_2 \longrightarrow -CH{=}CH-CHBr- + HBr$$

These reactions have been shown to occur to a greater extent in polar solvents than in non-polar solvents[45,46]. In PC, each bromide ion released would be expected to combine with more bromine to produce stable tribromide ions, thus compounding the error produced by unwanted substitution reactions. A measure of the substitution taking place should be possible by determination of either the bromide

Table VI. - Recoveries Obtained in Titration of Olefinic Compounds with Bromine in Propylene Carbonate[a]

Compound	Temperature				
	-45°C	-20°C	0°C	+25°C	+50°C
Allyl amine				118	
Allyl alcohol		132	112	113	141
Allyl ether				109	
Vinyl butyrate	161	102	102	95	89
1- and 2-Octene (mixed isomers)		124	104	100	103
Cyclohexene		132	106	98	98
Oleic acid			106	102	108
Linoleic acid				95[b]	

a Values presented are percentage recoveries based on 1:1 reactions between bromine and all of the compounds with the exceptions of allyl ether and linoleic acid. Values for these two compounds are calculated on the basis of a 2:1 reaction.

b Calculated from the position of the second of two potential breaks.

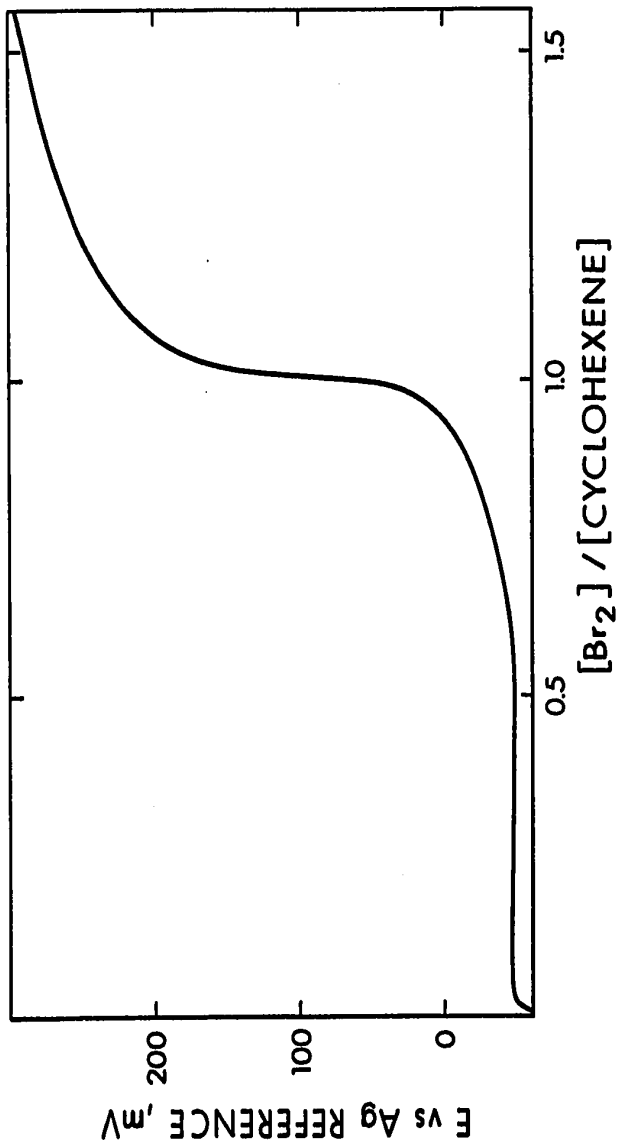


Figure 12. Potentiometric Titration of Cyclohexene with Bromine in Propylene Carbonate

or the acid present in solution after titration with bromine.

The concentration of bromide or tribromide in a PC solution containing an excess of bromine can be determined by potentiometric titration with silver perchlorate using a silver indicating electrode (Figure 4). By this method, the 0.5M bromine solution being used as the titrant in the determination of olefins was found to contain approximately 0.01M bromide. Therefore it was necessary to subtract from the amount of bromide found in solution after bromination of an olefin the amount of bromide added with the titrant.

An attempt was also made to determine the amount of acid released on bromination of an olefin in PC to establish whether or not the bromide found was being released as hydrogen bromide. Titrations with solutions of tetraethylammonium hydroxide in PC are complicated by the fact that tetraethylammonium hydroxide was found to react with bromine. Tetraethylammonium hydroxide consumes approximately one equivalent of bromine in PC. The reaction postulated is

$$2OH^- + 2Br_2 \longrightarrow Br_3^- + OBr^- + H_2O$$

Thus, to determine the acid released in addition reactions by this method, the amount of excess bromine must be

estimated in order to calculate the quantity of titrant reacting with bromine. The amount of acid found agrees, within the expected experimental error, with the amount of bromide found by titration with silver perchlorate. Since determination of bromide is more convenient and accurate, its concentration was used to measure the amount of substitution occurring rather than determination of the acid released.

The high results in the titration of several of the compounds listed in Table VI at room temperature, and the generally high recoveries obtained for all compounds at reduced temperatures, were found to be accompanied by formation of large amounts of hydrogen bromide. At -20°C, 0.48 equivalent of bromide per equivalent of cyclohexene was produced upon bromination. At room temperature, allyl alcohol consumed 1.13 equivalents of bromine with the formation of 0.34 equivalent of bromide. These results establish that the cause of high recoveries tabulated in Table VI is the occurrence of bromine substitution as a side reaction.

Analytical bromine addition reactions are often performed at reduced temperatures in an effort to suppress bromine substitution. Such a procedure is not effective in PC since reduction of the temperature caused bromine consumption to increase dramatically in every instance, though the temperature at which the increase occurred

varied from compound to compound.

This increase in substitution at low temperatures may be caused by differences in the temperature coefficient of the rates of the competing addition and substitution reactions. It appears that the rate of addition reactions is reduced at low temperatures relative to substitution reactions, so that the latter are able to compete to a greater degree.

Addition of a base such as pyridine to a PC solution of an olefin before titration with bromine was found to enhance the rate of substitution. This is as expected, because pyridine will accept protons released in the substitution reaction. In the presence of pyridine (3 moles per mole of cyclohexene) cyclohexene consumed 1.18 equivalents of bromine at room temperature and 1.67 equivalents at -20°C. Allyl alcohol consumed 1.95 equivalents of bromine at room temperature when 5 equivalents of pyridine were added prior to titration.

An attempt was made to apply a direct titration with bromine to the determination of the degree of unsaturation of fixed oils of vegetable origin. Most of the oils investigated were not sufficiently soluble in PC to allow titration in that solvent alone. However, all were found to be soluble in mixtures of chloroform and PC; sufficient chloroform was therefore added to bring the oils into solution before each titration. Approximately 30% (v/v)

chloroform was necessary to dissolve 1% of oil in chloroform—PC mixtures.

The results of titration of a variety of fixed oils are shown in Table VII. The results are reported as iodine values, the grams of iodine taken up by 100 g of the oil. Iodine values are used rather than bromine values because the degree of unsaturation of fixed oils is commonly expressed in this way in pharmaceutical and industrial literature. Two distinct potential breaks occurred in the titration of several oils; in these instances iodine values calculated from the amount of bromine required for reaching each of the endpoints are included. Potentiometric titration curves of corn oil and castor oil are shown in Figures 13 and 14. Also appearing in Table VII are iodine values determined on the same oil samples by the official British Pharmacopoeia method[35]. In this procedure, an excess of iodine monochloride is allowed to react with the oil for 30 minutes in a solvent composed of a mixture of carbon tetrachloride and glacial acetic acid. The excess iodine monochloride is subsequently determined by addition of an aqueous iodide solution and titration of the liberated iodine with sodium thiosulfate.

Linoleic acid, a major constituent of linseed oil, was also titrated with bromine in a mixture of chloroform and PC. Two potential breaks were seen in this titration also, the first after the addition of 1.52 equivalents of

Table VII. - Results Obtained in Titration of Fixed Oils with Bromine in Propylene Carbonate

Oil	Iodine Value Calculated From First Endpoint	Iodine Value Calculated From Second Endpoint	Iodine Value Determined by Iodine Monochloride Method[35]	Expected Range of Iodine Values[47]
Castor	111	a	88	81 - 91
Olive	91	a	85	79 - 88
Corn	109	141	118	111 - 128
Peanut	88	101	95	88 - 98
Cottonseed	101	128	108	103 - 111
Linseed	155	183	179	175 - 202

[a] Only one potential break seen in potentiometric titration.

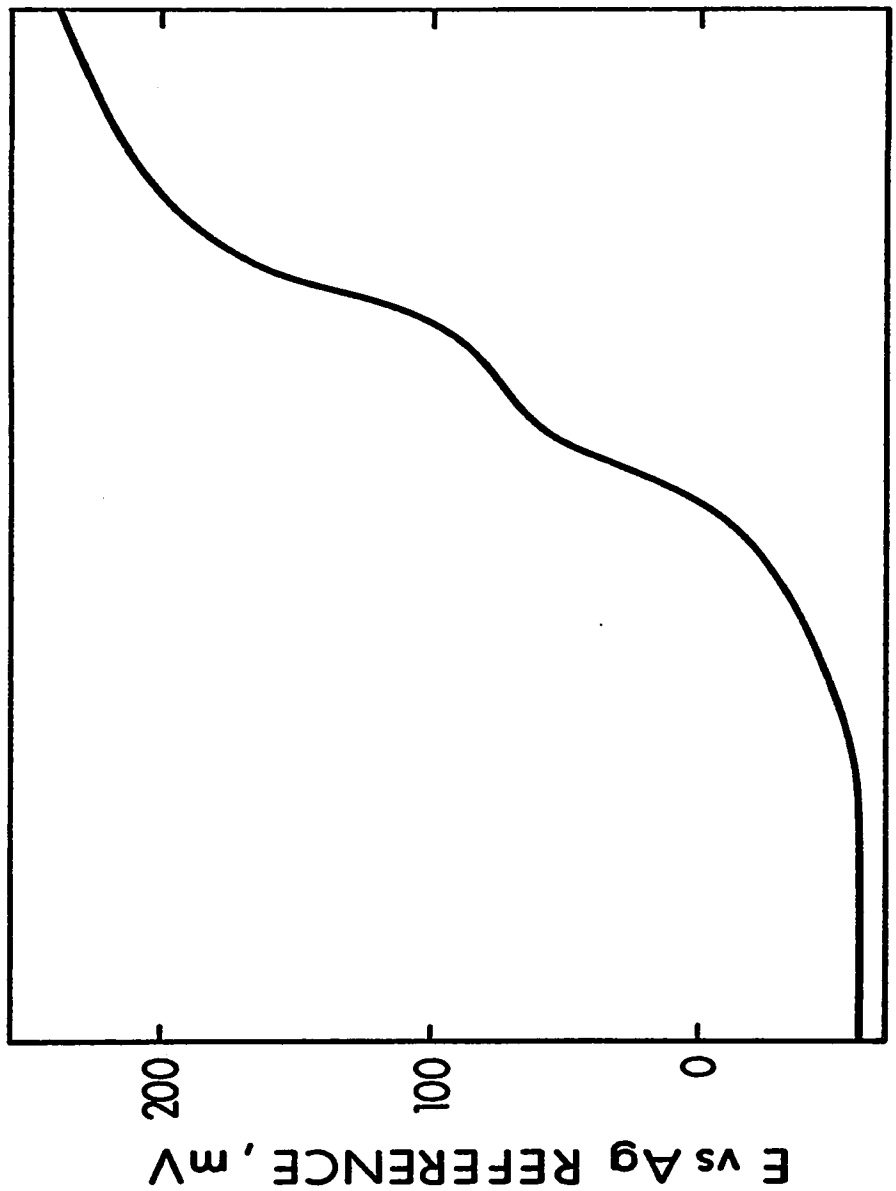


Figure 13. Potentiometric Titration of Corn Oil with Bromine in Propylene Carbonate–Chloroform Mixture

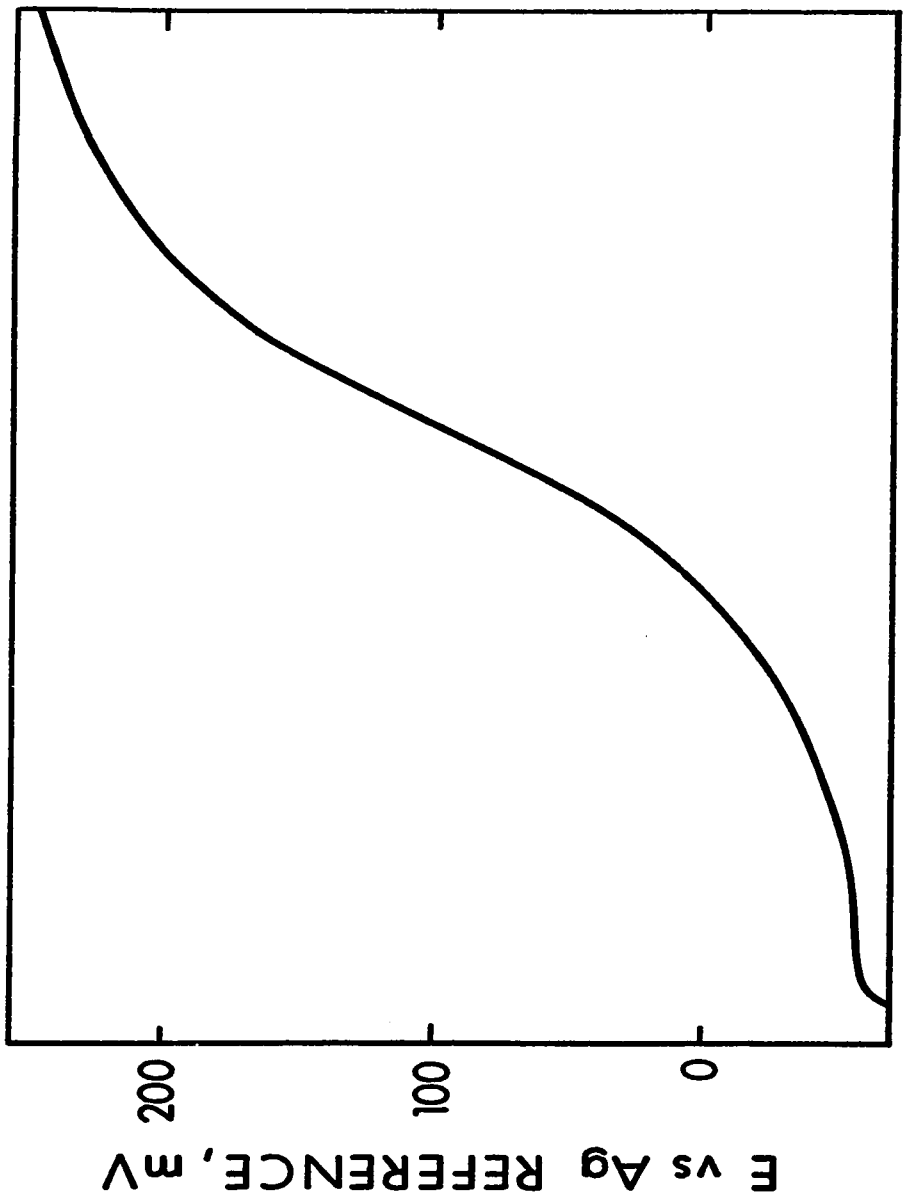


Figure 14. Potentiometric Titration of Castor Oil with Bromine in Propylene Carbonate–Chloroform Mixture

bromine (76% recovery) and the second after the addition of 1.90 equivalents of bromine (95% recovery). It thus appears that the second of the two potential breaks seen in this titration, and perhaps also in the titration of oils, is more indicative of the true degree of unsaturation than is the first.

The iodine value of fixed oils as determined by reaction with iodine monochloride or monobromide is reported to be reliable when the double bonds are not conjugated, but where conjugated double bonds are present the reaction is not complete[48]. The oils investigated here (Table VII) contain from 5% to 94% of fatty acids possessing conjugated double bonds[49]. The major unsaturated fatty acids in most of the oils investigated are oleic acid and linoleic acid, both of which have been shown to react essentially quantitatively with bromine in PC. Iodine values determined by direct titration with bromine in PC are generally 5% to 25% higher than those determined by addition of an excess of iodine monochloride in a non-polar solvent. It appears that the difference between the two methods is probably due to more quantitative reaction between bromine and unsaturated sites in the fatty acids, although there may be some tendency in PC for bromine to undergo substitution reactions. The procedure proposed thus had advantages over existing methods in that it is both faster and appears to be a more accurate measure of the degree of unsaturation.

Part IV. OXIDATION BY CERIUM(IV) IN PROPYLENE CARBONATE

BACKGROUND

Since its introduction as a titrimetric oxidizing agent in 1927 by Martin[50], quadrivalent cerium has become one of the more popular analytical oxidants. The cerium(IV) salt most commonly used for the preparation of titrant solutions is ammonium hexanitratocerate(IV), $(NH_4)_2Ce(NO_3)_6$, because it can be prepared conveniently in pure form and is readily soluble in acid solutions. The formal potential of the cerium(IV)—(III) couple is 1.44 V in 1M H_2SO_4 and 1.70 V in 1M $HClO_4$[51]. Solutions of cerium(IV) in concentrated acid are stable if protected from light. Titrations with cerium(IV) are usually performed in strongly acidic media; the equivalence point may be determined potentiometrically, amperometrically, or visually with indicators such as iron (II)-1,10-phenanthroline. A summary of aqueous cerimetric methods is available[52].

Cerium(IV) is also a strong oxidant in nonaqueous solvents. Hinsvark and Stone[53] first proposed the use of ammonium hexanitratocerate(IV) in glacial acetic acid as a volumetric reagent. The solubility of the salt in this solvent was found to be about 0.05M. Disadvantages of the system included the need to standardize the titrant daily because it decreased in strength at a rate of about 3% per

day, and the necessity for the oxidations to be carried out in the presence of a high concentration of perchloric acid to produce sufficiently rapid reaction rates.

In acetonitrile ammonium hexanitratocerate(IV) has a formal reduction potential of 0.755 V vs. a silver—0.01M silver nitrate in acetonitrile reference electrode[54] and so is also a convenient analytical oxidant. A 0.05M solution of ammonium hexanitratocerate(IV) in acetonitrile was found to be stable over a period of several days[55]. Addition of acetic acid to the acetonitrile solution increases the cerium(IV) reduction potential and the rate of cerium(IV) oxidation of most substances, which is often quite slow in pure acetonitrile. The increase in reaction rate is caused by acetate ion catalysis rather than by solvent effects because the addition of sodium acetate has the same rate-enhancing effect[56]. A review of analytical cerium(IV) oxidations in acetic acid, acetonitrile, and mixtures of these two solvents is available[2].

Since cerium(IV) has been shown to be a strong oxidant in nonaqueous solvents, a study of its use as a titrant in PC was undertaken. Because of its high dielectric constant, good solvent properties, and stability, PC was considered to offer some advantage over the two previously used solvents.

EXPERIMENTAL

Reagents and Apparatus

Propylene carbonate was purified as previously described in Part II. PC used to study the effect of solvent moisture content on the stability of cerium(IV) solutions was transferred to a dry box (Kewaunee Scientific Equipment) and dried by slow passage through a 25—cm column of Linde 5A molecular sieves. The sieves were dried under vacuum at 150°C for 12 hours prior to use. Cerium(IV) solutions were prepared by dissolution of pure ammonium hexanitratocerate(IV) in PC and stored in glass stoppered bottles. Solutions prepared using dried PC were stored in a dry box until use.

Ammonium hexanitratocerate(IV) (purity assay 100.00%, G. Frederick Smith Chemical Company) was oven dried for two hours at 85°C before use. Ferrocene (Arapahoe Chemicals) was used as received. Potassium iodide, sodium iodide, thiourea, hydroquinone, and dextrose were all reagent grade and were used as received.

Titrant delivery and potential recording were carried out with a Metrohm Model E436 automatic titrator. The potentiometric titration cell and electrode assembly described in Part II were used, with the exception that the silver—0.01M silver perchlorate in PC reference electrode was replaced by an aqueous saturated calomel reference electrode isolated from the cell solution with a

0.1M lithium perchlorate in PC bridge.

Thermometric titrations were carried out in a 50-ml beaker imbedded in a large styrofoam block. The solutions were stirred magnetically during titration. Temperature changes were followed with a thermistor (Fenwal Electronics Inc., #GB3251) sealed into the end of a thin glass tube with silicone rubber cement (General Electric, RTV). A bridge circuit similar to the one described by Linde, Rogers, and Hume[57] was assembled to allow potentiometric recording of the thermistor output. The apparatus was calibrated by immersing the thermistor in a water bath controlled to ±0.01°C and measuring at several temperatures the resistance of the thermistor with a Leeds and Northrup conductance bridge; the potential of the bridge circuit was measured with an Orion Model 801 digital pH meter. The resistance of the thermistor at 25°C was 2190Ω and its sensitivity was 0.039Ω/Ω/°C. The output of the bridge circuit changed 27.9 mV/°C.

RESULTS AND DISCUSSION

Stability of Titrant

The stability of a solution of cerium(IV) in PC was assessed by titration of samples of ferrocene after varying periods of storage (Table VIII). The effect of the addition of several acids on the stability of the titrant was also studied.

The decrease in strength of the cerium(IV) solution to which no acid was added may be partially due to formation of stable cerium(IV) hydroxide species through reaction with water absorbed from the atmosphere, as no special precautions were taken to protect the solution from atmospheric moisture. This possibility is supported by the observation that the titer of a 0.1M cerium(IV) solution prepared with dry distilled PC and stored in a dry box was found to decrease by less than 1% per day over several days. A 0.5M cerium(IV) solution was also used for some titrations; its stability was approximately the same as that of the more dilute solutions.

Reaction with Ferrocene

Ferrocene has been proposed for use as a primary standard for determining the concentration of copper(II) in acetonitrile[58]. It is readily soluble in acetonitrile, available in pure form, stable on storage, and is cleanly oxidized to the ferricenium ion with the loss of a single

Table VIII. - Effect of Acid on the Stability of Cerium(IV) Solutions in Propylene Carbonate[a]

Days After Preparation	[Ce(IV)] in PC	[Ce(IV)] in 0.1M HNO_3 in PC	[Ce(IV)] in 0.1M $HClO_4$ in PC
0[b]	0.095	0.094	0.068
1	0.090	0.090	0.063
2	0.088	0.085	0.052
3	0.087	0.082	0.048
4	0.083	0.080	0.045
5	0.079	0.076	0.040

a Value given in each instance is the cerium(IV) molar concentration as determined by titration of ferrocene. All solutions were prepared to be 0.1M in cerium(IV).

b The first titration was performed immediately after preparation of the titrant.

electron. Since ferrocene was found to be very soluble in PC also, a study of its utility for the standardization of cerium(IV) solutions in PC was undertaken.

A single, sharp potential break is seen in the potentiometric titration of ferrocene with cerium(IV) in PC (curve a, Figure 15). However, the endpoint for freshly prepared solutions of ammonium hexanitratocerate(IV) in distilled PC indicates a cerium(IV) concentration between 90% and 95% of that calculated from the weight of ammonium hexanitratocerate(IV) added, assuming a 1:1 reaction between ferrocene and cerium(IV).

If addition of titrant is interrupted in the region after the potential break in a titration of ferrocene with 0.5M cerium(IV), the potential decreases from about +900 mV to +600 mV within two minutes and remains steady at the lower value. If addition of titrant is resumed the potential immediately rises to the higher value, but drops again if the titration is once more interrupted. Curve b in Figure 15 plots the potential values observed when the titration was completed by addition of 0.125-ml increments of titrant, with a several minute wait after each addition. After more than three equivalents of cerium(IV) per mole of ferrocene were added, the potential remained steady for at least 30 minutes.

From this evidence it appears that oxidation of ferrocene by cerium(IV) is proceeding past the ferricenium

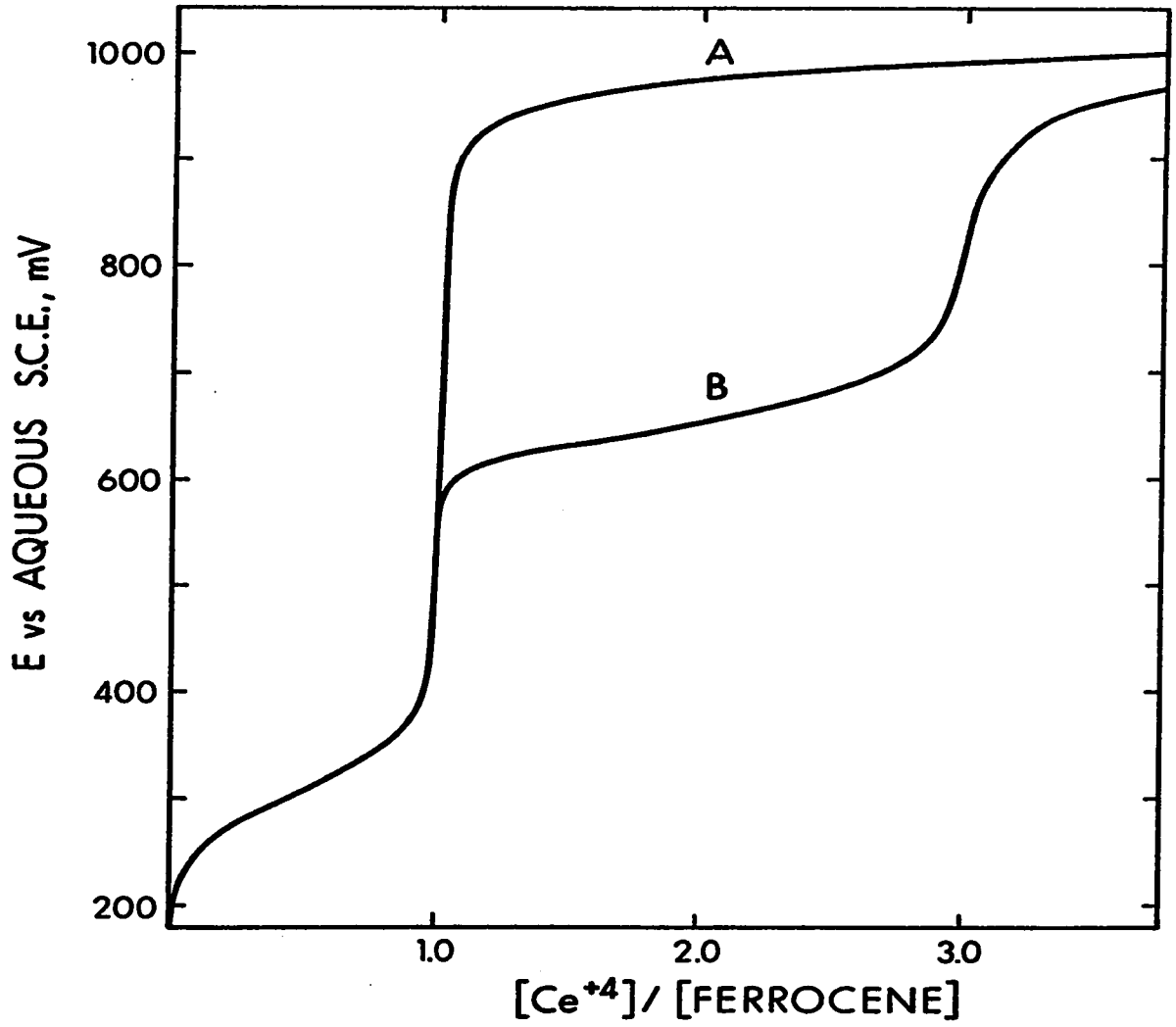


Figure 15. Potentiometric Titration of Ferrocene with Cerium(IV) in Propylene Carbonate: Rapid and Continuous (a), and Slow with Intermittant Addition of Titrant (b)

ion stage in a second slow step. The first break occurs at a 1:1 molar ratio corresponding to oxidation of ferrocene to ferricenium ion. The second slow reaction, which requires the addition of two more equivalents of cerium(IV), may be oxidation of the cyclopentadienyl moieties attached to the iron(III) in the ferricenium ion to produce one free iron(III) ion plus two equivalents of cyclopentadiene. The 5% to 10% difference between the cerium(IV) concentration of recently prepared titrant as determined by titration of ferrocene and that calculated from the weight of ammonium hexanitratocerate(IV) used may thus be partially due to non-stoichiometric reaction with ferrocene. Partial oxidation of the ferricenium ion under the conditions of a fast titration would lead to consumption of slightly more than one mole of cerium(IV) per mole of ferrocene.

Reaction with Iodide

Because of the stability (log K_f = 7.9) of the triiodide ion in PC[59], the potentiometric titration curve resulting from oxidation of iodide would be expected to show two potential breaks. The first break should occur upon oxidation of two-thirds of the iodide, corresponding to formation of the stable triiodide ion:

$$3I^- \rightleftharpoons I_3^- + 2e^-$$

A second potential break should occur upon oxidation of the triiodide ion to iodine:

$$2I_3^- \rightleftharpoons 3I_2 + 2e^-$$

A typical curve resulting from the potentiometric titration of iodide with a freshly prepared solution of 0.5M ammonium hexanitratocerate(IV) in PC is shown in curve a, Figure 16. The first break occurs as expected, but the second break does not occur until 1.05 to 1.10 equivalents of cerium(IV) per equivalent of iodide have been added. The late occurrence of this endpoint may be caused by reaction of a portion of the cerium(IV) with an impurity in the solvent to produce a complex that is a sufficiently strong oxidant to convert iodide to triiodide, but not strong enough to oxidize triiodide to iodine. An example of such a reaction is hydrolysis of cerium(IV) by traces of water remaining in the PC to form one or more cerium(IV) hydroxide species. The postulate that the error is caused by impurities in the solvent is supported by the fact that in a similar titration of iodide with 0.1M cerium(IV) in technical grade PC, the first endpoint was 10% late and the second endpoint was 40% late.

The endpoint in titrations of iodide with cerium(IV) in PC can also be determined thermometrically. The titration curve resulting from titration of 0.4 millimole of

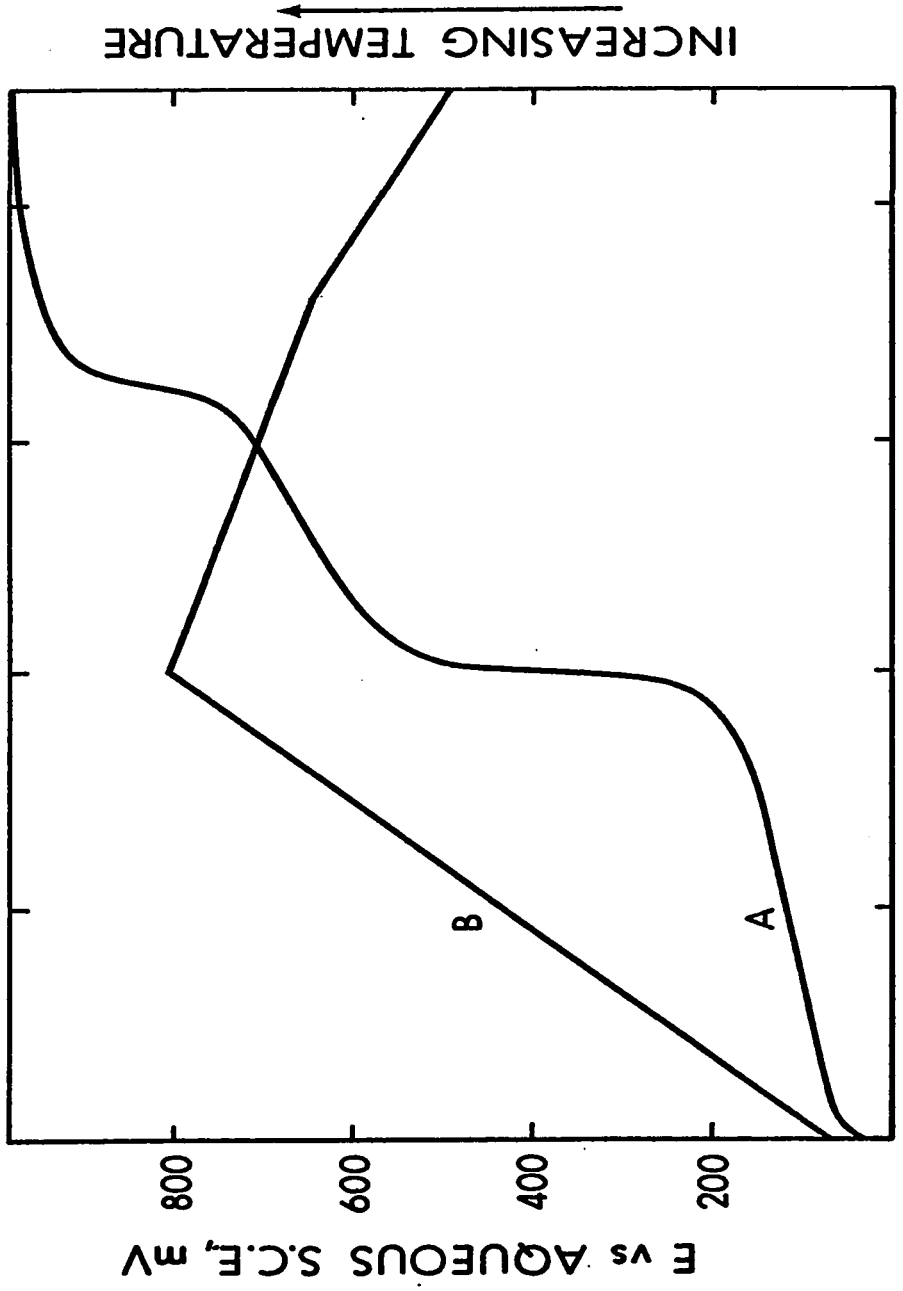
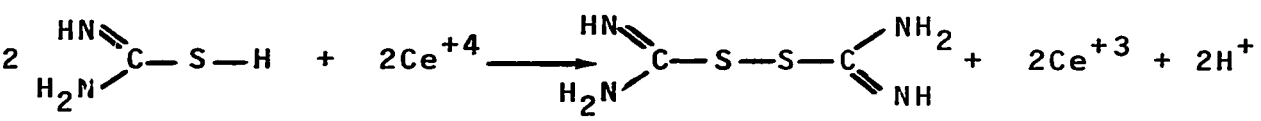


Figure 16. Potentiometric (a) and Thermometric (b) Titration of Iodide with Cerium(IV) in Propylene Carbonate

potassium iodide in 10 ml of PC with 0.1M cerium(IV) is shown in curve b of Figure 16. A reversal of slope is seen after the addition of two-thirds of an equivalent of cerium(IV) per equivalent of iodide. This indicates that oxidation of iodide to triiodide is exothermic while the oxidation of triiodide to iodine is endothermic. The second endpoint, indicated by a slight change in the slope of the line, occurs after addition of 1.2 equivalents of cerium(IV). The increased lateness of the second endpoint in this titration compared to that in a titration with 0.5M cerium(IV) supports the theory that the titer of cerium(IV) solutions is being reduced because of reaction of cerium(IV) with water. The level of impurities other than water in distilled PC is not sufficiently high to account for such a large error.

Reaction with Thiourea

Thiourea can be determined by titration with a solution of cerium(IV) in PC. A sharp, large (600 mV) potential break occurred after the addition of 0.98 equivalent of cerium(IV) per equivalent of thiourea. The 1:1 stoichiometry of the reaction indicates formation of the expected disulfide:

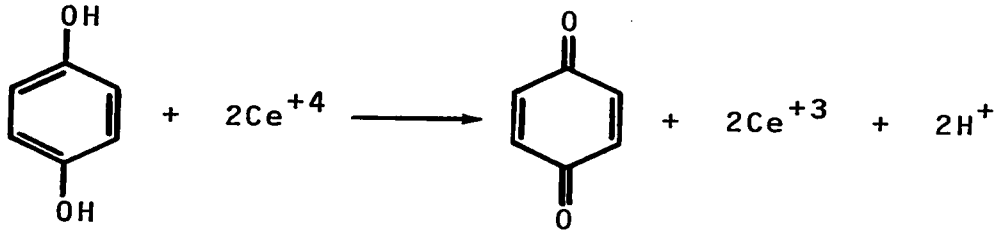


The small error in the position of the endpoint is probably caused by impurities in the sample of thiourea used.

Since the reaction between thiourea and cerium(IV) proceeds rapidly even under anhydrous conditions, the disulfide product apparently acts as a base capable of accepting two protons to produce a species of the form $\left[(H_2N)_2CS\right]_2^{+2}$. This behavior has been reported for thiourea oxidation in other aprotic solvents such as acetonitrile[60].

Reaction with Hydroquinone

Hydroquinone is not oxidized by cerium(IV) in anhydrous PC because PC is too weakly basic to accept the protons released in the reaction



The addition of water to the hydroquinone solution in PC provides a suitable proton acceptor and the oxidation goes to completion. Apparently cerium(IV) oxidizes hydroquinone so rapidly that hydrolysis is not a complication.

The curve shown in Figure 17 illustrates the titration of hydroquinone in an 8% (v/v) water in PC solvent system with 0.5M cerium(IV) in PC. The potential break

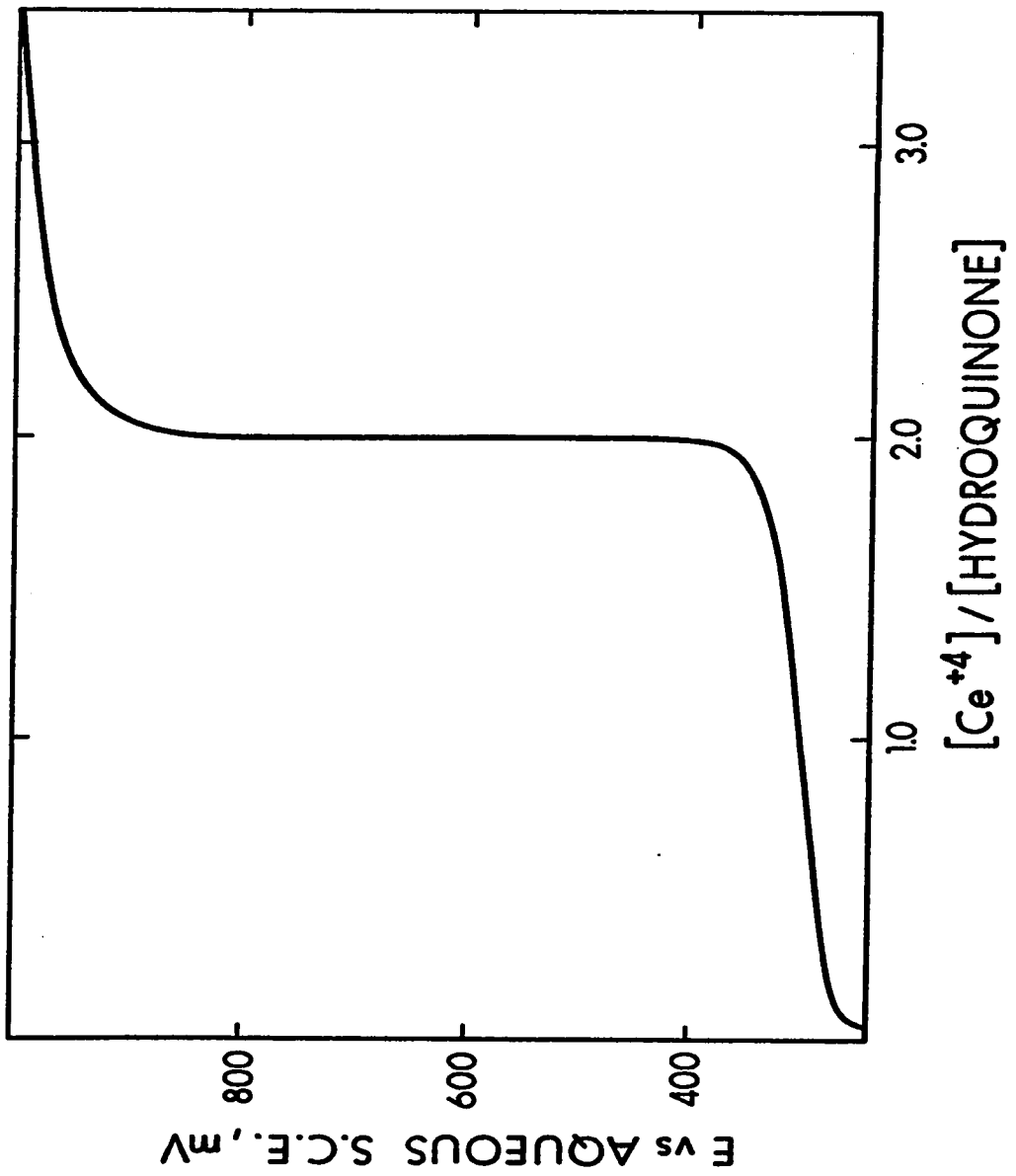


Figure 17. Potentiometric Titration of Hydroquinone with Cerium(IV) in Propylene Carbonate–Water Mixture

occurs after the addition of two equivalents of cerium(IV). The reaction does not go to completion unless a large excess of water is present; the potential break occurs after the addition of only 1.7 equivalents of cerium(IV) in a titration of 0.7 millimole of hydroquinone in the presence of 10 millimoles of water in PC.

Determination of the concentration of cerium(IV) in PC by titration with a solution of hydroquinone is also possible. In a series of five titrations with 0.25M hydroquinone of solutions of ammonium hexanitratocerate(IV) in PC containing 2% water, an average cerium(IV) recovery of 99.6% with a standard deviation of 0.2% was obtained.

Reaction with Dextrose

Dextrose is insoluble in PC at room temperature, but slightly soluble at 100°C. The yellow color of a cerium(IV) solution in PC is discharged when it is added to an excess of dextrose at 100°C. Attempts to assay dextrose in PC by addition of excess cerium(IV) at elevated temperatures, followed by titration of the excess cerium(IV) with a solution of hydroquinone, proved unsuccessful because cerium(IV) reacts with PC at elevated temperatures. By titration with hydroquinone, 0.1M solutions of cerium(IV) in PC were found to decrease in strength by 12% when maintained at 60°C for 15 minutes before titration, and by 60% when heated to 100°C for 15 minutes before titration.

Part V. OTHER OXIDIZING AGENTS IN PROPYLENE CARBONATE

To establish the possible utility of PC as a solvent for analytical electron-transfer reactions, a number of conventional aqueous oxidizing agents were surveyed as titrants.

EXPERIMENTAL

Technical grade PC (Jefferson Chemical Co.) was used for most of the titrations discussed in this section. Distilled PC, where used, was prepared according to the method outlined in Part II.

Hydrated iron(III) perchlorate ($Fe(ClO_4)_3 \cdot 6H_2O$, Alfa Inorganics, Inc.) was used as received. Attempts to dry iron(III) perchlorate by heating in an oven at 115°C and by heating under vacuum at 60°C proved unsuccessful; a mixture of violet and yellow crystals resulted in each instance. The iodine and potassium permanganate were reagent grade. Lead(IV) acetate was prepared by reaction of lead(IV) oxide with glacial acetic acid in the presence of acetic anhydride[61]. The product was recrystallized from glacial acetic acid and dried in vacuum. The purity of the lead(IV) acetate was found to be 100.1% by titration of primary standard arsenic trioxide[62].

Potentiometric titrations were carried out using a Metrohm Model E436 automatic titrator with titration cells

as described earlier (Part II). An aqueous saturated calomel reference electrode and a 0.1M lithium perchlorate in PC bridge were employed.

RESULTS AND DISCUSSION

Iron(III) Perchlorate

Iron(III) has been found to be a powerful oxidant in acetonitrile; the formal reduction potential of the iron(III)—(II) couple in acetonitrile is estimated to be 1.57 V vs. a silver—0.01M silver nitrate in acetonitrile reference electrode[63].

In the present study, a titration of ferrocene with 0.1M iron(III) perchlorate in technical grade PC gave a potential of 1.05 V vs. an aqueous saturated calomel reference electrode after addition of 1.5 equivalents of titrant. In a similar titration in which 0.1M ammonium hexanitratocerate(IV) was used as the titrant (curve a, Figure 15), the potential after the addition of 1.5 equivalents of cerium(IV) was 0.96 V; this indicates that iron(III) is a slightly stronger oxidant than cerium(IV) in PC.

The stability of solutions of iron(III) perchlorate in technical grade PC was assessed by titration of samples of ferrocene after various periods of storage (Table IX). All solutions were prepared to be 0.1M in iron(III), assuming the iron(III) perchlorate salt to be the hexahydrate, and were stored in clear glass bottles on a laboratory bench top.

Table IX.- Stability of Iron(III) Solutions in Propylene Carbonate

Days After Preparation	[Fe(III)][a]
0[b]	0.098
1	0.099
3	0.093
4	0.093
5	0.090
6	0.088

[a] Value given in each instance is the iron(III) molar concentration as determined by titration of ferrocene. All solutions were prepared to be 0.1M in iron(III).

[b] The first titration was performed immediately after preparation of the titrant.

A gas was steadily evolved from iron(III) solutions in PC on storage, making it difficult to accurately perform titrations with the automatic titrator. The gas was identified as carbon dioxide by mass spectral analysis. It was concluded that the decrease in molarity of iron(III) with time was caused by slow oxidation of PC by iron(III) to carbon dioxide and other oxidation products, or catalysis by iron(III) of hydrolysis of propylene carbonate.

Lead(IV) Acetate

Lead(IV) acetate is a powerful oxidant in nonaqueous solvents, the formal reduction potential being about 1.6 V in perchloric acid[64]. In water it hydrolyzes too readily to be useful. It has been used extensively as a titrant in electron-transfer reactions in glacial acetic acid[65,66].

Dissolution of lead(IV) acetate in either technical grade or distilled PC which has been exposed to the atmosphere for any length of time results in the immediate development of a dark brown color owing to formation of lead(IV) oxide according to the reaction

$$(CH_3COO)_4Pb + 2H_2O \longrightarrow PbO_2 + 4CH_3COOH$$

A colorimetric procedure for the determination of water in nonaqueous solvents at concentrations below 100 ppm is based on this reaction[67]. A lead(IV) acetate solution prepared in a dry box using distilled PC passed through a

column of dry molecular sieves just before use was only slightly yellow in color, but the intensity of the color rapidly increased and the solution turned brown when it was removed from the dry box.

Since reduction of lead(IV) to lead(II) involves two electrons per mole, and oxidation of ferrocene to ferricenium ion releases one electron per mole, two moles of ferrocene should be oxidized by each mole of lead(IV) acetate. In titrations of ferrocene with 0.05M lead(IV) acetate in distilled, dry PC, the endpoint occurs after the addition of 2.6 moles of lead(IV) acetate per mole of ferrocene instead of at a molar ratio of 0.5 as anticipated. Thus, if the stoichiometry of the reaction is that expected, the titrant contains only about a fifth as much lead(IV) as was originally added. When the same lead(IV) acetate solution is used to titrate ferrocene one day later, the endpoint occurs after the addition of 6.6 moles of lead(IV) per mole of ferrocene (calculated on the basis of the weight of lead(IV) acetate originally added during preparation of the titrant). Thus a further 60% decrease in the strength of the titrant took place in 24 hours. It appears that solutions of lead(IV) acetate in PC are not sufficiently stable for use as a conventional titrant.

Iodine

Iodine is a relatively weak oxidant in aqueous solution; the formal reduction potential for the reaction

$$I_2 + 2e^- \rightleftharpoons 2I^-$$

is 0.53 V. Tomicek and Valcha[68] attempted to determine ascorbic acid by titration with iodine in glacial acetic acid, but were unsuccessful because the potential break was too small.

An attempt was made to determine the oxidizing power of iodine in PC. Addition of iodine to a solution of ferrocene in PC resulted in the formation of the characteristic dark blue-green color of ferricenium ion, indicating oxidation of ferrocene by iodine in PC. A titration of ferrocene in distilled PC with 0.05M iodine yielded a potential break after the addition of 1.63 moles of iodine per mole of ferrocene. For the reaction between iodine and ferrocene corresponding to

$$3I_2 + 2Fc \longrightarrow 2Fc^+ + 2I_3^-$$

where Fc is ferrocene and Fc^+ is the ferrocenium ion, the endpoint should occur after the addition of 1.5 equivalents of iodine. Thus the strength of the titrant is about 92% of the value calculated on the basis of the weight of

iodine taken.

Potassium Permanganate

Potassium permanganate was found to be sufficiently soluble in PC to allow preparation of a 0.1M solution. When a few drops of permanganate solution were added to a solution of ferrocene in PC, no oxidation occurred as evidenced by the absence of the blue-green color of the ferricenium ion. However, when a drop of concentrated aqueous perchloric acid was added, the solution turned blue-green and a brown precipitate was produced. In the presence of acid, it appears that permanganate is reduced to manganese dioxide with the simultaneous oxidation of ferrocene to ferricenium ion.

A solution containing one millimole of ferrocene and two millimoles of perchloric acid in technical grade PC was titrated with 0.1M potassium permanganate in PC. A potential break occurred after the addition of 0.39 millimole of permanganate rather than after the 0.33 millimole predicted for the reduction of permanganate to manganese dioxide. The concentration of permanganate in the titrant as found by titration was thus only 85% of that calculated from the weight of potassium permanganate used.

Part VI. SUMMARY

(1) The analytical utility of PC as a solvent for oxidation-reduction and bromination reactions was investigated. Oxidizing agents studied include bromine, ammonium hexanitratocerate(IV), iron(III) perchlorate, lead(IV) acetate, iodine, and potassium permanganate.

(2) A method was developed for the quantitative determination of phenols and aromatic amines by direct titration with bromine in PC. Anthranilic acid, aniline, m-phenylenediamine, and 8-hydroxyquinoline can all be determined directly because they possess basic sites that accept the protons released in the substitution reactions. Other phenols and aromatic amines can be determined after addition of pyridine. Phenols, including phenol, p-nitrophenol, p-cresol, and resorcinol, and aromatic amines such as aniline, p-toluidine, and p-phenetidine can all be accurately determined in the presence of up to a three-fold excess of pyridine. Larger excesses of pyridine reduce the size of the potential break at the end-point through formation of a bromine—pyridine complex; the log of the formation constant of this complex was measured at 25°C and a value of 2.74 ± 0.03 was obtained.

(3) Bromine in PC also can be used to determine olefinic compounds. Cyclohexene, octene, vinyl butyrate, oleic acid, and linoleic acid react stoichiometrically at room temperature, but at reduced temperatures consume excessive amounts of bromine. High recoveries were obtained for allyl amine, allyl alcohol, and allyl ether at all temperatures. Over-consumption of bromine is accompanied by the formation of hydrogen bromide; this suggests that the error is caused by bromine substitution as a competitive reaction. Direct titration with bromine in a mixture of PC and chloroform can be applied to the determination of the degree of unsaturation of fixed oils such as castor oil, peanut oil, corn oil, and linseed oil. Advantages of this method over those presently used are a reduction in the time required for each determination and a more accurate measure of the degree of unsaturation of oils containing conjugated double bonds.

(4) Solutions of bromine in PC were found to be sufficiently stable for use as a titrant; the strength of such solutions decreased by less than 0.3% per day when stored in a closed system to prevent bromine evaporation and protected from light. The formation constant of the tribromide ion in PC was determined by potentiometric titration of bromide with bromine. A log K value of 7.23 $\pm$ 0.01 was measured at 25°C.

The bromine—bromide reaction is convenient for standardization of solutions of bromine.

(5) Solutions of ammonium hexanitratocerate(IV) in PC were used to titrate ferrocene, iodide, thiourea, and hydroquinone. Because of hydrolysis to what is postulated to be a series of cerium(IV)-hydroxy species, the strength of the titrant decreases steadily and varies with the reduction potential of the compound being determined.

(6) Iron(III) perchlorate is a more powerful oxidant than cerium(IV) in PC. However, solutions of iron(III) perchlorate in PC are too unstable to allow use as a titrant because of slow oxidation of the solvent to carbon dioxide and other products.

(7) Lead(IV) acetate is unsuitable as an oxidizing titrant in PC because it is rapidly hydrolyzed by traces of water in the solvent to form lead dioxide.

(8) Potassium permanganate is not reduced by ferrocene in anhydrous PC. After the addition of aqueous acid to the solution, permanganate is reduced to manganese dioxide. However, the presence of acid promotes decomposition of the solvent.

BIBLIOGRAPHY

1. G. Scatchard, Chem. Rev., 10, 229 (1932).
2. B. Kratochvil, Crit. Rev. Anal. Chem., 1, 415 (1971).
3. Jefferson Chemical Company, Propylene Carbonate Technical Bulletin (1960).
4. W.S. Harris, Ph.D. Thesis, University of California, Berkeley, California, 1958.
5. R. Payne, private communication quoted in J.N. Butler, R.J. Jasinski, D.R. Cogley, H.L. Jones, J.C. Synnott, and S. Carrol, Final Report, Contract F19628-68-C-0052, United States Air Force, 1970.
6. J. Courtot-Coupez and M. L'Her, C.R. Acad. Sci., Paris, Ser. C, 271, 357 (1970).
7. R.J. Parker and H.L. Yeager, Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, Personal Communication (1972).
8. K. Murata, Y. Yokoyama, and S. Ikeda, Anal. Chem., 44, 805 (1972).
9. T. Fujinaga and K. Izutsu, Pure Appl. Chem., 27, 274 (1971).
10. R.J. Jasinski and S. Kirkland, Anal. Chem., 39, 1663 (1967).
11. S.G. Meibuhr, B.E. Nagel, and R. Gatrell, Energy Convers., 10, 29 (1970).
12. J. Courtot-Coupez and M. L'Her, Bull. Soc. Chim. Fr., 1970, 1631.
13. R.T. Folley, L.E. Helgen, and L. Schubert, Sci. Tech. Aerosp. Rep., 4, 701 (1966).
14. A.N. Dey and B.P. Sullivan, J. Electrochem. Soc., 117, 222 (1970).
15. C.R. Noller, "Chemistry of Organic Compounds", 3rd ed., W.B. Saunders Company, Philadelphia, Pa., 1965, pp. 525-526.
16. Reference 15, p. 554.

17. R. Benedikt, Ann., 199, 127 (1879).

18. J. Thiele and H. Eichwede, Chem. Ber., 33, 673 (1900).

19. W.M. Lauer, J. Amer. Chem. Soc., 48, 442 (1926).

20. I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Vol. III, Interscience Publishers Inc., New York, N.Y., 1957, pp. 534-564.

21. H. Leffmann, Ed., "Allen's Commercial Organic Analysis", 4th ed., Vol. III, P. Blakiston's Son and Co., Philadelphia, Pa., 1910, pp. 480-482.

22. T. Callan and J.A.R. Henderson, J. Soc. Chem. Ind., London, 41, 161 (1922).

23. A.W. Francis and A.J. Hill, J. Amer. Chem. Soc., 46, 2498 (1924).

24. A.W. Francis, J. Amer. Chem. Soc., 48, 1631 (1926).

25. M.M. Sprung, Ind. Eng. Chem., Anal. Ed., 13, 35 (1941).

26. P.B. Sweetser and C.E. Bricker, Anal. Chem., 24, 1107 (1952).

27. A.K. Ingberman, Anal. Chem., 30, 1003 (1958).

28. C.O. Huber and J.M. Gilbert, Anal. Chem., 34, 247 (1962).

29. T. Williams, J. Krudener, and J. McFarland, Anal. Chim. Acta, 30, 155 (1964).

30. E. Kirowa-Eisner and E. Gileadi, J. Electroanal. Chem., 25, 481 (1970).

31. J. Courtot-Coupez and M. L'Her, Bull. Soc. Chim. Fr., 1969, 675.

32. Reference 15, pp. 472-474.

33. I. Heilbron, Ed., "Dictionary of Organic Compounds", 4th ed., Vol. I, Eyre and Spottiswoode, Ltd., London, 1965, p. 243 and p. 418.

34. A. Polgar and J.L. Jungnickel, in "Organic Analysis", Vol. III, J. Mitchell, Ed., Interscience Publishers Inc., New York, N.Y., 1956, pp. 206-255.

35. "The British Pharmacopoeia", The Pharmaceutical Press, London, 1968, pp. 1266-1267.

36. F. Said, M.M. Amer, A.K.S. Ahmed, and A.A. Said, J. Pharm. Pharmacol., 16, 210 (1964).

37. K. Uhrig and H. Levin, Ind. Eng. Chem., Anal. Ed., 13, 90 (1941).

38. P.C. McIlhiney, J. Amer. Chem. Soc., 16, 275 (1894).

39. A.W. Francis, Ind. Eng. Chem., 18, 821 (1926).

40. H.P. Kaufmann and E. Hansen-Schmidt, Arch. Pharm. (Weinheim), 263, 32 (1925).

41. F.A. Leisey and J.F. Grutsch, Anal. Chem., 28, 1553 (1956).

42. I.M. Kolthoff and F.A. Bovey, Anal. Chem., 19, 498 (1947).

43. B. Braae, Anal. Chem., 21, 1461 (1949).

44. F. Baumann and D.D. Gilbert, Anal. Chem., 35, 1133 (1963).

45. J. Bloeseken and E.T. Gelber, Rec. Trav. Chim., 46, 158 (1927); Chem. Abstr., 21, 1628 (1927).

46. C.F. Van Duin, Rec. Trav. Chim., 45, 345 (1926); Chem. Abstr., 20, 2441 (1926).

47. L.G. Chatten, Ed., "Pharmaceutical Chemistry", Vol. I, Marcel Dekker Inc., New York, N.Y., 1966, p. 408.

48. Reference 47, p. 419.

49. H.G. Kirschenbauer, "Fats and Oils", 2nd ed., Reinhold Publishing Corp., New York, N.Y., 1960, pp. 188-189.

50. J. Martin, J. Amer. Chem. Soc., 49, 2133 (1927).

51. G.F. Smith, "Cerate Oxidimetry", The G. Frederick Smith Chemical Co., Columbus, Ohio, 1964, p. 27.

52. H.A. Laitinen, "Chemical Analysis", McGraw-Hill, New York, N.Y., 1960, Chapter 20.

53. O.N. Hinsvark and K.G. Stone, Anal. Chem., 28, 334 (1956).

54. G.P. Rao and A.R.V. Murthy, J. Phys. Chem., 68, 1573 (1964).

55. G.P. Rao and A.R.V. Murthy, Z. Anal. Chem., 177, 86 (1960).

56. B. Kratochvil, M. Tipler, and B. McKay, Talanta, 13, 951 (1966).

57. H.W. Linde, L.B. Rogers, and D.N. Hume, Anal. Chem., 25, 404 (1953).

58. B. Kratochvil and P.F. Quirk, Anal. Chem., 42, 492 (1970).

59. J. Courtot-Coupez and M. L'Her, C.R. Acad. Sci., Paris, Ser. C, 266, 1286 (1968).

60. B. Kratochvil, D.A. Zatko, and R. Markuszewski, Anal. Chem., 38, 770 (1966).

61. G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry", 2nd ed., Vol. I, Academic Press, New York, N.Y., 1963, p. 767.

62. A. Berka, J. Janata, and J. Zyka, Collect. Czech. Chem. Commun., 29, 2242 (1964).

63. B. Kratochvil and R. Long, Anal. Chem., 42, 43 (1970).

64. A. Berka, V. Dvorak, I. Nemec, and J. Zyka, J. Electroanal. Chem., 4, 150 (1962).

65. A. Berka and J. Zyka, Collect. Czech. Chem. Commun., 24, 105 (1959).

66. G. Piccardi, Talanta, 11, 1087 (1964).

67. C.D. Thompson, F.D. Bogar, and R.T. Foley, Anal. Chem., 42, 1474 (1970).

68. O. Tomicek and J. Valcha, Collect. Czech. Chem. Commun., 16, 113 (1951).

APPENDIX A

Derivation of Expressions Required for the Determination of Tribromide Ion Formation Constant in Propylene Carbonate

Determination of β_2

During the addition of the first half equivalent of silver perchlorate in the titration of bromide in PC with silver ion (Figure 4), the initial reaction occurring is

$$Ag^+ + 2Br^- \rightleftharpoons AgBr_2^- \qquad (1)$$

β_2, the equilibrium constant for this reaction, is defined by the expression

$$\beta_2 = \frac{[AgBr_2^-]}{[Ag^+][Br^-]^2} \qquad (2)$$

Rearranging,

$$[Ag^+] = \frac{[AgBr_2^-]}{\beta_2[Br^-]^2} \qquad (3)$$

The potential measured at a silver electrode is determined by the Nernst equation

$$E = E^{\circ'}_{Ag/Ag^+} + 0.0591 \log [Ag^+] \qquad (4)$$

Substituting Equation 3 into Equation 4 and expanding,

$$E = E^{\circ'}_{Ag/Ag^+} + 0.0591 \log [AgBr_2^-] - 2(0.0591)\log[Br^-] - 0.0591 \log \beta_2 \quad (5)$$

In the region $0<x<0.5$, where x = the ratio of silver added to initial bromide present,

$$[AgBr_2^-] = xC_{Br^-} \quad (6)$$

and

$$[Br^-] = (1-2x)C_{Br^-} \quad (7)$$

where C_{Br^-} is the molar concentration of bromide ion before the start of the titration ($x = 0$). Equations 6 and 7 assume that β_2 is sufficiently large that all the silver added in this region is converted to the $AgBr_2^-$ form. Also, dilution effects have been neglected.

Substituting Equations 6 and 7 into Equation 5,

$$E = E^{\circ'}_{Ag/Ag^+} + 0.0591 \log (xC_{Br^-}) - 2(0.0591)\log(1-2x)C_{Br^-} - 0.0591 \log \beta_2 \quad (8)$$

Collecting like terms,

$$E = E^{\circ'}_{Ag/Ag^+} - 0.0591 \log C_{Br^-} - 0.0591[2 \log(1-2x)-\log x] - 0.0591 \log \beta_2 \quad (9)$$

Determination of K_p

During the addition of the second half equivalent of silver perchlorate in the titration of bromide in PC (Figure 4), the reaction occurring is

$$AgBr_2^- + Ag^+ \rightleftharpoons 2AgBr \qquad (10)$$

K_p, the equilibrium constant of this reaction is defined by the expression

$$K_p = [Ag^+][AgBr_2^-] \qquad (11)$$

Rearranging,

$$[Ag^+] = \frac{K_p}{[AgBr_2^-]} \qquad (12)$$

Substituting Equation 12 into Equation 4 and expanding,

$$E = E^{o'}_{Ag/Ag^+} - 0.0591 \log [AgBr_2^-] + 0.0591 \log K_p \qquad (13)$$

In the titration region $0.5<x<1$, where x is as defined previously,

$$[AgBr_2^-] = (1-x)C_{Br^-} \qquad (14)$$

Substituting Equation 14 into Equation 13 and expanding,

$$E = E^{o'}_{Ag/Ag^+} - 0.0591 \log C_{Br^-} - 0.0591 \log (1-x) + 0.0591 \log K_p \qquad (15)$$

Determination of K_{sp}

Division of Equation 11 by Equation 2 yields

$$\frac{K_p}{\beta_2} = \frac{[Ag^+]^2[AgBr_2^-][Br^-]^2}{[AgBr_2^-]} \qquad (16)$$

Cancelling terms and taking the square root

$$\sqrt{\frac{K_p}{\beta_2}} = [Ag^+][Br^-] \qquad (17)$$

The product on the right hand side of Equation 17 is defined as K_{sp}, the solubility product of AgBr. Thus,

$$K_{sp} = \sqrt{\frac{K_p}{\beta_2}} \qquad (18)$$

Determination of K_f by Titration of a Bromine-Bromide Solution with Silver Perchlorate

K_f, the formation constant of the tribromide ion, is defined by the expression

$$K_f = \frac{[Br_3^-]}{[Br^-][Br_2]} \qquad (19)$$

which is the equilibrium constant of the reaction

$$Br^- + Br_2 \rightleftharpoons Br_3^- \qquad (20)$$

Rearranging Equation 19,

$$[Br_3^-] = K_f[Br_2][Br^-] \qquad (21)$$

In a solution to which bromine and bromide have been added

$$[Br_2] = C_{Br_2} - [Br_3^-] \qquad (22)$$

where C_{Br_2} is the molar concentration of bromine before reaction with bromide to produce tribromide according to Equation 20.

Substituting Equation 22 into Equation 21 and rearranging,

$$[Br_3^-] = \frac{K_f C_{Br_2}[Br^-]}{1 + K_f[Br^-]} \qquad (23)$$

During the titration of a mixture of bromine and bromide with silver perchlorate in the region $0<x<1$ where x again is the ratio of silver added to initial bromide present,

$$[Br^-] = (1-x)C_{Br^-} - [Br_3^-] \qquad (24)$$

Substituting Equation 23 into Equation 24,

$$[Br^-] = (1-x)C_{Br^-} - \frac{K_f C_{Br_2}[Br^-]}{1 + K_f[Br^-]} \qquad (25)$$

Rearranging,

$$\frac{K_f[Br^-]^2 + [Br^-] + K_f C_{Br_2}[Br^-]}{1 + K_f[Br^-]} = (1-x)C_{Br^-} \qquad (26)$$

Multiplying both sides by $(1 + K_f[Br^-])$ and collecting terms,

$$K_f[Br^-]^2 + \left\{1 + K_f C_{Br_2} - (1-x)K_f C_{Br^-}\right\}[Br^-] = (1-x)C_{Br^-} \qquad (27)$$

To proceed further in the derivation, the following simplifying assumptions must be made:

a) Since the concentration of free bromide ion in a solution containing an equivalent number of moles of bromine will be very low if K_f is large, the term containing $[Br^-]^2$ in the left hand side of Equation 27 will be negligible compared to the term containing $[Br^-]$, and can therefore be neglected.

b) In the coefficient of $[Br^-]$ on the left hand side of Equation 27, 1 is assumed negligible compared to $K_f C_{Br_2}$ or $K_f C_{Br^-}$ if K_f is large and the initial concen-

trations of Br_2 and Br^- are greater than 10^{-3} or so, and can therefore be neglected.

If $C_{Br_2} = C_{Br^-}$, that is, equimolar quantities of bromine and bromide are added initially to the solution, then

Equation 27 reduces to

$$xK_f[Br^-] = (1-x) \qquad (28)$$

Rearranging,

$$[Br^-] = \frac{1-x}{xK_f} \qquad (29)$$

Equation 29 is incorporated into the potential measurement expression during titration of bromine-bromide mixtures in the following way:

$$K_{sp} = [Ag^+][Br^-] \qquad (30)$$

Taking the logarithm of each side and rearranging,

$$\log[Ag^+] = \log K_{sp} - \log[Br^-] \qquad (31)$$

Substituting Equation 31 into Equation 4,

$$E = E^{\circ'}_{Ag/Ag^+} + 0.0591 \log K_{sp} - 0.0591 \log[Br^-] \qquad (32)$$

Substituting Equation 29 into Equation 32 and rearranging,

$$E = E^{\circ'}_{Ag/Ag^+} + 0.0591 \log K_{sp} + 0.0591 \log K_f - 0.0591[\log(1-x) - \log x] \quad (33)$$

Determination of $E^{\circ'}_{Br_3^-/Br^-}$

Before the endpoint ($0<x<1$) in the potentiometric titration of bromide with bromine, the potential at a platinum indicating electrode is determined by the Nernst equation

$$E = E^{\circ'}_{Br_3^-/Br^-} + \frac{0.0591}{2} \log[Br_3^-] - \frac{3(0.0591)}{2} \log[Br^-] \quad (34)$$

corresponding to the half reaction

$$3Br^- \rightleftharpoons Br_3^- + 2e^- \quad (35)$$

During the titration in this region,

$$[Br_3^-] = xC_{Br^-} \quad (36)$$

and

$$[Br^-] = (1-x)C_{Br^-} \quad (37)$$

Substituting Equations 36 and 37 into Equation 34 and collecting terms,

$$E = E^{\circ'}_{Br_3^-/Br^-} - 0.0591 \log C_{Br^-} + \frac{0.0591}{2}\left[\log x - 3 \log(1-x)\right] \quad (38)$$

Determination of $E^{\circ'}_{Br_2/Br_3^-}$

After the endpoint ($1<x<\infty$) in the potentiometric titration of bromide with bromine, the potential at a platinum indicating electrode is determined by the Nernst equation

$$E = E^{\circ'}_{Br_2/Br_3^-} + \frac{3(0.0591)}{2} \log[Br_2] - 0.0591 \log [Br_3^-] \quad (39)$$

corresponding to the half reaction

$$2Br_3^- \rightleftharpoons 3Br_2 + 2e^- \quad (40)$$

During the titration in this region,

$$[Br_3^-] = C_{Br^-} \quad (41)$$

and

$$[Br_2] = (x-1)C_{Br^-} \quad (42)$$

Substituting Equations 41 and 42 into Equation 39 and collecting terms,

$$E = E^{\circ'}_{Br_2/Br_3^-} + \frac{0.0591}{2} \log C_{Br^-} + \frac{3(0.0591)}{2} \log(x-1) \quad (43)$$

Determination of K_f from $E^{\circ'}_{Br_3^-/Br^-}$ and $E^{\circ'}_{Br_2/Br_3^-}$

In a solution containing bromine, bromide and tribromide, the two Nernst equations, Equations 34 and 39, determine the same potential and can therefore be equated:

$$E^{\circ'}_{Br_3^-/Br^-} + \frac{0.0591}{2} \log \frac{[Br_3^-]}{[Br^-]^3} = E^{\circ'}_{Br_2/Br_3^-} + \frac{0.0591}{2} \log \frac{[Br_2]^3}{[Br_3^-]^2} \qquad (44)$$

Rearranging,

$$E^{\circ'}_{Br_2/Br_3^-} - E^{\circ'}_{Br_3^-/Br^-} = \frac{3(0.0591)}{2} \log \frac{[Br_3^-]}{[Br^-][Br_2]} \qquad (45)$$

Substituting Equation 19 into Equation 45,

$$E^{\circ'}_{Br_2/Br_3^-} - E^{\circ'}_{Br_3^-/Br^-} = \frac{3(0.0591)}{2} \log K_f \qquad (46)$$

Thus,

$$\log K_f = 11.30 \left[E^{\circ'}_{Br_2/Br_3^-} - E^{\circ'}_{Br_3^-/Br^-} \right] \qquad (47)$$

APPENDIX B

Data Required for the Determination of Tribromide Ion Formation Constant in Propylene Carbonate

Data for the determination of constants required in calculations of the value of the formation constant of the tribromide ion in PC from the intercept of straight-line plots are given in this Appendix. See Appendix A for the derivation of straight-line equations of the form $y = ax + b$ for this purpose. Potentials are expressed as mV vs. the silver–0.01M silver perchlorate in PC reference electrode.

Determination of β_2

Experimental conditions: titration of 0.3393 mmole of tetraethylammonium bromide in 60.0 ml of PC with 0.09826M silver perchlorate in the region $0<x<0.5$, where x = equivalents of silver perchlorate added.

Ml of Titrant Added	x 2 log(1-2x) - log x	y Potential
0.500	+0.542	-997.3
0.625	+0.352	-988.8
0.750	+0.168	-979.1
0.875	-0.018	-968.6
1.000	-0.214	-957.0
1.075	-0.340	-949.5
1.125	-0.429	-944.4
1.175	-0.523	-938.4
1.250	-0.677	-929.1
1.325	-0.851	-918.5
1.400	-1.054	-906.4
1.450	-1.214	-896.5
1.500	-1.402	-885.2
1.600	-1.633	-871.6
1.625	-1.936	-857.7
1.650	-2.134	-860.9

The slope and intercept of a plot of potential vs. [2 log(1-2x) - log x] were determined by least squares analysis of the data obtained between the addition of 0.750 ml and 1.600 ml of titrant. The values obtained were: slope, -60.1 mV; intercept, -969.7 mV.

Determination of K_p

Experimental conditions: titration of 0.3393 mmole of tetraethylammonium bromide in 60.0 ml of PC with 0.09826M silver perchlorate in the region $0.5<x<1.0$, where x = equivalents of silver perchlorate added.

	x	y
Ml of Titrant Added	log(1-x)	Potential
1.750	-0.307	-864.9
1.800	-0.320	-864.8
1.900	-0.347	-864.2
2.000	-0.376	-863.1
2.100	-0.407	-861.7
2.200	-0.440	-860.0
2.300	-0.476	-858.0
2.400	-0.516	-855.9
2.500	-0.559	-853.4
2.600	-0.607	-850.7
2.700	-0.661	-847.5
2.800	-0.723	-843.9
2.900	-0.795	-839.7
3.000	-0.882	-834.4
3.100	-0.991	-827.8
3.150	-1.057	-823.7
3.200	-1.135	-818.7
3.250	-1.231	-812.8
3.300	-1.354	-804.6
3.350	-1.526	-793.4
3.400	-1.815	-772.4
3.425	-2.092	-746.5

The slope and intercept of a plot of potential vs. log(1-x) were determined by least squares analysis of the data obtained between the addition of 2.600 ml and 3.300 ml of titrant. The values obtained were: slope, -61.4 mV; intercept, -888.3 mV.

Determination of K_f of Tribromide Ion by Titration of Bromine–Bromide Mixture with Silver Perchlorate

Experimental conditions: titration of 0.3393 mmole of tetraethylammonium bromide and 0.3393 mmole of bromine in 60.0 ml of PC with 0.09826M silver perchlorate in the region $0<x<1.0$, where x = equivalents of silver perchlorate added.

	x	y
Ml of Titrant Added	log(1-x) - log x	Potential
1.400	+0.199	-655.0
1.500	+0.149	-651.3
1.600	+0.100	-647.6
1.700	+0.051	-644.2
1.800	+0.003	-640.7
1.900	-0.045	-637.2
2.000	-0.094	-633.9
2.100	-0.144	-630.5
2.200	-0.193	-627.1
2.300	-0.244	-623.7
2.400	-0.297	-620.1
2.500	-0.352	-616.5
2.600	-0.410	-612.6
2.700	-0.471	-608.7
2.800	-0.538	-604.2
2.900	-0.610	-599.2
3.000	-0.691	-594.1
3.100	-0.784	-588.2
3.200	-0.890	-581.2
3.250	-0.953	-577.1
3.300	-1.024	-572.2
3.350	-1.107	-566.5
3.400	-1.205	-559.4

The slope and intercept of a plot of potential vs. [log(1-x) - log x] were determined by least squares analysis of data obtained between the addition of 1.600 ml and 3.300 ml of titrant. The values obtained were: slope, -66.7 mV; intercept, -640.3 mV.

Determination of $E^{\circ'}_{Br_3^-/Br^-}$ at 0°C

Experimental conditions: titration of 1.555 mmoles of tetraethylammonium bromide in 25.0 ml PC with 0.5926M bromine in the region $0<x<1.0$, where x = equivalents of bromine added.

Ml of Titrant Added	x log x - 3 log(1-x)	y Potential
0.125	-1.255	-308.3
0.250	-0.887	-300.8
0.375	-0.640	-293.4
0.500	-0.440	-287.6
0.625	-0.264	-282.0
0.750	-0.100	-276.7
0.875	+0.058	-271.8
1.000	+0.214	-267.0
1.125	+0.370	-262.0
1.250	+0.531	-256.9
1.375	+0.698	-251.8
1.500	+0.875	-246.4
1.625	+1.066	-240.6
1.750	+1.275	-234.1
1.875	+1.510	-226.7
2.000	+1.782	-218.3
2.125	+2.108	-208.2
2.250	+2.523	-194.6
2.375	+3.106	-175.2
2.500	+4.130	-133.8

The slope and intercept of a plot of potential vs. [log x - 3 log(1-x)] were determined by least squares analysis of data obtained between the addition of 0.250 ml and 2.250 ml of titrant. The values obtained were: slope, 31.1 mV; intercept, -273.6 mV.

Determination of $E^{o'}_{Br_3^-/Br^-}$ at 25°C

Experimental conditions: titration of 1.538 mmoles of tetraethylammonium bromide in 25.0 ml PC with 0.5989M bromine in the region $0<x<1.0$, where x = equivalents of bromine added.

Ml of Titrant Added	x log x - 3 log(1-x)	y Potential
0.125	-1.248	-307.4
0.250	-0.878	-296.0
0.375	-0.630	-288.2
0.500	-0.428	-281.9
0.625	-0.250	-276.2
0.750	-0.085	-270.9
0.875	+0.075	-265.8
1.000	+0.233	-261.0
1.125	+0.392	-255.9
1.250	+0.556	-250.5
1.375	+0.728	-244.9
1.500	+0.910	-239.1
1.625	+1.106	-232.7
1.750	+1.324	-225.6
1.875	+1.570	-217.6
2.000	+1.857	-208.3
2.125	+2.207	-196.5
2.250	+2.664	-180.6
2.375	+3.338	-154.3
2.500	+4.720	- 88.3

The slope and intercept of a plot of potential vs. [log x - 3 log(1-x)] were determined by least squares analysis of data obtained between the addition of 0.250 ml and 2.000 ml of titrant. The values obtained were: slope, 32.1 mV; intercept, -268.2 mV.

Determination of $E^{\circ\prime}_{Br_3^-/Br^-}$ at 50°C

Experimental conditions: titration of 1.243 mmoles of tetraethylammonium bromide in 25.0 ml of PC with 0.5205M bromine in the region $0<x<1.0$, where x = equivalents of bromine added.

Ml of Titrant Added	x log x - 3 log(1-x)	y Potential
0.125	-1.211	-302.2
0.250	-0.836	-290.0
0.375	-0.581	-281.2
0.500	-0.373	-274.4
0.625	-0.187	-268.0
0.750	-0.012	-262.2
0.875	+0.159	-256.3
1.000	+0.329	-250.6
1.125	+0.503	-244.7
1.250	+0.685	-238.4
1.375	+0.878	-231.8
1.500	+1.087	-225.0
1.625	+1.319	-217.1
1.750	+1.585	-208.1
1.875	+1.899	-197.3
2.000	+2.291	-183.9
2.125	+2.824	-166.1
2.250	+3.689	-134.5
2.375	+6.790	- 39.8

The slope and intercept of a plot of potential vs. [log x - 3 log(1-x)] were determined by least squares analysis of data obtained between the addition of 0.250 ml and 2.125 ml of titrant. The values obtained were: slope, 33.9 mV; intercept, -261.7 mV.

Determination of $E^{\circ\prime}_{Br_2/Br_3^-}$ at 0°C

Experimental conditions: titration of 1.555 mmoles of tetraethylammonium bromide in 25.0 ml of PC with 0.5962M bromine in the region $1.0<x<\infty$, where x = equivalents of bromine added.

	x	y
Ml of Titrant Added	log(x-1)	Potential
2.625	-2.186	+ 73.4
2.750	-1.264	+155.2
2.875	-0.990	+178.1
3.000	-0.823	+193.4
3.125	-0.703	+204.4
3.250	-0.609	+213.1
3.375	-0.532	+220.6
3.500	-0.466	+227.0
3.625	-0.409	+232.5
3.750	-0.359	+237.6
3.875	-0.314	+242.4
4.000	-0.273	+246.5
4.125	-0.235	+250.4
4.250	-0.201	+254.2
4.375	-0.169	+257.5
4.500	-0.139	+260.8
4.625	-0.112	+263.9
4.750	-0.085	+266.9
4.875	-0.061	+269.6
5.000	-0.038	+272.3

The slope and intercept of a plot of potential vs. log(x-1) were determined by least squares analysis of data obtained between the addition of 3.000 ml and 4.500 ml of titrant. The values obtained were: slope, 98.9 mV; intercept, 273.7 mV.

Determination of $E^{\circ'}_{Br_2/Br_3^-}$ at 25°C

Experimental conditions: titration of 1.538 mmoles of tetraethylammonium bromide in 25.0 ml of PC with 0.5989M bromine in the region $1.0<x<\infty$, where x = equivalents of bromine added.

Ml of Titrant Added	x log(x-1)	y Potential
2.625	-1.654	+101.0
2.750	-1.150	+150.7
2.875	-0.922	+171.7
3.000	-0.774	+186.1
3.125	-0.664	+196.9
3.250	-0.576	+205.5
3.375	-0.503	+212.7
3.500	-0.440	+219.0
3.625	-0.386	+224.6
3.750	-0.337	+230.0
3.875	-0.293	+234.2
4.000	-0.254	+238.5
4.125	-0.217	+242.4
4.250	-0.184	+245.9
4.375	-0.153	+249.4
4.500	-0.124	+252.5
4.625	-0.096	+255.6
4.750	-0.071	+258.4
4.875	-0.047	+261.2
5.000	-0.024	+263.8

The slope and intercept of a plot of potential vs. log(x-1) were determined by least squares analysis of data obtained between the addition of 2.625 ml and 5.000 ml of titrant. The values obtained were: slope, 99.9 mV; intercept, 264.3 mV.

Determination of $E^{o'}_{Br_2/Br_3^-}$ at 50°C

Experimental conditions: titration of 1.243 mmoles of tetraethylammonium bromide in 25.0 ml of PC with 0.5205M bromine in the region $1.0<x<\infty$, where x = equivalents of bromine added.

Ml of Titrant Added	x log(x-1)	y Potential
2.500	-1.329	+106.2
2.625	-1.003	+141.5
2.750	-0.819	+161.9
2.875	-0.691	+175.6
3.000	-0.591	+186.2
3.125	-0.511	+194.8
3.250	-0.443	+202.0
3.375	-0.384	+208.4
3.500	-0.332	+213.8
3.625	-0.286	+219.0
3.750	-0.244	+223.6
3.875	-0.206	+227.8
4.000	-0.171	+231.7
4.125	-0.138	+235.4
4.250	-0.108	+238.7
4.375	-0.080	+241.9
4.500	-0.053	+244.8
4.625	-0.032	+247.7
4.750	-0.004	+250.4
4.875	+0.017	+252.9
5.000	+0.039	+255.3

The slope and intercept of a plot of potential vs. log(x-1) were determined by least squares analysis of data obtained between the addition of 2.500 ml and 5.000 ml of titrant. The values obtained were: slope, 108.8 mV; intercept, 250.4 mv.

APPENDIX C

Determination of Formation Constant of Pyridine–Bromine Complex in Propylene Carbonate

The formation constant of the complex formed between pyridine (Py) and bromine in PC was determined by analysis of potentiometric titration curves resulting from titration of mixtures of tetraethylammonium bromide and pyridine with bromine. Addition of pyridine has no effect on the portion of the titration curve before the endpoint. In this region the potential is controlled by the bromide–tribromide couple; apparently pyridine does not react with either of these species. After the endpoint, the potential is controlled by the bromine–tribromide couple. The presence of pyridine in solution decreases the potential measured in this area, indicating that the concentration of free bromine is decreased by reaction with pyridine:

$$Br_2 + Py \rightleftharpoons Py\text{-}Br_2$$

The formation constant of this species is defined by the expression

$$K = \frac{[Py\text{-}Br_2]}{[Br_2][Py]}$$

Values of this constant may be calculated as follows. In a titration of 1.246 millimoles of tetraethylammonium bromide and 1.662 millimoles of pyridine in 25.0 ml of PC with 0.4839M bromine, the endpoint occurred after the addition of 2.575 ml of titrant. The potential after the addition of 3.250 ml of titrant (total volume of solution = 28.250 ml) was found to be +0.080 V vs. a silver–0.01M silver perchlorate in PC reference electrode. The concentration of free bromine can be calculated by the Nernst equation

$$E = E^{\circ'}_{Br_2/Br_3^-} + \frac{0.0591}{2} \log \frac{[Br_3]^3}{[Br_3^-]^2}$$

since the only unknown quantity in the equation is the bromine concentration. The known quantities are:

$$E = +0.080 \text{ V}$$

$$E^{\circ'}_{Br_2/Br_3^-} = +0.300 \text{ V}$$

$$[Br_3^-] = \frac{1.246}{28.25} = 4.411 \times 10^{-2} \text{M}$$

Thus,

$$[Br_2] = 4.118 \times 10^{-4} \text{M}$$

The concentration of the pyridine–bromine complex may be calculated from the difference between the quantity of bromine added beyond the endpoint and the quantity of free bromine calculated above.

$$[Py\text{-}Br_2] = \frac{[(0.4839)(3.250-2.575)] - [(4.118\times10^{-4})(28.25)]}{28.25}$$

$$= 1.115 \times 10^{-2} M$$

The concentration of free pyridine may be calculated from the difference between the quantity of pyridine originally added and the quantity of pyridine–bromine complex calculated above.

$$[Py] = \frac{1.662 - (1.115\times10^{-2})(28.25)}{28.25}$$

$$= 4.768 \times 10^{-2} M$$

Substituting these values into the expression for the formation constant yields:

$$K = \frac{(1.115 \times 10^{-2})}{(4.118\times10^{-4})(4.768\times10^{-2})} = 568$$

Similar calculations were carried out at other points in the region after the endpoint in the titration of pyridine–bromide mixtures with bromine in PC. The results are presented on the following page.

The formation constant measured in this way may be in error if a reaction such as bromination of pyridine is occurring. The value of the formation constant is somewhat higher than those measured in a number of other solvents, where K values tend to range from 50 to about 200.

Data for Determination of the Formation Constant of Pyridine–Bromine Complex in Propylene Carbonate

Mmoles of Pyridine Added[a]	Volume of Titrant Added (ml)	Potential[b]	Log Formation Constant
1.662	3.250	0.080	2.75
3.429	3.500	0.066	2.71
3.429	4.000	0.084	2.74
3.429	5.000	0.110	2.77
15.104	4.000	0.020	2.75

a In all instances, pyridine plus 1.246 millimoles of tetraethylammonium bromide in 25.0 ml of PC were titrated with 0.4839M bromine.

b Expressed as V vs. silver–0.01M silver perchlorate in PC reference electrode.