$$\text{ketone} + \text{Hg } ^3P_1 \longrightarrow \text{ketone}_m{}^3 + \text{Hg } ^1S_0 \qquad (11)$$

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.

Production of Trapped Radicals from Alkyl Halides in Organic Glasses by Dissociative Electron Attachment and by Photodissociation[1]

R. F. C. Claridge and J. E. Willard

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 $(RX + e^- \rightarrow R + X^-)$ 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; C_2H_5Cl, 40; C_2H_5Br, 25; C_2H_5I, ≤ 5; i-C_3H_7Cl, 20; n-C_3H_7Cl, 10; i-C_4H_9Cl, 20; n-C_4H_9Cl, 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 C_2H_5I 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 $(RX + e^- \rightarrow RX^-)$ and to dissociative electron capture $(RX + e^- \rightarrow R + X^-)$.

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 used[4] 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 $RI > RBr > RCl$.

Hamill and co-workers[5] 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

(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.

(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).

experiments, using benzyl chloride as the only solute, they have demonstrated growth of the known spectrum of the benzyl radical, both during radiolysis and as a result of photobleaching of the solvated electron spectrum following radiolysis.[5c] Confirmation that the radicals were formed by dissociative electron attachment was provided by a purely photochemical experiment in which the electrons came from the photoionization of 3×10^{-3} mole % N,N-dimethyl-p-phenylenediamine (DMPD) in 2-methyltetrahydrofuran (MTHF), containing 2 mole % benzyl chloride,[6] at 77°K. The known spectra of both DMPD+ and the benzyl radical were observed in the polar solvent MTHF but did not appear when the same experiment was carried out in nonpolar 3-methylpentane (3-MP).

Similar use of the optical spectra of simple alkyl radicals to study their formation by dissociative electron attachment from alkyl halides is precluded because the spectra of the radicals, unlike that of benzyl, do not occur in a readily accessible region. We have, therefore, used electron spin resonance to determine whether radicals are produced by dissociative capture of photoionized electrons by methyl, ethyl, propyl, and butyl halides, and by carbon tetrachloride in an organic glass at 77°K. Because of conflicting evidence in the literature on the relative efficiency of electron attachment by different alkyl halides, we have compared the radical yields from chlorides, bromides, and iodides. Concurrently with the photoelectron tests, we have done experiments to determine whether radicals can be formed in sufficient concentration for e.s.r. observation by the direct photodissociation of CH_3I or C_2H_5I in a 3-MP glass at 77°.

Experimental Section

Phillips Pure Grade 3-methylpentane was used after further purification. Methods of purification included: (1) mechanical stirring with 100% H_2SO_4 followed by washing and fractional distillation on a Todd column; (2) passing through a 4-ft. column of freshly activated alumina followed by fractional distillation of the first portion of the effluent; and (3) passing through a preparative gas chromatography column. All three methods reduced the onset of ultraviolet absorption for degassed samples of 1-cm. thickness from about 2700 to about 2200 Å. Matheson CH_3Cl, CH_3Br, and C_2H_5Cl were used as received. The other alkyl halides were Eastman White Label, further purified in most cases by passage through activated alumina and fractional distillation or by gas chromatography. Eastman tetramethylene-p-phenylenediamine ([CH_3]$_2$NC$_6$-H$_4$N[CH_3]$_2$) (TMPD), received as the hydrochloride, was extracted from alkaline aqueous solution with purified 3-MP, and the desired amount of alkyl halide was added. The 3-MP solution was then either dried with $MgSO_4$ or placed directly in an e.s.r. tube which was then attached to the vacuum line.

Drying was carried out on the vacuum line by distilling the 3-MP and halide through P_2O_5 and pumping on the residual TMPD in the sample tube at room temperature before distilling back the volatile components. Those alkyl halides which are gases at room temperature were added at this point.

(6) M. Kondo, M. R. Ronayne, J. P. Guarino, and W. H. Hamill, J. Am. Chem. Soc., 86, 1297 (1964).

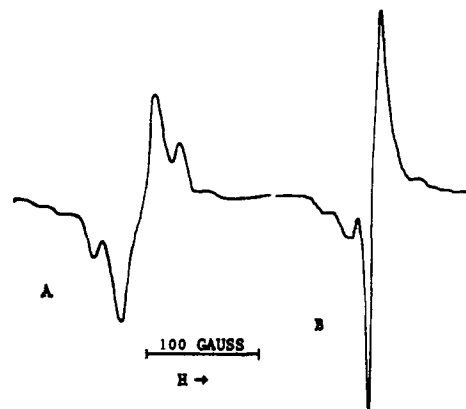Figure 1. (A) Signal from ultraviolet irradiation of 1.3×10^{-4} mole fraction of TMPD in 3-MP at 77°K. This is the signal designated as "background" in Figure 2; (B) signal from irradiation of TMPD in more highly purified 3-MP and also from γ-radiolysis of highly purified 3-MP. A and B received approximately the same irradiation dose. A was measured at a sensitivity about 13 times that of B.

Two sources of illumination were used. The first was a Bausch and Lomb monochromator set to deliver a band width of about 300 Å. with an intensity on the area of the sample of about 2×10^{14} photons sec.$^{-1}$ centered at 3450 Å. The other was a 100-w. AH4 medium-pressure mercury lamp with quartz envelope and quartz collimating lens. This was used without filter when radiation absorbed by the alkyl iodides was desired and with a Pyrex filter when radiation absorbed only by the TMPD was desired. When used with the filter to irradiate a 3-MP–TMPD–C_2H_5Cl glass, it produced ethyl radicals at a rate 13 times faster than the rate with the monochromator. TMPD in organic glasses at 77°K. has an absorption maximum at 3200 Å. with molar absorbancy index of ca. 3×10^3.[7]

Illumination was done with the sample in a quartz dewar in the e.s.r. cavity. A Varian 4500 e.s.r. spectrometer with 100-kc. modulation was used.[8] The spectra were recorded as the first derivative signal. Relative radical concentrations were estimated from peak heights. Line separations in gauss were estimated from the known line separation (507 gauss) of the hydrogen doublet induced in quartz sample tubes by γ-irradiation.

Results and Discussion

Control Experiments. Three laboratories[9] have reported the e.s.r. spectrum of the TMPD cation in aqueous solution to consist of 13 quintets with 7.4-gauss splitting between centers of the quintets. A broad unresolved e.s.r. spectrum with a sharp central line was observed[10] from a rigid solution of TMPD in 2-MP glass which had been exposed to ultraviolet irradiation at 77°K.

In the present work a spectrum such as that shown in Figure 1A or 1B was observed whenever 1.3×10^{-4} mole

(7) A. C. Albrecht and W. T. Simpson, *ibid.*, 77, 4454 (1955).
(8) We wish to thank Professor R. N. Dexter of the Physics Department for valuable assistance with problems concerned with the operation of the e.s.r. equipment.
(9) (a) S. I. Weissman, *J. Chem. Phys.*, 22, 1135 (1954); (b) T. R. Tuttle, Jr., *ibid.*, 30, 331 (1959); (c) K. H. Hauser, *Z. Naturforsch*, 14a, 425 (1959).
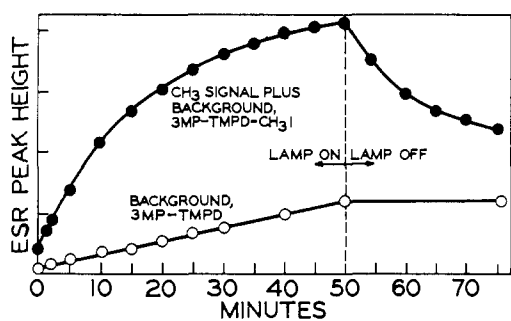(10) E. Dolan, *J. Chem. Phys.*, 37, 2508 (1962).

Figure 2. Upper curve: growth of methyl radical e.s.r. signal with time of irradiation of 3-MP-TMPD-CH₃I glass at 77°K. using monochromator set at 3450 Å.; right-hand side shows decay after turning off the lamp. Lower curve: effect of similar irradiation and dark period on spectrum of Figure 1A produced from 3-MP-TMPD glass at 77°K.
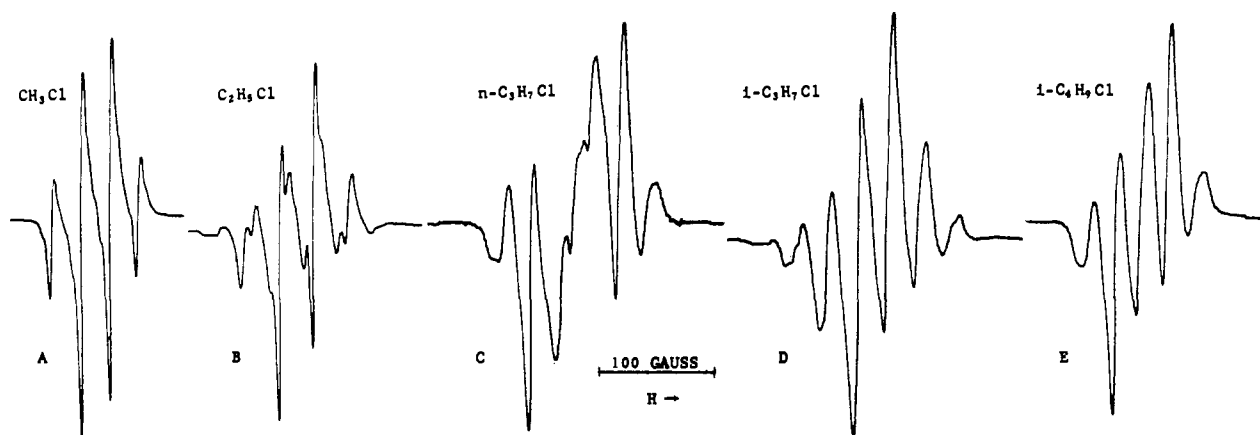
tense to interfere with the much stronger signal given by the alkyl radicals from dissociative capture when alkyl chlorides or bromides were present in the glass. It was also weaker than the methyl radical signal from methyl iodide (Figure 2).

Irradiation of 3-MP glasses containing 0.4–1.0 mole % of any one of the alkyl halides used in this work did not induce any e.s.r. signals when the monochromator was used at 3450 Å., or the Pyrex filter was used with the Hg lamp.

E.s.r. Spectra Produced. Selected e.s.r. spectra obtained following irradiation at 77°K. of 3-MP glass containing 1.3×10^{-4} mole fraction of TMPD and 4×10^{-3} mole fraction of alkyl halide are shown in Figure 3. CH₃Cl, CH₃Br, CH₃I, C₂H₅Cl, C₂H₅Br, C₂H₅I, n-C₃H₇Cl, i-C₃H₇Cl, n-C₃H₇I, i-C₃H₇I, n-

Figure 3. E.s.r. spectra from the irradiation of 3-MP-TMPD glass containing 4×10^{-3} mole fraction of alkyl chloride; all irradiations for 5 min. at 77°K. with filtered mercury lamp; TMPD present at 1.3×10^{-4} mole fraction; different e.s.r. sensitivity used on different spectra.

fraction of TMPD in 3-MP was irradiated at 3450 Å. for 4 min. with the monochromator. Spectra of the type of Figure 1A grew linearly with time of irradiation as shown in Figure 2. When irradiation was stopped, the signal intensity showed no sign of rapid decay. Spectra of the type of Figure 1B were observed in some samples of 3-MP-TMPD glass following radiation at 3450 Å. and in some samples of 3-MP following radiolysis with Co⁶⁰ γ-rays. These seemed to be samples which had received the most rigorous drying and purification. The sharp line never appeared in the presence of alkyl halides. Similar lines observed from the γ-radiolysis of 3-MP glass[11] and from the photolysis of TMPD in 2-MP[10] have been attributed to trapped electrons. This assignment is plausible. There is, however, some difficulty in explaining inhibition of the line by low levels of impurities, in view of evidence, to be discussed below, that the photoionized electrons from TMPD do not escape far from the parent TMPD⁺ ion. Careful study has been made of a similar line attributed to solvated electrons in MTHF.[12]

The species responsible for the spectrum of Figure 1A is presumed to be either an electron-scavenging impurity in the 3-MP or a radical formed as a result of energy available from the neutralization of the TMPD⁺ cation. This signal was not sufficiently in-

C₄H₉Cl, i-C₄H₉Cl, and CCl₄ were tested after 5-min. exposures to the filtered mercury arc. Of these all except the propyl iodides gave convincing evidence for radical formation by dissociative electron capture.

Methyl Halides. Methyl chloride, bromide, and iodide each gave a four-line spectrum, like Figure 3A, attributable to methyl radicals. This spectrum is similar to those reported for methane irradiated with Co⁶⁰ at 4°K. and measured at 20°K.[13] and for liquid methane undergoing electron irradiation at 97°K.[14] The relative intensities of the spectra produced from methyl chloride, bromide, and iodide for equal illuminations were approximately 10:3:1. This indicates that the relative efficiency of dissociative electron capture under these conditions is in this ratio and is in the reverse order to the dissociation cross sections observed for alkyl halides in liquid pentane,[3] and to the rate of capture in aqueous solutions.[4]

It is of interest that radiolysis of pure methyl chloride at 77°K. yields an e.s.r. spectrum of some ten lines,[13,15] in contrast to the four-line spectrum of Figure 3A. This indicates a relatively complex radiolytic mechanism for the pure material, with a predominant radical other than CH₃.

(11) D. Fueki and Z. Kuri, *J. Am. Chem. Soc.*, 87, 923 (1965).
(12) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, 43, 876 (1965).

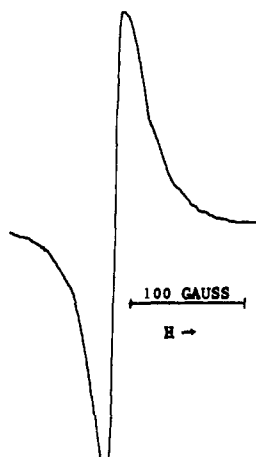(13) B. Smaller and M. Matheson, *J. Chem. Phys.*, 28, 1169 (1958).
(14) R. W. Fessenden and R. H. Schuler, *ibid.*, 39, 2147 (1963).
(15) P. B. Ayscough and C. Thomson, *Trans. Faraday Soc.*, 58, 1477 (1962).

Figure 4. E.s.r. spectrum of CCl_3 radical formed by ultraviolet irradiation of 3-MP glass containing 1.3×10^{-4} mole fraction of TMPD and 4×10^{-3} mole fraction of carbon tetrachloride.
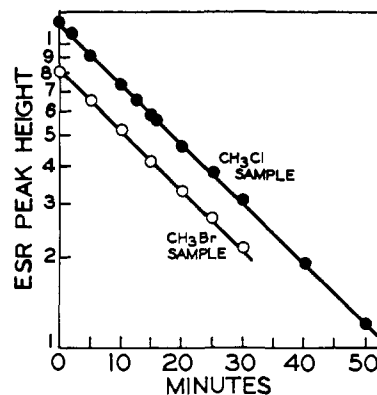

Figure 5. Log (e.s.r. peak height) vs. time for decay of methyl radicals. Points show the observed peak height minus the long-lived background: ●, radicals from irradiation of 3-MP–TMPD–CH_3Cl; O, radicals from irradiation of 3-MP–TMPD–CH_3Br.

Ethyl Halides. Each of the ethyl halides gave a 12-line ethyl radical spectrum. The spectra for ethyl chloride and ethyl bromide were indistinguishable (Figure 3B) in every respect except intensity, while that from ethyl iodide was much weaker but, when measured at high intensity, showed the same features superimposed on the background signal of Figure 1A. The intensity ratio $C_2H_5Cl:C_2H_5Br:C_2H_5I$ was estimated to be about 40:24:4, relative to CH_3Cl as 100.

Ethyl radical spectra with 12 lines having splittings similar to Figure 3B have been reported for ethane,[13] ethylene,[13] and ethyl chloride[13,15,16] irradiated with Co^{60} γ-rays at 77°K., and for liquid ethane during irradiation with electrons.[14] By contrast, the spectra observed from γ-irradiated ethyl iodide glass[17] at 77°K. and from X-irradiated mercury diethyl[18] consist of six symmetrical lines indicating line broadening or equal coupling of the unpaired electron with each of the five protons in the ethyl radical. Also, the spectrum of γ-irradiated ethyl bromide at 77°K. is unsymmetrical with structure on the low-field side of the six-line spectrum.[15,17,19] It has been suggested[19] that this structure may result from interaction of the unpaired electron with bromine in a bromine-containing radical.

Propyl and Butyl Halides. The characteristic eight-line spectrum of isopropyl radical[15] (Figure 3D) was produced by irradiation of 3-MP–TMPD glass containing isopropyl chloride. Isobutyl chloride gave the spectrum of Figure 3E, attributable to isobutyl radical.[15,20] n-Propyl chloride as additive gave the spectrum of Figure 3C, and the pattern when normal butyl chloride was used was very similar. It appears that this spectrum may be the six-line normal alkyl radical spectrum observed in glassy normal alkyl halides[15,17] superimposed on a stronger-than-usual background spectrum of the type of Figure 1A.

In the case of both the propyl and the butyl compounds, the signal from the iso form was 50–100% greater than that from the normal. The ratio of the

intensities from CH_3Cl, C_2H_5Cl, n-C_3H_7Cl, and n-C_4H_9Cl was approximately 100:40:10:10. Both isopropyl iodide and n-propyl iodide gave much weaker signals than the corresponding chlorides. These were difficult to distinguish from background under the conditions of these tests.

Carbon Tetrachloride. The broad single line shown in Figure 4 was obtained when carbon tetrachloride was the additive. This is identical with the spectrum we have observed when solid carbon tetrachloride at 77°K. is irradiated with Co^{60} γ-rays, and which S. Aditya of our laboratory has observed when HI dissolved in a mixture of CCl_4 and C_2H_5Br in the solid state at 77°K. was photolyzed with 2500-Å. radiation. It appears, therefore, that it must be attributed to the CCl_3 radical and that its production in the 3-MP–TMPD–CCl_4 system is evidence for the reaction $CCl_4 + e^- \rightarrow CCl_3 + Cl^-$. Other authors[21] have reported "broad bands" from CCl_4 following γ-irradiation at 77°K.

Methyl Radical Decay Kinetics. When the logarithm of the intensity of the methyl radical spectrum from irradiation of CH_3Cl or CH_3Br in the 3-MP–TMPD matrix was plotted against time, after subtraction of the intensity of the long-lived background signal of the species shown in Figure 1A, the straight lines of Figure 5 were obtained. These lines indicated that the decay of methyl radicals from either CH_3Cl or CH_3Br is first order with a half-life of 16 min. After correction is made for the background signal, approximately the same half-life is indicated by the growth and decay of the methyl radical concentration from photolysis of 3-MP–TMPD–CH_3I glass illustrated in Figure 2. The fact that the half-lives for these three experiments were the same, while the concentrations of methyl radicals differed by a ratio of some 60:20:1, shows that the radicals are not removed by combination with other methyl radicals, since the latter are distributed at random through the glass and the rate of combination with them would be second order. It is also clear that the rate of radical removal is independent of whether the partner fragment formed with each radical is Cl^-, Br^-, or I^-. Hypotheses which may be postulated to explain the pseudo-first-order decay are considered below.

(16) S. V. Filseth, Ph.D. Thesis, University of Wisconsin, 1962.

(17) H. W. Fenrick, S. W. Filseth, A. L. Hanson, and J. E. Willard, *J. Am. Chem. Soc.*, **85**, 3731 (1963).

(18) W. Gordy and C. G. McCormack, *ibid.*, **78**, 3243 (1956).

(19) F. W. Mitchell, B. C. Green, and J. W. T. Spinks, *J. Chem. Phys.*, **36**, 1095 (1962).

(20) P. P. Ayscough and H. E. Evans, *J. Phys. Chem.*, **68**, 3066 (1964).

(21) N. Leray and J. Roncin, *J. Chem. Phys.*, **42**, 800 (1965).

(1) Radical removal by hydrogen abstraction from 3-MP or TMPD. This is highly improbable at 77°K., from activation energy considerations, and also because there is no growth of an e.s.r. signal corresponding to the formation of a new radical.

(2) Radical removal by combination with the X^- ion to form CH_3X^-. This possibility cannot be excluded. It would require zero or equal energies of activation for the reactions of the methyl radical with each of the three different halide ions and would require that the radical and ion always be trapped within the same solvent cage,[22] and that the CH_3X^- ion give no observable e.s.r. signal.

(3) Radical removal by either a stepwise or concerted reaction of the type $TMPD^+ + I^- \rightarrow TMPD + I$, $CH_3 + I \rightarrow CH_3I$. This, like the second alternative, requires equal probability of reaction with the different halide ions, and requires that the reactant partners be within the same solvent cage.[22]

Qualitative observations we have made on the decay of methyl radicals formed both by the γ-ray radiolysis of 3-MP glass containing CH_3I and by the photolysis with 2537-Å. radiation of a similar solution indicate that the half-life at 77°K. is about the same as that in Figure 5. This implies that the recombination rate of paired fragments in the parent cage is not related to the presence of TMPD or to the presence of negative charge on the halogen.

The evidence suggests that the rate-determining step in the decay of trapped methyl radicals in systems of the type discussed here may be a rearrangement of the planar methyl radical structure to a geometry more favorable for combination with a highly reactive partner within the same solvent cage.

All other radicals which we have observed in this work decay much more slowly than the methyl radicals, the rate for ethyl radicals being about 10%/hr., and for the others still slower.

Dissociation Step. The requirement that the $TMPD^+$, CH_3, and I^- be in the same solvent cage is not implausible if the TMPD exists in a complex with CH_3I at the time of light absorption. A number of considerations make the $TMPD–CH_3X$ complex hypothesis attractive. One is the fact that it allows for the dissociation step without requiring the migration of the photoionized electron, which is necessary if the alkyl halide is dispersed at random in the glass. Evidence that electrons trapped in 3-MP at 77°K. do not migrate readily is given by the stability of their optical spectra,[5] by photoconductivity experiments,[24] and by the stability of e.s.r. peaks such as those of Figure 1B. Migration of the electrons would result in their disappearance by neutralization on encounter with the cations. Electroluminescence experiments on ultraviolet-irradiated 3-MP–TMPD solutions show that repeated application of a unidirectional electric field[24] produces lumines-

cence only on the first application, but that reversal of the field produces a second luminescence. This is interpreted as evidence for trapping of electrons in close proximity to the parent ion.

Direct dissociation of the RX molecules by absorption of photons from the filtered mercury lamp has been shown not to occur, by the fact that radicals are not produced in irradiations of 3-MP–RX glasses without TMPD present. However, the photons absorbed by TMPD from the filtered source are of sufficient energy to dissociate the C–X bonds, and so the possibility must be considered that dissociation to R and X occurs through energy transfer. The fact that the optical spectrum of $TMPD^+$ grows in parallel with that of benzyl radical when 3-MP–TMPD glass containing benzyl chloride is irradiated[5c] is evidence in favor of a mechanism involving ionization and electron attachment, rather than energy transfer between neutral species.

A question of considerable interest is why the efficiency of dissociative electron attachment in the systems reported here increases in the order RI < RBr < RCl, which is the reverse of that deduced from radiolyses in liquid hydrocarbons[3] and the reverse of the rate constants for reaction of solvated electrons with aqueous alkyl halides.[4] It agrees in some cases but not in others with the order of electron attachment efficiency deduced from studies in which alkyl halide solutes compete with biphenyl or naphthalene for electrons[5b] produced by radiolysis. We have also observed that CCl_4, CH_3Cl, and C_3H_7Cl in 3-MP glass at 77°K. are efficient in reducing the yield of I_2 and CH_4 produced from CH_3I during radiolysis, indicating their effectiveness in competing with CH_3I for electrons. Since complexing of the alkyl halides would not be a determining factor in the latter system, it does not appear that differences in ease of complexing of TMPD with the different alkyl halides used in the present work is adequate to explain the observed differences in probability of dissociative electron attachment. It is known from mass spectrometric evidence[25] that kinetic as well as thermodynamic factors are important in determining the probability of the dissociative capture process. Thus, the appearance potential for Cl^- from gaseous CH_3Cl is 10 e.v., while the appearance potentials for Br^- and I^- from CH_3Br and CH_3I are zero.[25] It appears that the nature of the trapping of the alkyl halide molecule in the solid matrix as compared to its condition in the liquid state may serve to alter the cross section for the dissociative capture process.

Caging effects may also influence the yields in the solid state. The probability of the halide ion escaping from its radical partner depends on the energy available in excess of the C–X bond energy, on the size of the halogen and of the radical, on their relative masses, on the degrees of freedom available to take up energy in the radical, and on the density and composition of the cage walls. It has been shown,[26] however, that only 0.08 of those C_2H_5I molecules which absorb 2537-Å. radiation (113 kcal./mole) in liquid C_2H_5I at 200°K. escape from the parent I atom. Extrapolation of

(22) The fact that all of the methyl radicals decay with the same half-life (Figure 5) indicates that they are similarly positioned with respect to the event that produces decay. If the decay is by combination with the X^- formed when the CH_3 was formed, the two must be within the same solvent cage since, if they were separated by one molecular diameter or more, the probability of recombination would be much less[23] than the 100% recombination observed.

(23) R. M. Noyes, *J. Chem. Phys.*, 18, 999 (1950).

(24) (a) G. E. Johnson and A. C. Albrecht, Abstracts of papers presented at the International Conference on Photosensitization in Solids, Illinois Institute of Technology, Chicago, Ill., June 1964; (b) G. E. Johnson, Ph.D. Thesis, Cornell University, 1965.

(25) V. H. Diebeler and R. M. Reese, *J. Res. Natl. Bur. Std.*, 54, 127 (1955).

(26) R. H. Luebbe, Jr., and J. E. Willard, *J. Am. Chem. Soc.*, 81, 761 (1959).

data at 300 and 200°K. indicates an escape yield of only 5×10^{-4} at 77°K. This is a further argument in favor of the conclusion that the R and X⁻ species formed in the present work are trapped in the same solvent envelope.

Radical Production by Photodissociation of Alkyl Iodides in 3-MP at 77°K. Methyl iodide and ethyl iodide at 0.005 mole fraction in 3-MP glass at 77°K. were each photolyzed for 4 min. with the unfiltered radiation of the Hg lamp. The former produced the sharp four-line spectrum characteristic of methyl radicals, which decayed with a half-life similar to that for CH_3 radicals produced by the photoionization process and discussed above. Two additional lines outside the methyl lines did not decay as rapidly and, when the methyl signal had disappeared, proved to be part of a 3-methylpentyl radical spectrum. This 3-methylpentyl radical spectrum was similar to that produced[27] by the attack on 3-MP of hot H atoms from

the photolysis of HI. It is attributed to the abstraction of hydrogen from 3-MP by hot methyl radicals formed by the photolysis of CH_3I. Hot reactions of methyl radicals from the photolysis of gaseous CH_3I[28a] and of CH_3I in liquid cyclohexane,[28b] in alkene glasses at 77°K.[28c] and in inert gas matrices at 20°K.,[28d] have been demonstrated earlier. The spectrum from the photolysis of C_2H_5I in 3-MP has six lines with intensity ratios which are characteristic of both ethyl[17] and 3-methylpentyl[27] radicals. The line splittings are *ca.* 24 gauss, slightly less than those observed for ethyl (*ca.* 27 gauss). These splittings and the detailed shape of specific lines are characteristic of the 3-MP radical, suggesting a high efficiency of H abstraction by hot ethyl radicals from the photolysis of C_2H_5I in this system.

(28) (a) G. M. Harris and J. E. Willard, *ibid.*, 76, 4678 (1954); (b) R. F. Pottie, W. H. Hamill, and R. R. Williams, Jr., *ibid.*, 80, 4224 (1958); (c) P. B. Ayscough and H. E. Evans, *Trans. Faraday Soc.*, 60, 801 (1964); (d) C. D. Bass and G. C. Pimental, *J. Am. Chem. Soc.*, 83, 3754 (1961).

(27) S. Aditya and J. E. Willard, *J. Am. Chem. Soc.*, in press.

The Hydrogen Bromide Catalyzed Isomerization of *n*-Butenes. II.[1] Kinetic Investigation

Allan Maccoll and R. A. Ross

Contribution from the William Ramsay and Ralph Forster Laboratories, University College, London, England. Received June 15, 1965

The kinetics of the hydrogen bromide catalyzed isomerization of butene-1 to butene-2 has been studied in a static system over the temperature range 559–656°K. The reaction is predominantly homogeneous and molecular with the kinetic form: rate of isomerization of butene-1 = k_2[butene-1][HBr]. The Arrhenius equation over this temperature range is log k_2 = 11.86 − 26,300/2.3RT, where k_2 is in units of mole⁻¹ cc. sec.⁻¹.

Introduction

Hydrogen bromide is known to catalyze the dehydration of alcohols in the gas phase and these reactions have been claimed to be molecular.[2] As one guide to mechanism in these reactions the olefin distribution from unsymmetrical alcohols has been investigated. In the case of *t*-pentyl alcohol the equilibrium proportions of the three methylbutenes were found,[3] clearly indicating isomerization of the olefins by hydrogen bromide. The equilibrium proportions of the *n*-butenes were found as the products from *sec*-butyl alcohol and hydrogen bromide,[2] again suggesting isomerization.

The olefin distribution found in the dehydrobromination of *sec*-butyl bromide also indicated isomerization by the halide formed.[4] Hydrogen bromide has been

shown to catalyze the isomerization of cyclopropane,[5] the kinetic behavior being similar to that found in the catalyzed alcohol dehydrations. The catalyzed isomerization of *n*-butene by hydrogen bromide is now reported.

Experimental Section

The materials and apparatus have been described previously.[1] The Pyrex reaction vessel was "conditioned" by allowing a mixture of butenes to remain in it for a few days at ~450°. This resulted in a transparent, amber-colored coating being deposited uniformly on the surface. Air was rigorously excluded from the apparatus and a small amount of reaction mixture was generally left in the vessel between runs and overnight, the vessel only being fully evacuated just prior to the start of a run. Taps on the vacuum line were greased with Apiezon M grease except those that came in contact with reaction products, which were greased with B.D.H. Fluorube A grease.

Procedure. Butene-1 was normally admitted to the reaction vessel first and its pressure measured (no detectable reaction occurs below ~450°). Hydrogen bromide was admitted from a much higher pressure at zero time. Any temperatue change, measured with a glass-covered thermocouple probe inside the reaction vessel, is less than 0.2°.

At the end of a run the products were expanded into an evacuated 5-l. flask containing 10 g. of $Ba(OH)_2$[5]

(1) Part I: A. Maccoll and R. A. Ross, *J. Am. Chem. Soc.*, 87, 1169 (1965).

(2) See, *e.g.*, R. L. Failes and V. R. Stimson, *J. Chem. Soc.*, 653 (1962), and previous papers in the series.

(3) V. R. Stimson and E. J. Watson, *ibid.*, 3920 (1960).

(4) A. Maccoll and R. H. Stone, *ibid.*, 2756 (1961).

(5) R. A. Ross and V. R. Stimson, *ibid.*, 1602 (1962).