

This comparison shows that the products ethane, isopentane, and 2,2-dimethylbutane are observed to be formed in both cases in yields in excess of the calculated values, in fact they are not expected at all at low dose rates. On the other hand these are exactly the products one would expect to form in reaction 12 considering that the radicals present are methyl, isobutyl, and neopentyl. Further the yields of ethane, isopentane, and 2,2-dimethylbutane observed at low dose rate are in the ratio 1:0.12:0.67 and in light of the radical yields we would expect the ratio of these yields to be 1:0.14:0.67 if methyl radicals were combining with the other radicals at this dose rate. Since at these low dose rates methyl radicals are known to predominantly abstract we conclude that regions of high dose rate exist; that is these products are formed by combination of methyl and other radicals in the tracks of the ionizing particle. Further evidence of the molecular nature of these products comes from the observation that the yield of ethane in 30 mM iodine solution is 0.35,⁴ and the yield of 2,2-dimethylbutane is 0.20 in the presence of 1 mM oxygen, only slightly below the yields in neat neopentane.⁴ This reduction of yields is characteristic and to be expected at high concentrations of scavenger.

It is of interest to use this data to calculate the fraction of methyl radicals formed initially which escape the track, $N(\text{CH}_3)/N(\text{CH}_3)_0$; $N(\text{CH}_3)$ is the methyl radical yield and is observed to be 2.3 and $N(\text{CH}_3)_0$ is the sum of the methyl radical yield plus the molecular methyl radical yield, the latter is the yield of methyl radicals which combine with other radicals in the track. The molecular methyl radical yield is $\geq 2G(\text{C}_2\text{H}_6) + G(\text{isopentane}) + G(\text{2,2-dimethylbutane}) = 1.2$; it may be larger than this to the extent that methyl radicals also combine with hydrogen atoms in the track. The yield of methyl radicals which react with *t*-butyl radicals has been neglected since this represents a back reaction to neopentane, the extent of which cannot be directly measured. Thus the molecular methyl radical yield is equal to or greater than 1.2 or $N(\text{CH}_3)/N(\text{CH}_3)_0 \leq 0.66$. This value is remarkably close to the corresponding value of 0.62 for OH radicals observed in low LET radiolysis of water.²⁵ If this interpretation is correct it would be extremely interesting to measure the yields of these characteristic products as a function of solute concentration and LET and compare the experimental results with the expectations of diffusion theory.

(25) P. J. Dyne and J. M. Kennedy, *Can. J. Chem.*, **36**, 1518 (1958).

Photoisomerization of 1,6-Heptadiene Sensitized by Mercury 6(³P₁) Atoms¹

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The decomposition of 1,6-heptadiene photosensitized by mercury 6(³P₁) atoms has been studied in the pressure range from 3 to 65 mm. In addition to free-radical products and a polymer which accounted for 95% of the decomposition, six isomers were observed. Four of these were identified as 4-cyclopropylbutene-1, bicyclo[3.2.0]heptane, bicyclo[3.1.1]heptane, and 1-methyl-2-vinylcyclobutane. Thus, in this system, an isomerization which gives rise to a cyclopropyl derivative (as in other unconjugated diolefins) as well as a parallel process which gives a cyclobutyl derivative (as in monoolefins) are observed. It is tentatively suggested that the present system may not be unique in this respect and that two such pathways may be operative in the mercury-photosensitized isomerization of other unconjugated diolefins as well.

Introduction

The photoisomerization of mono- and diolefins sensitized by mercury 6(³P₁) atoms has been the subject of many recent studies. In monoolefins, the process generally proceeds with the migration of a hydrogen. Avrahami and Kebarle² proposed that in a molecule

in which several kinds of protons are available the migratory aptitude will be determined by the order 1,4 > 1,3 > 1,2. Placzek and Rabinovitch³ have reviewed all of the results to which this hypothesis is applicable and come to the conclusion that it is, in general, a valid statement although not a highly selective one. These authors have also pointed out that the mercury-sensitized isomerizations of diolefins seem to be exceptional in that the 1,2 migration of hydrogen atoms is the only process that is to be observed, although 1,3 and 1,4 migrations are equally possible. The three examples that are known to date are: 1,4-pentadiene,⁴ 1,5-hexadiene,⁵ and 1,5-cyclo-octadiene.⁴ If the cyclic compound is dropped from the discussion (since it is almost the only one for which data are available), there are only two exceptions. Of these 1,4-pentadiene may be really thought of as in a class by itself. In this molecule, apart from the 1,2 transfer which is observed, the other possibility is a 1,3 transfer which would give a product with a conjugated diene system. This product may undergo secondary reactions more rapidly than the reactant. This limits the exceptional behavior to 1,5-hexadiene.

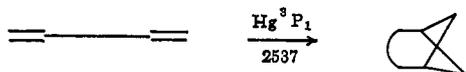
(3) D. W. Placzek and B. S. Rabinovitch, *Can. J. Chem.*, **43**, 820 (1965).

(4) R. Srinivasan, *J. Am. Chem. Soc.*, **86**, 3318 (1964).

(5) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963).

(1) Paper IV on "Mercury Photosensitized Reactions in Diolefins."
(2) M. Avrahami and P. Kebarle, *J. Phys. Chem.*, **67**, 354 (1963).

The present study of the mercury-sensitized isomerization of 1,6-heptadiene was undertaken to see whether diolefins do fall in line with the Avrahami and Kebarle rule or not.² It may be pointed out that in all three of the diolefins which had been studied previously a second isomerization reaction, which can be written as



gave rise to a valence tautomer. The yield of this reaction was strongly pressure dependent (just as the hydrogen-transfer products are) but did not show a maximum.

Experimental Section

1,6-Heptadiene was obtained from K & K Laboratories (Plainview, N. Y.). It was fractionated on a 23-plate spinning-band column to give a middle cut boiling over a narrow range of temperature. This material was dried and degassed before use. Analysis by vapor phase chromatography showed that it contained 0.5% of an impurity that remained unchanged during sensitized decomposition of the 1,6-heptadiene.

2-Ethylcyclopentanone from K & K Laboratories was used as obtained. Its purity, as determined by vapor phase chromatography analysis, was about 98%. Runs were carried out in a static system. The light source was a bank of seven General Electric G8T5 lamps arranged circularly around the cell. Two cylindrical cells 8.0×22 cm. and 4.3×25 cm. were used. Their useful volumes and dead space volumes were 1090 and 35 ml. in one case, and 300 and 70 ml. in the other. The light source was calibrated with a uranyl oxalate actinometer. The geometry of the source resulted in maximum intensity at the axis of the cell and the minimum at the edge of the cell. As a result, the smaller cell had a higher intensity per unit volume by a factor of 1.5. Runs made at the same pressure in both cells established that this difference in intensity had no detectable effect on the quantum yields. The actual intensities in the two cells were 0.95 and 1.55×10^{17} quanta/ml./min. The power supply to the light source was regulated by a constant voltage transformer.

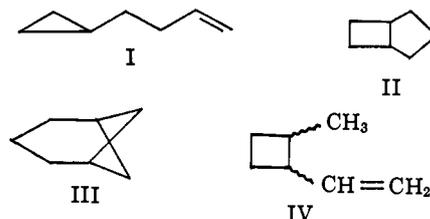
Analyses were made on a Perkin-Elmer 154D vapor chromatograph fitted with a Ucon oil 550 column, 2 m. long, maintained at 40° . Since the total yield of isomers was less than 10%, the conversion of 1,6-heptadiene had to be kept to as high a value as 50%. There is no reason to suspect that secondary decomposition of the isomers occurred. Essentially similar results were obtained when a flow system was used to remove the products from the reaction zone as rapidly as they were formed.

Results

Products. Photolysis of 1,6-heptadiene sensitized by mercury gave rise to free radical products, several isomers, and a liquid polymer. The free radical processes dominated over the whole pressure range in which the system was studied although their importance decreased with an increase in pressure. No more than 1 in 30 molecules of 1,6-heptadiene that were photolyzed underwent isomerization. There were no less than six

isomers, of which only four could be identified with some degree of certainty. These were:

(i) 4-Cyclopropylbutene-1 (I). Its molecular weight was 96 as determined by mass spectrometry. In its infrared spectrum it showed absorptions at 1640, 990, and 915 cm^{-1} which indicated the presence of a vinyl group, and at 3050 and 1018 cm^{-1} which suggested a cyclopropyl group. The molecule was identified by comparing its infrared spectrum with that of an authentic sample.⁶



(ii) Bicyclo[3.2.0]heptane (II). Its molecular weight was 96 as determined by mass spectrometry. It showed no unsaturation in its infrared or n.m.r. spectra. The formula C_7H_{12} demands the presence of two rings. Since a cyclopropyl group (or proton on such a group) was not evident in the spectra the structure was limited to II or III. It was established that the material was II by comparison of the infrared spectrum with that of an authentic sample.⁷

(iii) Bicyclo[3.1.1]heptane (III). Its molecular weight was 96 as determined by mass spectrometry. It showed no unsaturation in its infrared or ultraviolet spectra. Since a cyclopropyl group was not evident in the infrared spectrum, the probable structures were reduced to one, namely III.

(iv) 1-Methyl-2-vinylcyclobutane (IV). Its molecular weight was 96 as determined by mass spectrometry. The infrared spectrum showed absorptions at 1645, 1002, and 911 cm^{-1} which were indicative of a vinyl group, and at 1376 cm^{-1} which showed a methyl group. The n.m.r. spectrum consisted of three sets of absorptions centered at τ 4.45, 8.25 (broad), and 9.08 (doublet) of areas in the ratio 1:1:2. This would fit in well with structure IV which has three olefinic protons, three methyl protons attached to a carbon with one proton on it, and six other protons all of which are on a cyclobutane ring. The doubling of the infrared absorptions and the n.m.r. absorptions due to the methyl protons suggested that the compounds were probably a mixture of the *trans* and *cis* isomers in comparable amounts. The material gave a rather broad single peak in a vapor phase chromatograph but no special effort was made to resolve the two isomers. The quantitative data reported in Table I are for the mixture.

Pressure Dependence. In Table I, the rates of formation of hydrogen and six isomers as well as the rate of disappearance of 1,6-heptadiene are given as a function of the initial pressure of the hydrocarbon.

The total quantum yield for the formation of all of the isomers reached a constant value of 0.015 in the pressure range from 21 to 65 mm. At lower pressures it decreased. In contrast, the quantum yield for the

(6) The authors wish to thank Dr. H. E. Simmons for the infrared spectrum of I.

(7) The authors wish to thank Professor William G. Dauben for the infrared spectrum of II.

Table I. Rates of Formation of Products in Mercury-Photosensitized Isomerization of 1,6-Heptadiene^a

Pressure of 1,6-heptadiene, mm.	Time, min.	Rates of formation of product							Rate of disappearance of 1,6-heptadiene
		H ₂	4-Cyclopropylbutene-1	Methylvinylcyclobutane	Bicyclo-[3.2.0]-heptane	Bicyclo-[3.1.1]-heptane	Isomer V	Isomer VI	
3.0	1.0	0.488	0.081	0.050	0.016	0.026	0.034	0.014	...
10.7	3.9	0.319	0.169	0.100	0.079	0.087	...	0.025	96.7
15.0	5.0	0.253	0.171	0.113	0.118	0.105	...	0.019	98.8
21.4	7.0	0.348	0.137	0.120	0.161	0.082	0.021	0.027	...
25.0	8.0	...	0.193	0.088	0.165	0.065	...	0.017	...
36.0	12.0	0.232	0.182	0.074	0.206	0.063	0.009	0.020	...
46.5	14.0	0.188	0.224	0.118	0.304	0.079	0.012	0.019	13.7
65.0	20.0	0.221	0.175	0.112	0.320	0.073	0.012	0.010	...

^a Rates in $\mu\text{moles/min.}$ in 300 ml.; yields corrected for intensity changes.

disappearance of 1,6-heptadiene decreased to 0.3 at 46 mm. from a value of 0.6 at 15 mm.

In Figure 1 the reciprocal of the quantum yields for the two most important isomers and for hydrogen are plotted as a function of pressure. There is some reason to believe (based on the infrared spectra) that the near leveling-off of the plot for 4-cyclopropylbutene-1 is due to the presence of a second product which begins to interfere at the minimum point.

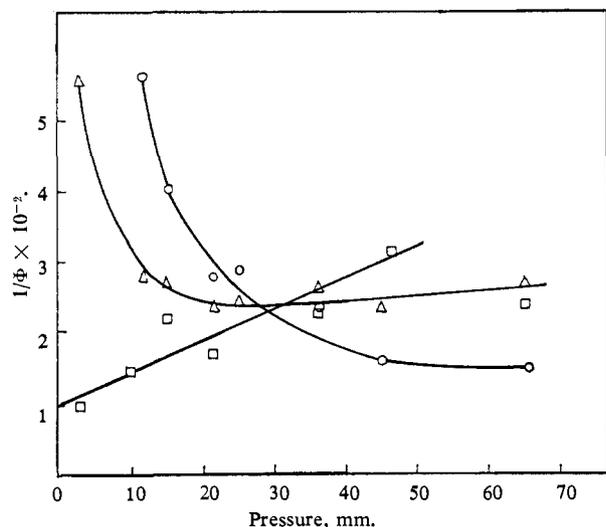


Figure 1. Stern-Volmer plots for three of the products from 1,6-heptadiene: \square , hydrogen; Δ , 4-cyclopropylbutene-1; \circ , bicyclo-[3.2.0]heptane.

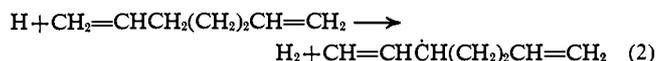
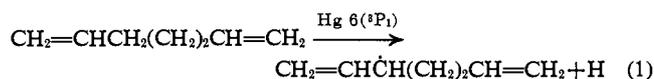
The photolysis of 2-ethylcyclopentanone by mercury sensitization gave rise to numerous gaseous and liquid products. Of this only the C₄ fraction was separated and analyzed by gas chromatography. There were three major compounds, of which two were identified as 1-butene and *n*-butane, respectively. The third compound, which has a molecular weight of 56, showed infrared absorptions at 1020 (cyclopropyl) and 1376 cm⁻¹ (CH₃) and none that was indicative of unsaturation. The spectrum agreed with the published spectrum of methylcyclopropane.⁸ The amounts of methylcyclopropane and 1-butene were in the ratio of 1:2.

Discussion

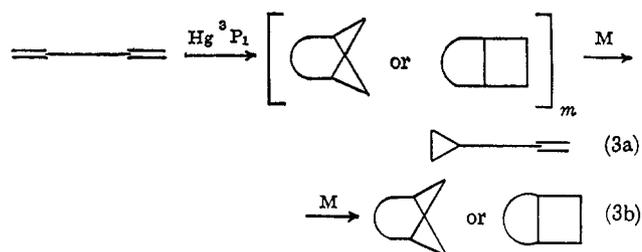
Before the mechanism of isomerization of 1,6-heptadiene is considered, it is appropriate to note that

(8) F. E. Condon and D. E. Smith, *J. Am. Chem. Soc.*, **69**, 965 (1947).

the principal mode of decomposition of the molecule is by secondary reactions which are brought on by free radical processes. The Stern-Volmer plot shows that at zero pressure the only important primary process is the splitting off of a hydrogen atom, which then would form molecular hydrogen by the abstraction of a second proton.

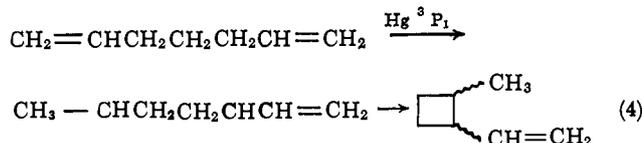


The several isomerization reactions that are observed are best explained if it is postulated that unconjugated diolefins, on sensitization by Hg ³P₁ atoms, can isomerize in two distinct ways. These are: (type I) a hydrogen-transfer reaction which is primarily determined by the length of the chain as proposed by Avrami and Kebarle²; (type II) a valence isomerization to give a "hot" cyclobutane derivative which, depending on the pressure, either rearranges to a ω -cyclopropyl-1-olefin or a thermalized bicyclic compound. The process can be written as



It should be stressed at this point that this classification of sensitized isomerizations is purely tentative and is based on the 1,6-heptadiene system only.

The product of the type I process in 1,6-heptadiene is 1-methyl-2-vinylcyclobutane. The reaction can be represented as

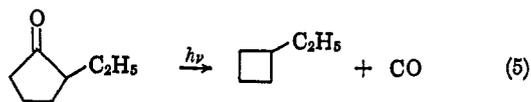


The occurrence of this reaction shows that unconjugated diolefins are capable of undergoing sensitized hydrogen transfer in the same fashion as monoolefins. It is also comforting to note that while 1-5, 1-4, and

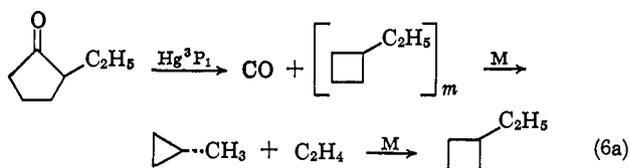
1-3 migrations are all possible in the molecule, the only product that was formed in identifiable amounts was the one that would have been predicted on the basis of Avrahami and Kebarle's hypothesis. The formation of the *cis* and *trans* isomers in comparable yield parallels the formation of *cis*- and *trans*-1,2-dimethylcyclopropane from 1-pentene.³ The occurrence of the type I process in 1,5-hexadiene should give rise to 1-vinyl-2-methylcyclopropane if the present hypothesis is correct. A re-examination of this system seems worthwhile.

The mechanism of the type II process, as given here, is an elaboration of an earlier concept.⁵ It was proposed that the excited molecule of the diene that is produced on sensitization by a Hg ³P₁ atom possesses considerable vibrational energy, and that this energy content determines its mode of decomposition. It is now believed that this excited state has the structure of a hot bicyclic compound. Since such bicyclic products are actually isolated in this instance and in other instances,^{4,5} and since the cycloaddition of olefins to give cyclobutane derivatives is a well-known photochemical process,⁹ the postulated structure for the excited state is a reasonable one.¹⁰

The isomerization of the hot bicyclic intermediate to a cyclopropyl olefin is a novel rearrangement. It would be simple to prove it if it were possible to excite a bicyclic compound such as II by Hg ³P₁ atoms. Unfortunately, since such molecules are saturated, photosensitization would merely lead to the loss of a hydrogen atom or molecule. Instead, it was attempted to produce a hot cyclobutane derivative by an alternative source. The photolysis of 2-ethylcyclopentanone may be expected to give ethylcyclobutane.¹¹



On bringing about the same reaction by mercury photosensitization, it was observed that methylcyclopropane was one of the products. This reaction may be written as



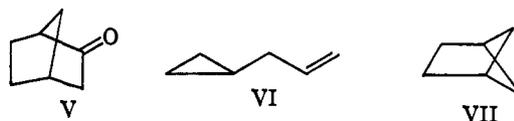
and is entirely analogous to (3). It may also be pointed out that in the decomposition of norcamphor (V) by Hg ³P₁ atoms allylcyclopropane (VI) is formed in significant yield along with bicyclo[2.1.1]hexane (VII).¹² The rearrangement of cyclobutanes to cyclopropyl compounds has some parallel in carbonium ion chemistry.

(9) For a review see A. Schonberg, "Preparative Organic Photochemistry," Springer-Verlag, Berlin, 1958.

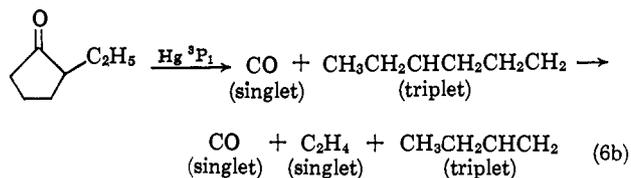
(10) It is somewhat surprising that more bicyclo[3.2.0]heptane than bicyclo[3.1.1]heptane is formed as the latter has a strain-free cyclohexane ring in it. Perhaps the rates of formation of these two products is not determined by the small difference in strain energy.

(11) For a review see R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963).

(12) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4923 (1961).

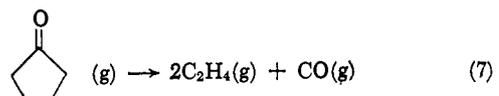


A referee has pointed out that the sensitized photolysis of 2-ethylcyclopentanone is capable of an alternative interpretation. If reaction 6a were written as

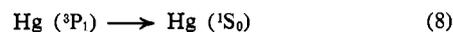


then the last species is required by the spin conservation rule to be a triplet and could indeed be the same species as formed in the photosensitized decomposition of butene-1. This interpretation would not only eliminate the formation of a vibrationally excited ethylcyclobutane as an intermediate, but it would show that the formation of methylcyclopropane in the photosensitized decomposition of 2-ethylcyclopentanone is not related to the isomerization of unconjugated diolefins by Hg ³P₁ atoms.

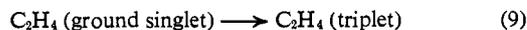
It is, first of all, necessary to examine the validity of reaction 6b. The reaction



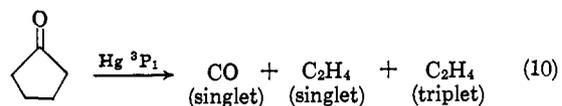
has $\Delta H = +44.89$ kcal./mole at 25° according to the data that are available on the heats of formation,¹³ while the transition



is exothermic by 112.7 kcal./mole. The transition



is endothermic by 80 kcal./mole,¹⁴ if the excitation is not accompanied by an internal twisting of the molecule. If the triplet state is twisted, the reaction will be endothermic by only about 50 kcal./mole. The over-all reaction



will be endothermic by 12 kcal./mole (and hence not favored) or exothermic by 18 kcal./mole (and hence favored) depending on the nature of the triplet that is formed.

A more powerful consideration which cannot be ignored under actual experimental conditions is that both reactions 10 and 6a may proceed through the initial formation of an excited ketone molecule. There is some evidence to show that this is true both in cyclopentanone and in norcamphor.¹⁵ Since the 0 → 0 absorption of the triplet of these ketones lies about 70 kcal./mole above the ground state, the process

(13) P. Sellers and S. Sunner, *Acta. Chem. Scand.*, **16**, 46 (1962); American Petroleum Institute Research Project 44.

(14) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(15) R. Srinivasan, unpublished work.



would give rise to a vibrationally excited triplet. Since even the singlet states of these ketones have been observed to undergo collisional quenching of the decomposition processes in the pressure range from 1 to 100 mm., the longer-lived triplet would almost certainly undergo some deactivation before it can take part in reaction 6a. The loss of 18 or more kcal./mole of vibrational energy would make reaction 6b unfavorable.

It is probable that reaction 6b can occur some of the time, especially at low pressures (less than 5 mm.) and high temperatures. The experiments on 2-ethyl cyclopentanone were carried out at a total pressure of

10 to 50 mm. The high proportion of methylcyclopropane to butene-1 must be noted.

It should be possible to rule for or against a process such as (6a) by the determination of quantum yields for the cyclobutyl, cyclopropyl, and diolefinic products from the mercury-photosensitized decomposition of a bicyclic ketone and (separately) the diolefin that originates from it. Deuteration studies would also help to establish whether the cyclopropyl product always originates from the diolefin when the starting material is the ketone.

Acknowledgment. The authors wish to thank Drs. E. B. Whipple and D. A. Arnold of the Union Carbide Research Institute for the n.m.r. spectra.

Production of Trapped Radicals from Alkyl Halides in Organic Glasses by Dissociative Electron Attachment and by Photodissociation¹

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin. Received July 23, 1965

The production of free radicals from alkyl halides by the dissociative electron attachment reaction ($\text{RX} + e^- \rightarrow \text{R} + \text{X}^-$) has been demonstrated, using electrons from the photoionization of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) in 3-methylpentane (3-MP) glass at 77°K. The radicals were detected by electron spin resonance. The relative yields for the same amount of light absorbed by TMPD are approximately: CH_3Cl , 100; CH_3Br , 30; CH_3I , 10; $\text{C}_2\text{H}_5\text{Cl}$, 40; $\text{C}_2\text{H}_5\text{Br}$, 25; $\text{C}_2\text{H}_5\text{I}$, ≤ 5 ; *i*- $\text{C}_3\text{H}_7\text{Cl}$, 20; *n*- $\text{C}_3\text{H}_7\text{Cl}$, 10; *i*- $\text{C}_4\text{H}_9\text{Cl}$, 20; *n*- $\text{C}_4\text{H}_9\text{Cl}$, 10. The methyl radicals produced from different parent species and at different concentrations all decay at a first-order rate with the same half-life (16 min.). This seems to require that decay is by combination with the parent partner and within the solvent cage where bond rupture occurred. Irradiation of solutions of CH_3I or $\text{C}_2\text{H}_5\text{I}$ in 3-MP glass at 77°K. with 2537-Å. radiation absorbed by the iodide produces alkyl radical spectra attributable to rupture of the C-I bond and to abstraction of H from 3-MP by hot CH_3 or C_2H_5 radicals. A sharp e.s.r. line, tentatively attributed to trapped electrons, is observed in both pure 3-MP radiolyzed with γ -rays at 77°K. and in TMPD solutions in 3-MP at 77°K. exposed to ultraviolet radiation absorbed by the TMPD, in accordance with reports from other laboratories.

Introduction

Alkyl halides all have electron affinities favorable to electron attachment ($\text{RX} + e^- \rightarrow \text{RX}^-$) and to dissociative electron capture ($\text{RX} + e^- \rightarrow \text{R} + \text{X}^-$).

(1) This work has been supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-32 and by the W. F. Vilas Trust of the University of Wisconsin.

Consequently, low concentrations may serve as electron scavengers in systems undergoing radiolysis. In so doing they often change the course of the radiolysis by increasing the lifetimes of positive ions, thus favoring ion molecule steps, by altering the chemistry of the neutralization step, and by serving as the source of new radicals. For this reason a detailed knowledge of the conditions under which electron attachment and dissociative electron capture occur is important.

Evidence for dissociative electron capture in the radiolysis of dilute solutions of alkyl halides in liquid hydrocarbons has been obtained by determining the yields of radioiodides formed when the solutions contain I_2 (I^{131}).^{2,3} Pulsed radiolysis of aqueous solutions of alkyl halides has been used⁴ to determine the relative rate constants for the reaction of different alkyl halides with hydrated electrons as indicated by the rate of disappearance of the hydrated electron spectrum. Both of these studies indicate that the relative effectiveness of alkyl halides in reacting with electrons is in the order $\text{RI} > \text{RBr} > \text{RCl}$.

Hamill and co-workers⁵ have studied the relative electron-capturing effectiveness of different alkyl halides as solutes in organic glasses undergoing radiolysis, by observing their ability to compete for electrons with solutes such as biphenyl and naphthalene, which form negative ions with known optical spectra. In other

(2) R. R. Williams, Jr., and W. H. Hamill, *Radiation Res.*, **1**, 158 (1954).

(3) P. R. Geissler and J. E. Willard, *J. Am. Chem. Soc.*, **84**, 4627 (1962).

(4) A. Sgutka, J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, **69**, 289 (1965).

(5) (a) M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962); (b) J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962); (c) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussions Faraday Soc.*, **36**, 169 (1963).