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THE UNIVERSITY OF ALBERTA

THE GEOMETRICAL ISOMERIZATION OF BUTENYL RADICALS

BY

BURKHARD STREHLKE

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
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UNIVERSITY OF ALBERTA
EDMONTON, ALBERTA

FALL, 1971

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

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

THE GEOMETRICAL ISOMERIZATION OF BUTENYL RADICALS

submitted by BURKHARD STREHLKE in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

Four azo-butenes were synthesized and thermolized in the gas phase at 125.7°. The butenyl radicals produced are not capable of hydrogen abstraction from the parent azo compound or the dienes formed. The diene products from the three isomeric azo-butenes, formed from the combination of two radicals, show small but still significant retention of configuration. The isomerization of the butenyl radicals can effectively compete with the combination process. Examination of the diene yields gives a value of K = 1.54 for the equilibrium constant for the process

It can be seen that the butenyl radical is 1.4 times more reactive at its primary end than at its secondary end and that the 3-methylbutenyl radical is 3.2 times more reactive at its primary end than at its tertiary end. From the thermolysis carried out in solution, where a higher degree of stereoselectivity is observed, it can be seen that differences of reactivity between the *cis*- and *trans*-butenyl radicals are negligible at 125.7°.

The barrier for *cis-trans* isomerization can be calculated to be 20 kcal mole^{-1} from the kinetic studies of the three isomeric azo-butenes in the gas phase.

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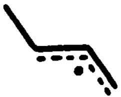

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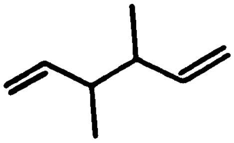

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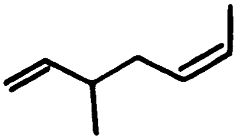

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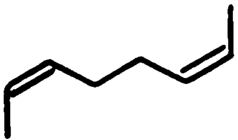

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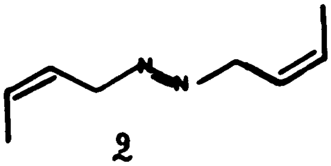

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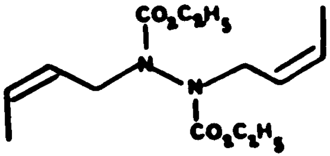

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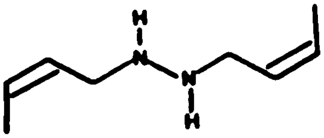

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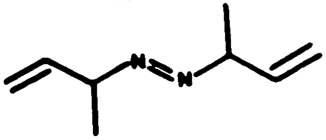

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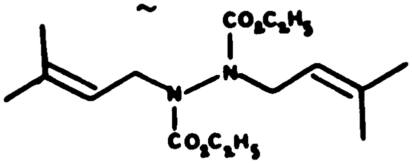

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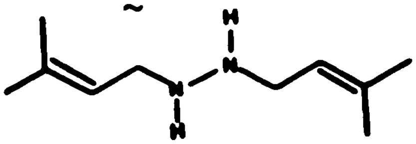

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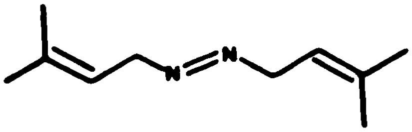

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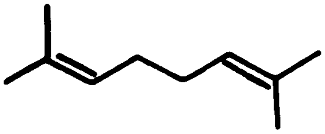

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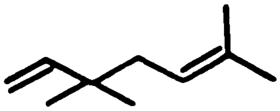

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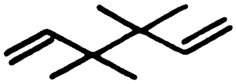

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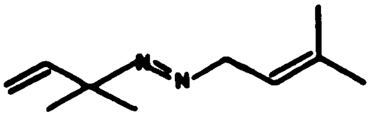

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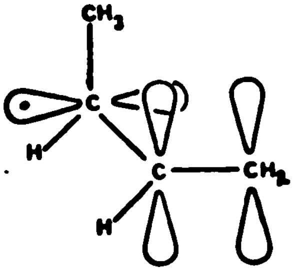

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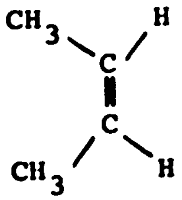
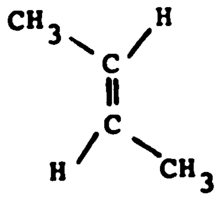
HISTORICAL

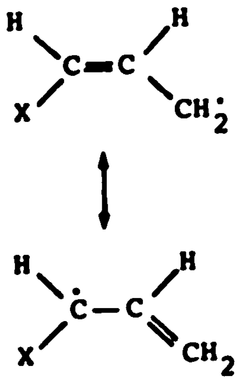
The geometrical isomerization of multiple bonds is best exemplified by the *cis* to *trans* isomerization of olefins. For the 2-butenes this process requires an

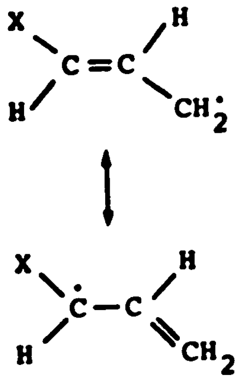




activation energy of 62.8 kcal $mole^{-1}$ (1). The analogous isomerization process for the allyl radical has been detected but not measured.

Since simple Hückel molecular orbital calculations give a π bond order of 0.70711 (2) for the allyl radical then





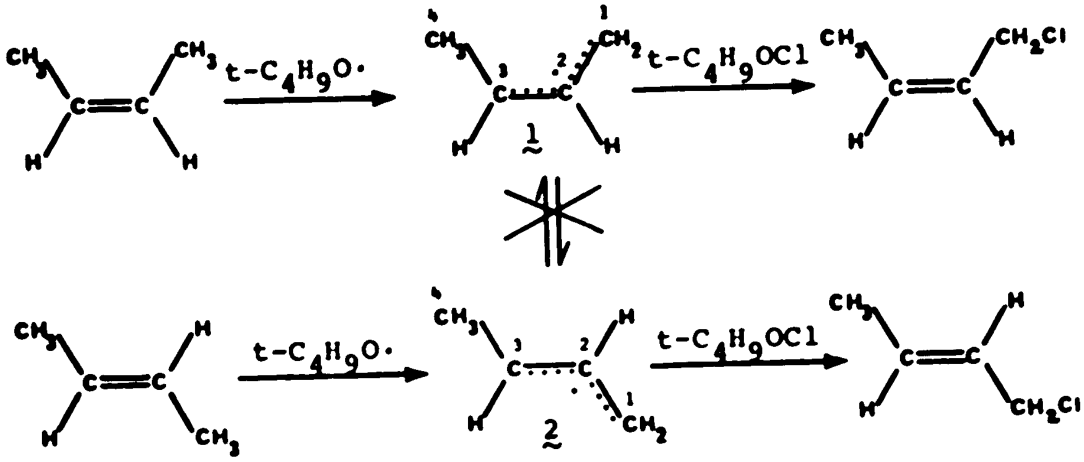
one may naively expect an activation energy of 44.4 kcal $mole^{-1}$ for the isomerization of the allyl radical.

Several attempts to estimate this value have been made using heats of formation and estimates of the allylic resonance energy. Some directly relevant studies are reviewed in this section.

A. Butenyl Radicals

Butenyl radicals have been generated in solution and investigated by several workers.

Walling and Thaler (3) in 1961 showed that free radical chlorination of *cis*-2-butene with *t*-butyl hypochlorite gave *cis*-1-chloro-2-butene and 3-chloro-1-butene and only small amounts of addition products. Similarly *trans*-2-butene gave *trans*-1-chloro-2-butene, 3-chloro-1-butene and minor amounts of addition products.



They concluded that the observed variation in the ratios of products from the three butenes is not compatible with the idea that the olefins yield a common allylic radical, Table I. This and the observed complete retention of *cis-trans* geometry was explained on the assumption that "*cis-* and *trans*-allylic radicals are able to retain their stereochemistry until they react with *t*-butyl hypochlorite to yield the observed products".

Since the butenyl radical is an ambident species it is interesting to note that the reactivity is not the same at each of the centers carrying the unpaired electron. Table II gives the ratios obtained by Walling and Thaler (3) for the three olefins. The smaller value of the ratio arising from the *cis*-2-butene was attributed to steric hindrance to attack on C_1 of the *cis*-butenyl radical (1) being greater than that on C_1 of the *trans*-butenyl radical (2).

Balaceanu (4) and coworkers in 1963 reported on the liquid phase oxidation of 1-butene and *cis*- and *trans*-2-butene at temperatures between 65° and 80°C.

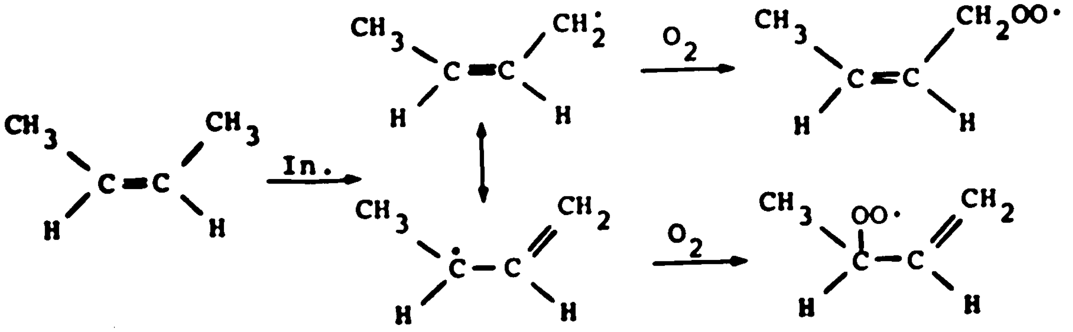


TABLE I

Composition of allylic chlorides from free-radical chlorination of butenes (3)

Compound	Temp. (°C)	1-chloro-2-butene (%)	3-chloro-1-butene (%)	Addition Product (%)
cis-2-butene	-78.5	65.0±0.0[a]	35.0±0.0	16.4±0.2
	40	63.2±1.1[a]	36.8±1.1	16.9±0.9
trans-2-butene	-78.5	83.1±0.2[b]	16.9±0.2	trace
	40	73.2±0.3[b]	26.8±0.3	3-4
1-butene	-78.5	73.9±0.1[c]	26.1±0.1	trace
	40	69.1±0.3[c]	30.9±0.3	3.3

[a] *cis* isomer only.

[b] *trans* isomer only.

[c] mixtures of *cis* and *trans*, at 40°C 65 + 5% *trans*.

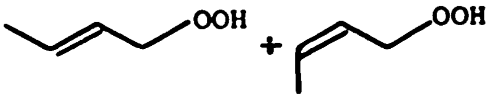
TABLE II

Ratio of attack at C_1 to C_3 of the butenyl radical in *t*-butyl hypochlorite chlorination (3)

Compound	Temperature	Ratio
1-butene	40	2.24
cis-2-butene	40	1.72
	-78.5	1.85
trans-2-butene	40	2.73
	-78.5	4.90

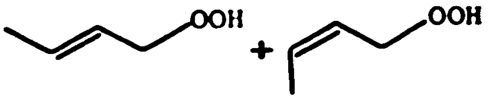
The reaction was carried out with molecular oxygen using azobisisobutyronitrile (AIBN) as an initiator and the products after reduction with $LiAlH_4$ were analyzed by gas chromatography. Three isomeric alcohols corresponding to the three isomeric hydroperoxides were found in the case of the butenes.

Starting with *cis*-2-butene containing 6.1% of the *trans*-isomer they obtained 52.6% of the 1-hydroperoxy-2-butene of which 34.2% was *cis*, and 47.4% 3-hydroperoxy-1-butene. Taking impurities into consideration this gave a ratio of



= 1.75

Similarly they obtained from *trans*-2-butene containing 5% of the *cis*-isomer 54.8% of the 1-hydroperoxy-2-butene of which 90.4% was *trans*, and 45.8% 3-hydroperoxy-1-butene and hence a ratio of



= 11.0

Oxidation of 1-butene appeared to give only *trans*-1-hydroperoxy-2-butene besides 3-hydroperoxy-1-butene.

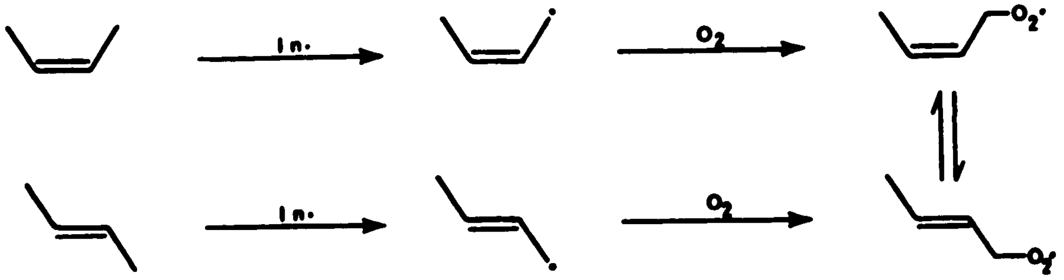
From these data the authors calculated values for the stereoselectivity for the *cis*-2-butene going to *cis*-1-hydroperoxy-2-butene and for the *trans*-2-butene going to *trans*-1-hydroperoxy-2-butene, the values being 36.5% and 91.8%, respectively.

For the positional isomerization the ratios for

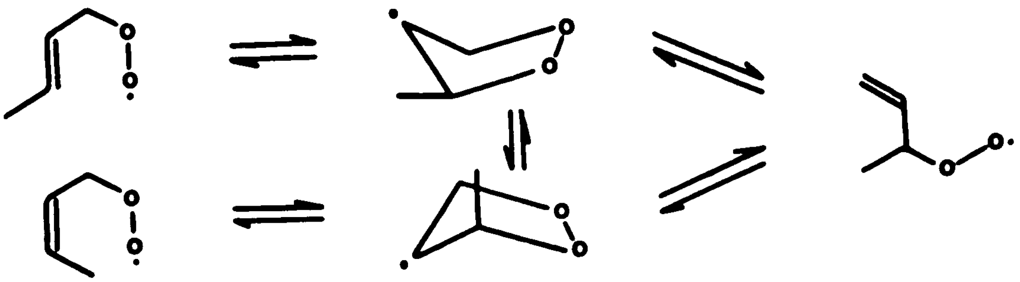
$CH_3CH(OOH)CH=CH_2 \div CH_3CH=CHCH_2OOH$

are for 1-butene ≈9 and for *cis*- and *trans*-2-butene ≈1.

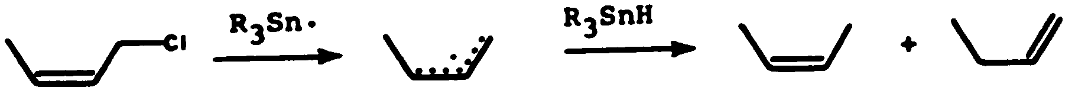
The authors, on the basis of Walling and Thaler's work (3) and assuming that the reaction of oxygen with the allylic radical is very fast, suggested that the isomerization is occurring at the hydroperoxy radical stage.

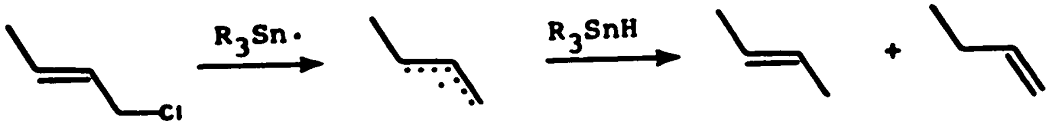


A reversible intramolecular cyclization could account for such an isomerization.



In 1967 Denney and coworkers (5) reported on the *cis-trans* isomerization of allylic radicals. Several allylic chlorides were treated with triphenyltin hydride. Abstraction of halogen by triphenyltin radical to give an allylic radical is followed by reaction with triphenyltin hydride to give the hydrocarbons.





The reactions were carried out at 80°C in hydrocarbon solvents with AIBN as initiator; by varying the absolute concentrations of reactants (concentrations of allylic chloride and triphenyltin hydride were kept equivalent) the lifetime of the intermediate radicals could be varied. The results are summarized in Table III. If the concentrations of starting materials are kept low enough, all the pairs of allylic chlorides give the same products. At intermediate concentrations incomplete isomerization is observed. Although it was not possible to assign rate constants to these isomerizations, they nevertheless conclude that the barrier to rotation in allylic radicals

TABLE III

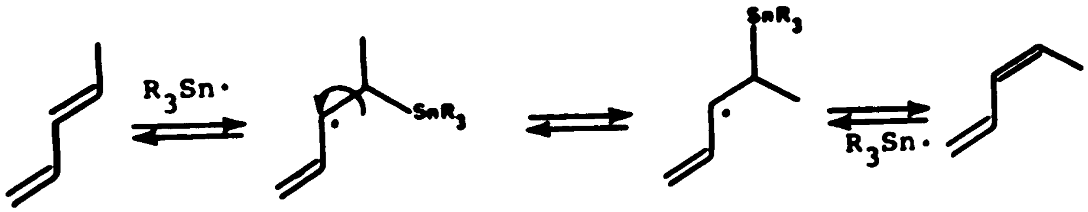
Composition of butenes from dechlorination of allylic chlorides with triphenyltin hydride at 80° (5)

compound	concentration	1-butene (%)	*cis*-2-butene (%)	*trans*-2-butene (%)
cis-$CH_3CH=CH-CH_2Cl$	0.027	34	25	41
(containing 12% of the *trans* isomer)	0.0135	35	24	41
trans-$CH_3CH=CH-CH_2Cl$	0.27	28	23	49
	0.027	36	22	42
	0.0135	36	23	41

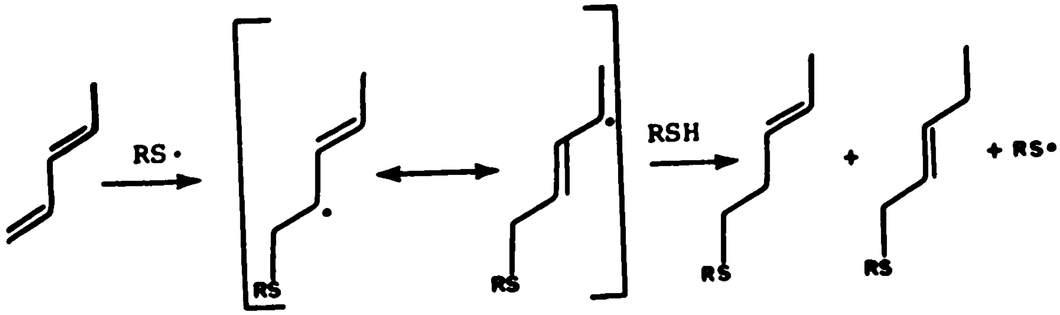
is not large, and that the interconversions can compete effectively with the reaction with triphenyltin hydride.

Again positional isomerization is observed. At low concentrations the ratio for 2-butene÷1-butene is about 1.94.

However, in the same year a paper by Neumann and coworkers (6) presented evidence for a reversible addition of triphenyltin radical to olefins. If *trans*-1,3-pentadiene (2 fold excess) was treated with triphenyltin hydride, they recovered 3% of *cis*-1,3-pentadiene and if *cis*-1,3-pentadiene was treated with triphenyltin hydride, the recovered pentadiene was 55% *trans*. Thus, reversible addition of the triphenyltin radical can lead to *cis*-*trans* isomerization via rotation of the tetrahedral carbon.



In 1965 Thaler and coworkers (7) studied the stereochemical course of the addition and cooxidation reactions of thiols with *cis*- and *trans*-1,3-pentadiene. Free radical addition of different thiols to 1,3-pentadiene demonstrated that the major products were the 1,2- and 1,4-adducts, formed from the attack of the thiol radical on C-1 of the diene:



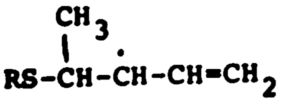
Only minor products resulted from attack at C-4 which was attributed to the greater stability of the disecondary allylic radicals relative to that of the primary-secondary radicals:

$$RS-CH_2-\dot{C}H-CH=CH-CH_3$$

$$\updownarrow$$

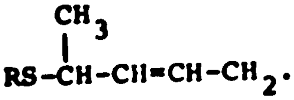
$$RS-CH_2-CH=CH-\dot{C}H-CH_3$$

disecondary



$$RS-\overset{\overset{\displaystyle CH_3}{|}}{C}H-\dot{C}H-CH=CH_2$$

$$\updownarrow$$

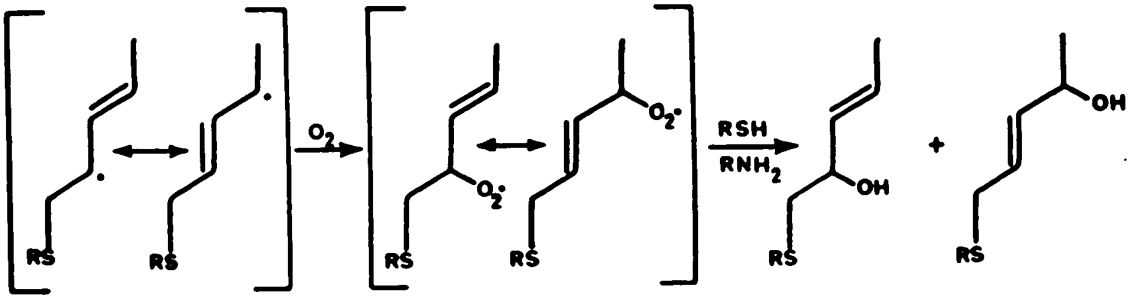


$$RS-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH=CH-CH_2\cdot$$

primary-secondary

Both 1,2- and 1,4-adducts were formed in similar quantities since the reactive positions of the allylic radical intermediate were both secondary.

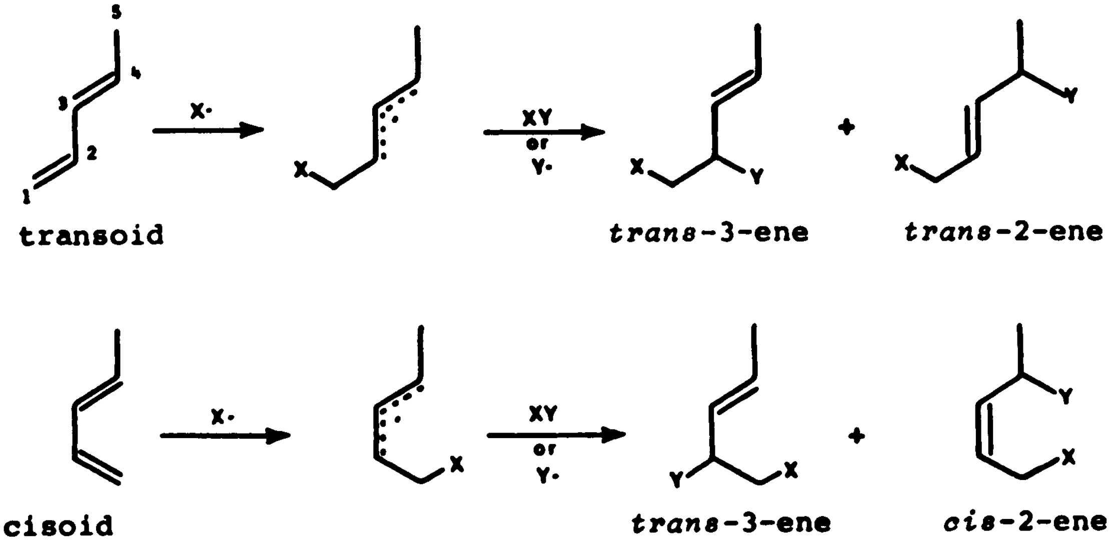
In the cooxidation reactions the allylic radicals were also formed by the action of the thiyl-radical on the 1,3-pentadiene, but these then combine with oxygen to form peroxy radicals which in turn remove a hydrogen atom from the thiol to give hydroperoxide and regenerate the thiyl radical.



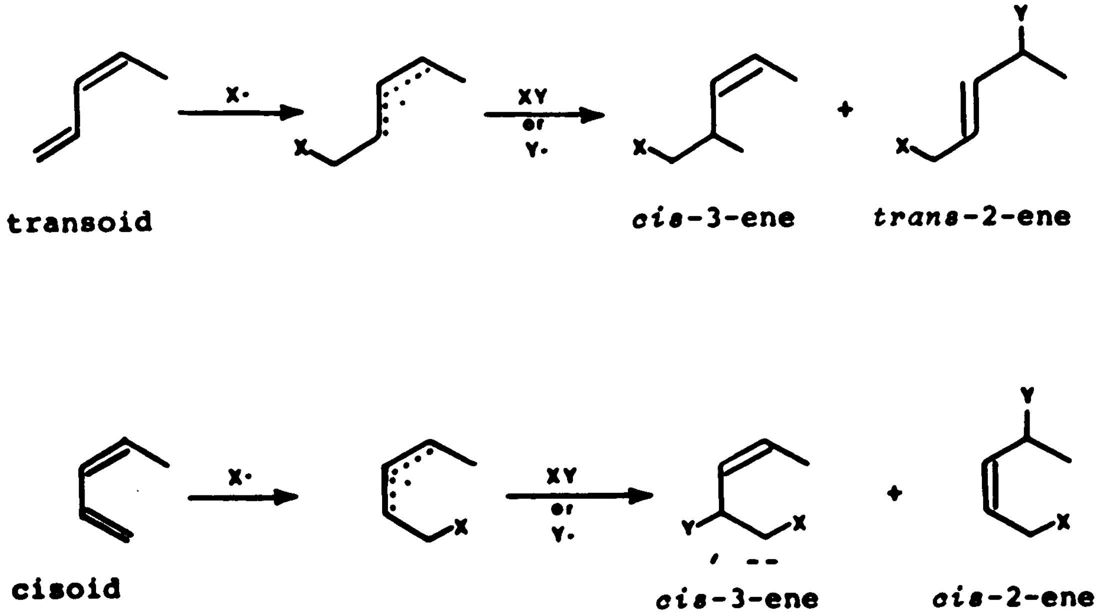
In the presence of catalytic amounts of amine the hydroperoxides are immediately reduced by excess thiol to allylic alcohols. Thus the same allylic intermediates resulting from the addition of thiyl-radical to 1,3-pentadiene would be involved in both the thiol addition and the cooxidation reactions. The authors can then, by assuming that the products are not isomerized after their formation and that the dienes do not undergo isomerization prior to reaction with the attacking radical, take the stereochemical configuration of the 1,2-adducts as a direct measure of the retention of configuration of the intermediate allylic radicals. The stereochemistry of the 1,4-adducts would be determined by the rotational conformation of the reacting dienes (Scheme I).

Scheme I

Configurations of *trans*-1,3-pentadiene



Configurations of *cis*-1,3-pentadiene

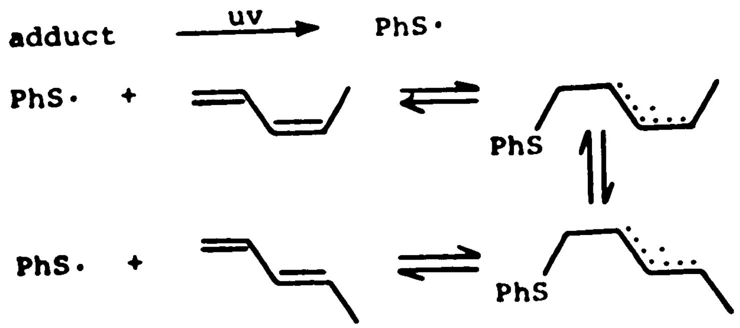


Cooxidation with benzenethiol gave predominantly products resulting from the attack of the thiyl radical at C-1. Examination of the stereochemistry of the 1,2-addition products revealed that their formation had been completely stereospecific: *cis*-1,3-pentadiene gave the *cis*-2-ene product while *trans*-1,3-pentadiene gave the *trans*-2-ene product only. The 1,3-pentadiene was found not to isomerize under these conditions. These facts were taken as an indication that the allylic radical intermediate combines rapidly with the oxygen diradical and the authors suggested that the addition of thiyl radical to diene in the presence of oxygen is an irreversible process. Thus they calculated that the *cis*- and *trans*-isomers react at approximately the same rate with the thiyl radical ($k_{cis}/k_{trans} = 0.94 \pm 0.04$).

Addition of aromatic thiols to the dienes also exhibited a high degree of stereospecificity. The 1,2-adduct from *cis*-1,3-pentadiene was 92% *cis* while the 1,2-adduct from *trans*-1,3-pentadiene was 96% *trans*. However analysis of recovered excess diene showed that considerable isomerization of diene had occurred. The unreacted starting 1,3-pentadiene was almost 40% *trans* when initially pure *cis*, and up to 10% *cis* when initially pure *trans*-1,3-pentadiene was used. Several control runs led the authors to an explanation for the better than 90%

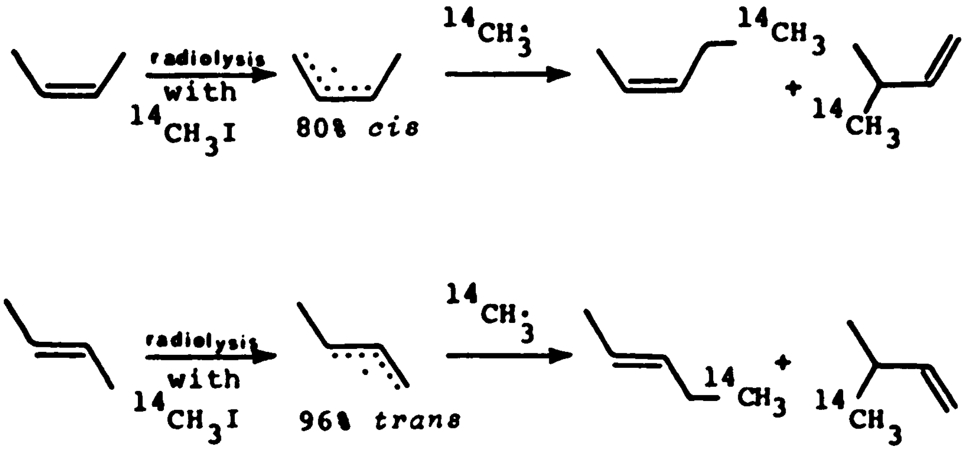
retention of configuration in the addition reaction while the starting diene was isomerized to more than 40%. They found that the vast majority of product was formed before an appreciable amount of isomerization had taken place, but that the degree of isomerization increased markedly as the thiol concentration approached zero. The photo-initiated reaction of benzenethiol with 1,3-pentadiene showed again a high degree of stereospecificity while recovered excess diene was completely equilibrated (85% *trans*, 15% *cis*). Ultraviolet irradiation of 1,3-pentadiene alone had no effect, however, when some benzenethiol-pentadiene adduct was added and the solution irradiated, the 1,3-pentadiene was readily isomerized to the equilibrium mixture.

A mechanism involving addition of a thiyl radical, formed from the adduct, to the diene was used to explain these results. The allylic radicals in the absence of thiol are not readily consumed and the radicals are long lived and have opportunity to rotate:



When aliphatic thiols were used in the addition reaction the unreacted excess 1,3-pentadiene was recovered unchanged, however, in this case the 1,2-adducts showed little stereospecificity; some preference for *cis*-3-ene from *cis*-diene and *trans*-3-ene from *trans*-diene suggested that, while the intermediate allylic radicals undergo considerable isomerization under these conditions, they are still not interconverting freely. An interpretation of these data was based on the differences in stability of the aromatic and aliphatic thiyl radicals. Thus, the addition of PhS· to the diene would be expected to be more reversible than the addition of $CH_3S\cdot$. If such a reversible addition occurred many times for each reaction step, the smallest amount of rotation of the intermediate allylic radical would cause significant isomerization of the remaining diene. The fact that the addition reaction with benzenethiol was highly stereospecific, whereas the addition of methanethiol showed little or no stereospecificity was explained by the different lifetimes of the intermediate allylic radicals in both cases. If these radicals are not consumed rapidly, they have opportunity to rotate and the stereospecificity of the reaction is destroyed. Aromatic thiols possess a weak sulfur-hydrogen bond compared to aliphatic thiols because the resulting thiyl radical of the former thiol can be strongly stabilized by resonance with the aryl group.

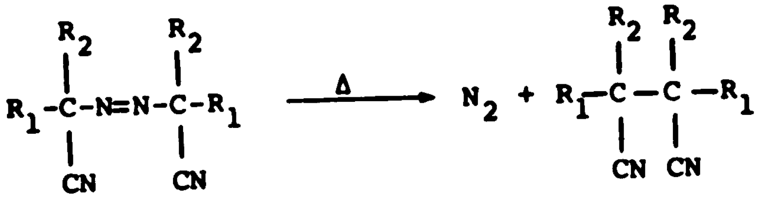
In 1965 Holroyd and Klein (8) reported on the radiolysis of 1-butene and *cis*- and *trans*-2-butene at -88°. Trapping butenyl radicals formed in this manner by $^{14}CH_3\cdot$ they found that the products were formed with high retention of configuration. Thus they reported that 96% of the butenyl radicals formed from *trans*-2-butene are in the *trans* configuration, whereas from *cis*-2-butene 80% are in the *cis*-configuration.



In comparing the ratios of 2-pentene-C^{14} to 3-methyl-1-butene-C^{14} for the reaction starting with *trans*-2-butene with that starting with *cis*-2-butene, they found that the intermediate radicals react slightly differently. Starting with *trans*-2-butene the ratio was found to be 2.04±0.02, but starting with *cis*-2-butene the ratio was found to be 1.67±0.02. The differences were attributed to steric effects. In a control experiment hydrogen atoms added to butadiene gave after scavenging with $^{14}CH_3\cdot$ radicals a ratio of 2-pentene-C^{14} to 3-methyl-1-butene-C^{14} of 1.90. Interestingly, no *cis*-2-pentene was formed in this reaction. The ratio in 1-butene was found to be 2.24±0.08, whereas from a mixture of equal amounts of *cis*- and *trans*-2-butenyl radicals a ratio of 1.86 would be expected. This was taken as evidence for the reaction of 1-butenyl radicals with $^{14}CH_3\cdot$ to give 2-pentene-C^{14}. Again, as Walling and Thaler (3) had observed, the *trans*-species was observed to yield more product by reaction at the terminal carbon than does the *cis*-species.

B. Gas Phase Thermolysis of Azoalkanes

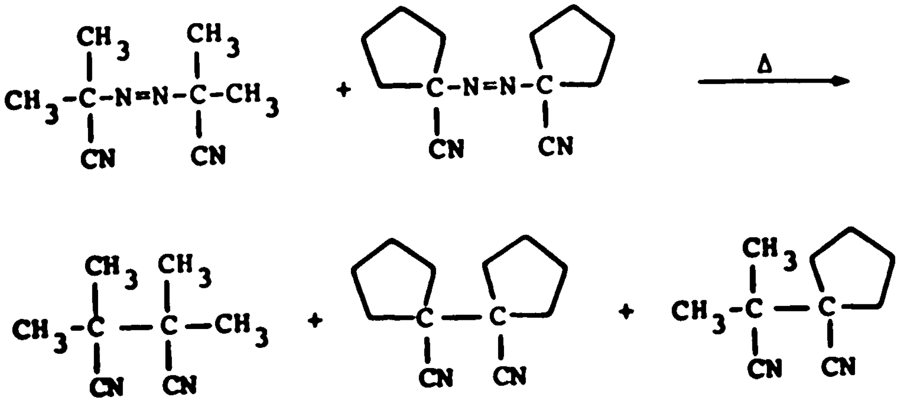
A large body of information on the thermolysis of azoalkanes is available in the literature. Under the influence of heat or light azoalkanes fragment into alkyl free radicals and molecular nitrogen (9). Thermolysis of azomethane, the parent compound of the azoalkanes, produces apart from nitrogen, methane and ethane as the principal products, with minor amounts of ethylene and higher hydrocarbons (10). The presence of methyl radicals has been indicated by the fact that the initial products of thermal and photochemical decomposition are capable of removing metallic mirrors (11) and that azomethane initiates the thermal decomposition of ethane and propane (12). In 1951 Overberger and Berenbaum (13) reported that the thermolysis of diastereomeric azo compounds gave identical mixtures of *racemic* and *meso* products:



$$R_1\text{-}\overset{R_2}{\underset{CN}{C}}\text{-}N{=}N\text{-}\overset{R_2}{\underset{CN}{C}}\text{-}R_1 \xrightarrow{\Delta} N_2 + R_1\text{-}\overset{R_2}{\underset{CN}{C}}\text{-}\overset{R_2}{\underset{CN}{C}}\text{-}R_1$$

rac or *meso* *rac* and *meso*

The authors also observed that mixtures of azo-bis-nitriles yielded both symmetrical and mixed dinitriles:



The initially formed free radicals obtained from decomposition of azoalkanes not only combine to give the corresponding alkane, but can also undergo further processes such as radical disproportionation, addition to the nitrogen-nitrogen double bond (9,10,14) of the azoalkane or hydrogen abstraction from the azoalkane:

$$\begin{array}{lcl}
R{-}N{=}N{-}R & \xrightarrow{\Delta} & 2R\cdot + N_2 \\
R\cdot + R\cdot & \xrightarrow{\text{Recomb.}} & R{-}R \\
R\cdot + R\cdot & \xrightarrow{\text{Disprop.}} & \text{olefin + alkane} \\
R\cdot + R{-}N{=}N{-}R & \xrightarrow{\text{Add.}} & R{-}\underset{\overset{|}{R}}{N}{-}\dot{N}{-}R \\
R\cdot + R'{-}CH_2{-}N{=}N{-}R & \xrightarrow{\text{Abstr.}} & R{-}H + R'{-}\dot{C}H{-}N{=}N{-}R
\end{array}$$

Recently, Crawford and Al-Sader (15) have shown that allyl radicals, produced upon the thermolysis of 3,3'-azo-1-propene, dimerize to produce 1,5-hexadiene.

Only a trace of propene (<0.1%) was formed which is indicative of the low probability of the allyl radical to abstract hydrogen and of little or no chain induced decomposition via a scheme analogous to that observed in the azomethane thermolysis (10). There was some evidence for a reversible addition of the allyl radical to the azo starting material which was, however, much slower than the thermolysis reaction.

C. Allylic Resonance Energy (ARE)

The allylic resonance energy is defined as the difference between the bond dissociation energy of a C-H bond allylic to a double bond and the analogous bond in a saturated paraffin (16).

In 1953 Franklin and Field (17) calculated the resonance energy of the allyl radical using both the valence bond and the LCAO - molecular orbital methods and obtained values of 18 kcal mole^{-1} and 17 kcal mole^{-1} respectively. An independent calculation was carried out by using Sehon and Szwarc's (18) value of 62 kcal mole^{-1} as the energy required to remove a methyl radical from 1-butene and Roberts and Skinner's (19) value of 32 kcal mole^{-1} for the heat of formation of a methyl radical. The heat of formation of the allyl radical could thus be calculated to be 30 kcal mole^{-1}. The heat of formation of the allyl radical without resonance was calculated using Franklin's (20) method and found to be 49 kcal mole^{-1}. Thus the value for the resonance energy of the allyl radical was estimated to be 19 kcal mole^{-1}.

Values for the ARE have been estimated from various kinetic parameters of vinyl- and methylene-substituted compounds (Table IV).

In 1962 Benson and coworkers (21) suggested a value of 15 kcal mole^{-1} for the ARE. For cyclopropane and simple alkyl-cyclopropanes the overall activation energies for processes such as

$$\text{Ring} \rightleftarrows \text{Biradical} \longrightarrow \text{Olefin}$$

are of the order of 65 kcal mole^{-1} (22). Similar values are found for cyclobutane and its alkyl derivatives (22). In comparing the activation energies for the thermolysis of vinylcyclopropane to give cyclopentene (23) and of methylenecyclobutane to give allene and ethylene (24) the surprising difference of ≈15 kcal mole^{-1} was accounted for by assuming that nearly complete resonance energy is developed in the biradical obtained from vinylcyclopropane whereas in the biradical from methylenecyclobutane the hydrogen-atoms in the methylene-radical are not in the same plane as the vinyl-group, but almost at right angles, and thus the resonance energy contribution is almost zero.

Unpublished results by Doering (25) for the reaction:

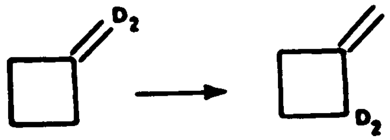


TABLE IV

Values for the allylic resonance energy from bond-dissociation energies

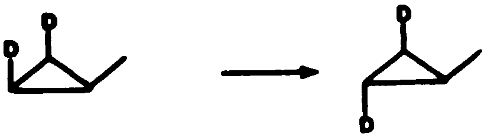
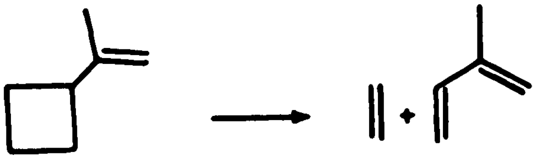
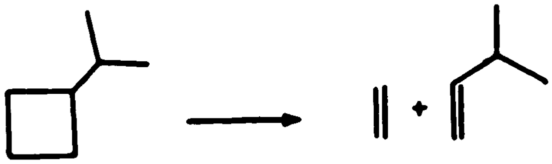
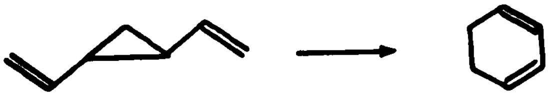
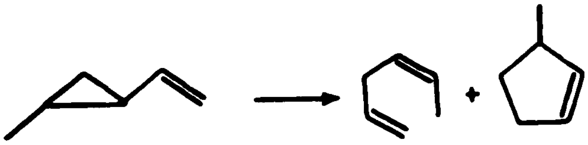
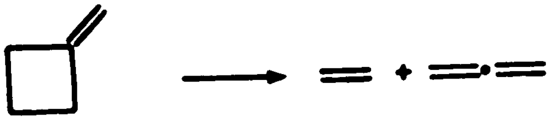
Reaction	E_a kcal mole^{-1}	ARE kcal mole^{-1}	Ref.
$CH_3CH_2CH=CH_2 + I \rightarrow CH_3\dot{C}HCH=CH_2 + HI$	12.4	12.6*	(26)
$CH_3CH_2CH_3 + I \rightarrow CH_3\dot{C}HCH_3 + HI$	25.0		(27)
	47.1	13.4*	(28)
	60.5		(29)
	51.0	11.6*	(30)
	62.6		(31)

TABLE IV (cont'd)

Values for the allylic resonance energy from bond-dissociation energies

Reaction	E_a kcal mole^{-1}	ARE kcal mole^{-1}	Ref.
	32.1	16.5*	(32)
	48.6		(33)
	32.2	8.8*	(34)
	41.0		(35)
	49.6	13.7*	(23)
	63.3		(24)

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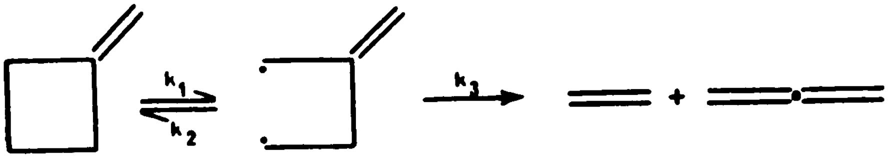
* These values are actually for butenyl rather than allyl radicals.

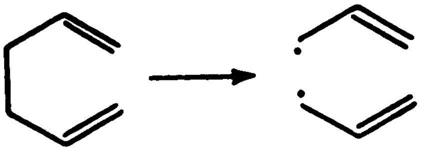
which has an activation energy of 49.5 kcal $mole^{-1}$ suggest that the ring closure from the biradical is very fast relative to fragmentation i.e. k_3 is very much smaller than k_2. The degenerate rearrangement is probably a



concerted $\sigma_a^2 + \Pi_s^2$ reaction and does not involve complete homolytic cleavage of the C-C bond in the transition state.

In 1964 Benson and coworkers (26) suggested from their study of the iodine atom catalyzed positional isomerization of 1-butene a value of 12.6 kcal $mole^{-1}$ for the allylic resonance energy. A value of 12.4±0.3 kcal $mole^{-1}$ was found for the activation energy for the iodine atom attack on 1-butene. When subtracted from the value 25.0±0.5 kcal $mole^{-1}$ for the analogous reaction of iodine atom with propane (27), the value of 12.6 kcal $mole^{-1}$ for the ARE is obtained. The overall uncertainty is claimed not to be greater than ±1 kcal.

ARE values have also been obtained from heats of formations of the allyl radical. Homer and Lossing (36), in a detailed study,mass spectrometrically obtained a value of $\Delta H_f^\circ = 33.0$ kcal $mole^{-1}$ for the allyl radical from the process:



and calculated a value of 17.8 kcal/mole for the ARE.

In 1969 Golden (37) calculated from transition state theory and values obtained by Denney and coworkers (5) for the geranyl-neryl system that at 180°C the *trans* radical has the lower heat of formation by ∿0.3 kcal $mole^{-1}$ and that the *cis* has ∿2.3 gibbs $mole^{-1}$ more entropy. The value for the equilibrium constant showed that at 80°C the *cis* form of the radical is slightly more stable than the *trans* form, a rather unexpected result.

The direct measurement of the equilibrium constant for the process

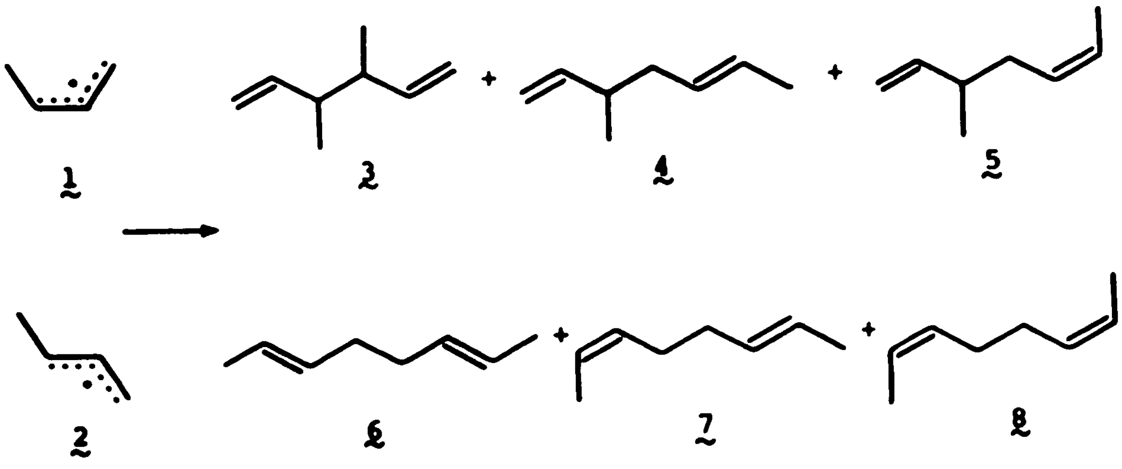
$$M + 2\ \text{allyl} \underset{k_d}{\overset{k_r}{\rightleftharpoons}} 1{,}5\text{-hexadiene} + M$$

at two different temperatures was reported by Golden, Benson and Gac in 1969 (38). These combined with the known entropy changes for the reaction yielded a value of 9.6 kcal $mole^{-1}$ for the allylic resonance energy. Although this value might be uncertain by as much as 2 or 3 kcal $mole^{-1}$, they conclude that this result "must surely lay to rest any thought that allylic resonance energy is much greater than 12 kcal mole^{-1}.

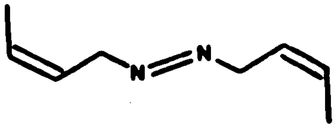
OBJECTIVE

In light of the low value for the allylic resonance energy of 10 - 12 kcal mole^{-1} the configurational stability of butenyl radicals seems to be surprising. None of the studies on the isomerization of butenyl radicals, however, were done in the gas phase at temperatures above 100°C.

Recently Crawford and Al-Sader (15) have shown that allyl radicals are formed upon thermolysis of 3,3'-azo-1-propene and combine to give 1,5-hexadiene. Propene was formed in less than 1% during this reaction, suggesting the absence of any significant amount of hydrogen abstraction and of any chain induced decomposition. By analogy, the following products can be expected from coupling of *cis*- and *trans*-butenyl radicals:



A study of (*Z*,*Z*,*E*)-4,4'-azo-2-butene (9) and (*E*,*E*,*E*)-4,4'-azo-2-butene (10) should yield some information on the configurational stability of butenyl radicals in the gas



(9)

(10)

phase by analysis of the diene products. If the butenyl radicals are able to retain their stereochemistry until recombination occurs, the only products from (9) should be (3), (5) and (8), and from (10) should be (3), (4) and (6). If however isomerization does occur, all of the diene isomers may be expected starting from either (9) of (10). If the lifetime of the butenyl radicals were long enough to establish an equilibrium mixture, an identical product distribution would be expected starting from either (9) or (10). Investigation of the products from thermolysis of the azo compounds in solution should show an increase in stereospecificity, if cage recombination occurs and the radicals are formed initially in their *cis*- or *trans*-configuration, respectively.

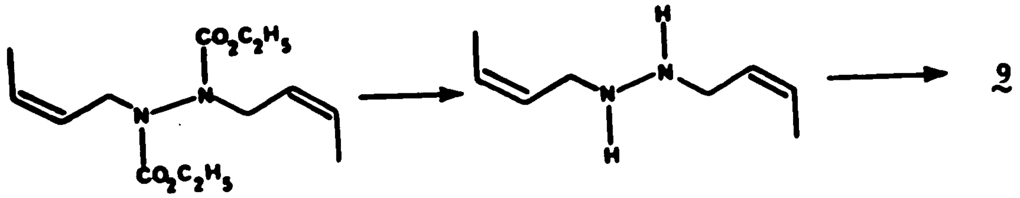
From kinetic data for the unimolecular decomposition of these azo-compounds, it is anticipated that a value for the barrier for *cis-trans*-isomerization of the butenyl radicals can be obtained.

The azo compounds as butenyl radical precursors were selected since thermolysis occurs at a conveniently low temperature, and surface reactions seldom cause any problem. The thermolysis can be readily carried out in the gas phase with nitrogen added, so that the formed free radicals can be deactivated by collision with nitrogen molecules, and the mean free path is decreased so as to reduce the possible influence of the wall upon the intermediate.

RESULTS

A. Synthesis

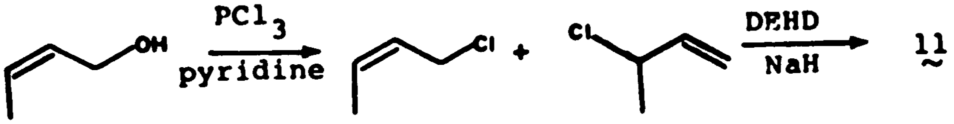
(Z,Z,E)-4,4'-azo-2-butene 9 was prepared by the mercuric oxide oxidation of the corresponding hydrazine. The latter was obtained from the hydrolysis of the diethyl-N,N'-di-(*cis*-2-butene-1-yl)-bicarbamate (11) using potassium hydroxide in 95% ethanol. The procedure was essentially that described by Crawford and Al-Sader (15). It was found that after three hours of refluxing only partial hydrolysis had occurred, accounting for the low yield (41%) reported by the authors. Extending the reflux period to 15 hours improved the yield to about 75%.



11 12

The bicarbamate was prepared in an analogous manner to that described by Crawford and Al-Sader (15). The 1-chloro-*cis*-2-butene was allowed to react with the dianion of diethyl-hydrazodicarboxylate (DEHD), generated by the reaction of sodium hydride with DEHD in dry 1,2-

dimethoxyethane (DME) under a nitrogen atmosphere. The 1-chloro-*cis*-2-butene was obtained by the addition of *cis*-2-buten-1-ol to phosphorous trichloride in the presence of pyridine (40). During this reaction about 5% of 3-chloro-1-butene was formed, however, complete removal of it is not necessary since it will not alkylate the dianion of DEHD.



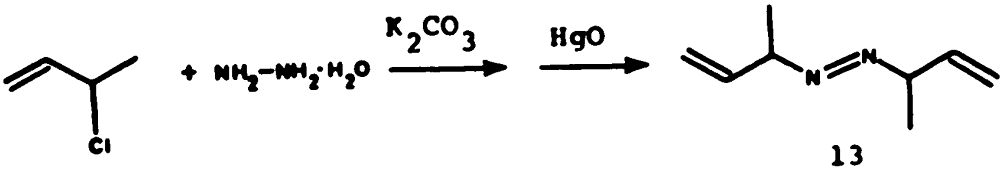
Pure *cis*-2-buten-1-ol was obtained from the hydrogenation of commercially available 2-butyn-1-ol in the presence of Lindlar catalyst followed by preparative gas chromatography (gc) on a 3,3'-oxidipropionitrile (ODPN) column. The nmr spectrum of **9** is shown in Figure 1.

The (E,E,E)-4,4'-azo-2-butene was prepared in an analogous manner except that the starting material was *trans*-2-buten-1-ol. This was obtained by subjecting a commercially available mixture of *cis*- and *trans*-2-buten-1-ol to preparative gc on the ODPN column. The

FIGURE 1: nmr spectrum (100 MHz) of 9.

nmr spectrum of 10 is shown in Figure 2.

During the course of the investigation it became evident, that knowledge of the product distribution from the thermolysis of (E)-3,3'-azo-1-butene (13) and the kinetic parameters for this process would be of interest. The synthesis of this azo compound could not be accomplished in the manner described before, since direct alkylation of DEHD does not occur with 3-chloro-1-butene. Synthesis via methyl-vinylketazine was unsuccessful because the initially formed hydrazone undergoes immediate cyclization. The alkylation of acetaldazine with vinyl lithium was attempted but failed. The azo compound, however, was formed in very low yield by the direct allylation of hydrazine hydrate with 3-chloro-1-butene in the presence of potassium carbonate, at 30°, and subsequent mercuric oxide oxidation.



13

A variety of compounds were formed although not identified, but the 3,3'-azo-1-butene could be separated

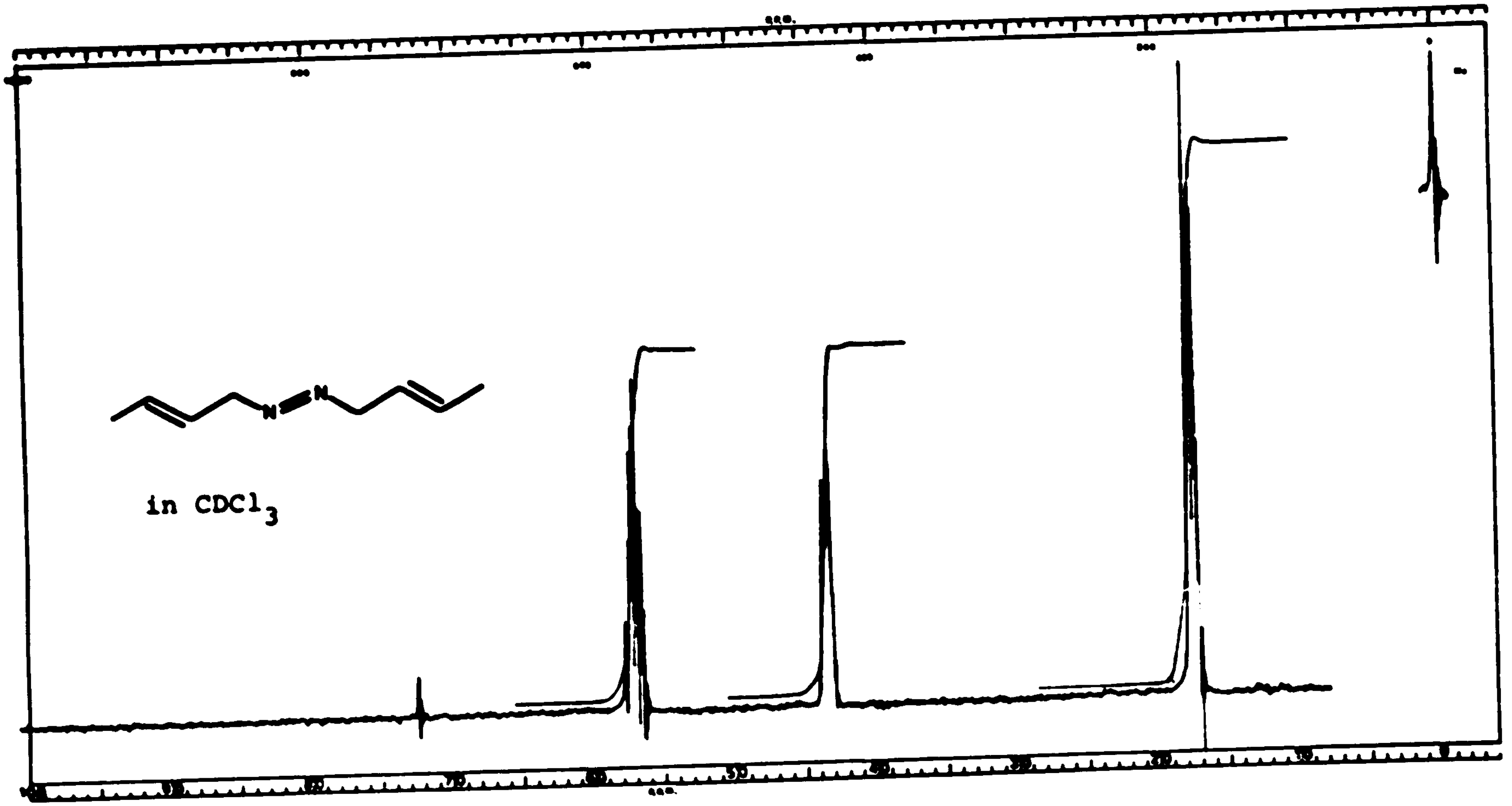
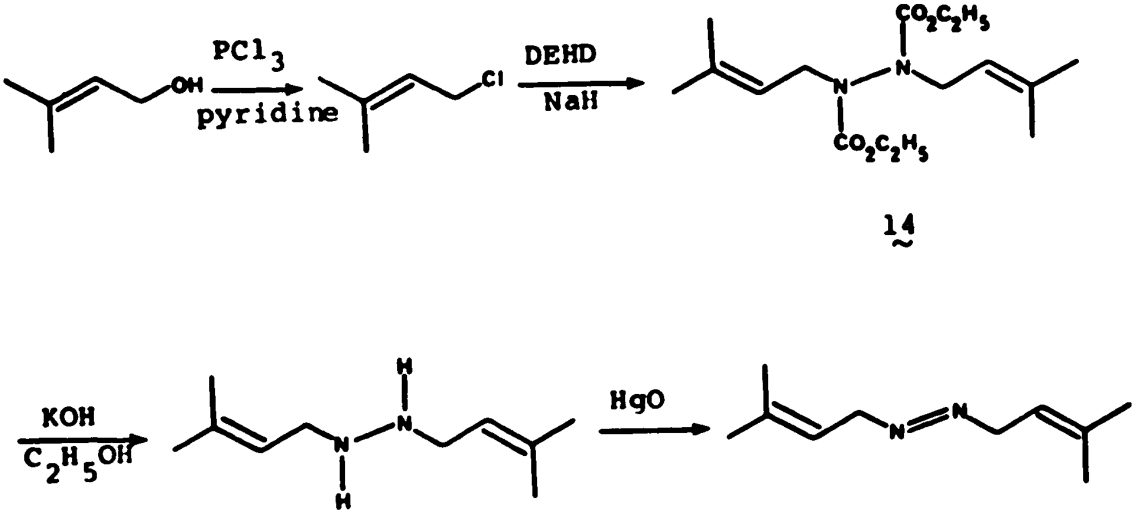


FIGURE 2: nmr spectrum (100 MHz) of 10.

from the mixture by preparative gc. The nmr spectrum of 13 is shown in Figure 3.

The (*E*)-4,4'-azo-(2-methyl)-2-butene (15) was prepared in the same manner as the 4,4'-azo-2-butenes, except that 3-methyl-2-buten-1-ol was used as the starting alcohol; it was prepared by the lithium aluminum hydride reduction of the methyl ester of senecioic acid. The nmr spectrum of 16 is shown in Figure 4.



14

15

16

B. Thermolysis and Analysis of Products

The thermolyses of the azo compounds were carried out in a 1200 ml Pyrex glass vessel, situated in a well thermostated air bath. The temperature at 120 -

FIGURE 3: nmr spectrum (100 MHz) of 13.

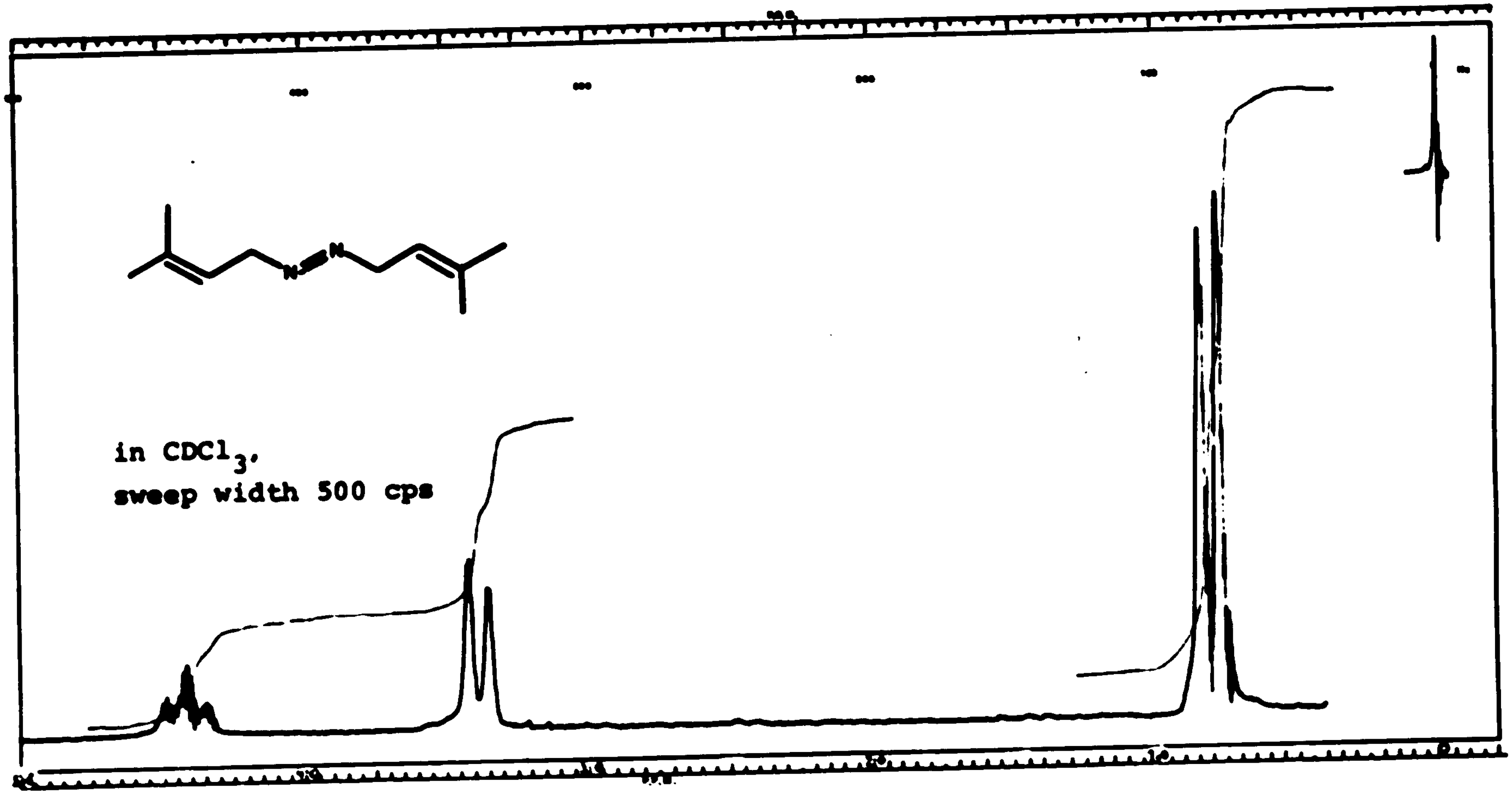


FIGURE 4: nmr spectrum (100 MHz) of $\underset{\sim}{16}$.

130°C could be controlled to within ±0.01°C. Samples of 5 µl of the azo compound were introduced and nitrogen was added to obtain an initial pressure of 100 mm.

Thermolysis products were trapped with liquid nitrogen and analyzed by gc. Peak areas were obtained from a Hewlett Packard Model 3370 A electronic integrator, directly connected to the flame ionization detector of the gc.

The product distribution and standard deviations from compounds 9 , 10 and 13 are shown in Table V, for the individual results see Appendix A. The peaks were identified in the manner described by Doering and Roth (40). Compounds 3 and 13 are actually mixtures of *meso* and *rac* as indicated by gc. Although no baseline separation of *meso* and *rac* 3 could be obtained at a column temperature of 25°C it appears that they are formed in approximately a 1:1 ratio. All other thermolysis products and the azo compounds themselves were cleanly separated, see Figure 5.

Control runs showed that no isomerization occurred prior to fragmentation of the azo compounds. At 60% completion recovered samples of the azo compounds were judged unchanged by nmr and gc. This fact rules out a reversible azo to diazene (41) rearrangement at this temperature. Crawford and Al-Sader (15), in their study

TABLE V

Product distribution and standard deviations from the thermolysis of 9 , 10 and 13 at 125.70°±0.01°

(100 torr nitrogen added in 1200 ml vessel)

Azo Compound	% Yield (standard deviation) 3	4	5	6	7	8
9	16.99	28.31	18.59	11.91	17.67	6.54
	(0.21)^{a}	(0.06)^{a}	(0.08)^{a}	(0.03)^{a}	(0.11)^{a}	(0.07)^{a}
10	17.20	28.66	18.36	12.20	17.47	6.12
	(0.28)^{b}	(0.15)^{b}	(0.17)^{b}	(0.17)^{b}	(0.21)^{b}	(0.06)^{b}
13	17.05	28.83	18.48	11.94	17.64	6.08
	(0.19)^{c}	(0.08)^{c}	(0.07)^{c}	(0.07)^{c}	(0.13)^{c}	(0.01)^{c}

[a] Obtained from 10 samples (see Appendix A)

[b] Obtained from 11 samples (see Appendix A)

[c] Obtained from 12 samples (see Appendix A)

Values are not rounded off for computational purposes.

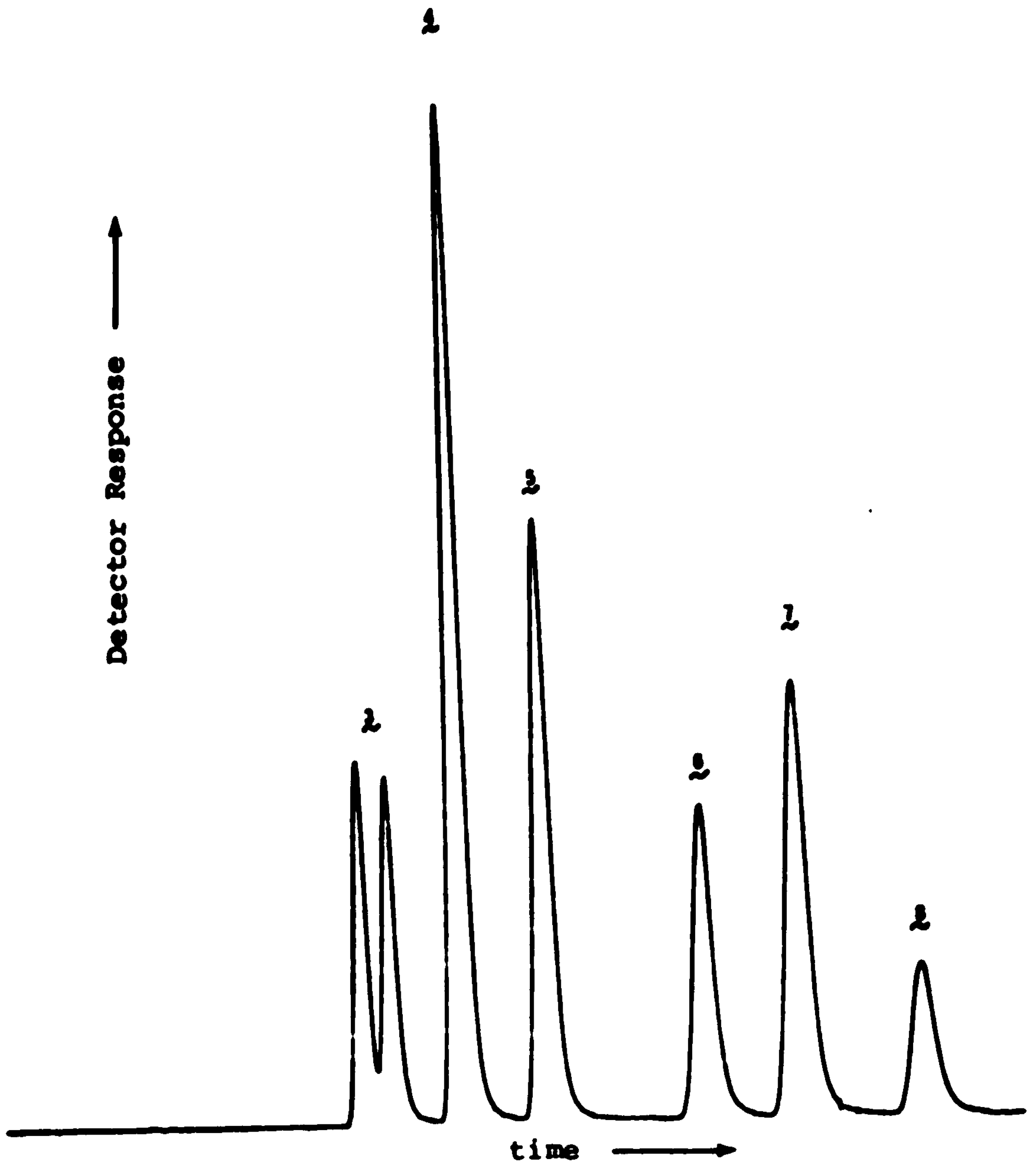
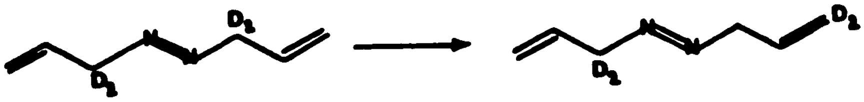


FIGURE 5: Gas chromatogram of the products from the thermolysis of 9 at 125.7° obtained on the 150 ft ODPN capillary column at 25°.

of 3,3'-azo-1-propene-3,3-d_2 had observed some scrambling of the deuterium from the α,α-position to the γ,γ-position of the allyl groups.



A process, responsible for this type of rearrangement was not detected for the azo-butenes. Such a process would show as either positional or geometrical isomerization of the butenyl groups in the azo compound, or both.

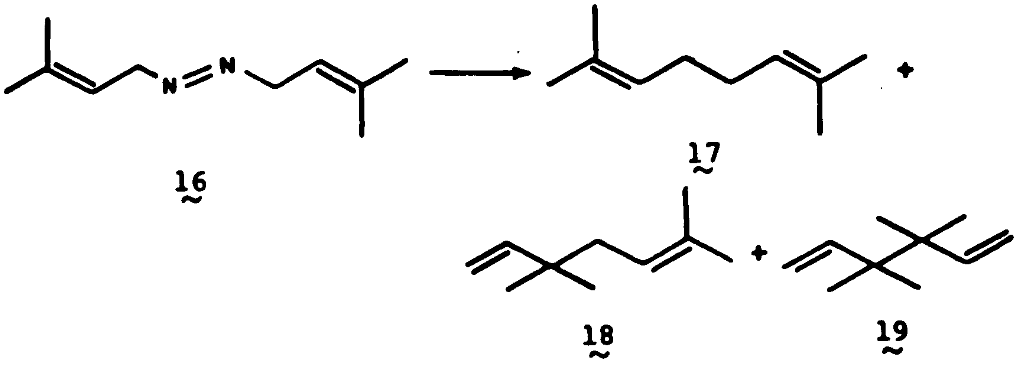
Changes of the surface of the reaction vessel as well as change in the surface to volume ratio did not alter the product distribution significantly.

In another control experiment, isomerization of the diene products was proven to be of no importance under the reaction conditions. This is in agreement with the results of Doering and Roth (40) who reported that **3** undergoes the Cope rearrangement only at temperatures of 200°C and above.

As Crawford and Al-Sader (15) had observed for the allyl radical, the butenyl radical does not abstract hydrogen to any degree since only minute amounts of butenes (less than 0.3%) are formed.

The product distribution from thermolysis of the azo compounds 9 and 10 in dihydronaphthalene and decahydronaphthalene is shown in Table VI.

Product distribution from 16 and standard deviations are shown in Table VII, the individual values are given in Appendix A.



The dienes were identified by heating a mixture of 17, 18 and 19 of known composition to 180° for two hours. Under these conditions 19 is expected to undergo the Cope rearrangement to give 17 . The composition of the mixture after heating is enhanced in 17 , unchanged in 18 and reduced in 19.

The same hydrocarbons in a slightly different ratio were obtained by Baldwin and coworkers (41) when the unsymmetrical azo compound 20 was heated to 75° for 60

TABLE VI

Product distribution from thermolysis of (Z,Z,E)-4,4'-azo-2-butene (9) and (E,E,E)-4,4'-azo-2-butene (10) in solution at 122.50±0.01°

		% Yield					
Compound	Solvent	3	4	5	6	7	8
9	dihydro-haphthalene	15.7	7.5	37.1	3.4	8.3	28.0
	decahydro-naphthalene	16.4	11.6	35.7	4.9	9.2	22.1
10	dihydro-naphthalene	15.8	36.3	6.3	28.2	9.3	4.0
	decahydro-naphthalene	16.4	33.8	12.9	23.2	10.7	3.0

minutes.

20

TABLE VII

Product distribution from the thermolysis of azo-butene (16) at 114.99±0.01°C (100 torr nitrogen added in 1200 ml glass vessel)[a,b]

	% yield (standard deviation)		
Compound	(17)	(18)	(19)
(16)	60.11 (0.19)	33.84 (0.20)	6.05 (0.06)

[a] obtained from six samples (see Appendix A).

[b] values are not rounded off for computational purposes.

(C) Kinetic Measurements

The kinetic studies of compounds 9, 10, 13 and 16 were carried out in the stainless steel reactor used by Al-Sader (42) and Mishra (43) and devised by Smith (44). The increase in pressure was measured by the increase of the electromotive force (emf) as indicated on a strip chart recorder. The pressure reading was converted into emf via a calibrated transducer.

The rate constant of a first order gas phase reaction of the type

$$A \xrightarrow{k} \text{products}$$

is given (45) by the equation

$$k = \frac{2.303}{t} \text{ Log } \frac{P_\infty - P_o}{P_\infty - P_t} \qquad (1)$$

where k is the first order rate constant, t is the time and P is the actual pressure inside the reactor.

The relationship between the emf caused by the pressure change on the transducer and the pressure inside the reactor was found to be linear throughout the range in which the studies were carried out, and can be expressed by

$$E = aP' + b \qquad (2)$$

where a and b are proportionality constants.

The observed pressure in the system used is

$$P_{obs} = P - P_x \qquad (3)$$

where P_x is a constant quantity, namely the pressure required to push the diaphragm from its equilibrium position against the needle. Combining equations 2 and 3 we get for the emf

$$E = a(P - P_x) + b \qquad (4)$$

or for the pressure

$$P = \frac{E - b}{a} + P_x \qquad (5)$$

Substituting equation 5 into equation 1 we get for the rate constant

$$k = \frac{2.303}{t} \text{Log} \frac{E_\infty - E_0}{E_\infty - E_t} \qquad (6)$$

where E_∞ is the transducer emf at 100% completion, i.e. after 100 half lives and E_t is the emf at time t in seconds.

The quantity $(E_\infty - E_0)$ is a constant and thus equation 6 becomes

$$k = -\frac{2.303}{t} \text{Log} (E_\infty - E_t) + C \qquad (7)$$

Plotting Log $(E_\infty - E_t)$ versus time gives a straight line with a slope equal to $-\frac{k}{2.303}$ from which the rate constant can be obtained. Between 10 and 28 points were taken off the chart record between 20 and 80% completion (Figure 6 and Appendix B).

For the evaluation of error limits the least square method was employed (46).

Equation 7 can be rewritten as

$$y = bx + a \qquad (8)$$

where $y = \text{Log}(E_\infty - E_t)$, $b = -\frac{k}{2.303}$, $x = t$ and $a = C = \text{Log}\ (E_\infty - E_0)$.

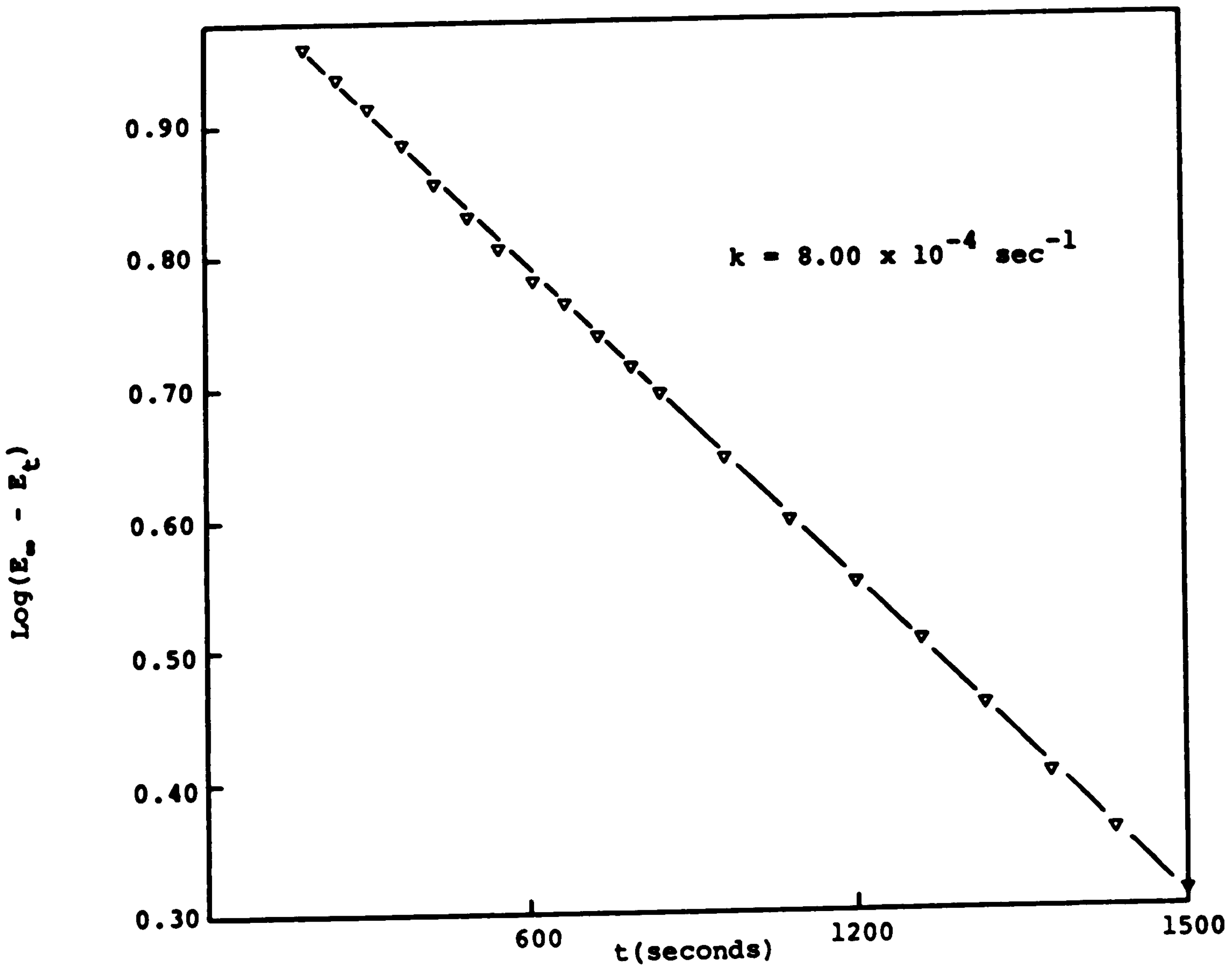


FIGURE 6: Plot of Log(E_∞ - E_t) versus time for the thermolysis of 9 at 140.3°.

The least square analysis gives the best fit values for the slope

$$b = -\frac{k}{2.303} = \frac{n\sum xy - \sum x\sum y}{n\sum x^2 - (\sum x)^2} \qquad (9)$$

and for the intercept

$$a = \mathrm{Log}(E_\infty - E_o) = \frac{\sum x^2\sum y - \sum x\sum xy}{n\sum x^2 - (\sum x)^2} \qquad (10)$$

The probable error in b can be shown to be

$$P_b = P_y \sqrt{\frac{n}{n\sum x^2 - (\sum x)^2}} \qquad (11)$$

where

$$P_y = 0.6745\sqrt{\frac{\sum(y-a-bx)^2}{n-2}} \qquad (12)$$

Rate constants for the thermolysis of the azo compounds 9, 10, 13 and 16 are shown in Table VIII, the individual values for the emf on which the calculations are based are given in Appendix B.

From the Arrhenius equation

$$k = A\cdot e^{-\frac{E_a}{RT}} \qquad (13)$$

which can be rewritten to give

$$\mathrm{Log}\,k = -\frac{E_a}{2.303RT} + \mathrm{Log}\,A \qquad (14)$$

TABLE VIII

Rate constants for the thermolysis of (*Z*,*Z*,*E*)-4,4'-azo-2-butene (**9**), (*E*,*E*,*E*)-4,4'-azo-2-butene (**10**), (*E*)-3,3'-azo-1-butene (**13**) and (*E*)-4,4'-azo-(3-methyl)-2-butene (**16**)[a]

Compound	Temperature (°C)	10^4 x k (sec^{-1})
9	140.30±0.05	8.00±0.06
	148.20±0.05	18.1 ±0.2
	148.60±0.05	18.2 ±0.1
	159.80±0.05	56.2 ±0.1
10	140.50±0.05	5.98±0.03
	141.60±0.05	7.28±0.04
	148.80±0.05	12.01±0.05
	160.00±0.05	36.1 ±0.3
13	125.60±0.05	10.58±0.04
	135.00±0.05	29.5 ±0.1
	135.20±0.05	30.0 ±0.3
	140.00±0.05	50.9 ±0.5
16	134.90±0.05	7.59±0.08
	140.20±0.05	14.57±0.11
	142.70±0.05	18.50±0.08
	148.80±0.05	38.3 ±0.4

[a] see Appendix B

it can be seen that a plot of Log k versus $\frac{1}{T}$ should give a straight line with the slope being equal to $-(2.303R)^{-1}E_a$.

For the evaluation of this slope the rate constants at the two extreme temperatures were used. For the error limits the upper limit of one rate constant was used with the lower limit of the other and vice versa. This method gives a satisfactory evaluation of the errors since the precision of each point is incorporated (47). In a least square analysis the two extreme points are dominant in the calculation of the slope, if only three points are available.

For a gas phase reaction the enthalpy of activation is given by

$$\Delta H^{\ddagger} = E_a - nRT \tag{15}$$

where n is the order of the reaction (45). Thus for a first order reaction, equation 15 reduces to

$$\Delta H^{\ddagger} = E_a - RT \tag{16}$$

From the transition state theory (45) the first order rate constant can be expressed by

$$k = \frac{k' \cdot T}{h} \quad e^{+\frac{\Delta S^{\ddagger}}{R}} \cdot \quad e^{-\frac{\Delta H^{\ddagger}}{RT}} \tag{17}$$

where $\Delta S^{\ddagger}$ is the entropy of activation, k' is Boltzmann's constant and h is Planck's constant. Combining equations 13, 16 and 17 we obtain

$$\Delta S^{\ddagger} = 2.303R \text{ Log } \frac{A \cdot h}{k' \cdot T \cdot e} \tag{18}$$

or

$$\Delta S^{\ddagger} = 2.303R \left[\text{Log } \frac{h}{k' \cdot T \cdot e} + \text{Log } A\right] \tag{19}$$

Equation 19 was used to calculate the entropy of activation at 150°C. The activation energies and the entropies of activation are shown in Table IX.

TABLE IX

Kinetic parameters for the thermolysis of azobutenes 9, 10, 13 and 16 [a]

Compound	E_a (kcal $mole^{-1}$)	Log A	$\Delta S^{\ddagger}$(150°) (e.u.)
9	35.54±0.25[b]	15.69±0.13[b]	10.6±0.6
10	31.20±0.25[b]	13.30±0.13[b]	-0.4±0.6
13	35.48±0.30[b]	16.57±0.16[b]	14.2±0.8
16	39.73±0.50[b]	18.16±0.27[b]	21.9±1.2

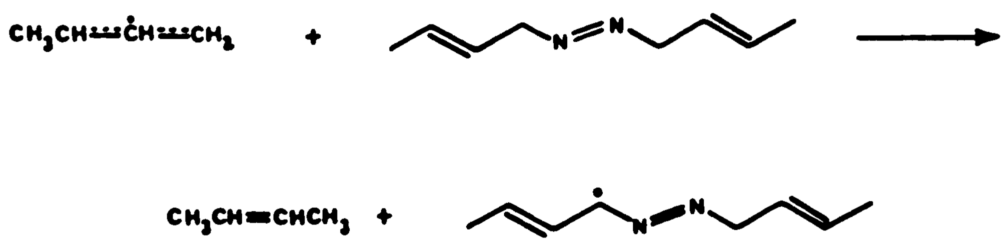
[a] see Appendix B for calculations

[b] values are not rounded off for computational purposes

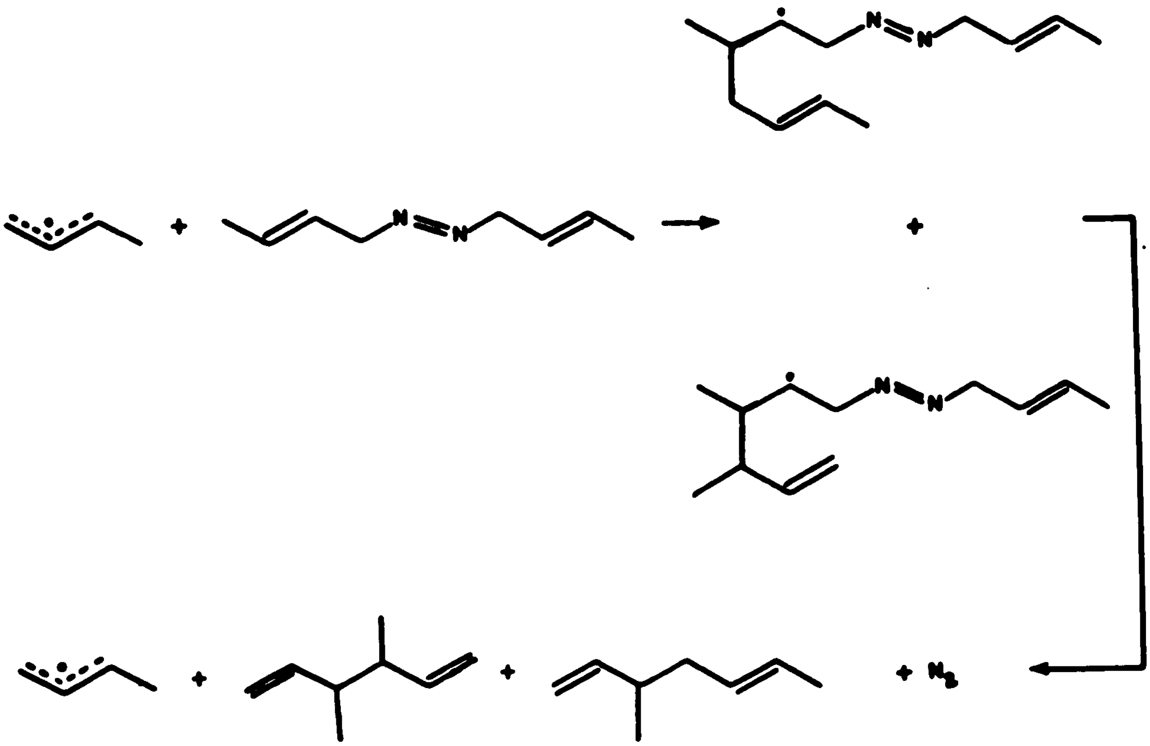
DISCUSSION

(A) Mechanism of Product Formation

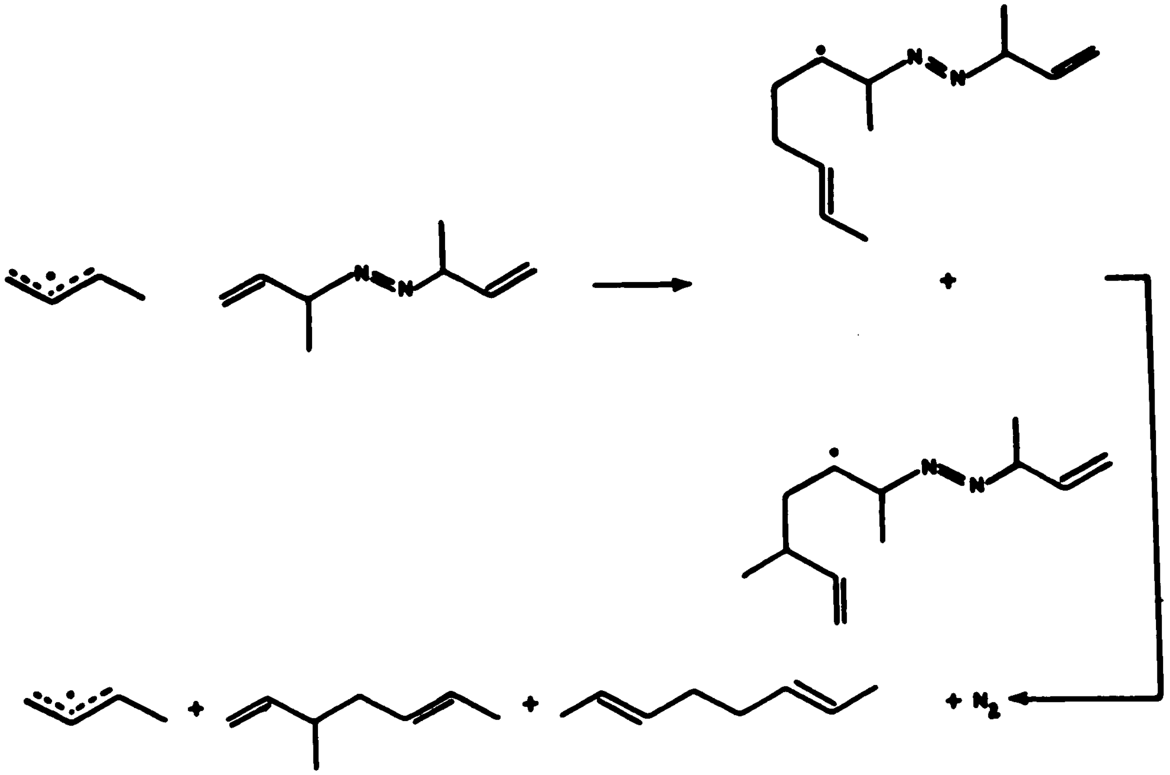
In excellent agreement with the results of Crawford and Al-Sader (15), the thermolysis of the azobutenes **9**, **10**, **13** and **16** is not complicated by induced decomposition. The butenyl radicals, as has been observed for the parent allyl radical, seem to be unable to abstract hydrogen from the azo compounds, or from the products, to form butene. An analogous reaction is believed to be responsible for the induced decomposition of azomethane (10). In no instance was the total yield of butenes higher than 0.3%.



Decomposition however could also be induced via an addition of a butenyl radical to a carbon-carbon double bond in the azo compound. Neglecting *cis-trans* isomerism it can be seen that such a process would lead to 3,4-dimethyl-1,5-hexadiene 3 and the 3-methyl-1,5-heptadienes 4 and 5 starting with either (Z,Z,E)-4,4'-azo-2-butene (9) or (E,E,E)-4,4'-azo-2-butene (10)

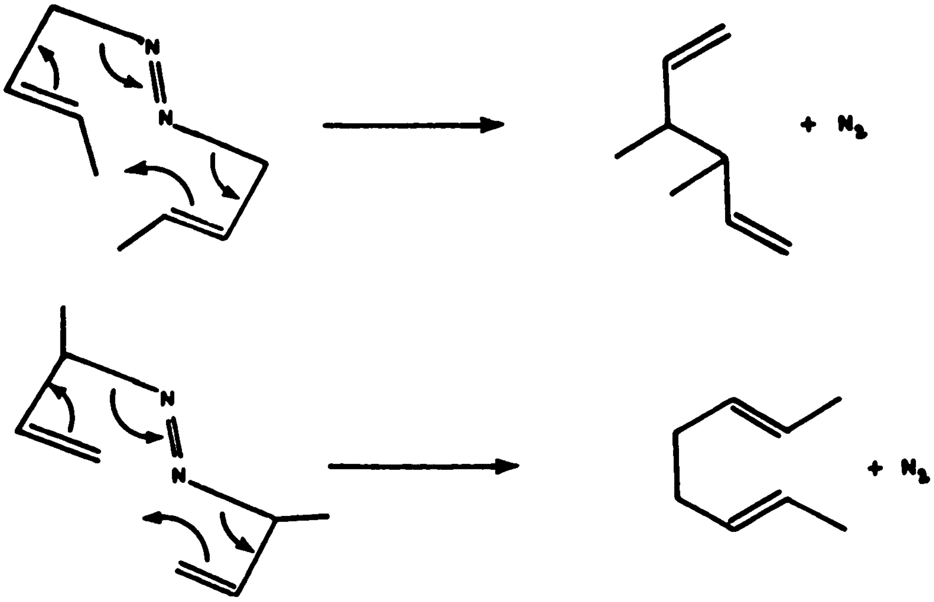


For (E)-3,3'-azo-1-butene (13) an identical process would lead to the 3-methyl-1,5-heptadienes 4 and 5 and the 2,6-octadienes 6, 7 and 8.



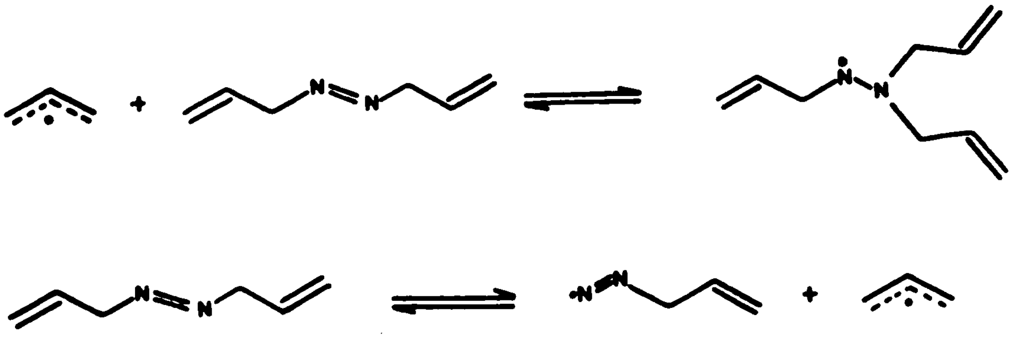
From Table V it can be seen that the total yield of 3,4-dimethyl-1,5-hexadiene and 3-methyl-1,5-heptadiene from the azobutenes 9 and 10 is actually lower than that from the azo compound 13, 63.89% from 9, 64.22% from 10 and 64.36% from 13. Similarly the total yield of 3-methyl-1,5-heptadienes and 2,6-octadienes from 13 (82.97%) is not significantly different than that from 9 (83.02%) and 10 (82.81%).

The same product argument can be used to rule out a molecular reaction of the type



As can be seen such a process would produce only 3,4-dimethyl-1,5-hexadiene from the azo-2-butenes 9 and 10 whereas the azo-1-butene 13 would lead to only the octadienes. The formation of the 3-methyl-heptadienes could not be explained by such a molecular process alone.

The absence of a reversible addition of a butenyl radical to the azo double bond as well as a reversible one bond fragmentation is signalled by the fact that all azo compounds could be recovered unchanged when the thermolysis was allowed to proceed to partial completion. Either or both of these reactions were suggested by Crawford and Al-Sader (15) to be responsible for the observed 3% deuterium scrambling during the thermolysis of 3,3'-azo-1-propene-3,3-$\underline{d}_2$.



Either process would isomerize the starting azobutene as well and must be below the level of detectability in the present study since the recovered azo compounds were always judged unchanged by nmr and gc.

A possibility to consider is that the isomerization of the butenyl radicals takes place at the wall of the reaction vessel. Neither a change in surface nor a change in surface to volume ratio altered the product proportions significantly, Table X. Aging of the glass vessel also had no effect.

The distance a radical can diffuse in its mean lifetime can be calculated (48) from the equation

$$x \cong \sqrt{t_D \cdot D} \qquad (20)$$

where t_D is the mean lifetime and D is the diffusion constant (48) which in turn is given by

TABLE X

Product distribution from (*Z*,*Z*,*E*)-4,4'-azo-2-butene (**9**), (*E*,*E*,*E*)-4,4'-azo-2-butene (**10**) and (*E*)-3,3'-azo-1-butene (**13**) in a 25 ml glass vessel at 125.50° without nitrogen added

	% Yield					
Compound	**3**	**4**	**5**	**6**	**7**	**8**
9	17.5	28.3	18.8	11.6	17.2	6.6
10	16.7	28.0	18.4	12.2	17.9	6.7
13	16.7	27.6	18.6	12.1	18.1	6.9

$$D = \frac{3}{32} \cdot \frac{1}{N \cdot J_{12}^2} \left(\frac{8k'T}{\Pi\mu}\right)^{\frac{1}{2}} \qquad (21)$$

where J_{12} is the average molecular radius, N is the total number of molecules present per unit volume and μ is the reduced mass, i.e.

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad (22)$$

In the present case the butenyl radicals travel through nitrogen molecules thus

$$\frac{1}{\mu} = \frac{1}{28} + \frac{1}{55}$$

or $\mu = 18.6.$

Taking the values $J_1 = 2\text{Å}$ and $J_2 = 5\text{Å}$ as the molecular radii for the nitrogen molecule and the butenyl radical, respectively, we obtain $J_{12} = 3.5\text{Å}$.

The number of molecules of nitrogen can be calculated from

$$N = n \cdot N_A \qquad (23)$$

where n is the number of moles and N_A is Avogadro's number. The number of moles of nitrogen in a 1200 ml vessel at 130° is given by

$$n = \frac{P \cdot V}{R \cdot T} \qquad (24)$$

From the values given, the diffusion constant was calculated

$$D = 0.0278 \text{ cm}^2 \text{ sec}^{-1}$$

Using van den Bergh and Callear's (49) value of 8.5×10^{12} cm^3 mole^{-1} sec^{-1} for the rate constant for the recombination of allyl radicals, the mean lifetime of the butenyl radicals can be calculated from

$$t_D = \frac{1}{k_{comb} \cdot [R\cdot]} \tag{25}$$

Steady state approximations for the process

$$R\text{-}N{=}N\text{-}R \xrightarrow{k_1} 2R\cdot + N_2 \xrightarrow{k_{comb}} R\text{-}R$$

give

$$k_1[\text{azo}] = k_{comb}[R\cdot]^2 \tag{26}$$

and

$$[R\cdot] = \sqrt{\frac{k_1[\text{azo}]}{k_{comb}}} \tag{27}$$

where [azo] refers to the initial concentration of the azo compound, about 2.4×10^{-5} mole l^{-1}, and $[R\cdot]$ refers to the total concentration of all butenyl radicals. Using equations 25 and 27 and the value of 1.65×10^{-4} for k_1 (see Table XI), the mean lifetime was found to be

$$t_D = 0.17 \text{ sec.}$$

TABLE XI

Rate constants for the thermolysis of azobutenes 9, 10, 13 and 16 at 125.7°

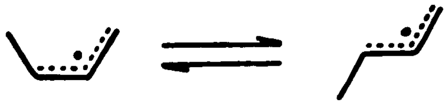
Compound	k x 10^4 (sec^{-1})
(9)	1.65
(10)	1.61
(13)	10.73
(16)	2.47

The distance travelled by the butenyl radical during this mean lifetime can be calculated now from equation 20

$$x = \sqrt{t_D \cdot D} = 0.069 \text{ cm.}$$

The reaction vessel had a radius of 6.5 cm. Since the volume of a sphere with radius 6.5 cm is 1149 cm^3 as compared to 1097 cm^3 for a sphere with radius 6.4 cm, it follows that more than 95% of the butenyl radicals were never in contact with the wall.

The almost identical product distribution from 9, 10 and 13 indicates that the butenyl radicals have come to almost complete equilibrium in the gas phase at 125°C before combination occurs



However, some degree of retention of configuration is still observed. Thus (Z,Z,E)-4,4'-azo-2-butene (9) produces slightly higher yields of 3-methyl-(Z)-1,5-heptadiene (5) and (Z,Z)-2,6-octadiene (8) than does (E,E,E)-4,4'-azo-2-butene (10). Similarly 10 produces more 3-methyl-(E)-1,5-heptadiene (4) and (E,E)-2,6-octadiene

(6) than does 9. Application of the *t-test* (50) confirms that these differences are significant.

The *t-test* is used for the comparison of averages. An estimate for the variance of two sets of values

$x_1, x_2, \ldots\ldots, x_n$ (with average $\bar{x}$)

and

$y_1, y_2, \ldots\ldots, y_m$ (with average $\bar{y}$)

is given by

$$s^2 = \frac{\sum x_i^2 - \frac{(\sum x_i)^2}{n} + \sum y_i^2 - \frac{(\sum y_i)^2}{m}}{(n-1) + (m-1)} \qquad (28)$$

The value for t can then be calculated from

$$t = \frac{\bar{x}-\bar{y}}{s} \sqrt{\frac{n \cdot m}{n+m}} \qquad (29)$$

for $(n + m - 2)$ degrees of freedom. The measure t thus is the ratio of the difference between the averages to the standard deviation of this difference. Values for t with confidence limits are available in tabulated form (50) and shown in Table XII.

Values of t calculated from the product distribution from thermolysis of the azobutenes 9 and 10 are given in Table XIII. A value for t exceeding that at the critical 99% confidence limit signals a significant

TABLE XII

Critical values of *t* with confidence levels (50)

Degrees of freedom	95% confidence level	99% confidence level
17	2.110	2.898
18	2.101	2.878
19	2.093	2.861
20	2.086	2.845
21	2.080	2.831
22	2.074	2.819

TABLE XIII

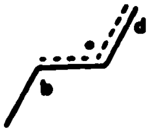
Calculated *t* values from the comparison of the averages of the diene yields from (*Z*,*Z*,*E*)-4,4'-azo-2-butene with those from (*E*,*E*,*E*)-4,4'-azo-2-butene

Diene	Degrees of freedom	*t*
3	19	1.956
4	19	7.150
5	19	4.030
6	19	5.577
7	19	2.772
8	19	14.66

difference between the two averages compared. Thus it can be seen that with 99% confidence the product distribution from **9** is different from that of **10**. All yields of dienes from **9** involving combination of a butenyl radical with a *cis*-butenyl radical are higher than those from **10**.

(B) Evaluation of the Equilibrium Constant for the *cis-trans* Isomerization of the Butenyl Radicals

An interesting statistical model can be envisaged. Both the *cis*- and *trans*-butenyl radical have two centers of reactivity.

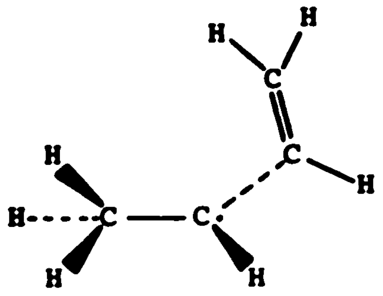


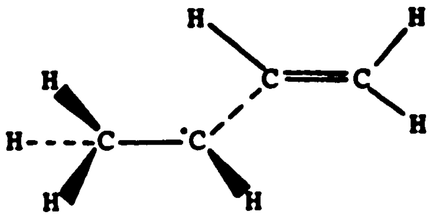
The studies cited in the historical section (3,8) showed that the ratio of the reactivities at the primary versus the secondary end of the butenyl radical is larger for the *trans*-radical **2** than for the *cis*-radical **1**. Thus

$$\frac{d}{b} > \frac{c}{a}$$

The difference was attributed to steric effects; the methyl group shields the primary position in the *cis*-

radical more than does the methyl group in the *trans*-radical. On the other hand the steric factors to attack at the secondary center will not be greatly different in 1 and 2.





If the mole fractions of 1 and 2 in the mixture are given by x and y respectively then the total yield of product is given by equation

$$[(a+c)x + (b+d)y]^2 = 1.0 \tag{30}$$

if the diene distribution is also given in mole fractions. Statistical terms of this equation can be associated with each of the dienes formed by combination of two butenyl radicals. Since the yield of 3,4-dimethyl-1,5-hexadiene is given by the term $(ax + by)^2$ we can use the yield of 3 to evaluate (ax + by) and obtain (ax + by) = 0.4122 from azobutene 9. The formation of 3-methyl-(E)-1,5-heptadiene is given by 2(ax + by)dy; using the value for (ax + by) calculated above we obtain dy = 0.3434.

From equation 30 we then obtain

$$(a+c)x + (b+d)y = 1.0 \qquad (31)$$

which allows us to calculate a value for cx, i.e. $cx = 0.2444$. These values can now be used to calculate the yields of **5**, **6**, **7** and **8** and we obtain 0.2015, ($[2(ax + by)\,cx]$); 0.1179 ($[d^2y^2]$); 0.1679, ($[2cxdy]$); and 0.0597, ($[c^2x^2]$); as compared to the observed values 0.1859, 0.1191, 0.1767 and 0.0654 respectively.

As can be seen the agreement of predicted and observed yields is quite good, although the model is rather crude. Similarly the term dy can be obtained from the yield of (*E*,*E*)-2,6-octadiene in which case the yields of **4**, **5**, **7** and **8** can be predicted. The results for these calculations are shown in Table XIV.

The ratio of $\frac{d \cdot y}{c \cdot x}$ can similarly be calculated in different ways e.g.

$$\frac{dy}{cx} = \frac{[\mathbf{6}]}{[\mathbf{8}]} = \frac{[\mathbf{4}]}{[\mathbf{5}]} \quad \text{etc.}$$

The values for $\frac{dy}{cx}$ calculated in this manner are shown in Table XV. Because of the partial retention of configuration the values calculated from the product distribution of **10** are always slightly larger than those calculated from **9**. In order to estimate a value for

TABLE XIV

Predicted diene distribution from statistical treatment of the diene composition from the thermolysis of (*Z*,*Z*,*E*)-4,4'-azo-2-butene (9), (*E*,*E*,*E*)-4,4'-azo-2-butene (10) and (*E*)-3,3'-azo-1-butene (13)

Azo compound	Diene	Statistical term for formation of diene	Term used in calculation	Numerical value	Diene yield predicted (%)	Diene yield observed (%)
9	3	$(ax + by)^2$	$(ax + by)$	0.4122	-	-
	4	$2(ax + by)dy$	dy	0.3434	-	-
	5	$2(ax + by)cx$	-	-	20.15	18.59
	6	d^2y^2	-	-	11.79	11.91
	7	$2cxdy$	-	-	16.79	17.67
	8	c^2x^2	-	-	5.97	6.54
9	3	$(ax + by)^2$	$(ax + by)$	0.4122	-	-
	4	$2(ax + by)dy$	-	-	28.45	28.31
	5	$2(ax + by)cx$	-	-	20.01	18.59

TABLE XIV

Azo compound	Diene	Statistical term for formation of diene	Term used in calculation	Numerical value	Diene yield predicted (%)	Diene yield observed (%)
	6	d^2y^2	dy	0.3451	-	-
	7	2cxdy	-	-	16.75	17.67
	8	c^2x^2	-	-	5.89	6.54
10	3	$(ax + by)^2$	(ax + by)	0.4147	-	-
	4	2(ax + by)dy	dy	0.3456	-	-
	5	2(ax + by)cx	-	-	-	-
	6	d^2y^2	-	-	11.94	12.20
	7	2cxdy	-	-	16.59	17.47
	8	c^2x^2	-	-	5.75	6.12
	3	$(ax + by)^2$	(ax + by)	0.4147	-	-
	4	2(ax + by)dy	-	-	28.97	28.66

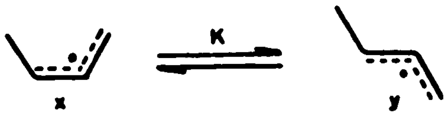
TABLE XIV

Azo compound	Diene	Statistical term for formation of diene	Term used in calculation	Numerical value	Diene yield predicted (%)	Diene yield observed (%)
10	5	$2(ax + by)cx$	-	-	19.57	18.36
	6	d^2y^2	dy	0.3493	-	-
	7	$2cxdy$	-	-	16.49	17.47
	8	c^2x^2	-	-	5.57	6.12
13	3	$(ax + by)^2$	$(ax + by)$	0.4129	-	-
	4	$2(ax + by)dy$	dy	0.3491	-	-
	5	$2(ax + by)cx$	-	-	19.65	18.48
	6	d^2y^2	-	-	12.19	11.94
	7	$2cxdy$	-	-	16.62	17.64
	8	c^2x^2	-	-	5.66	6.08

TABLE XIV

Azo compound	Diene	Statistical term for formation of diene	Term used in calculation	Numerical value	Diene yield predicted (%)	Diene yield observed (%)
13	3	$(ax + by)^2$	$(ax + by$	0.4129	-	-
	4	$2(ax + by)dy$	-	-	28.53	28.83
	5	$2(ax + by)cx$	-	-	19.95	18.48
	6	d^2y^2	dy	0.3455	-	-
	7	$2cxdy$	-	-	16.69	17.64
	8	c^2x^2	-	-	5.84	6.08

the equilibrium constant K, the ratio $\frac{d}{c}$ has to be evaluated.



$$K = \frac{k_{ct}}{k_{tc}} = \frac{y}{x} \qquad (32)$$

From the results of the thermolysis in solution, Table VI , it can be seen that the yield of 3,4-dimethyl-1,5-hexadiene is basically the same for compounds 9 and 10, confirming that there is little or no difference in the reactivity at the secondary end of the butenyl radicals 1 and 2 at 125°.

Any difference in reactivity at the primary end of the *cis*- and *trans*-butenyl radical should be reflected in the yield of the heptadienes. Thus if the reactivity at the primary end of the *trans*-butenyl radical was greater than that at the primary end of the *cis*-butenyl radical the ratio of 3-methyl-(Z)-1,5-hexadiene to 3,4-dimethyl-1,5-hexadiene starting with (Z,Z,E)-4,4'-azo-2-butene should be smaller than the ratio of 3-methyl-(E)-1,5-hexadiene to 3,4-dimethyl-1,5-hexadiene starting with (E,E,E)-4,4'-azo-2-butene, i.e.

if d > c

then

$$\frac{[5]\text{ from } 9}{[3]\text{ from } 9} < \frac{[4]\text{ from } 10}{[3]\text{ from } 10} \qquad (33)$$

Similarly the ratio of dimethylhexadiene:methylheptadiene: octadiene would be different for the two azo compounds. From the results of the thermolysis of 9 and 10 in dihydronaphthalene, see Table VI, the ratio of 3-methyl-(*Z*)-1,5-heptadiene to 3,4-dimethyl-1,5-hexadiene from 9 is calculated to be 2.36 and the ratio of 3-methyl-(*E*)-1,5-hexadiene to 3,4-dimethyl-1,5-hexadiene from 10 is 2.31. The ratio 3:(4 + 5):(6 + 7 + 8) from 9 is equal to 1.00:2.84:2.53 as compared to 1.00:2.71:2.64 for the same ratio from 10. The almost identical values for these ratios rule out that d is much different from c. A good approximation for the ratio of $\frac{d}{c}$ is then given from the product distribution of the thermolysis of 9 and 10 in solution by

$$\frac{[4]\text{ from } 10}{[3]\text{ from } 10} \div \frac{[5]\text{ from } 9}{[3]\text{ from } 9}$$

which gives $\frac{d}{c} = 0.98$. A value for $\frac{d}{c}$ smaller than 1.00 is not expected and reflects the uncertainties in the product distribution from the thermolysis in solution. Nevertheless, at 125.7° the value for $\frac{d}{c}$ is not much

TABLE XV

Equilibrium constant for the *cis-trans* isomerization of butenyl radicals calculated from the product distribution of (Z,Z,E)-4,4'-azo-2-butene (9) and (E,E,E)-4,4'-azo-2-butene (10)

Compound	Diene yields used	Statistical term	K; $(\frac{dy}{cx})$
9	$\frac{[4]}{[5]}$	$\frac{(ax + by)dy}{(ax + by)cx}$	1.52
	$\frac{[6]^{1/2}}{[8]^{1/2}}$	$\left(\frac{d^2y^2}{c^2x^2}\right)^{1/2}$	1.35
	$\frac{1}{2}\ \frac{[7]}{[8]}$	$\frac{1}{2}\ \frac{2cxdy}{cxcx}$	1.35
	$2\ \frac{[6]}{[7]}$	$2\ \frac{dydy}{2cxdy}$	1.35
10	$\frac{[4]}{[5]}$	$\frac{(ax + by)dy}{(ax + by)cx}$	1.56
	$\frac{[6]^{1/2}}{[8]^{1/2}}$	$\left(\frac{d^2y^2}{c^2x^2}\right)^{1/2}$	1.41
	$2\ \frac{[6]}{[7]}$	$2\ \frac{dydy}{2cxdy}$	1.40

TABLE XV

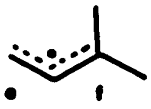
Compound	Diene yields used	Statistical term	K; $(\frac{dy}{cx})$
13	$\frac{[4]}{[3]}$	$\frac{(ax + by)dy}{(ax + by)cx}$	1.56
	$\frac{[6]^{\frac{1}{2}}}{[8]^{\frac{1}{2}}}$	$\left(\frac{d^2y^2}{c^2x^2}\right)^{\frac{1}{2}}$	1.40
	$\frac{1}{2}\ \frac{[7]}{[8]}$	$\frac{1}{2}\ \frac{2cxdy}{cxcx}$	1.45
	$2\ \frac{[6]}{[7]}$	$2\ \frac{dydy}{2cxdy}$	1.35

larger than 1.00, which is in good agreement with the results of Walling and Thaler (3), who observed that the differences in reactivities at the primary end of the two butenyl radicals 1 and 2 decrease with increasing temperature. Thus the value for $\frac{d}{c}$ in their studies was found to be 2.65 at -78.5° and 1.59 at 40° (Table II).

The value for the equilibrium constant K is thus given by the ratios $\frac{dy}{cx}$ shown in Table XV. The value for K calculated from the 3-methyl-(E)-1,5-heptadiene to 3-methyl-(Z)-1,5-heptadiene ratio is preferred because both dienes are formed by combination of the primary end of the butenyl radicals 1 and 2 with the secondary end of other butenyl radicals. Since the value for K is affected by the partial retention of configuration, the mean of the two values calculated for 9 and 10, K = 1.54 will be used for the remainder of the calculations.

From the above values it can also be seen that the reactivity at the primary end of the butenyl radical is greater by a factor of 1.4 than that at the secondary end at 125.7°.

This model can also be applied to the radical formed from the azo compound 16. If the two reactive sites are marked with e and f, e.g.



then the total diene yield is given by

$$z^2(e + f)^2 = 1.0 \tag{34}$$

and since z, the molar fraction of the radical is equal to 1

$$(e + f)^2 = 1.0 \tag{35}$$

Again the statistical terms are associated with the dienes formed and e calculated from the yield of 2,6-dimethyl-2,6-octadiene; the predicted yields for the 3,3,6-trimethyl-1,5-heptadiene and 3,3,4,4-tetramethyl-1,5-hexadiene can then be calculated. The results are shown in Table XVI. Again the agreement of predicted and observed yields is quite good. The reactivity at the primary end of the methylbutenyl radical can be seen to be greater by a factor of 3.2 than that at the tertiary end at 115.0°.

(C) Kinetic Parameters

The activation energy for the thermolysis of 3,3'-azo-1-propene is 36.1 kcal mole^{-1} with an entropy of activation $\Delta S^{\ddagger}$, of 10 e.u. (15). From Table IX it is evident, that only the values of the E_a and $\Delta S^{\ddagger}$ for the thermolysis of $\underset{\sim}{9}$ and $\underset{\sim}{13}$ are comparable to those for the thermolysis of 3,3'-azo-1-propene. In comparison the values for the thermolysis of $\underset{\sim}{10}$ are quite unexpected and no attempt is made to explain this discrepancy until

TABLE XVI

Predicted diene distribution from statistical treatment of the diene composition from the thermolysis of (E)-4,4'-azo-(3-methyl)-2-butene (16)

Diene	Statistical term for formation of diene	Term used in calculation	Numerical value	Diene yield predicted (%)	Diene yield observed (%)
(17)	e^2	e	0.7753	-	-
(18)	2ef	-	-	34.84	33.84
(19)	f^2	-	-	5.05	6.05
(17)	e^2	-	-	56.86	60.11
(18)	2ef	-	-	37.09	33.84
(19)	f^2	f	0.2460	-	-

more information is available. Although steric factors are known to play an important role in the decompositions of azo compounds (51), these alone cannot be responsible for the observed results. The high values for E_a and $\Delta S^{\ddagger}$ for the azobutene $\underset{\sim}{16}$ could possibly be caused by the slow vaporization of the azo compound after injection into the kinetic vessel. A study of this compound will be undertaken in a different vessel and with a different analysis method. The kinetic parameters for the azo compounds are used to calculate the rate constants at 125.7° and the values are shown in Table XI.

It is of interest that the *meso*- and *rac*-isomers of $\underset{\sim}{13}$ fragment at a slightly different rate, demonstrating the importance of steric factors. When the mixture of the two isomers, obtained from the synthesis, was heated to 125.7° for 30 minutes (about three halflives), the composition of the mixture changed from 40% for the isomer moving faster on the ODPN capillary column and 60% of the other to 50% each. Thus the isomer moving faster on the column reacts approximately 1.2 times faster than the other. Differences in rate constants for *meso*- and *rac*- azo compounds have been observed before (52).

(D) Evaluation of the Energy Barrier to *cis-trans* Isomerization of Butenyl Radicals

In section (A) of the discussion a value for the mean half-life of the butenyl radicals under the reaction conditions was obtained. This value in combination with the partial retention of configuration can be used to estimate the energy barrier to *cis-trans* isomerization. Using the yields for 3-methyl-(E)-1,5-hexadiene from **10**, 28.66%, and that for 3-methyl-(Z)-1,5-hexadiene from **9**, 18.59% as the equilibrium values we can calculate that the isomerization of the butenyl radicals from **10** has come to 98.8% completion and that of the butenyl radicals from **9** to 98.8% completion, both of these being minimum values. It can be shown by the *t*-test that the value of 28.52% with the standard deviation 0.06 is not significantly different at the 99% confidence limit from 28.66% with the standard deviation 0.15. Similarly the value 18.42% with the standard deviation 0.17 is not significantly different from 18.59% with standard deviation 0.08. Thus the isomerization could have come to 99.6% completion as a maximum value, above which no differences would have been detected as significant.

Thus we obtain that the mean lifetime of the radicals is approximately six to eight times larger than that for the isomerization, i.e.

$$8\tau_{\frac{1}{2}\mathrm{isom}} \leq \tau_{\frac{1}{2}\mathrm{recomb}} \leq 6\tau_{\frac{1}{2}\mathrm{isom}}$$

The mean lifetime, calculated before, gives for the halflife of the butenyl radicals

$$\tau_{\frac{1}{2}\mathrm{recomb}} = \ln 2 \times t_D = 0.12 \text{ sec}$$

and the limiting values 0.015 sec^{-1} and 0.02 sec^{-1} are obtained for $\tau_{\frac{1}{2}\mathrm{isom}}$.

The halflife of a first order reaction is given by

$$\tau_{\frac{1}{2}} = \frac{\ln 2}{k} \tag{36}$$

where k is the first order rate constant

$$k = \frac{\ln 2}{\tau_{\frac{1}{2}}} \tag{37}$$

The rate constant for the isomerization process k_{isom} can thus be calculated:

$$46.2 \text{ sec}^{-1} > k_{\mathrm{isom}} > 34.6 \text{ sec}^{-1}$$

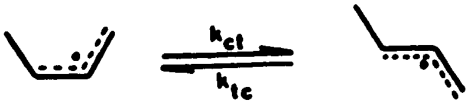
For a process approaching equilibrium

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B$$

the rate constant can be shown (53) to be

$$k_{AB} = k_A + k_B \tag{38}$$

This gives for the *cis-trans* isomerization of the butenyl radicals



$$k_{isom} = k_{ct} + k_{tc} \tag{39}$$

In connection with the equilibrium constant

$$K = \frac{k_{ct}}{k_{tc}} = 1.54$$

values for k_{ct} and k_{tc} can be obtained:

$$28.0 \text{ sec}^{-1} > k_{ct} > 21.0 \text{ sec}^{-1}$$

$$18.2 \text{ sec}^{-1} > k_{tc} > 13.6 \text{ sec}^{-1}$$

The change in free energy in going from the initial state to the transition state (45) is given by the equation

$$\Delta G^{\ddagger} = 2.303RT \text{ Log } \frac{k'T}{h} - 2.303RT \text{ Log } k \tag{40}$$

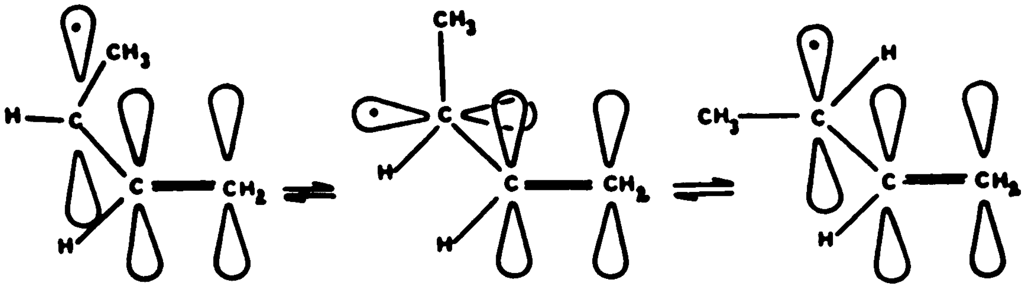
Using equation 40 values for the energy barrier to *cis-trans* isomerization can be calculated and are shown in Table XVII.

TABLE XVII

Energy barrier to *cis-trans* isomerization of the butenyl radicals

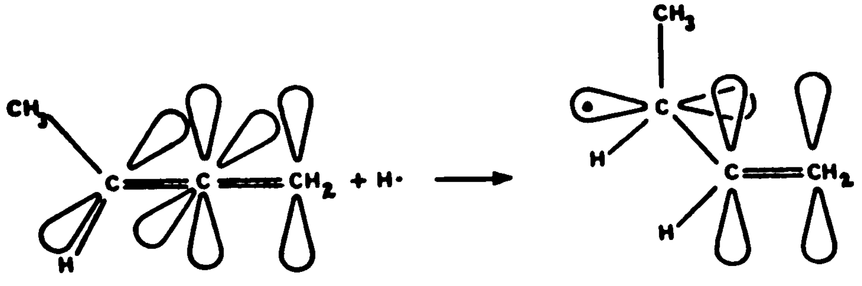
Reaction	$\Delta G^{\ddagger}$ upper limit (kcal mole^{-1})	$\Delta G^{\ddagger}$ lower limit (kcal mole^{-1})
cis → *trans*	21.2	20.9
trans → *cis*	21.5	21.3

A calculation for the barrier to rotation in the butenyl radical may be carried out using existing data in the literature. The transition state for *cis-trans* isomerization is assumed to be a twisted structure 21 with zero overlap between the p orbital on C_3 and the π bond between C_1 and C_2:



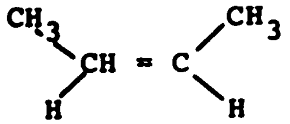
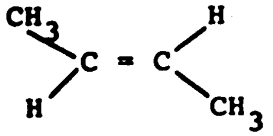
21

A transition state such as 21 can also be thought of as that obtained from the hypothetical addition of a hydrogen atom to C_2 of 1,2-butadiene; again the p-orbitals do not overlap:



The difference between the heat of formation of 21, $(\Delta H_f^\circ)_{21}$ and the heats of formation of 1 and 2 will approximate the barrier to rotation in the allylic radical.

Since the heat of formation of 1,2-butadiene, $\Delta H_f^\circ = 38.77$ kcal mole^{-1} (54), and of the hydrogen atom, $\Delta H_f^\circ = 52.1$ kcal mole^{-1} (55), are known, we can calculate the heat of formation of 21 if we knew the change in enthalpy for the addition of a hydrogen atom to C_2 of 1,2-butadiene. An approximate value for this can be obtained from calculated values for processes such as:

		ΔH°_{298} (a)
$CH_2 = CH_2 + H\cdot$	$\rightarrow CH_3 - CH_2\cdot$	-38.9 kcal mole^{-1}
$CH_3 - CH = CH_2 + H\cdot$	$\rightarrow CH_3 - \dot{C}H - CH_3$	-39.6 kcal mole^{-1}
$CH_3CH_2CH = CH_2 + H\cdot$	$\rightarrow CH_3CH_2\dot{C}H - CH_3$	-39.5 kcal mole^{-1}
 $+ H\cdot$	$\rightarrow CH_3 - CH_2 - \dot{C}HCH_3$	-37.8 kcal mole^{-1}
 $+ H\cdot$	$\rightarrow CH_3CH_2 - \dot{C}H - CH_3$	-36.8 kcal mole^{-1}

Since in all the above cases the newly formed carbon-hydrogen bond is sp^3 rather than sp^2, as in the case of the hydrogen atom addition to 1,2-butadiene, another -6 kcal mole^{-1}, the difference between an sp^3 and an sp^2 carbon-hydrogen bond, have to be added to the above values for ΔH°_{298}. Thus, if the reaction between 1,2-butadiene and hydrogen atoms is exothermic by 42 kcal mole^{-1} we can calculate $(\Delta H^\circ_f)_{\underset{\sim}{21}}$ according to

$$(\Delta H^\circ_f)_{\underset{\sim}{21}} = (\Delta H^\circ_f)_{\text{hydrogen}} + (\Delta H^\circ_f)_{\text{1,2-butadiene}} + \Delta H^\circ_{298}$$

The value for $(\Delta H^\circ_f)_{\underset{\sim}{21}}$ thus obtained is 47.9 kcal mole^{-1}.

(a) calculated from Benson and O'Neal (56) group additive values for heats of formations.

Subtracting from this the value for the calculated heat of formation of the *trans*-butenyl radical $\underset{\sim}{2}$ we obtain for the barrier to *trans-cis* isomerization a value of 17.6 kcal mole^{-1}. The analogous value for *cis-trans* isomerization is 16.6 kcal mole^{-1}.

It can be readily argued that the value of 6 kcal mole^{-1} used to correct for the difference between sp^2 and sp^3 is too large, and that the appropriate value is that fraction of the ethylene C-H bond dissociation energy (104 kcal mole^{-1}) (57) that the 38.9 kcal mole^{-1} of ethane represents relative to the bond dissociation energy of the ethane C-H bond (98 kcal mole^{-1}) (57). Then ΔH°_{298} is 41 kcal mole^{-1} and the calculated barrier is 19 kcal mole^{-1} and 18 kcal mole^{-1}, respectively.

It is interesting to note that hydrogen atom and methyl-radical attack on allene takes place on the terminal carbon atom to form a vinylic radical rather than on the central carbon atom in which case an allyl radical would be formed (58,59):

$$CH_2 = C = CH_2 + H\cdot \longrightarrow CH_2 = \dot{C} - CH_3$$

$$CH_2 = C = CH_2 + H\cdot \not\longrightarrow \dot{C}H_2 - CH = CH_2$$

CONCLUSIONS

(1) The almost identical product distribution from (Z,Z,E)-4,4'-azo-2-butene (9), (E,E,E)-4,4'-azo-2-butene (10) and (E)-3,3'-azo-1-butene suggests that the *cis*- and *trans*-butenyl radicals interconvert in the gas phase at 125.7° at a rate faster than that for combination. Thus the products arise from a "nearly equilibrated" reservoir of butenyl radicals. The results from thermolysis in the gas phase together with those from thermolysis in solution yield a value of 1.54 for the equilibrium constant of the *cis* ⇄ *trans* butenyl radical isomerization.

(2) The kinetic parameters, although as yet not rationalized, in conjunction with the equilibrium constant for the *cis-trans* isomerization of the butenyl radicals enable us to calculate the energy barrier for the *cis-trans* interconversion. The value of 20 kcal mole^{-1} is high as compared to the suggested value of 12 kcal mole^{-1} (38) for the allylic resonance energy, but explains the high degree of stereoselectivity in the reactions of butenyl radicals in solution at and below 40° (3,8).

EXPERIMENTAL

All boiling points are uncorrected.

Gas chromatographs used for purification of starting materials and azo compounds were a Nester Faust Model 850 "Prepkromatic" and a Wilkens Aerograph Autoprep Model A-700.

Analyses of products were carried out on a Perkin Elmer Model 900 gc, using a flame ionization detector directly connected to a Hewlett Packard Model 3370 A electronic integrator in conjunction with a Hewlett Packard Model 7127 A strip chart recorder. Columns used for analysis were 150 ft capillary columns with 0.01 in. inner diameter, wallcoated with β,β'-oxydipropionitrile (ODPN) or silicone gum SE 30.

The ultraviolet spectra were obtained using a Carey Model 14M spectrophotometer.

The nuclear magnetic resonance spectra were obtained using a Varian HR-100 spectrometer.

Exact masses were determined on an A.E.I. MS-9 mass spectrometer. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, University of Alberta (Edmonton).

(A) Reaction Vessel and Air Bath

A 1 l round bottom flask (Pyrex glass) connected to a vacuum line, situated in a well insulated air bath described in detail by Clark (60) was used as the reaction vessel. The total volume was 1200±50 ml. The temperature inside the bath was controlled by a Melabs proportional temperature controller and was measured by a Hewlett Packard Model 2801 A quartz thermometer. The probe (Serial No. S/N 974-21) was calibrated by the National Bureau of Standards. The value of 0.02° was subtracted from the readings, as this is the linearity correction in the 120° region. During a run the temperature could be held constant within ±0.01°C.

The azo compounds were introduced into the reaction vessel through an inlet system which was warmed to 60°C. Immediately after introduction of the compounds dry nitrogen was added to obtain an initial pressure of 100 torr inside the reaction flask. The initial concentration of the azo compound was about 2.4×10^{-5} mole l^{-1}.

(B) Analysis of Products

In each run 0.5 μl of sample was introduced into the injection port, the temperature of which was 70°C. The split ratio in the port was 170:1. Products from compounds $\underset{\sim}{9}$, $\underset{\sim}{10}$ and $\underset{\sim}{13}$ were analyzed on the

ODPN capillary column held at 25°. A typical gas chromatogram is shown in Figure 5. Products from 16 were poorly separated on the ODPN column, better results were obtained from the SE 30 column used at 50°.

The relative retention times of azo compounds 9, 10, 13 and their thermolysis products are given in Table XVIII. The analogous values for compound 16 and its products are given in Table XIX.

(C) Thermolysis in Solution

Azo compound (9) (10 mg) was added to 1,4-dihydronaphthalene (100 µl). The solution was placed in a capillary glass tube with an inner diameter of 0.2 cm, degassed, the tube sealed and heated for 120 min at 122.4°. In the same manner azo compound (9) was thermolyzed in decahydronaphthalene.

Azo compound 10 was treated in the manner described above for compound 9.

The product distribution from 9 and 10 are shown in Table VI.

(D) Kinetics

The kinetic vessel used is shown diagramatically in Figure 7. Samples were injected as neat liquids. Values were taken between 20 and 80% completion (see Appendix B).

TABLE XVIII

Relative retention times of (Z,Z,E)-4,4'-azo-2-butene (9), (E,E,E)-4,4'-azo-2-butene (10) and (E)-3,3'-azo-1-butene (13) and their thermolysis products

Column	Column Temp. (°C)	Helium flow rate (ml min^{-1})	Compound	Relative retention time [(Z,Z)-2,6-octadiene = 1.00]
150 ft ODPN	80	1.0	(9)	3.32
capillary	80	1.0	(10)	3.16
	80	1.0	(13)	1.18[a]
	40	1.0	(13)	1.44[a]
	25	1.0	(3)	0.49
	25	1.0	(4)	0.58
	25	1.0	(5)	0.65
	25	1.0	(6)	0.82
	25	1.0	(7)	0.89
	25	1.0	(8)	1.00

[a] Compounds (13) and (3) are mixtures of *meso* and *rac*, retention time is given for the faster moving compound.

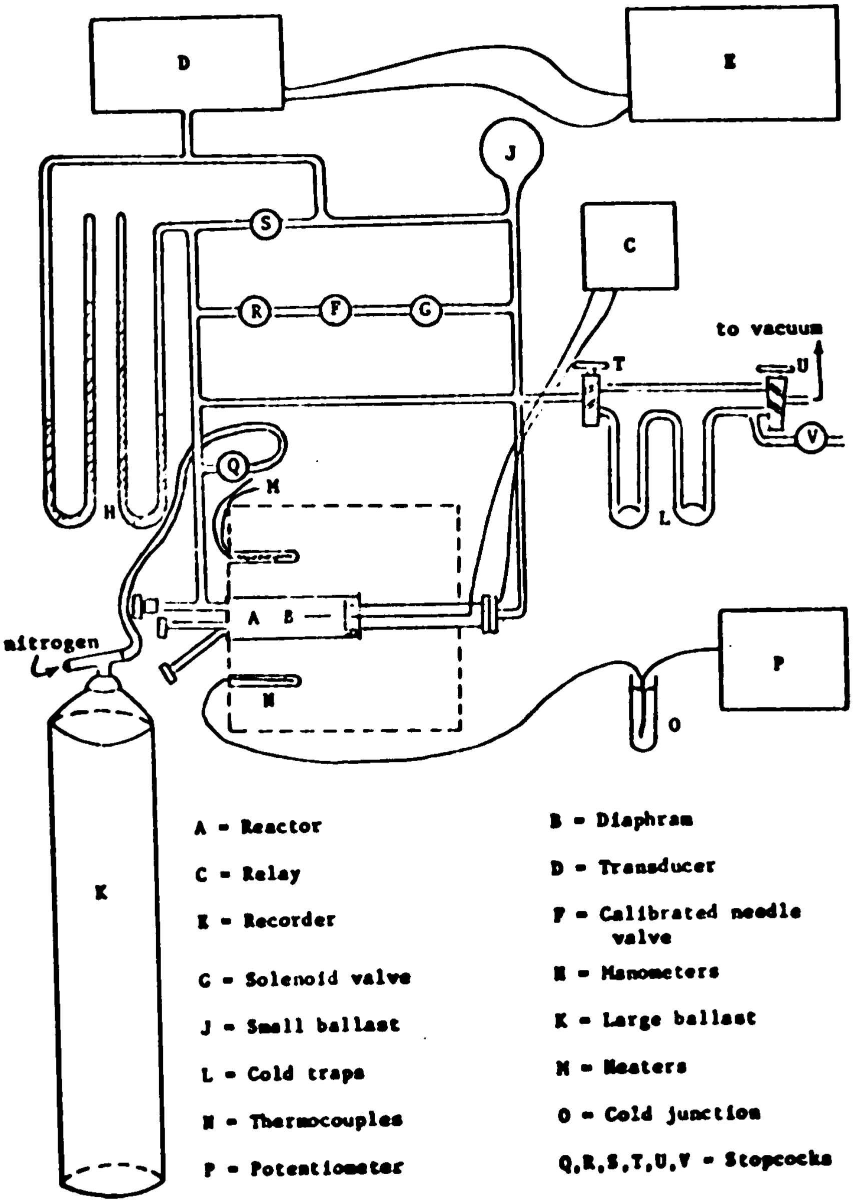
TABLE XIX

Relative retention times for (E)-4,4'-azo-(3-methyl)-2-butene (16) and its thermolysis products

Column	Column temp. (°C)	Helium flow rate (ml min^{-1})	Compound	Relative retention time (3,3,4,4-tetramethyl-1,5-hexadiene = 1.00)
150 ft SE 30 capillary	50	1.0	(16)	5.30
	50	1.0	(17)	0.52
	50	1.0	(18)	0.66
	50	1.0	(19)	1.00

FIGURE 7

Schematic diagram of the apparatus used for the kinetic studies



A = Reactor
C = Relay
E = Recorder
G = Solenoid valve
J = Small ballast
L = Cold traps
N = Thermocouples
P = Potentiometer

B = Diaphram
D = Transducer
F = Calibrated needle valve
H = Manometers
K = Large ballast
M = Heaters
O = Cold junction
Q,R,S,T,U,V = Stopcocks

(E) Preparations

(Z)-2-Buten-1-ol. The procedure used was essentially that of Hatch and Nesbitt (39). Lindlar catalyst (8.0 g) was added to a solution of 2-butyn-1-ol (25.0 g, 0.357 mole) in methanol (290 ml). The mixture was shaken with hydrogen (0.357 mole) at a pressure of 30 psi. The addition was complete in 1.5 hours. The solution was filtered and the methanol removed by distillation through a 30 cm Vigreux column. After the methanol had distilled off, the pressure was reduced to 60 torr and the fraction boiling between 62° and 65° was collected. Yield: 24.0 g (93%). A second run gave 25.0 g (97%). During the hydrogenation minor amounts of butanol and (E)-2-buten-1-ol were formed. The combined products therefore had to be further purified. Two successive purifications by preparative gc, using a 12 ft column with 0.75 in. inner diameter of 20% ODPN on Chromosorb W support, gave 25.0 gms. This was observed to be more than 99.9% pure. The column temperature was 100°, the helium flow rate 500 ml min^{-1}. The retention time of (Z)-2-buten-1-ol from air under these conditions was 18.0 minutes. The nmr spectrum showed a multiplet at 4.40τ, a doublet at 5.82τ, another doublet at 8.35τ and a singlet at 6.30τ of intensity 2:2:3:1.

1-Chloro-(Z)-2-butene. The procedure was essentially that of Hatch and Nesbitt (39). A mixture of (*Z*)-2-buten-1-ol (25.0 g, 0.347 mole) and pyridine (9.0 g, 0.114 mole) was added slowly with stirring and ice cooling to phosphorous trichloride (16.0 g, 0.116 mole). The product was washed successively with water, saturated sodium carbonate solution and water again. After drying over anhydrous potassium carbonate, distillation gave 21.0 g (67%) of 1-chloro-(*Z*)-2-butene along with 5% 3-chloro-1-butene, bp 80°. Removal of this impurity was not necessary, since the latter does not interfere in the next step. The nmr spectrum displayed a multiplet at 4.34τ, a doublet at 5.91τ and another doublet at 8.30τ of relative intensities 2:2:3.

Diethyl N,N'-di-((Z)-2-bu'en-1-yl)-bicarbamate (**11**). In a 1 *l* three necked flask equipped with mechanical stirrer, dropping funnel and nitrogen inlet tube, a suspension of DEHD (20.4 g, 0.116 mole) in dry DME (200 ml) (distilled immediately before use from lithium aluminum hydride) was stirred at room temperature. After 53.6% sodium hydride (10.4 g, 0.232 mole) was added in small portions under a nitrogen atmosphere, the mixture was stirred for three hours and a solution of 1-chloro-(*Z*)-2-butene (21.0 g, 0.232 mole) in dry DME (180 ml) was added slowly. A solution of sodium iodide (3.0 g, 0.02 mole) in dry DME (25 ml) was dropped into the suspension at a fast rate and the resulting mixture stirred under nitrogen overnight. Excess water was then added and the solution extracted four times with benzene. The combined benzene extracts were washed twice with a saturated sodium bisulfite solution, then twice with water. After drying over magnesium sulfate the benzene was removed under reduced pressure and the residue distilled under vacuum to yield 22.0 g (66%) of product with a bp of 102° at 0.4 torr. The nmr spectrum showed a multiplet at 4.40τ, a doublet at 5.90τ and a doublet at 8.35τ along with a quartet at 5.80τ and a triplet at 8.75τ for the ethylester function.

(Z,Z)-4,4'-Hydrazo-2-butene (12). In a 200 ml three necked flask equipped with a reflux condenser and nitrogen inlet tube, were placed potassium hydroxide (11.2 g, 0.2 mole), 95% ethanol (70 ml) and diethyl N,N'-di-((Z)-2-buten-1-yl)-bicarbamate (14.2 g, 0.05 mole) and the mixture refluxed under nitrogen for 15 hours. The precipitated potassium carbonate was filtered off and the solution concentrated under vacuum. Water was added and the solution extracted four times with ether. The combined ether extracts were dried over magnesium sulfate, the ether evaporated through a 30 cm Vigreux column and the residue distilled under vacuum. Obtained were 5.4 g (77%) of product, bp 37° at 0.7 torr. The nmr spectrum showed a multiplet at 4.40τ, a doublet at 6.50τ and a doublet at 8.30τ with the hydrazo protons at 6.40τ.

(a) (Z,Z,E)-4,4'-Azo-2-butene (9). To a well stirred suspension of red mercuric oxide (15.0 g, 0.062 mole) and sodium sulfate (15.0 g, 0.156 mole) in anhydrous ether (100 ml) there was added slowly, with ice cooling, a solution of (Z,Z,)-4,4'-hydrazo-2-butene (3.0 g, 0.02 mole) in anhydrous ether (150 ml). The mixture was stirred at 0° for 4.5 hours, after which it was allowed to warm to room temperature. The ether was removed by distillation through a 30 cm Vigreux column. Volatile materials in the residue were vapor transferred on a vacuum line and the distillate further purified by preparative gc. Good separation from all impurities in a reasonable time was obtained at 80° on a 10 ft column of 10% Ucon-insoluble on Fluoropak support. The product was finally trap to trap distilled under high vacuum. Obtained were 1.6 g (54%); the nmr spectrum is shown in Figure 1. The uv spectrum has a λ_{max} at 355 mμ (ε = 40 in methanol). Exact mass 138.1156; calculated for $C_8H_{14}N_2$ 138.1157.

Anal. Calcd. for $C_8H_{14}N_2$: C, 69.57; H, 10.14; N, 20.29

Found: C, 69.47 H, 10.05 N, 19.99

(E)-2-Buten-1-ol was obtained from two successive gc purifications of a commercially available mixture of (Z)- and (E)-2-buten-1-ol. The same column and conditions as described for the purification of (Z)-2-buten-1-ol were used. The retention time was 15.6 min from air. The nmr spectrum showed three multiplets at 4.33τ, 5.94τ and at 8.30τ respectively with the hydroxyl proton at 6.88τ of the relative intensities 2:2:3:1.

1-Chloro-(E)-2-butene. The compound was prepared in the manner described above for the *cis* isomer except that (E)-2-buten-1-ol (27.0 g, 0.375 mole) in pyridine (9.5 g, 0.12 mole) was added to phosphorous trichloride (17.5 g, 0.125 mole). Yield: 23.0 g (68%), bp 85°. The nmr spectrum showed a multiplet at 4.25τ, a doublet at 4.96τ and another multiplet at 8.28τ of relative intensities 2:2:3.

Diethyl N,N'-di-((E)-2-buten-1-yl)-bicarbamate was prepared in the manner described above for compound 12 except that 53.6% sodium hydride (11.4 g, 0.255 mole) was added to DEHD (22.4 g, 0.128 mole) in dry DME (200 ml) followed by the slow addition of 1-chloro-(E)-2-butene (23.0 g, 0.255 mole) in DME (180 ml). Finally a solution of sodium iodide (3.0 g, 0.02 mole) in dry DME (25 ml) was added, the mixture stirred overnight and then worked up as described above for 12 . Yield:

22.0 g (61%), bp 104° at 0.4 torr. The nmr spectrum showed a multiplet at 4.40τ, a doublet at 6.04τ and a multiplet at 8.33τ along with a quartet at 5.81τ and a triplet at 8.75τ for the ethyl ester group.

(E,E)-4,4'-Hydrazo-2-butene was prepared in the manner described above for the (Z,Z)-4,4'-hydrazo-2-butene except that a mixture of diethyl N,N'-di-((E)-2-buten-1-yl)-bicarbamate (14.2 g, 0.05 mole), and potassium hydroxide (11.2 g, 0.2 mole) in 95% ethanol (70 ml) was refluxed for 15 hours. Obtained were 5.2 g (74%), bp 40° at 0.5 torr. The nmr spectrum showed three multiplets at 4.50τ, 6.70τ and a triplet at 8.33τ with the hydrazo protons at 6.80τ.

(b) (E,E,E)-4,4'-Azo-2-butene (10) was prepared in the same manner as the (Z,Z,E) isomer 9 except that a solution of (E,E)-4,4'-hydrazo-2-butene (3.0 g, 0.02 mole) in anhydrous ether (150 ml) was added to a suspension of mercuric oxide (15.0 g, 0.062 mole) and sodium sulfate (15.0 g, 0.156 mole) in anhydrous ether (100 ml). Yield: 1.7 g (57%); the nmr spectrum is shown in Figure 2. The uv spectrum has a λ_{max} at 356 mμ (ε = 40 in methanol). Exact mass 138.1156; calculated for $C_8H_{14}N_2$ 138.1157.

Anal. Calcd. for $C_8H_{14}N_2$:	C, 69.57;	H, 10.15;	N, 20.29
Found:	C, 69.48;	H, 10.12;	N, 19.95.

(c) (*E*)-3,3'-Azo-1-butene (**13**). A mixture of 85% hydrazine hydrate (5.9 g, 0.1 mole), 50% ethanol (80 ml), potassium carbonate (20.0 g, 0.146 mole) and 3-chloro-1-butene (18.1 g, 0.2 mole) was stirred for 48 hours under nitrogen. The solution was filtered and the filtrate extracted five times with 50 ml portions of ether. The combined ether extracts were dried over sodium sulfate and concentrated to a volume of 100 ml, which was added to an ice-cooled well stirred suspension of red mercuric oxide (25.0 g, 0.1 mole), sodium sulfate (25.0 g, 0.26 mole) in anhydrous ether (160 ml). After six hours the mixture was allowed to warm to room temperature. The solution was filtered and the ether removed by distillation through a 30 cm Vigreux column.

Analysis of the residue by gc on the ODPN capillary column at 40° indicated the presence of at least 12 compounds. When the mixture was, however, injected into a hot injection port (250°), the typical pattern of the dienes **3**, **4**, **5**, **6**, **7** and **8** was observed and at the same time two peaks decreased in intensity. The retention times of these, 1.44 and 1.48 relative to (*Z*,*Z*)-2,6-octadiene, were markedly different from those of azo compounds **9** and **10**. The two compounds, which were present in the mixture to about 5%, were separated from the other components by preparative gc on a 12 ft ODPN column at 70° and then distilled under high vacuum. A mixture, 0.4 g (3%), of *meso* and *rac* (E)-3,3'-azo-1-butene was obtained. Separation of the isomers was not possible by preparative gc. From analysis on the ODPN capillary column it appears that the slower moving component constitutes 60% of the mixture. The nmr spectrum is shown in Figure 3. The uv spectrum has a λ_{max} at 358 mμ (ε = 28 in methanol). Exact mass 138.1157; calculated for $C_8H_{14}N_2$, 138.1157.

Anal. Calcd. for $C_8H_{14}N_2$: C, 69.57; H, 10.15; N, 20.29
Found: C, 69.59; H, 10.03; N, 20.24.

3-Methyl-2-buten-1-ol. A solution of methyl senecioate (51.0 g, 0.45 mole) in anhydrous ether (150 ml) was added slowly to a slurry of lithium aluminum hydride (9.1 g, 0.24 mole) in anhydrous ether (150 ml) and the mixture stirred at room temperature for three hours. The excess hydride was hydrolyzed with water and the metal hydroxides dissolved in 15% sulfuric acid. The organic layer was separated, dried over sodium sulfate and the ether removed on the rotary evaporator. Distillation gave 30.0 g (78%), bp 134°, (lit. value 140° (61)).

1-Chloro-3-methyl-2-butene. This chloride was prepared in the manner described above for the 1-chloro-2-butenes except that 3-methyl-2-buten-1-ol (30.0 g, 0.349 mole) in pyridine (12.0 g, 0.154 mole) was added to phosphorous trichloride (16.0 g, 0.116 mole). Obtained were 26.0 g (71%) of product, bp 106-108°.

Diethyl N,N'-di-(3-methyl-2-buten-1-yl)-bicarbamate (14). The bicarbamate 14 was prepared in the manner described for 11 except that 53.6% sodium hydride (13.6 g, 0.303 mole) was added to DEHD (26.6 g, 0.151 mole) in dry DME (180 ml) followed by the slow addition of 1-chloro-3-methyl-2-butene (26.0 g, 0.303 mole) in dry DME (150 ml). Finally a solution of sodium iodide (3.0 g, 0.02 mole) in dry DME (25 ml) was added, the mixture stirred overnight and worked up as described above for 11 . Yield: 20.0 g (46%), bp 112-114° at 0.4 torr.

4,4'-Hydrazo-(3-methyl)-2-butene (15). The hydrazo compound was prepared in the manner described for the 4,4'-hydrazo-2-butenes, except that the bicarbamate 14 (10.0 g, 0.032 mole) was refluxed along with potassium hydroxide (7.2 g, 0.128 mole) in 95% ethanol (70 ml) for 15 hrs. The product 15 was used without further purification for the mercuric oxide oxidation.

(d) *(E)-4,4'-Azo-(3-methyl)-2-butene (16)*. The azo compound was prepared in the manner described above for the azo-2-butenes except that 4,4'-hydrazo-(3-methyl-2-butenes (3.7 g, 0.022 mole) in anhydrous ether (160 ml) was added to a suspension of mercuric oxide (20.0 g, 0.083 mole) and sodium sulfate (20.0 g, 0.208 mole) in anhydrous ether (140 ml). Purification by gc on a 5 ft Ucon-insoluble on Fluoropak support column yielded 1.4 g (38%) of **16**. The column temperature was 80°, the helium flow rate 200 ml min^{-1}; the retention time under these conditions was 28.0 min free from air. The nmr spectrum is shown in Figure 4; the uv spectrum had a λ_{max} at 362 mμ (ε = 42 in methanol). Exact mass 166.1472; calculated for $C_{10}H_{18}N_2$ 166.1470. Retention times of the azo compounds on preparative gc columns are given in Table XX.

Anal. Calcd. for $C_{10}H_{18}N_2$:	C, 72.29;	H, 10.84;	N, 16.87
Found:	C, 71.17;	H, 11.05;	N, 16.40

F. Control Experiments

(i) Samples of azo compounds **9**, **10** and **13** were recovered after the thermolysis had proceeded to between 20 and 60% completion and analyzed by nmr and gc. The chemical shift of the allylic protons in **9** is different from that of the allylic protons in **10** by 0.17τ. The azo compounds are also cleanly separated by gc on the ODPN capillary column. Neither nmr nor gc gave any indication that the starting azo compound had isomerized prior to fragmentation.

(ii) Azo compound 9 (30 mg) was heated to 148° in the presence of a mixture of the octadienes (5 mg) with the composition 6 : 44%, 7 : 44.5% and 8 11.5%. Under the same conditions azo compound 9 (30 mg) gave the octadienes in the following proportions: 6 : 27.1%, 7 : 44.4% and 8 : 28.5%. From these results the octadiene distribution for the thermolysis of 9 in the presence of the octadienes can be calculated to 6 : 33.5%, 7 : 44.4% and 8 : 22.1% under the condition that the olefins do not isomerize during the reaction. The octadiene distribution found was 6 : 33.1%, 7 : 44.1% and 8 : 22.8%.

(iii) Thermolyses of 9 , 10 and 13 were also carried out at 125.5° in 25 ml cylindrical pyrex glass vessels without the addition of nitrogen. The product distributions were not significantly different from those obtained from the thermolysis in the 1200 ml vessel with nitrogen added and are shown in Table X.

(iv) The azo compound 16 was heated at 115.0° for 30 min. The product distribution was found to be 17 : 60.13%, 18 : 33.81% and 19 : 6.06% which is not significantly different from the distribution when 16 was heated for 3 hours (see Table VII).

(v) When a mixture of the dienes in the proportion **17** : **18** : **19** = 62.3:32.8:4.9 was heated to 180° for 2 hours rearrangement was observed. Diene **19** underwent the Cope rearrangement to yield **17** . The product distribution was found to be **17** : 64.7%, **18** : 32.6% and **19** : 2.7%.

(vi) The reaction products were trapped out with liquid nitrogen and immediately analyzed by gc. In a control run the products from thermolysis were analyzed directly by a gc attached to the vacuum line. A Gow-Mac Model TR-2-B,W thermal conductivity cell was used with a Gow-Mac Model 40-50 power supply in conjunction with a Hewlett Packard Model 7127 A strip chart recorder equipped with a Disc Integrator. Although the diene products could not be separated on the column used (12 ft column with 1/8 in. inner diameter, the support was 10% ODPN on Chromosorb W), it could be seen that less than 0.3% butenes were formed during the reaction. Thus little or none of the low boiling butenes are lost during the transferral of products from the vacuum line.

TABLE XX

Retention times for (*Z*,*Z*,*E*)-4,4'-azo-2-butene (**9**), (*E*,*E*,*E*)-4,4'-azo-2-butene (**10**), (*E*)-3,3'-azo-1-butene (**13**) and (*E*)-4,4'-azo-(3-methyl)-2-butene (**16**) on preparative gc columns

Column	Temp. (°C)	Helium flow rate (ml min^{-1})	Compound	Retention time from air (min)
10 ft Ucon-insoluble on Fluoropak	80°	300	**9**	19.5
			10	16.8
12 ft ODPN on Chromosorb W	70°	500	**13**	31.0
5 ft Ucon-insoluble on Fluoropak	60°	300	**16**	28.0

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VITA

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In 1968 he married Claudia T. Ritzel and is presently an expectant father.

APPENDIX A

Product distribution from azo compounds 9, 10, 13 and 16

Product Distribution from Thermolysis of 9 at 125.70±0.01°

Run	3	4	5	6	7	8
I	17.06	28.39	18.72	11.75	17.54	6.55
II	16.98	28.27	18.68	11.83	17.64	6.60
III	16.64	28.23	18.70	11.97	17.80	6.66
IV	17.20	28.36	18.53	11.83	17.60	6.47
V	17.33	28.38	18.59	11.80	17.47	6.43
VI	17.13	28.31	18.54	11.88	17.63	6.51
VII	17.02	28.26	18.52	11.96	17.72	6.53
VIII	16.98	28.33	18.54	11.95	17.66	6.53
IX	17.01	28.38	18.57	11.94	17.66	6.44
X	16.91	28.27	18.55	11.97	17.76	6.54
XI	16.66	28.22	18.50	12.11	17.87	6.63
Mean	16.99	28.31	18.59	11.91	17.67	6.54
Standard deviation	0.21	0.06	0.08	0.03	0.11	0.07

Product Distribution from Thermolysis of 10 at 125.70±0.01°

Run	3	4	5	6	7	8
II	17.31	28.57	18.50	12.05	17.48	6.08
II	17.60	28.80	18.54	11.90	17.14	6.03
III	17.32	28.52	18.15	12.24	17.60	6.17
IV	17.15	28.51	18.47	12.38	17.37	6.12
V	17.31	28.85	18.27	12.19	17.31	6.07
VI	17.57	28.92	18.32	11.98	17.20	6.02
VII	17.06	28.55	18.64	12.18	17.45	6.12
VIII	16.95	28.66	18.22	12.30	17.70	6.17
IX	16.81	28.59	18.20	12.42	17.75	6.22
X	16.87	28.64	18.27	12.34	17.69	6.19
Mean	17.20	28.66	18.36	12.20	17.47	6.12
Standard Deviation	0.28	0.15	0.17	(0.17)	(0.21)	(0.06)

Product Distribution from Thermolysis of 13 at 125.70±0.01°

Run	3	4	5	6	7	8
I	17.03	28.86	18.52	11.91	17.64	6.06
II	17.32	28.87	18.49	11.83	17.45	6.03
III	17.03	28.75	18.45	11.99	17.72	6.06
IV	17.18	28.70	18.51	11.90	17.56	6.16
V	16.91	28.82	18.50	11.97	17.72	6.07
VI	16.78	28.74	18.59	11.98	17.79	6.13
VII	16.75	28.82	18.42	12.07	17.88	6.07
VIII	16.85	28.78	18.50	11.98	17.72	6.18
IX	17.28	28.98	18.34	11.90	17.48	6.03
X	17.15	28.86	18.41	11.94	17.55	6.09
XI	17.21	28.84	18.46	11.88	17.53	6.07
XII	17.07	28.88	18.54	11.88	17.63	6.00
Mean	17.05	28.83	18.48	11.94	17.64	6.08
Standard Deviation	0.19	0.08	0.07	0.07	0.13	0.01

Product Distribution from Thermolysis of 16 at 125.70±0.01°

Run	17	18	19
I	60.28	33.73	5.98
II	59.77	34.20	6.03
III	60.21	33.70	6.09
IV	59.99	33.89	6.12
V	60.14	33.86	6.00
VI	60.25	33.67	6.08
Mean	60.11	33.84	6.05
Standard deviation	0.19	0.20	0.06

APPENDIX B

Values of Log(E_∞ - E_t) and plots of Log(E_∞ - E_t) versus time and evaluation of the activation energies and Log A factors for the thermolyses of $\underset{\sim}{9}$, $\underset{\sim}{10}$, $\underset{\sim}{13}$ and $\underset{\sim}{16}$.

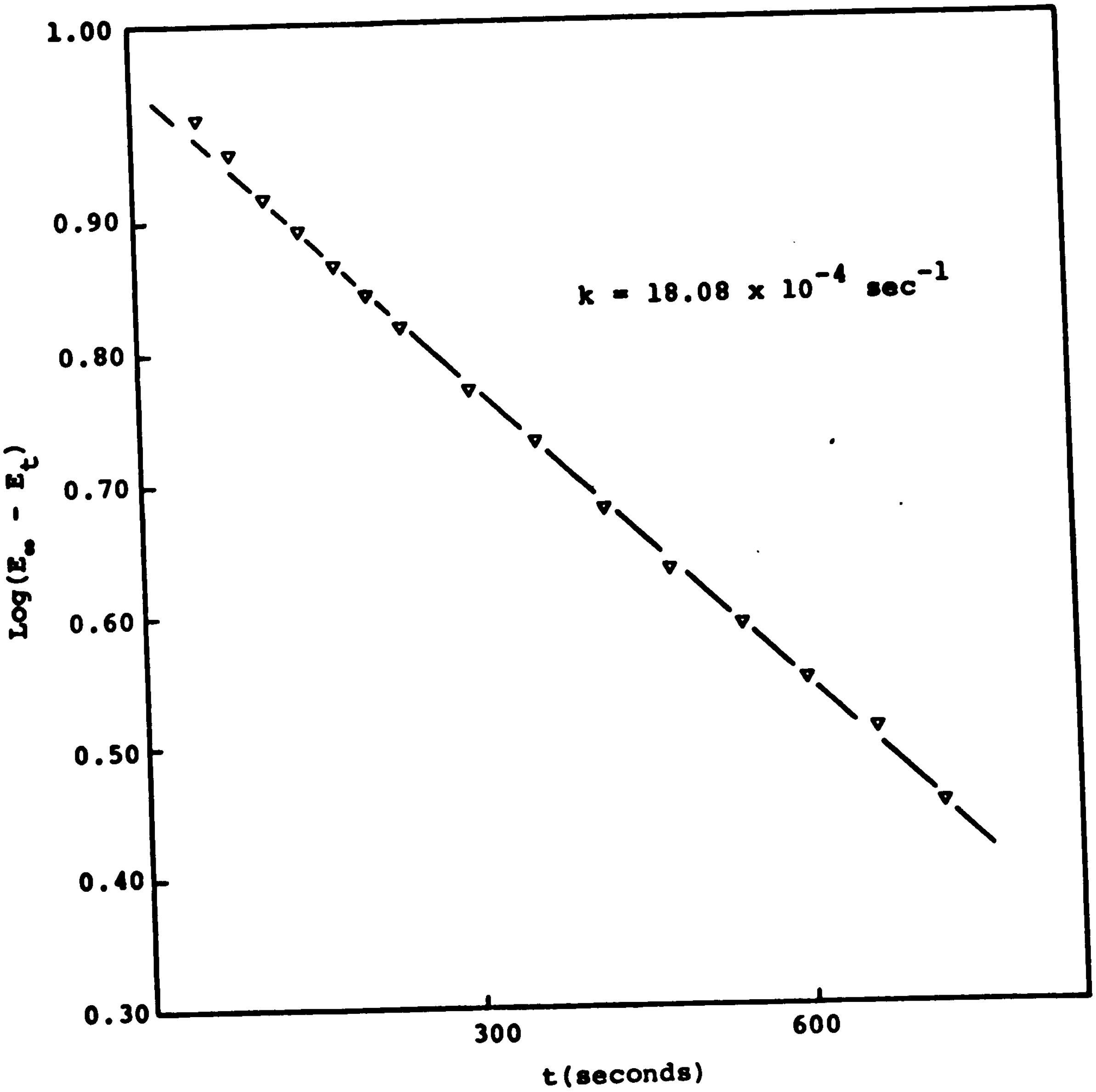
Values taken off the chart record for the evaluation of the rate constant for the thermolysis of **9** at 140.3°[a]

Time (sec)	E_t (cm)	$\mathrm{Log}(E_\infty - E_t)$
90	11.30	0.79239
120	11.50	0.77815
150	11.65	0.76716
180	11.80	0.75587
210	11.90	0.74819
240	12.00	0.74036
270	12.20	0.72428
300	12.35	0.71181
360	12.60	0.69020
420	12.85	0.66745
480	13.05	0.64836
540	13.25	0.62839
600	13.55	0.59660
660	13.70	0.57978
720	13.90	0.55630
780	14.00	0.54407
840	14.20	0.51851
900	14.40	0.49136
960	14.55	0.46982
1020	14.60	0.46240
1080	14.70	0.44716
1140	14.85	0.42325
1200	15.00	0.39794
1260	15.10	0.38021
1320	15.20	0.36173
1380	15.30	0.34242
1440	15.40	0.32222
1500	15.50	0.30103
∞	17.50	

[a] see Figure 5.

Points taken off the chart record for the evaluation of the rate constant of the thermolysis of **9** at 148.2°

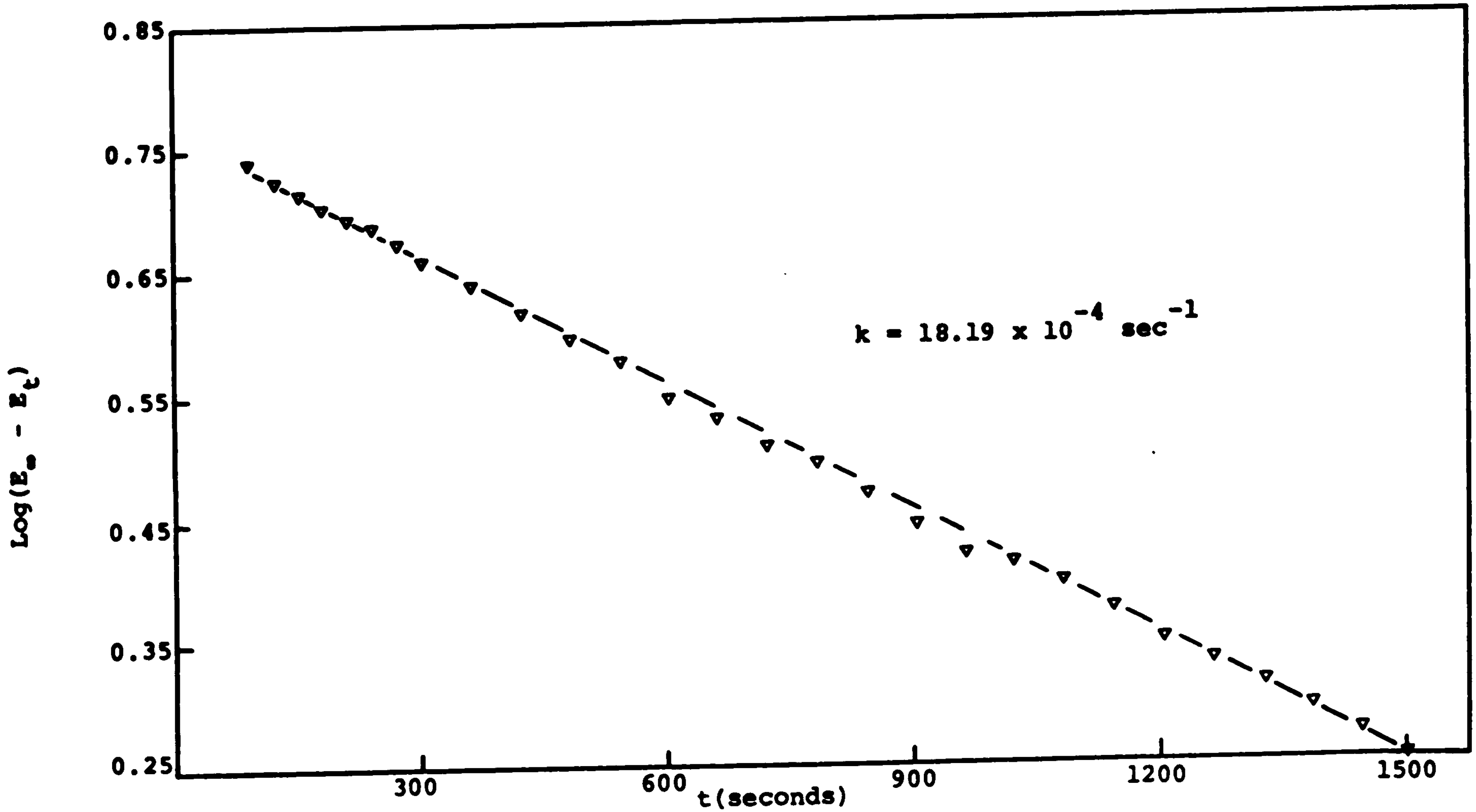
Time (sec)	E_t	$\log(E_\infty - E_t)$
120	13.60	0.98453
150	14.20	0.95665
180	14.85	0.92428
210	15.35	0.89762
240	15.80	0.87216
270	16.20	0.84819
300	16.60	0.82271
360	17.30	0.77452
420	17.80	0.73640
480	18.45	0.68124
540	18.95	0.63347
600	19.35	0.59106
660	19.70	0.55023
720	20.00	0.51188
780	20.40	0.45485
∞	23.25	-



Plot of $\text{Log}(E_\infty - E_t)$ versus time for the thermolysis of $\underset{\sim}{9}$ at 148.2°.

Points taken off the chart record for the evaluation of the rate constant for the thermolysis of $\underset{\sim}{9}$ at 148.6°

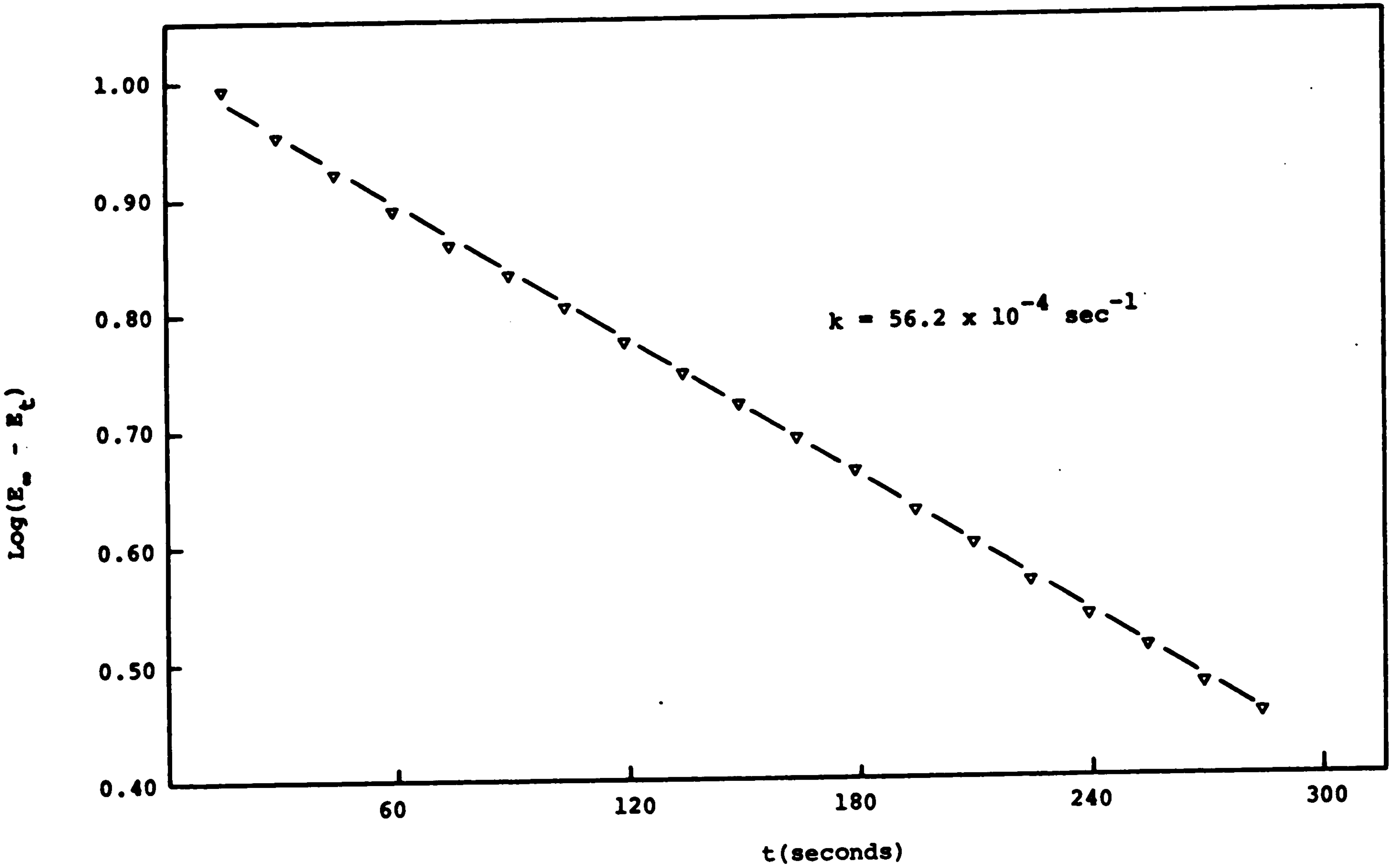
Time (sec)	E_t (cm)	$\text{Log}(E_\infty - E_t)$
90	13.30	0.90580
120	13.70	0.88366
150	14.10	0.86034
180	14.55	0.83251
210	15.00	0.80277
240	15.35	0.77815
270	15.65	0.75587
300	15.90	0.73640
330	16.20	0.71181
360	16.50	0.68574
390	16.75	0.66276
420	16.95	0.64345
480	17.45	0.59106
540	17.85	0.54407
600	18.20	0.49831
660	18.50	0.45485
720	18.80	0.40654
780	19.10	0.35218
840	19.30	0.31175
900	19.50	0.26717
∞	21.35	-



Plot of $\mathrm{Log}(E_\infty - E_t)$ versus time for the thermolysis of $\underset{\sim}{9}$ at 148.6°.

Points taken off the chart record for the evaluation of the rate constant for the thermolysis of **9** at 159.8°

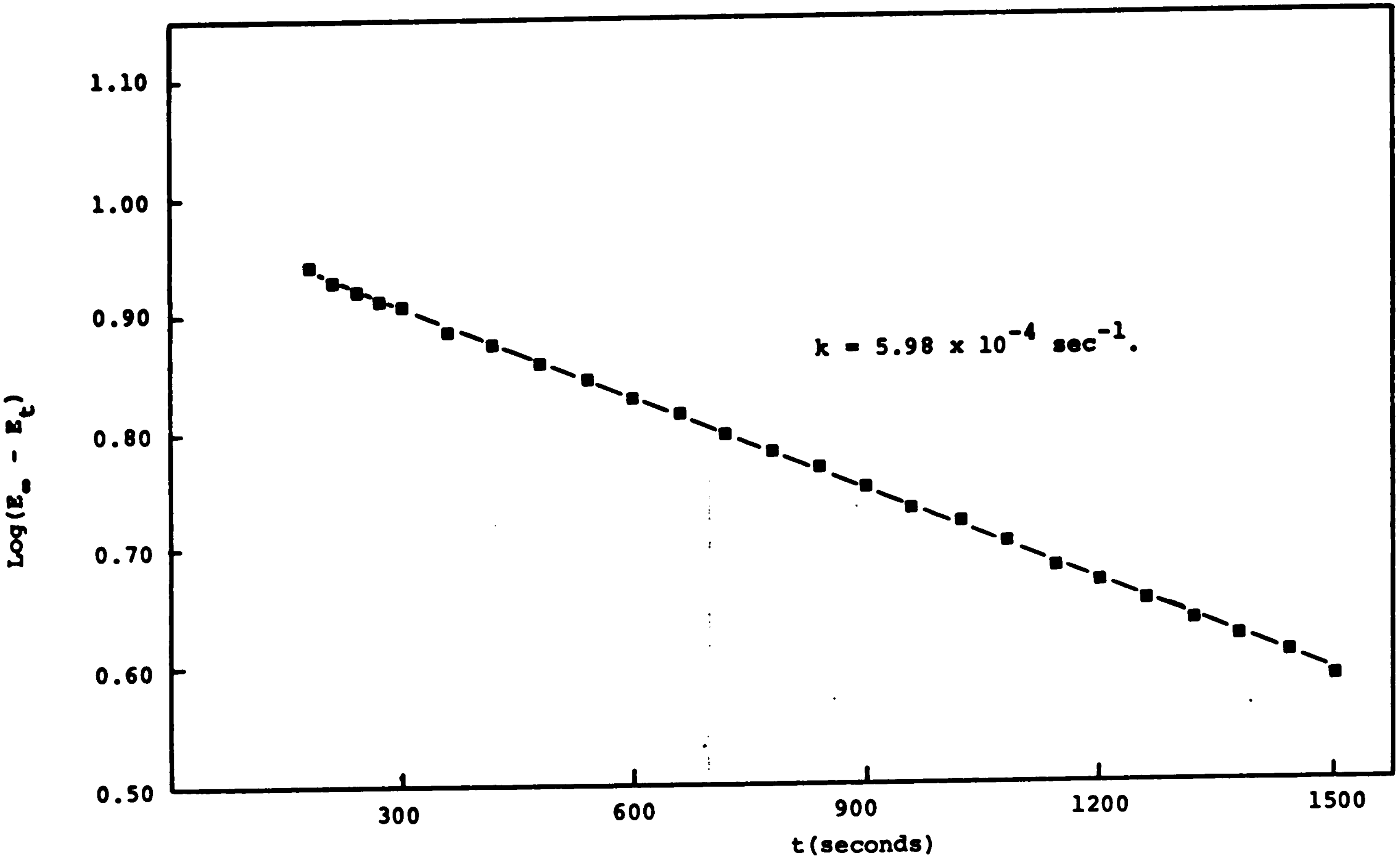
Time (sec)	E_t (cm)	$\mathrm{Log}(E_\infty - E_t)$
24	14.25	0.99343
36	15.10	0.95424
48	15.75	0.92168
60	16.35	0.88930
72	16.85	0.86034
84	17.30	0.83251
96	17.75	0.80285
108	18.15	0.77452
120	18.50	0.74819
132	18.90	0.71601
144	19.20	0.69020
156	19.50	0.66276
168	19.80	0.63347
180	20.10	0.60206
192	20.40	0.56820
204	20.65	0.53782
216	20.85	0.51188
228	21.05	0.48430
240	21.20	0.46240
∞	24.10	-



Plot of Log(E_∞ - E_t) versus time for the thermolysis of **9** at 159.8°.

Values taken off the chart record for the evaluation of the rate constant for the thermolysis of 10 at 140.5°

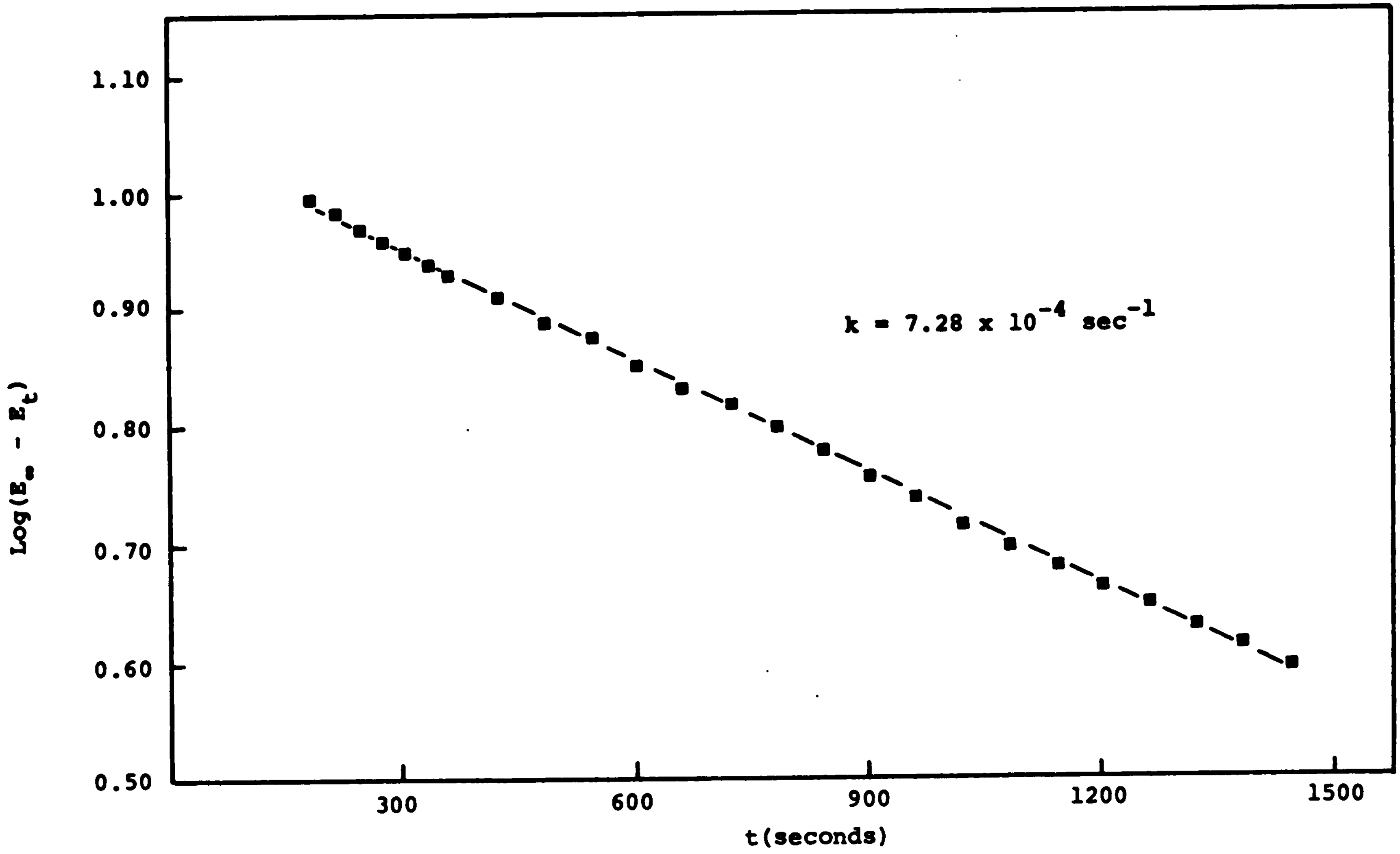
Time (sec)	E_t (cm)	Log($E_\infty - E_t$)
1180	12.85	0.94201
210	13.10	0.92942
240	13.25	0.92168
270	13.40	0.91381
300	13.50	0.90848
360	13.90	0.88649
420	14.10	0.87506
480	14.40	0.85733
540	14.60	0.84510
600	14.85	0.82931
660	15.05	0.81624
720	15.30	0.79934
780	15.50	0.78533
840	15.70	0.77085
900	15.95	0.75205
960	16.15	0.73640
1020	16.30	0.72428
1080	16.50	0.70757
1140	16.75	0.68574
1200	16.90	0.67210
1260	17.05	0.65801
1320	17.25	0.63849
1380	17.35	0.62839
1440	17.50	0.61278
1500	17.70	0.59106
∞	21.60	-



Plot of Log(E_∞ - E_t) versus time for the thermolysis of 10 at 140.5°.

Values taken off the chart record for the evaluation of the rate constant for the thermolysis of 10 at 141.6°

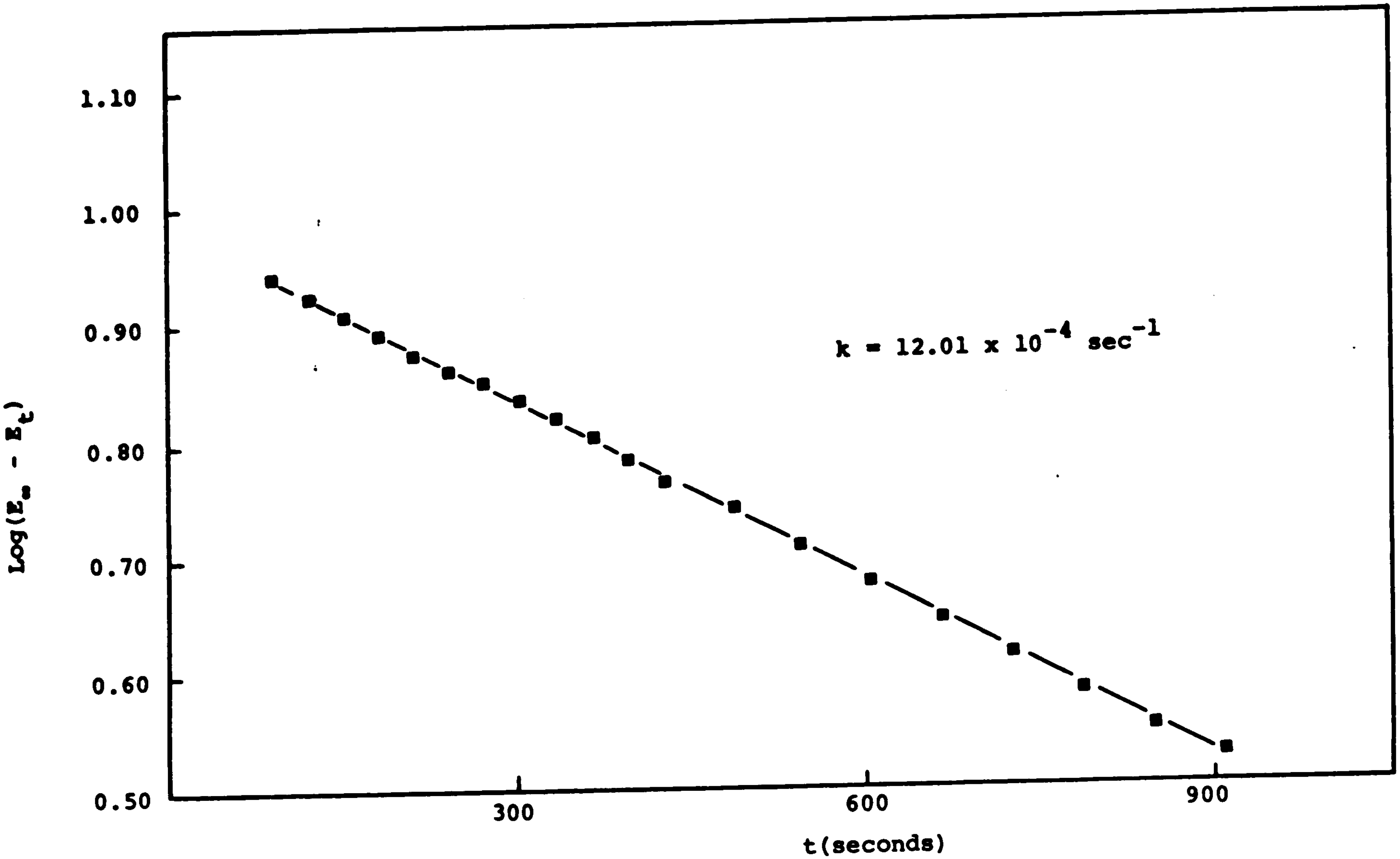
Time (sec)	E_t (cm)	$\text{Log}(E_\infty - E_t)$
180	14.60	0.99564
210	14.90	0.98227
240	15.20	0.96848
270	15.40	0.95904
300	15.60	0.94939
330	15.80	0.93952
360	16.00	0.92942
420	16.40	0.90848
480	16.75	0.88930
540	17.00	0.87506
600	17.40	0.85126
660	17.70	0.83251
720	17.90	0.81954
780	18.20	0.79934
840	18.50	0.77815
900	18.80	0.75587
960	19.00	0.74036
1020	19.30	0.71601
1080	19.50	0.69897
1140	19.70	0.68124
1200	19.90	0.66276
1260	20.05	0.64836
1320	20.25	0.62839
1380	20.40	0.61278
1440	20.55	0.59660
∞	24.50	-



Plot of Log(E_∞ - E_t) versus time for the thermolysis of **10** at 141.6°.

Values taken off the chart record for the evaluation of the rate constant for the thermolysis of **10** at 148.8°

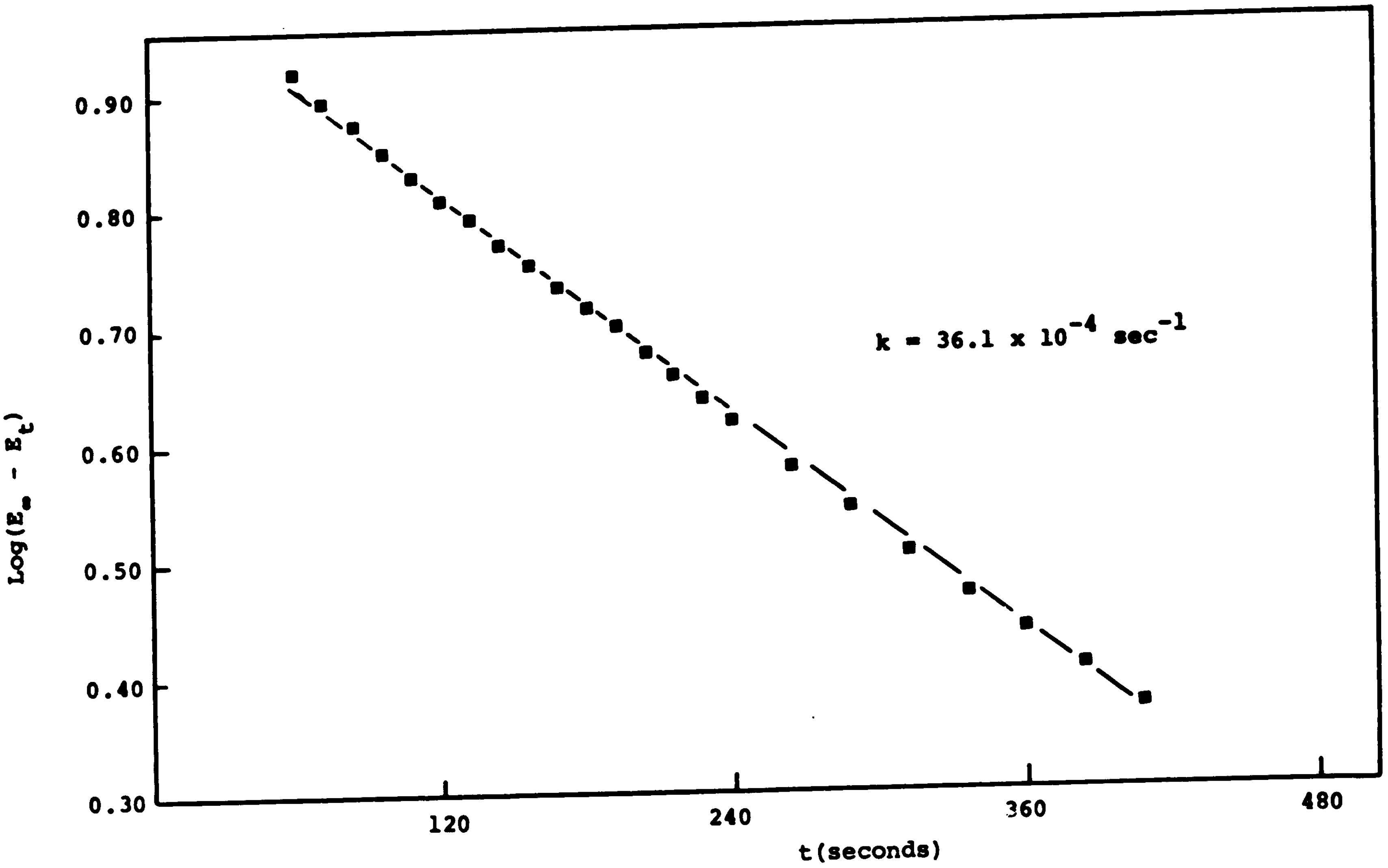
Time (sec)	E_t (cm)	$\text{Log}(E_\infty - E_t)$
90	11.95	0.94448
120	12.30	0.92686
150	12.60	0.91116
180	12.90	0.89487
210	13.20	0.87795
240	13.45	0.86332
270	13.65	0.85126
300	13.90	0.83569
330	14.20	0.81624
360	14.40	0.80277
390	14.70	0.78175
420	14.90	0.76716
480	15.25	0.74036
540	15.65	0.70757
600	16.00	0.67670
660	16.35	0.64345
720	1665	0.61278
780	16.95	0.57978
840	17.20	0.55023
900	17.40	0.52505
∞	20.75	



Plot of $Log(E_\infty - E_t)$ versus time for the thermolysis of 10 at 148.8°.

Values taken off the chart record for the evaluation of the rate constant for the thermolysis of 10 at 160.0°

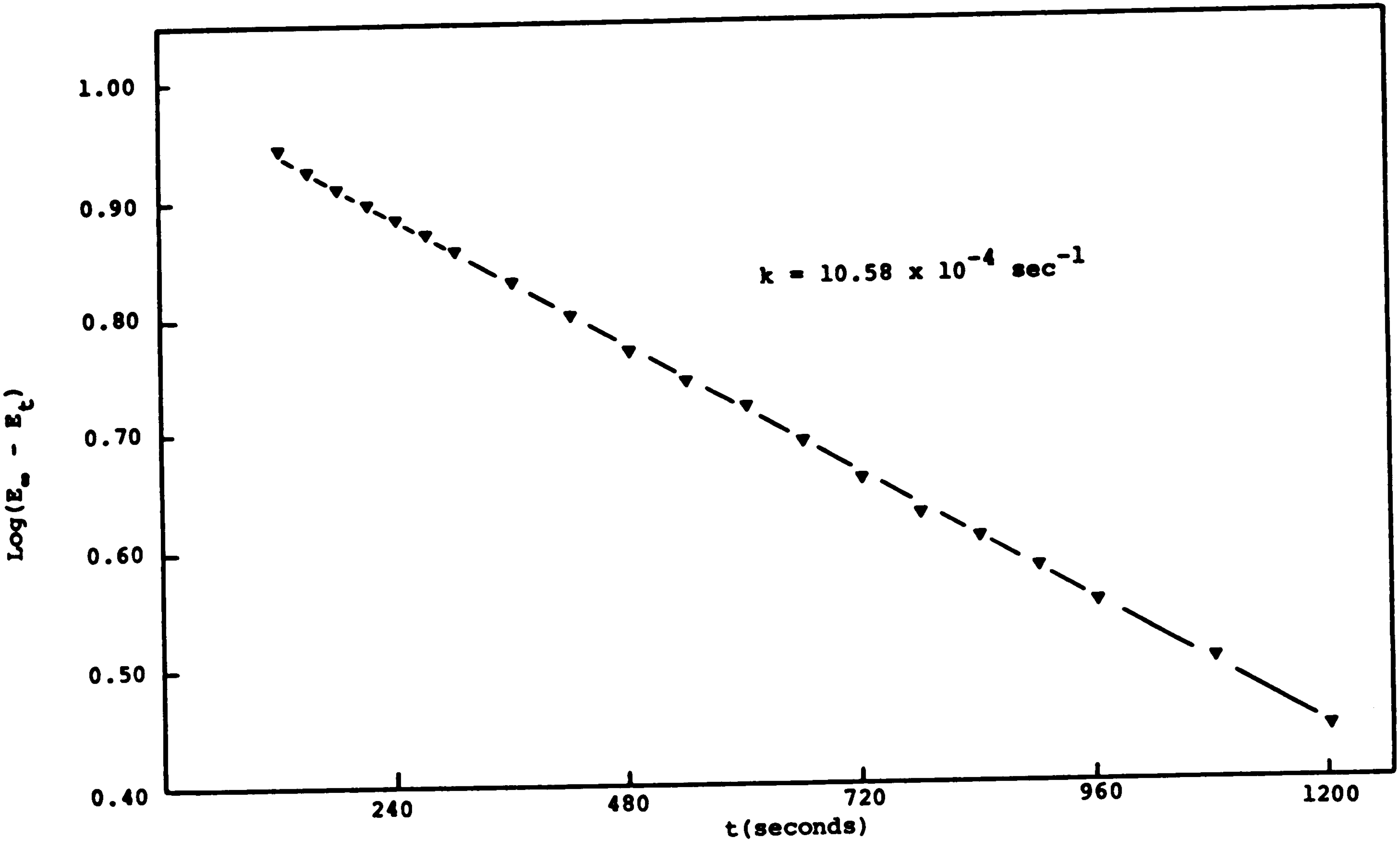
Time (sec)	E_t (cm)	Log(E_∞ - E_t)
60	13.30	0.91645
72	13.75	0.89209
84	14.10	0.87216
96	14.45	0.85126
108	14.80	0.82931
120	15.10	0.80956
132	15.35	0.79239
144	15.65	0.77085
156	15.90	0.75205
168	16.10	0.73640
180	16.35	0.71601
192	16.55	0.69897
204	16.80	0.67670
216	17.00	0.65801
228	17.20	0.63849
240	17.40	0.61805
264	17.75	0.57978
288	18.05	0.54407
312	18.35	0.50515
336	18.60	0.46982
360	18.80	0.43933
384	19.00	0.40654
408	19.20	0.37107
∞	21.55	0.37107



Plot of $\mathrm{Log}(E_\infty - E_t)$ versus time for the thermolysis of $\underset{\sim}{10}$ at 160.0°.

Values taken off the chart record for the evaluation of the rate constant for the thermolysis of **13** at 125.6°

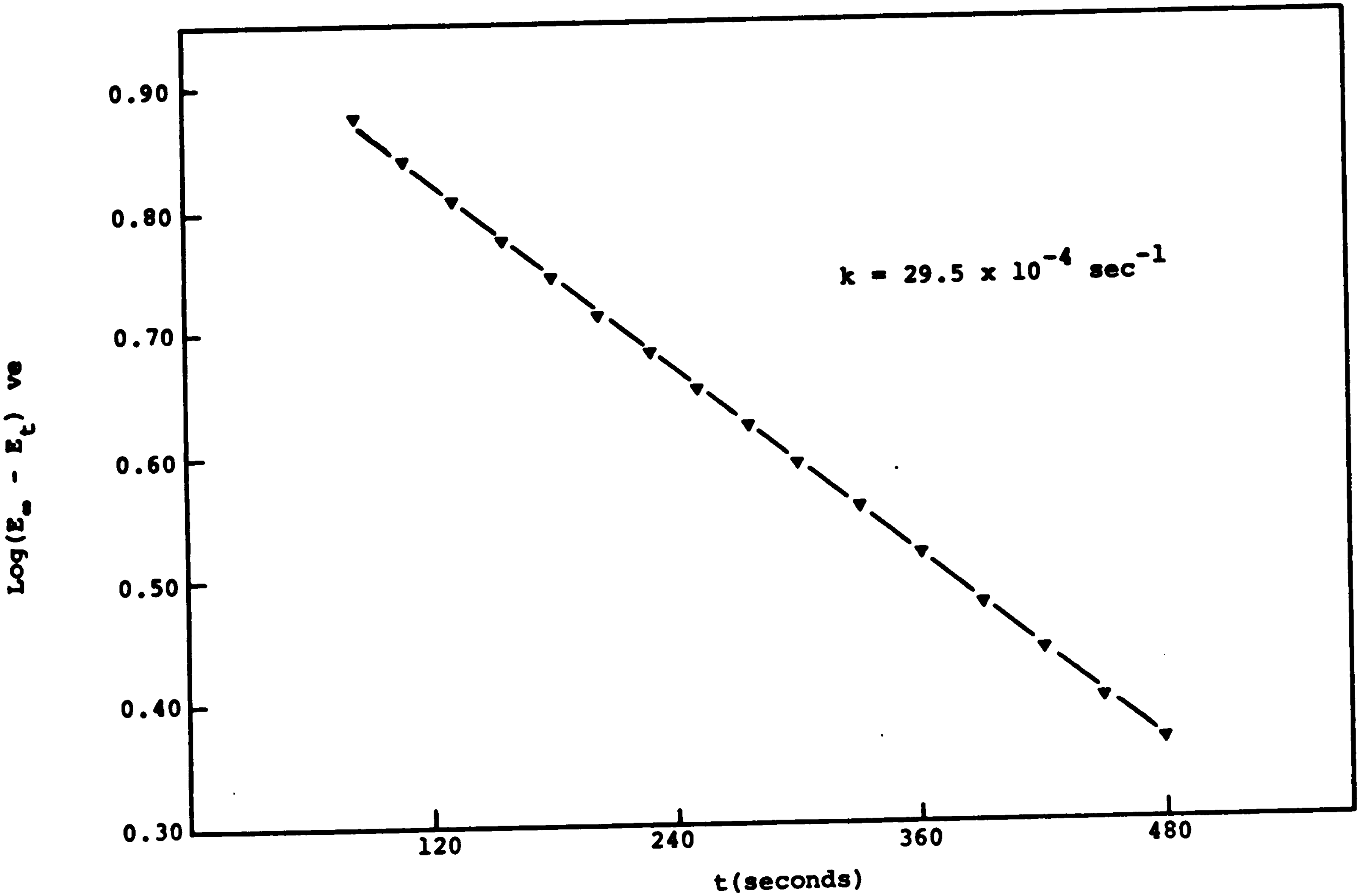
Time (sec)	E_t (cm)	$\mathrm{Log}(E_\infty - E_t)$
120	12.85	0.94694
150	13.20	0.92942
180	13.50	0.91381
210	13.75	0.90036
240	14.00	0.88649
270	14.20	0.87506
300	14.45	0.86034
360	14.90	0.83251
420	15.35	0.80277
480	15.80	0.77085
540	16.10	0.74819
600	16.40	0.72428
660	16.75	0.69461
720	17.10	0.66276
780	17.40	0.63347
840	17.60	0.61278
900	17.85	0.58546
960	18.10	0.55630
1080	18.50	0.50515
1200	18.90	0.44716
∞	21.70	



Plot of $\mathrm{Log}(E_\infty - E_t)$ versus time for the thermolysis of 13 at 125.6°.

Values taken off the chart record for the evaluation of the rate constant for the thermolysis of 13 at 135.0°

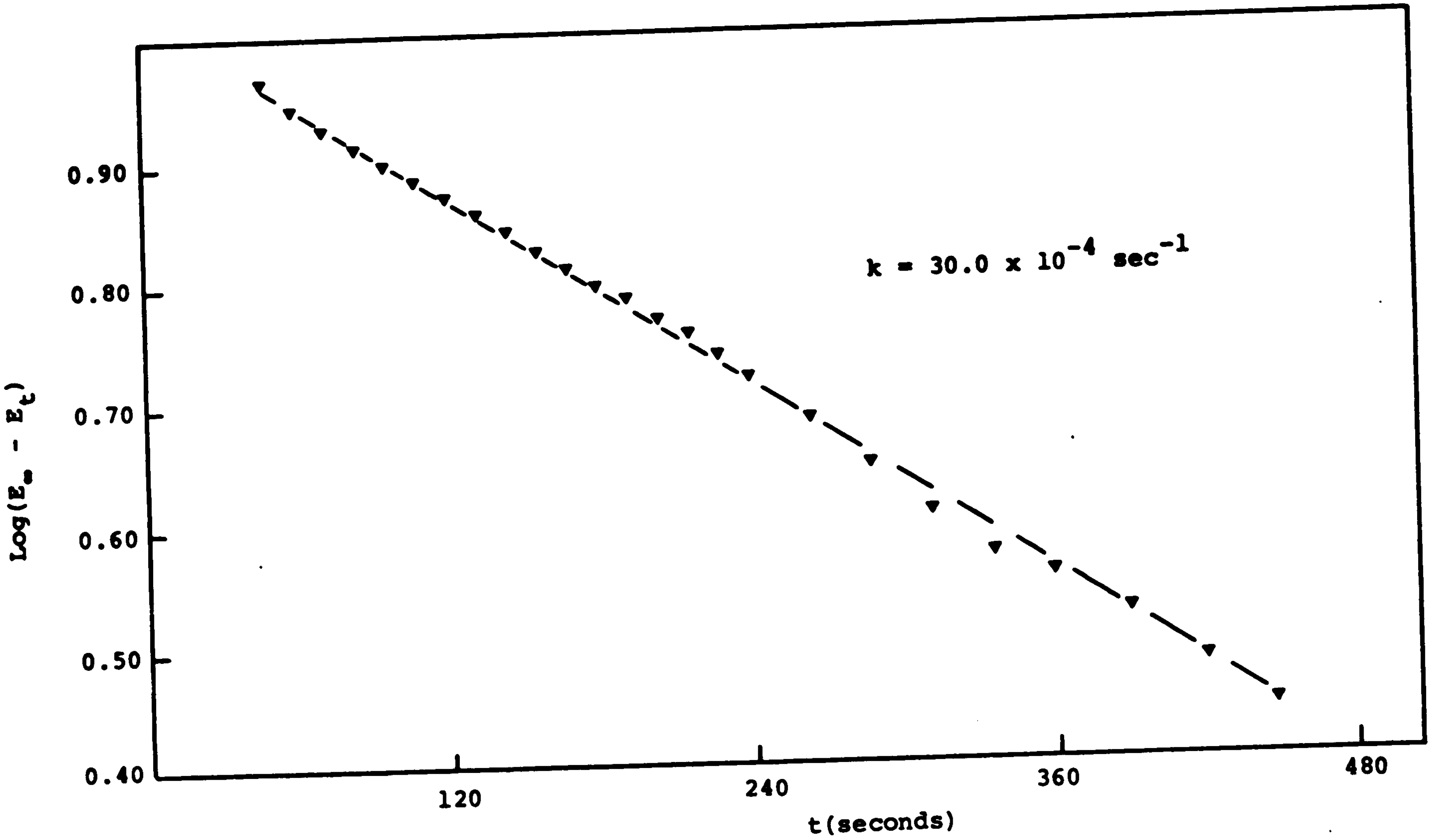
Time (sec)	E_t (cm)	$\text{Log}(E_\infty - E_t)$
84	14.10	0.87506
108	14.70	0.83885
132	15.20	0.80618
156	15.65	0.77452
180	16.05	0.74429
204	16.45	0.71181
228	16.80	0.68124
252	17.15	0.64836
276	17.40	0.62325
300	17.70	0.59106
330	18.00	0.55630
360	18.30	0.51851
390	18.60	0.47712
420	18.85	0.43933
450	19.10	0.39794
480	19.30	0.36173
∞	21.60	



Plot of Log(E_∞ - E_t) versus time for the thermolysis of 13 at 135.0°.

Values taken off the chart record for the evaluation of the rate constant for the thermolysis of **13** at 135.2°

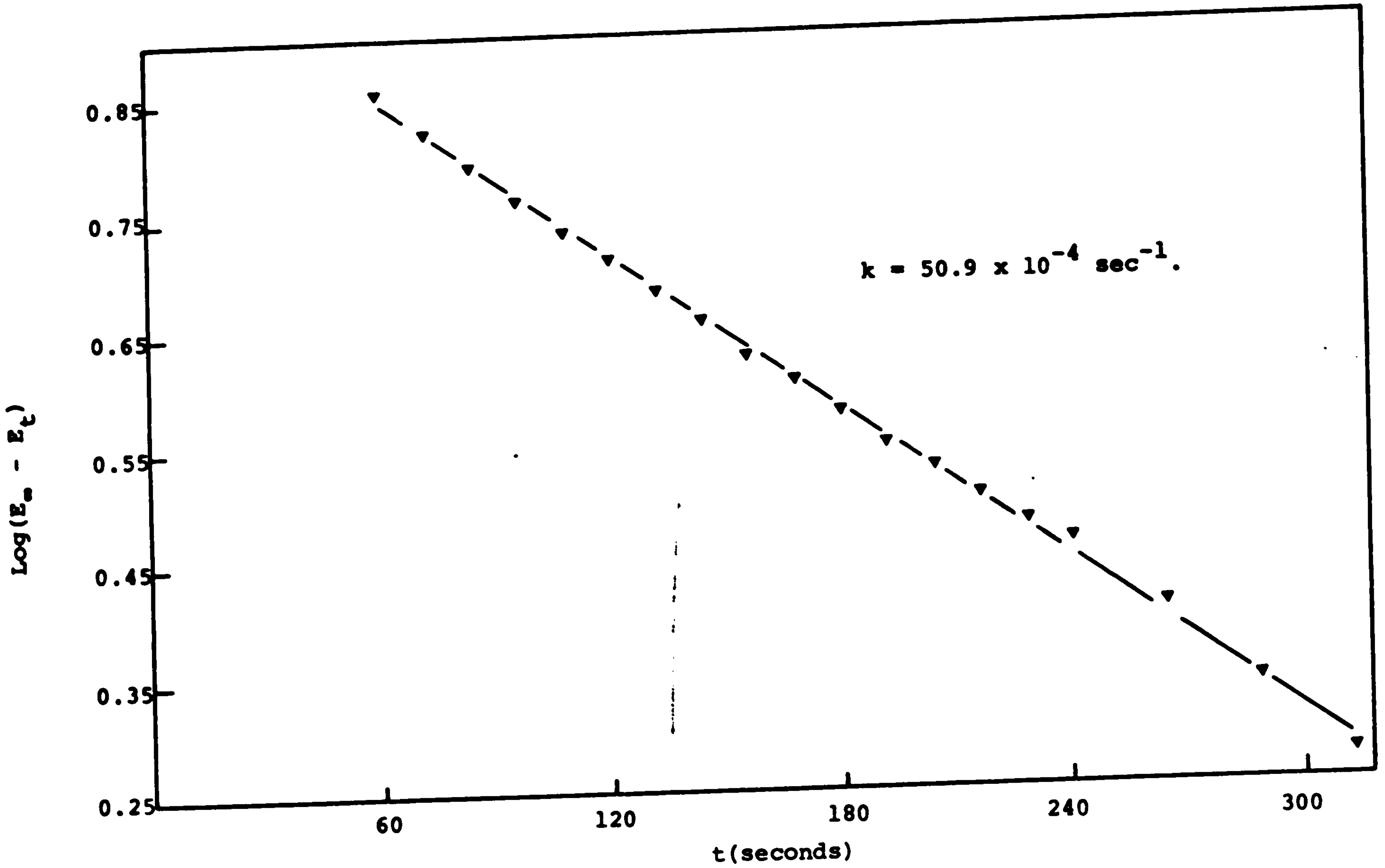
Time (sec)	E_t (cm)	$\text{Log}(E_\infty - E_t)$
48	14.40	0.97081
60	14.85	0.94939
72	15.20	0.93197
84	15.50	0.91646
96	15.75	0.90309
108	16.00	0.88930
120	16.25	0.87506
132	16.50	0.86034
144	16.75	0.84510
156	17.00	0.82931
168	17.25	0.81291
180	17.45	0.79934
192	17.60	0.78888
204	17.85	0.77085
216	18.00	0.75967
228	18.25	0.74036
240	18.50	0.72016
264	18.90	0.68574
288	19.30	0.64836
312	19.70	0.60746
336	20.00	0.57403
360	20.15	0.55630
390	20.40	0.52505
420	20.95	0.44716
480	21.15	0.41497
∞	23.75	



Plot of $\mathrm{Log}(E_\infty - E_t)$ versus time for the thermolysis of $\underset{\sim}{13}$ at 135.2°.

Values taken off the chart record for the evaluation of the rate constant for the thermolysis of **13** at 140.0°

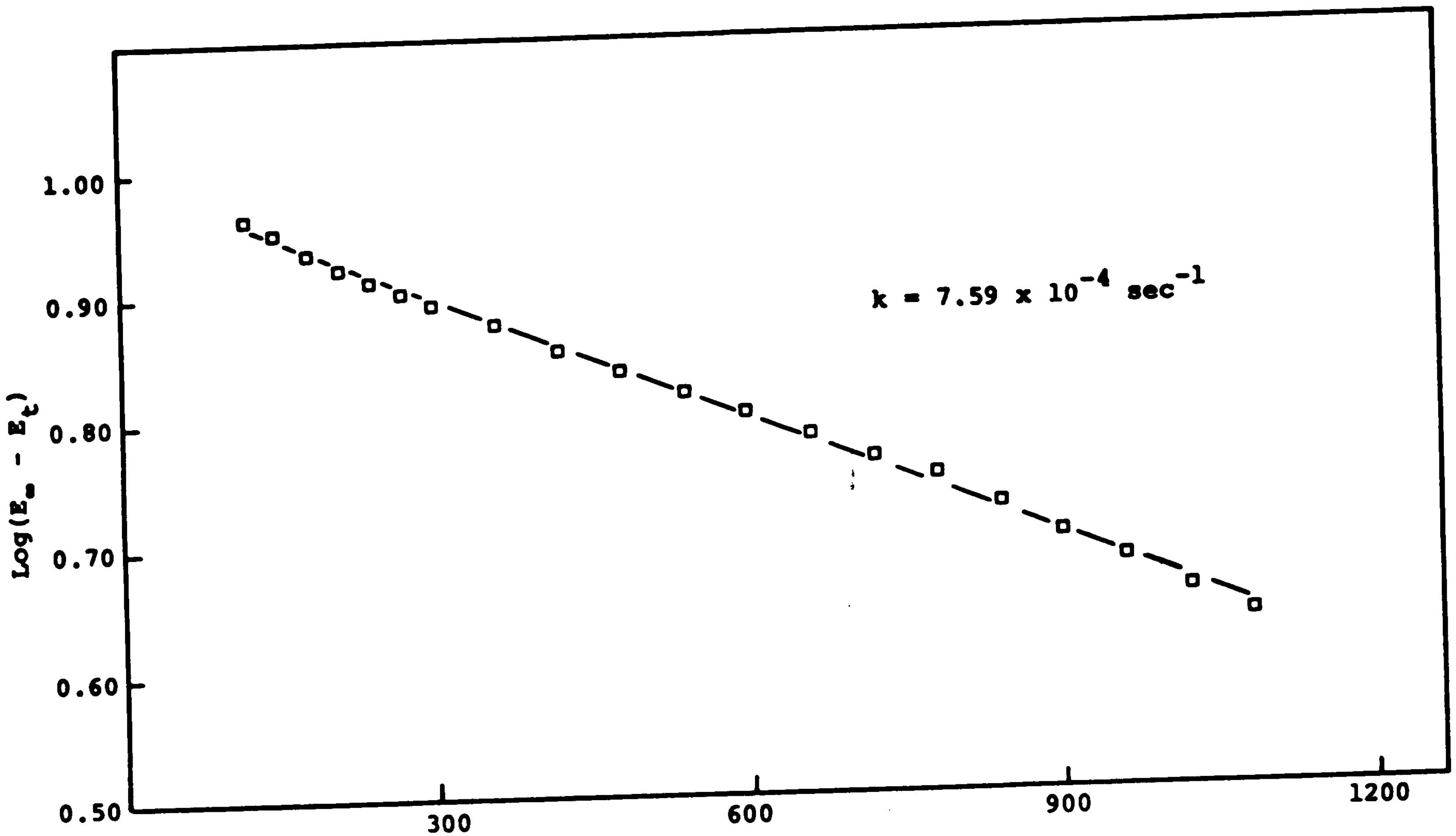
Time (sec)	E_t (cm)	$\log(E_\infty - E_t)$
60	15.95	0.85733
72	16.50	0.82282
84	16.90	0.79588
96	17.30	0.76716
108	17.70	0.73640
120	18.00	0.71181
132	18.30	0.68574
144	18.60	0.65801
156	18.90	0.62839
168	19.10	0.60746
180	19.35	0.57978
192	19.60	0.55023
204	19.75	0.53148
216	19.95	0.50515
228	20.10	0.48430
240	20.25	0.46240
264	20.60	0.40654
288	20.95	0.34242
312	21.25	0.27875
∞	23.15	-



Plot of Log(E_∞ - E_t) versus time for the thermolysis of 13 at 140.0°.

Values taken off the chart record for the evaluation of the rate constant for the thermolysis of 16 at 134.9°

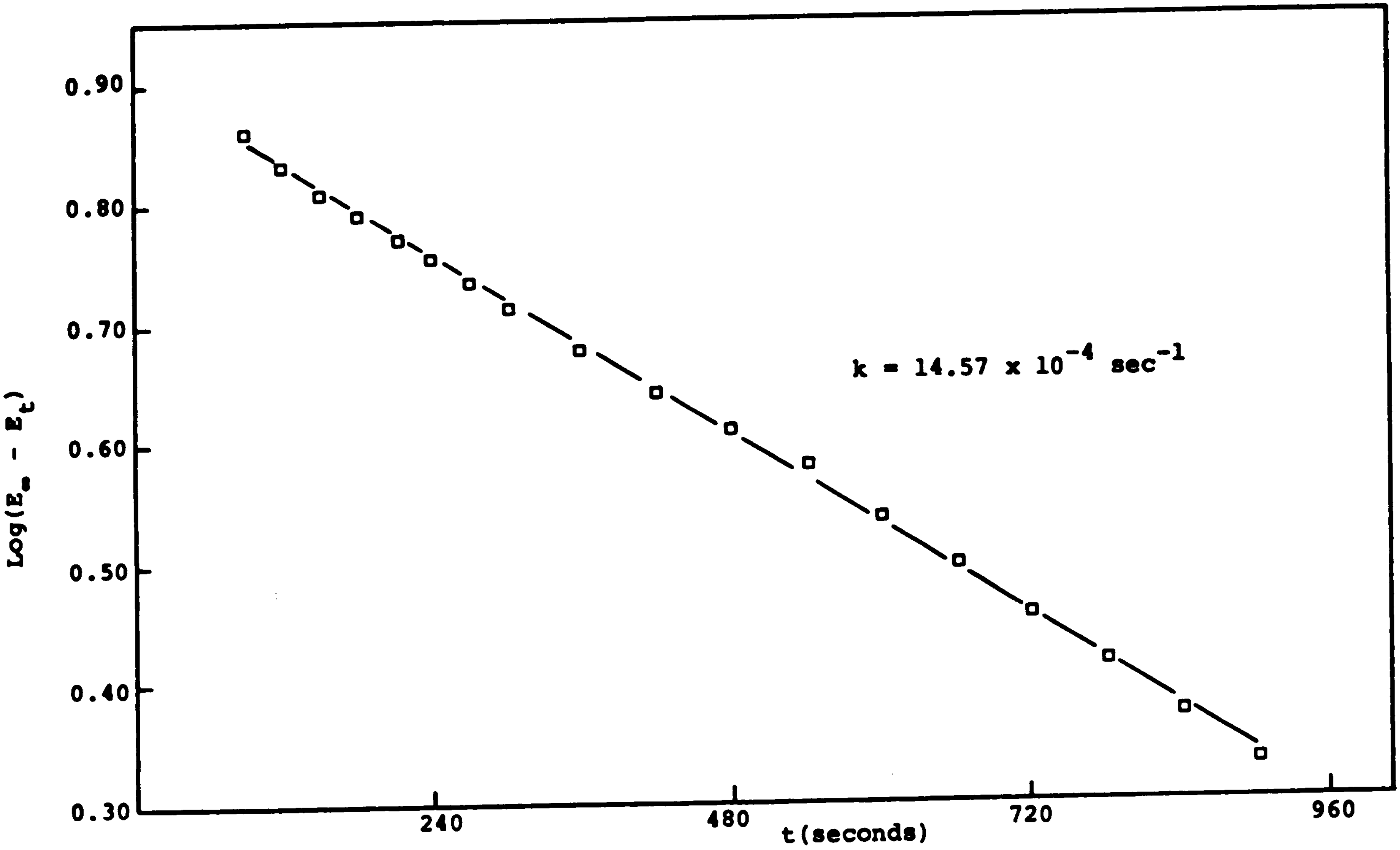
Time (sec)	E_t (cm)	Log(E_∞ - E_t)
120	14.20	0.96848
150	14.50	0.95424
180	14.80	0.93952
210	15.05	0.92686
240	15.25	0.91645
270	15.45	0.90580
300	15.60	0.89762
360	15.90	0.88081
420	16.30	0.85733
480	16.55	0.84198
540	16.85	0.82282
600	17.10	0.80618
660	17.35	0.78888
720	17.65	0.76716
780	17.85	0.75205
840	18.15	0.72835
900	18.45	0.70329
960	18.70	0.68124
1020	18.95	0.65801
1080	19.15	0.63849
∞	23.50	0.63849



Plot of Log(E_∞ - E_t) versus time for the thermolysis of **16** at 134.9°.

Values taken off the chart record for the evaluation of the rate constant for the thermolysis of 16 at 140.4°

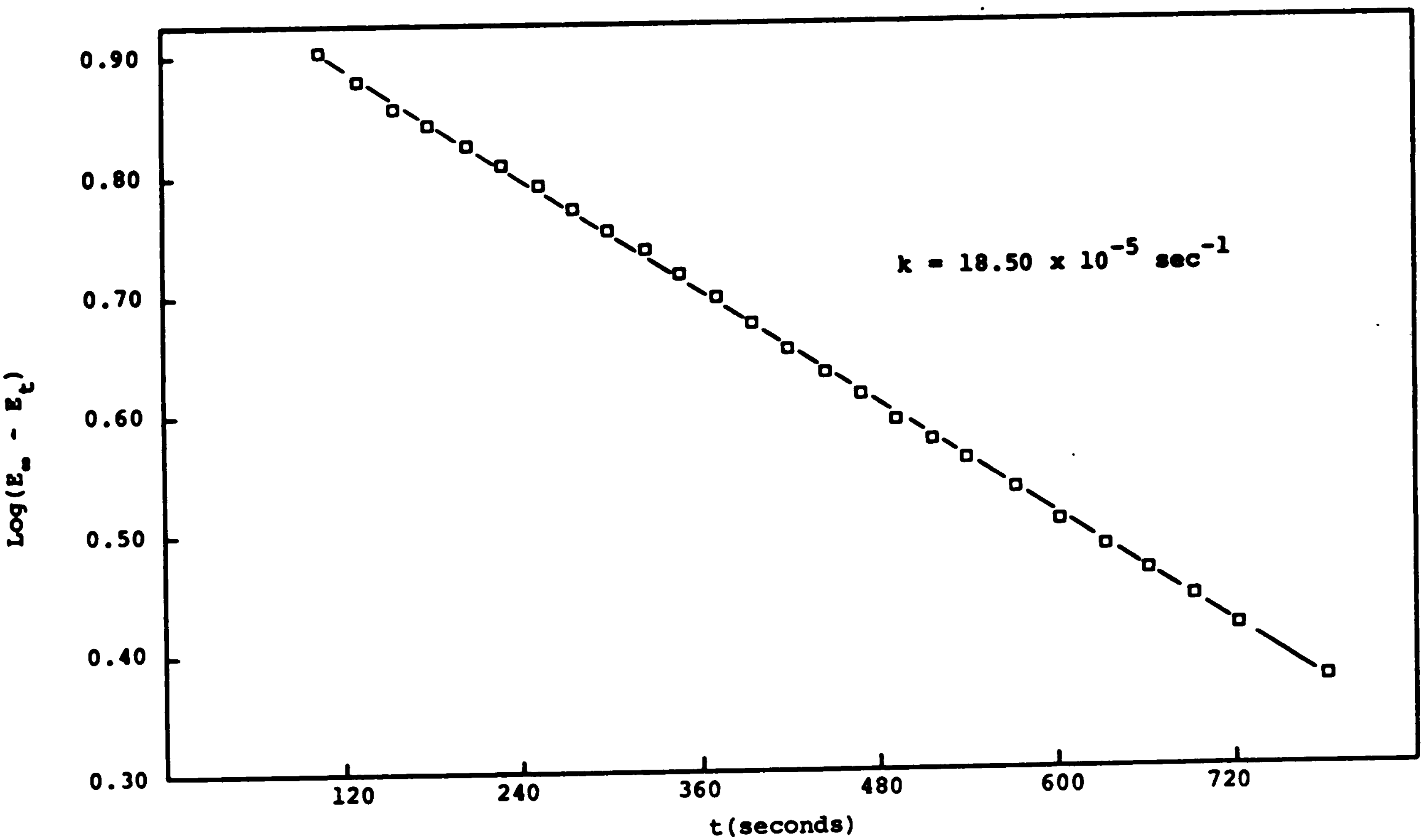
Time (cm)	E_t (cm)	$\mathrm{Log}(E_\infty - E_t)$
90	10.15	0.86034
120	10.60	0.83251
150	10.95	0.80956
180	11.20	0.79239
210	11.45	0.77452
240	11.70	0.75587
270	11.95	0.73640
300	12.25	0.71181
360	12.65	0.67670
420	13.00	0.64345
480	13.30	0.61278
540	13.65	0.57403
600	13.95	0.53782
660	14.25	0.49831
720	14.55	0.45485
780	14.80	0.41497
840	15.05	0.37107
900	15.25	0.33244
∞	17.40	-



Plot of $\text{Log}(E_\infty - E_t)$ versus time for the thermolysis of $\underset{\sim}{16}$ at 140.4°.

Values taken off the chart record for the evaluation of the rate constant for the thermolysis of 16 at 142.7°

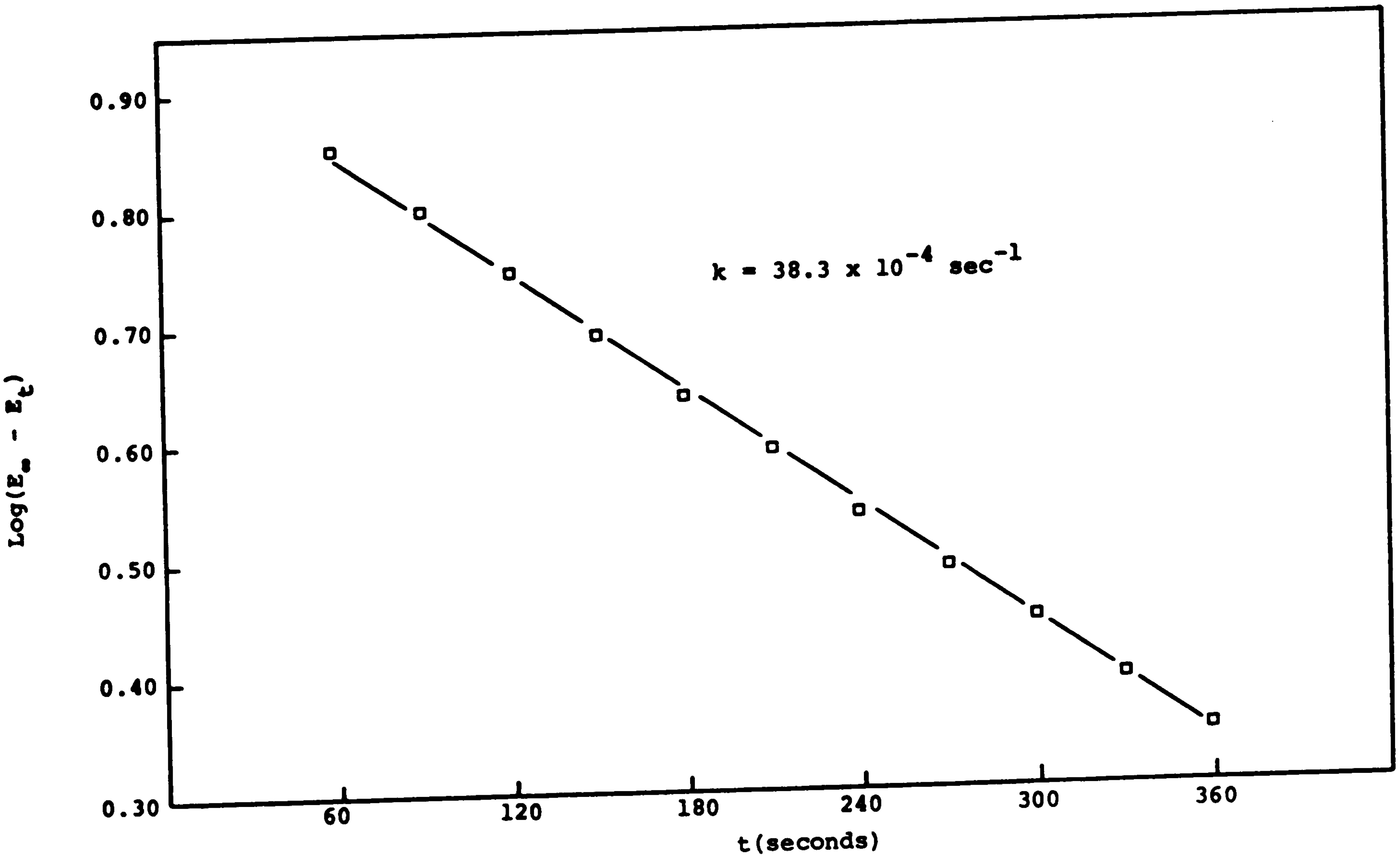
Time (sec)	E_t (cm)	$\text{Log}(E_\infty - E_t)$
108	14.95	0.90580
132	15.35	0.88366
156	15.70	0.86332
180	16.00	0.84510
204	16.30	0.82607
228	16.55	0.80956
252	16.80	0.79239
276	17.05	0.77452
300	17.30	0.75587
324	17.55	0.73640
348	17.80	0.71601
372	18.05	0.69461
396	18.30	0.67210
420	18.50	0.65321
444	18.70	0.63347
468	18.90	0.61278
492	19.10	0.59106
516	19.25	0.57403
540	19.40	0.55630
570	19.60	0.53148
600	19.80	0.50515
630	19.95	0.48430
660	20.10	0.46240
690	20.25	0.43933
720	20.40	0.41497
780	20.65	0.37107
∞	23.00	-



Plot of $\text{Log}(E_\infty - E_t)$ versus time for the thermolysis of 16 at 142.7°.

Values taken off the chart record for the evaluation of the rate constant for the thermolysis of 16 at 148.8°

Time (sec)	E_t (cm)	$\text{Log}(E_\infty - E_t)$
60	13.10	0.85126
90	13.90	0.79934
120	14.65	0.74429
150	15.30	0.69020
180	15.85	0.63849
210	16.30	0.59106
240	16.75	0.53782
270	17.10	0.49136
300	17.40	0.44716
330	17.70	0.39794
360	17.95	0.35218
∞	20.20	-



Plot of $\mathrm{Log}(E_\infty - E_t)$ versus time for the thermolysis of **16** at 148.8°.

(a) Values used for the calculation of the error limits in E_a and log A for azo compound **9**

	$k \times 10^4$ (sec^{-1})	-log k	$\frac{1}{T} \times 10^3$ (sec^{-1})	E_a (kcal $mole^{-1}$)	log A
lower limit	8.06	3.09367	2.419	35.29	15.56
	56.1	2.25306	2.310		
upper limit	7.94	3.10018	2.419	35.79	15.82
	56.3	2.24765	2.310		

Thus we obtain E_a = 35.54±0.25 kcal and log A = 15.69±0.13

(b) Values used for the calculation of the error limits in E_a and log A for azo compound **10**

	$k \times 10^4$ (sec^{-1})	-log k	$\frac{1}{T} \times 10^3$ (sec^{-1})	E_a (kcal $mole^{-1}$)	log A
lower limit	6.01	3.13549	2.411	30.95	13.17
	35.8	2.44563	2.309		

upper limit	5.95	3.14026	2.411	31.45	13.42
	36.4	2.43962	2.309		

Thus E_a = 31.20±0.25 kcal $mole^{-1}$ and log A = 13.30±0.13.

(c) Values used for the calculation of the error limits in E_a and log A for azo compound 13

	k x 10^4 (sec^{-1})	-log k	$\frac{1}{T}$ x 10^3 (sec^{-1})	E_a (kcal $mole^{-1}$)	log A
lower limit	10.62	2.97388	2.508	35.18	16.31
	50.4	2.29731	2.420		
upper limit	10.54	2.97716	2.508	35.78	16.63
	51.4	2.28912	2.420		

Thus E_a = 35.48±0.3 kcal $mole^{-1}$ and log A = 16.57±0.16.

(d) **Values used for the calculation of the error limits in E_a and log A for azo compound 16**

	k x 10^4 (sec^{-1})	-log k	$\frac{1}{T}$ x 10^3 (sec^{-1})	E_a (kcal $mole^{-1}$)	log A
lower limit	7.67	3.11520	2.451	39.23	17.89
	37.9	2.42113	2.370		
upper limit	7.51	3.12436	2.451	40.23	18.43
	38.7	2.41207	2.370		

Thus $E_a = 39.73 \pm 0.50$ kcal $mole^{-1}$ and log $A = 18.16 \pm 0.27$.