Reaction Intermediates in the Radiolysis of Alkyl Iodides in 3-Methylpentane Glass at 77°K[1]

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Abstract: At least six metastable species with absorption maxima in the 3000–8000-A range result from the γ irradiation of dilute solutions of alkyl iodides in 3-methylpentane (3-MP) glass at 77°K and below. The predominant species immediately after irradiation at 20 or 77°K decays within minutes at 77°K or above, accompanied by a sequence of growth and decay of other species. These are distinguished by differences in their stability with respect to aging and photobleaching and by the effect which charge scavengers have on their yields. Five of the species involve the alkyl radicals from the RI as well as the I atom, since only one peak is produced when HI is radiolyzed in 3-MP at 77°K. None of the same maxima are observed when the solute is a bromide or chloride. The sixth species, which grows following irradiation, appears to be I_2^-. All ten iodides tested give peaks consistent with an RI^+ species which converts to an $(RI)_n{}^+$ species, as suggested earlier[2] for CH_3I in 3-MP. γ-Irradiated solutions of alkyl iodides in methyltetrahydrofuran are transparent in the 3000–8000-A region, indicating that charge is stabilized on the solvent, or that $(RI)_n$ clusters are precluded by the polar nature of the solvent, or both. $G(I_2)$ from C_4H_9I and $G(CH_4)$ from CH_3I in 3-MP at 77°K are both greatly reduced by 10^{-2} mf CCl_4, consistent with the conclusion that their formation includes a dissociative electron capture step. Photolysis of HI or of n-C_4H_9I in 3-MP at 77°K produces neutral species absorbing in the 4000-A region which increase in concentration on standing at 80°K following photolysis.

Radiolysis of pure C_2H_5I, n-C_4H_9I, i-C_4H_9I, or n-$C_5H_{11}I$ in the glassy state at 80°K produces four trapped intermediates which show absorption maxima at approximately 7500, 5200, 4050, and 3500 A.[3] Incidental to a more extensive investigation of other compounds, Bertin and Hamill,[2] working with CH_3I and n-C_4H_9I dissolved in 3-MP glass at 77°K, have observed somewhat similar, but different, absorption peaks following γ irradiation. They have ascribed one of these to I^- and have suggested that others are formed by reactions requiring aggregates of RI molecules. The dilute solutions of polar RI molecules in a nonpolar solvent are of particular interest because they may favor aggregation effects, because charge or energy transfer from solvent to solute is necessary to give significant yields and because the results may be compared with those in a polar solvent such as methyltetrahydrofuran. We have, therefore, investigated factors affecting the spectra produced by the radiolysis of solutions of ten different alkyl halides in 3-MP glass. The studies show that the 390-mμ peak ascribed[2] to I^- is probably caused by I_2^-, that a decaying peak in the 4400-A region previously believed[2] to occur only with CH_3I is produced in all the alkyl iodides in 3-MP, and that reaction in $(RI)_n$ aggregates seems to be needed to explain the data. Additional peaks are further characterized.

Experimental Section

Phillips pure grade 3-methylpentane (3-MP), 2-methylpentane (2-MP), and alkyl halides were purified as described previously.[2-4] Eastman White Label methyltetrahydrofuran (MTHF) (stabilized with hydroquinone) was distilled *in vacuo* from sodium metal and stored *in vacuo* on a sodium mirror. Phillips pure grade cyclohexane was further purified by preparative gas chromatography. Gaseous HI was prepared on the vacuum line by dehydrating reagent grade aqueous HI with P_2O_5 and removing I_2 by contact with Ag powder.

All solutions were degassed by several cycles of freezing, pumping, and melting, and passed through P_2O_5 on the vacuum line. Samples to be irradiated at 77°K were sealed in 1-cm² quartz tubing, and immersed in liquid nitrogen to convert them to the glassy form. Irradiation and spectrophotometric examination were carried out as previously described.[3] The optical density of the irradiated quartz was less than 0.05 in the spectral range used. Dose rates from the Co^{60} source were about 2×10^{18} ev g^{-1} min^{-1} during the course of this work. When desired, the liquid nitrogen coolant was maintained at 67°K by bubbling He gas through it.

Samples to be irradiated at 20°K consisted of a layer of 3-MP glass $^1/_{16}$ in. thick contained between Suprasil quartz plates sealed with silicone cement to a $^1/_{16}$-in. thick copper spacer with a rectangular cavity in the center. A $^1/_{32}$-in. hole through the spacer at one end of the cavity allowed connection to a glass tube through which the cavity could be evacuated and filled prior to sealing off. The other end of the spacer contained a threaded projection for screwing into the cold finger of an Air Products and Chemicals Co. Cryotip refrigeration unit. The vacuum jacket for the refrigerated finger was designed to allow exposure of the cold sample to irradiation from the Co^{60} source at a dose rate of about 2×10^{17} ev g^{-1} min^{-1}, and to allow examination on the Cary spectrophotometer without interrupting operation of the cooling system. It was not usually possible to lower the 3-MP glass to 20°K without some cracking which lowered its transmission of light. For this reason the absorption spectra in these experiments were taken using a Sylvania Type DXL high-intensity lamp, in place of the usual spectrophotometer light source, and neutral density filters in the path of the reference beam.

Methane was determined by gas chromatography, using a 10-ft 5-mm i.d. column of 10% SF 96 silicone oil on Chromosorb P at 45°, after separating the low-boiling gases from the irradiated mixture by fractionation in a microstill.[5]

Iodine yields were found by extraction of the irradiated sample with 1 *N* KI and measurement of the I_3^- absorption in the aqueous layer.[6] To test for HI, the irradiated sample was extracted with water, and I_3^- was measured in the aqueous layer after adding an equal volume of 2 *N* KI containing KIO_3.

In the text below concentrations of additives are stated as mole fraction, abbreviated as mf.

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

(2) E. P. Bertin and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 1301 (1964).

(3) R. F. C. Claridge and J. E. Willard, *ibid.*, **88**, 2404 (1966).

(4) R. F. C. Claridge and J. E. Willard, *ibid.*, **87**, 4992 (1965).

(5) W. Van Dusen, Jr., and W. H. Hamill, *ibid.*, **84**, 3648 (1962).

(6) S. U. Choi and J. E. Willard, *J. Phys. Chem.*, **66**, 1041 (1962).

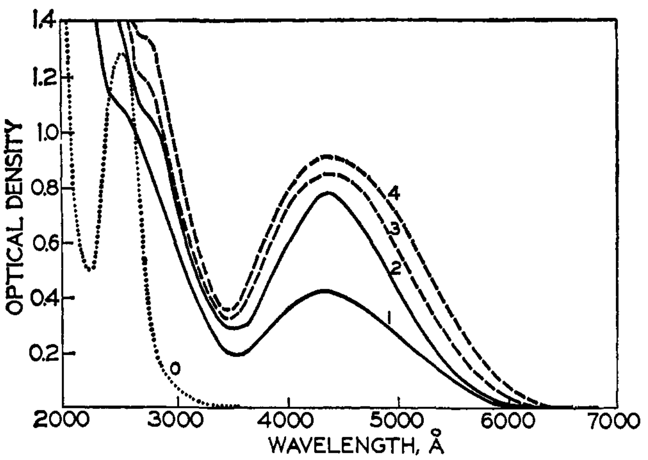

Figure 1. Spectra produced by photolysis of n-C_4H_9I in 3-MP glass at 80°K: (0) before photolysis, (1) 2.75-hr photolysis; (2) 6.5-hr photolysis, (3) 1-hr standing after 6.5-hr photolysis, (4) 2-hr standing after 6.5-hr photolysis. [n-C_4H_9I] = 1×10^{-4} mf.

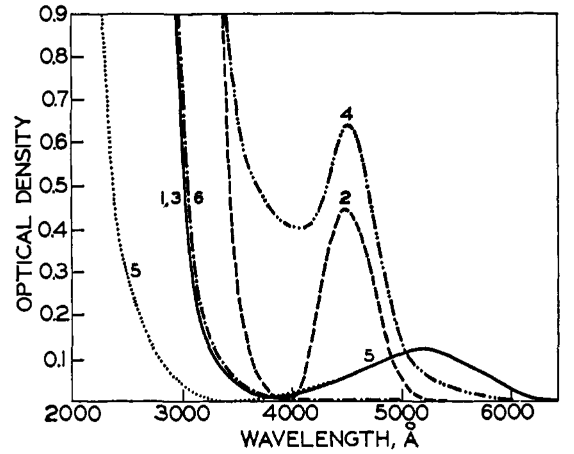

Figure 2. Spectra of stable species in 3-MP: (1) 1.1×10^{-2} mf n-C_4H_9I + 1.5×10^{-5} mf I_2 at 300°K, (2) same as (1) but at 80°K, (3) 1.1×10^{-2} mf C_4H_9I + 1.5×10^{-5} mf I_2 + 1.5×10^{-3} mf HI at 300°K, (4) same as (3) but at 80°K, (5) 1.5×10^{-3} mf HI + 1.5×10^{-6} mf I_2 at 300°K, (6) 1.1×10^{-2} mf n-C_4H_9I at 80°K.

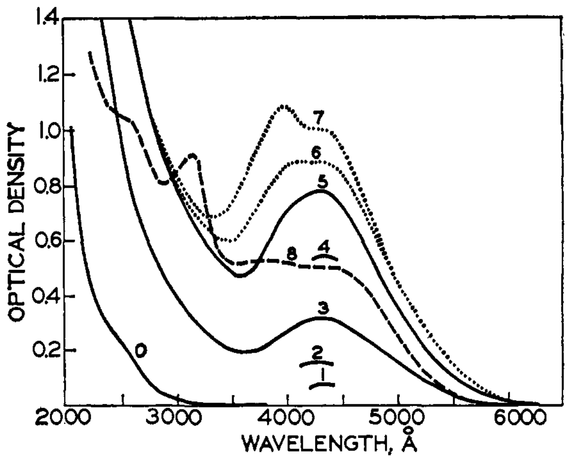

Figure 3. Spectra produced by photolysis of HI in 3-MP glass at 80°K: (0) before photolysis, (1) 0.5-hr photolysis, (2) 1.0-hr photolysis, (3) 2.0-hr photolysis, (4) 3.0-hr photolysis, (5) 4.0-hr photolysis, (6) 1-hr standing after 4-hr photolysis, (7) 2-hr standing after 4-hr photolysis, (8) melted and refrozen. [HI] = 1×10^{-4} mf.

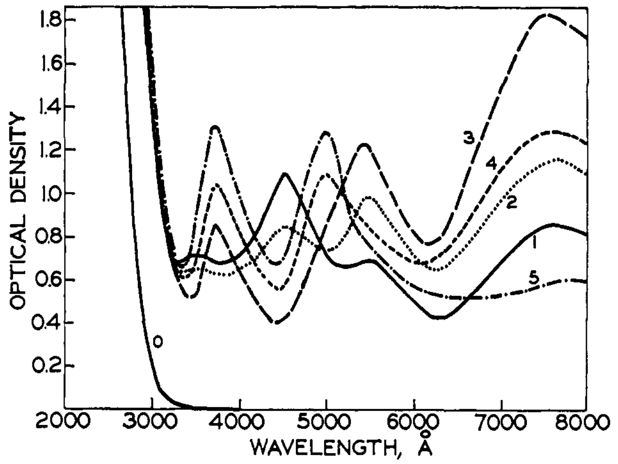

Figure 4. Spectra of γ-irradiated n-C_4H_9I in 3-MP at 80°K as a function of time after irradiation: (0) before irradiation, (1) immediately after irradiation, (2) 10-min standing at 80°K, (3) 30-min standing at 80°K, (4) 120-min standing at 80°K, (5) 400-min standing at 80°K. [n-C_4H_9I] = 1.1×10^{-2} mf; dose = 1×10^{19} ev g^{-1}.

Results

Spectra of Iodides and Iodine in 3-MP Glass without Irradiation and with Photolysis. Curve 0 of Figure 1 indicates that 10^{-4} mf n-C_4H_9I in 3-MP at 80° shows negligible absorption above 3000 A. At 10^{-2} mf significant absorption begins at about 3500 A (curve 6, Figure 2). The latter is moved to longer wavelength by the presence of I_2 (curve 2, Figure 2) or HI (curve 4, Figure 2). The presence of I_2 gives an absorption peak at 4500 A and that of HI increases absorption in the 3800–4100-A region. The 4500-A peak results from an RI–I_2 complex which is unstable in the same system at 300°K, and the enhanced absorption resulting from HI is also absent at 300°K (curves 1 and 3 of Figure 2, which fall on the same solid line). At 300°K a mixture of HI and I_2 in 3-MP shows no absorption above 3000 A except the 5200-A absorption of I_2 (curve 5, Figure 2).

3-Methylpentane containing 3.2×10^{-6} mf I_2 forms a clear glass at 80°K with an absorption maximum at 5100 A, having an extinction coefficient of 1.2×10^3 l. mole^{-1} cm^{-1}. The spectra of higher concentrations of I_2 in pure 3-MP are broad and show a continuous increase in absorption with decreasing wavelength, indicating that iodine precipitates. Impure 3-MP can retain more iodine in the clear glassy state than can be dissolved in the pure hydrocarbon. In the impure glasses the absorption maximum is shifted to 4500 A owing to complex formation, as in the case of the glasses containing n-C_4H_9I, illustrated in Figure 2.

Figures 1 and 3 show that photolysis of n-C_4H_9I and HI, respectively, in 3-MP at 80°K, using 2500-A radiation, produces neutral absorbing species which continue to grow in concentration for periods of hours following the photolysis.

Spectra of 3-MP Glass Containing Dissolved Iodides, Following Radiolysis at 77°K. Changes on Aging and Photobleaching. The prominent features of the spectra of γ-irradiated solutions of ten alkyl iodides, of HI, of a bromide, and of a chloride in 3-MP glass are summarized in Table I. Radiolysis was at 77°K and spectral observation at 80°K. Changes in the spectra of the iodides with time of aging in the dark after irradiation are illustrated in Figure 4, and changes with il-

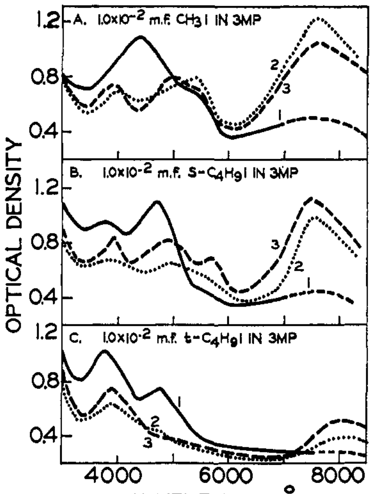

Figure 5. Spectra at 67°K as a function of photobleaching after γ irradiation: (1) after γ irradiation, (2) after 1.75-min bleaching, (3) after 3.5-min bleaching. Dose = 1×10^{19} ev g^{-1}.

lumination in Figure 5.[7] The plots are representative of the peak growth and decay behavior for all of the alkyl iodides. The positions of the maxima, except that at 3950 A, vary somewhat from compound to compound (Table I), and the relative intensities and rates of change of intensity also differ. Use of a 2-methylpentane matrix in place of 3-MP does not change the absorption maxima or qualitative growth and decay of peaks in tests with C_2H_5I and n-C_4H_9I.

Table I. Position of Absorption Maxima[a] Resulting from γ Irradiation of 10^{-2} mf Solutions of Alkyl Halides in 3-MP Glass at 77°K

CH_3I		3950	4400 (0.5)	5350	7650 (0.8)
C_2H_5I	3550 (wk)	3950	4450 (0.6)	5400	7500 (1.1)
n-C_3H_7I			4550 (0.6)		7650 (1.0)
n-C_4H_9I	3550 (wk)	3950	4550 (0.6)	5400	7600 (1.2)
n-$C_5H_{11}I$	3550	3950	4600 (0.6)		7600 (0.5)
n-$C_6H_{13}I$		3950	4600 (0.5)		7500 (0.3)
i-C_4H_9I	3650	3950	4650 (0.6)		7700 (1.1)
i-C_3H_7I	3800 (0.2)	3950	4625 (0.6)		7500 (1.1)
sec-C_4H_9I	3800 (0.2)	3950	4700 (0.6)		7500 (0.9)
t-C_4H_9I	3800 (0.4)	3950	4800 (0.3)		8000 (0.3)
HI		3950			
n-C_4H_9Br		3650			6000
n-C_4H_9Cl					

[a] Including peaks which grew in or decayed during 7 hr of standing at 80–83°K following 5 min of γ irradiation at a dose rate of 1.9×10^{18} ev g^{-1} min^{-1}. The numbers in parentheses indicate the optical density of the peaks in the 4500- and 3800-A regions at the time of the first reading (*ca.* 10 min after irradiation) and of the peak in the 7600-A region at the maximum reading obtained.

In comparison with the radiolyzed alkyl halide solutions in 3-MP glasses, the spectrum produced when HI is the solute is simple, as shown in Figure 6.

In all ten of the radiolyzed alkyl iodide–3-MP glasses the absorption peak in the 4400–4800-A region decayed by some 50% or more in 10 min in the dark at 80°K, while the peaks in the 7500- and 5500-A regions grew and a peak at 3950-A appeared. On longer standing further changes occurred. For example, in the n-C_4H_9I system, when the 4550-A peak had decayed completely, the 7600-A peak reached a maximum and then decayed slowly. At the same time the 5400-A peak decayed and a new peak appeared at 5000 A. After several hours of aging (line 5, Figure 4) the 3950- and 5000-A peaks were present with a smaller peak in the 7500-A region.

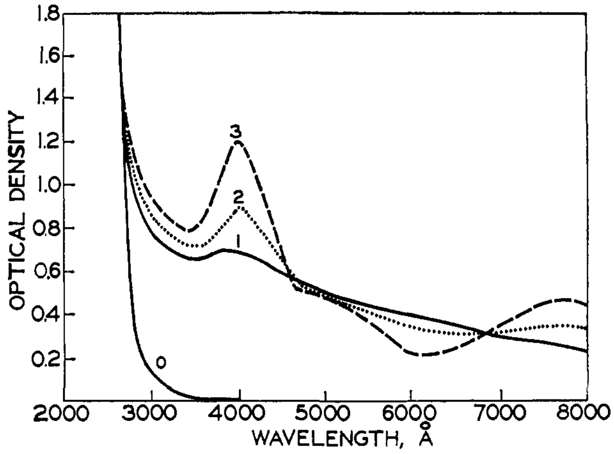

Figure 6. Spectra of γ-irradiated HI in 3-MP at 80°K as a function of time after irradiation: (0) before irradiation, (1) immediately after irradiation, (2) 30-min standing at 80°K, (3) 90-min standing at 80°K. [HI] = 1.3×10^{-2} mf; dose = 1×10^{19} ev g^{-1}.

At 77°K the rate of change of the spectra is appreciably slower than at the 80°K temperature used in the experiments of the preceding paragraph. At 67–70°K little change in intensity of the spectra occurred during several hours in the dark.

Photobleaching tests were made using the infrared analyzing beam of the Cary 14 spectrophotometer[8] filtered with Corning 1–69 and 2–62 filters to limit the spectral range to 6000–10,000 A.[9] The duration of each bleaching interval was 1.75 min, the time required to record this spectral range with the spectrophotometer. Following each such scan the spectrum from 3000 to 7000 A was recorded, using the visible ultraviolet source of the spectrophotometer. The intensity of the analyzing light in the latter region was too low to cause bleaching.

The iodides from methyl through butyl all showed nearly complete bleaching of the 4400–4800-A peak in 1.75 min. Three examples for solutions held in liquid N_2 at 67°K are shown in Figure 5. The systems containing the longer chain iodides, n-$C_5H_{11}I$ and n-$C_6H_{13}I$, were more resistant. For these systems the 7500-A peak was proportionately slow in growing. In all cases prolonged bleaching reduced the peak in the 7500-A region to a low value, as in the case of the pure alkyl iodides reported earlier,[2] but had little effect on the other remaining peaks.

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[7] The samples for these spectra and some of the data in Table I were not treated with P_2O_5. Where comparisons were made they did not differ from thoroughly degassed samples. The *sec*-C_4H_9I was Eastman White Label grade, treated only by shaking with P_2O_5.

[8] For analysis in the infrared region all of the radiation from the source enters the sample before entering the monochromator of the spectrophotometer. With a thermocouple imbedded in the organic glass reading 80°K the temperature rises to a steady state of 100°K when the full infrared analyzing light of the Cary spectrophotometer is allowed to fall on the glass, but only to 84° when the filter cutting off wavelengths above 10,000 A is used. The effect of heating and photobleaching is completely negligible when using the visible ultraviolet source, since the light passes through the monochromator before entering the sample.

[9] J. P. Guarino and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 777 (1964).

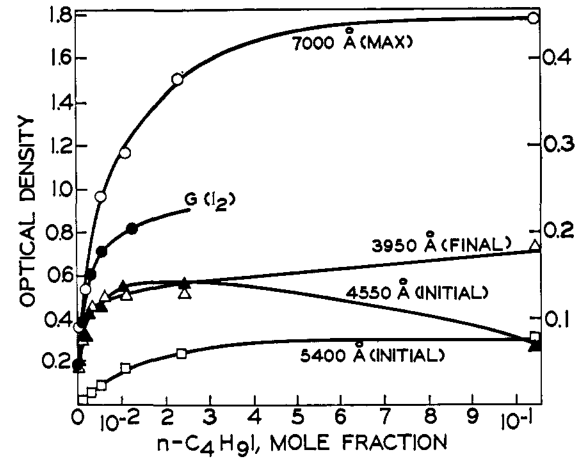

Figure 7. Effect of n-C_4H_9I concentration on spectral intensities and G (I_2) produced by γ irradiation of n-C_4H_9I in 3-MP at 80°K. Dose = 1×10^{19} ev g^{-1}.

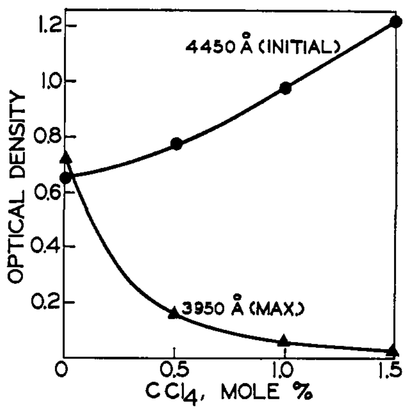

Figure 8. Effect of CCl_4 concentration on spectral intensity produced by γ irradiation of n-C_4H_9I in 3-MP at 80°K. [n-C_4H_9I] = 1×10^{-2} mf; dose = 1×10^{19} ev g^{-1}.

Spectra Following Radiolysis at 20°K. The spectrum of 2×10^{-2} mf C_2H_5I in 3-MP glass at 20°K following γ irradiation at 20°K consisted of a peak at 4500 A with some lesser absorption in the 5000–7000-A range, similar to curve 1 of Figure 4. There was no change in optical density after an hour in the dark at 20°K. On exposure to light centered in the 4500-A region, at 20°K, the 4500-A peak decayed while peaks at 5500 A and above 7000 A grew. This decay and growth is identical with that produced by illumination or aging at 80°K. It may be concluded that the species observed at 20°K are the same as those seen in the more extensive experiments at 80°K, and that the latter are not the product of less stable precursors which decay too fast to be seen at 80°K.

The experiments thus far done at 20°K also indicate that the 3950-A peak, which has been ascribed to I_2^-, does not grow in at 20° on illumination, as it does at 80°K. This is understandable if its growth requires the diffusion of I atoms and I^- ions.

Changes in Spectra with Increasing Temperature. The photoinduced changes shown in Figure 5 for samples at 67°K, as well as the changes which occur in the dark at 80°K (Figure 4), all occur spontaneously in short times above 80°K. In all cases the peak above 7000 A decays by 50% or more in 10 min at 88°K, accompanied by decrease of the 5400-A peak and increase of the 5000-A peak. At 103°K the 5000-A peak (Figure 4) begins to decay rapidly while at the same time the 3950-A peak is replaced by a peak at 3650 A, which, in turn, disappears at 163°K. Visible fluidity of the glass begins to be apparent at about 105°K. At about 200°K weak absorption at 4500 A attributed to $RI \cdot I_2$ (curve 3, Figure 3) becomes noticeable, being replaced at room temperature by the weaker absorption of I_2 in 3-MP at 5200 A.

Effect of Concentration of Alkyl Iodide. At low concentrations of alkyl iodide in 3-MP glass, absorption peaks of the type of Figures 4 and 5 must result from species formed by charge transfer or energy transfer from the 3-MP to the solute. An indication of the concentration dependence of this transfer is given in Figure 7.

Yields of C_2H_5 radicals as a function of C_2H_5I concentration in γ-irradiated 3-MP glass at 77°K, determined by Miriam Shirom of our laboratory using esr, give plots similar in shape to Figure 7, with the plateau region being reached at a concentration of about 8×10^{-3} mf.

Effects of Scavengers for Electrons and for Positive Charge. Hamill and co-workers[2,9] have shown that absorption attributable to negative ions in organic glasses may be reduced by electron scavengers, such as alkyl chlorides, and enhanced by additives which stabilize positive charge, while peaks due to cationic species are affected in the opposite manner. In the present work CCl_4 has been found to cause an increase in the initial optical density of the 4550-A peak and a decrease in the final yield of the 3950-A peak when n-C_4H_9I is radiolyzed in 3-MP glass (Figure 8). (The optical densities in Figure 8 have been adjusted to correct for the tails of adjacent peaks.) The CCl_4 also produces a sharp decrease in the initial values of the 5400-A absorption. The 4800-A peak which has been ascribed to CCl_4^+ in 3-MP–CCl_4 glasses[9] is not seen, although we observed this species in irradiated CCl_4–3-MP glasses containing no RI or containing HI. Effects qualitatively similar to those of Figure 8 are observed when n-C_4H_9Cl or CH_3Cl is used in place of CCl_4. The presence of 10^{-2} mf n-C_4H_9Cl with 10^{-2} mf CH_3I in 3-MP greatly reduces the 3950-A peak relative to that seen with CH_3I alone but does not affect the 4400-A peak. In all of these experiments the irradiation was for 5 min at a dose rate of 2×10^{18} ev g^{-1} min^{-1} at 77°K, the measurements being made at 80°K. The initial heights of the peaks were determined 5 min after the end of irradiation.

Benzene or 2-methylpentene-1 (2-MP-1) present with 1.4×10^{-2} mf C_2H_5I in 3-MP glass during irradiation reduces the initial intensity of the 4450-A peak, and, to a lesser extent, the intensities of the 5400- and 5000-A peaks (Figure 9).

I_2 and RH Yields. If the action of added CCl_4 during the irradiation of 3-MP glass containing alkyl halide is to capture electrons in competition with the process $RI + e^- \rightarrow R + I^-$, one might expect a reduction in $G(I_2)$ and G(RH) from the radiolysis. Such reduction occurs. Determinations of I_2 yields made by Clark L. Bair of our laboratory to test this point may be summarized as follows: (1) $G(I_2)$ is about 0.22 when 1.1×10^{-2} mf n-C_4H_9I is irradiated in 3-MP

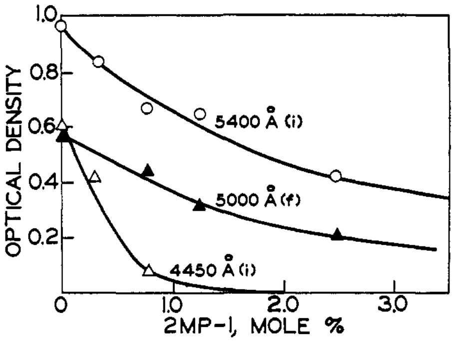

Figure 9. Effect of 2-MP-1 concentration on spectral intensity produced by γ irradiation of C_2H_5I in 3-MP at 80°K. $[C_2H_5I] = 1.4 \times 10^{-2}$ mf; dose $= 1 \times 10^{19}$ ev g^{-1}.

at 77°K for 5, 10, 15, or 20 min at a dose rate of 1.9×10^{18} ev g^{-1} min^{-1}; (2) at 3×10^{-4}, 6×10^{-4}, 15×10^{-4}, and 60×10^{-4} mf n-C_4H_9I, $G(I_2)$ is about 0.06, 0.11, 0.15, and 0.18, respectively, for 20-min irradiations (Figure 7); (3) $G(I_2)$ for 20-min irradiations of 1.1×10^{-2} mf n-C_4H_9I containing 0, 3.2×10^{-3}, 6.5×10^{-3}, and 1.3×10^{-3} mf CCl_4 was about 0.22, 0.18, 0.14, and 0.08, respectively.

$G(CH_4)$ which is 0.06 for pure 3-MP increased to 0.56 when 6.5×10^{-3} mf CH_3I was present in the 3-MP. When 10^{-2} mf CCl_4 was present with the CH_3I, the yield was 0.08. Similar experiments with polycrystalline cyclohexane gave a value of $G(CH_4)$ of 0.00 for the pure matrix, 0.48 with 6×10^{-3} mf CH_3I present, and 0.09 with both 6×10^{-3} mf CH_3I and 9×10^{-3} mf CCl_4 present. These results are consistent with the conclusion that by scavenging electrons the CCl_4 is preventing the formation of CH_3 radicals by dissociative electron attachment. Methane formation must occur by a hot reaction at the time of the dissociative process, or occur on warm-up, since the activation energy for H abstraction from 3-MP by thermal CH_3 radicals is presumably too high for this reaction to be significant at 77°K.

Effect of Solvent. In contrast to the spectra of Figure 4 for a 3-MP glass, solutions of 10^{-2} mf n-C_4H_5I or C_2H_5I in the polar solvent methyltetrahydrofuran (MTHF) showed no absorption in the 3500–7000-A region immediately after γ irradiation, or after standing for an hour at 80°K. On melting, a peak appeared at 3650 A, attributable to a complex of I_2 with MTHF or to I_3^-.

Discussion

Comparison with Previous Work. The only previous report[2] of the visible–ultraviolet absorption spectra of γ-irradiated iodides in 3-MP glass states: "Irradiation of iodine, hydrogen iodide, methyl iodide, n-butyl iodide, or p-diiodobenzene in 3-MP glass produces species with λ_{max} 770, 530, and 390 mμ. The band at 390 mμ is assigned to I^-. The band at 430 mμ in glasses containing methyl iodide does not appear with other alkyl iodides."

Our observations differ from these exploratory findings in the following ways. (1) All ten iodides tested show absorption in the 4200–4800-A region, corresponding to the "430-mμ" band for CH_3I. (This absorption decays at 80°K in the dark and decays faster under illumination.) (2) The evidence indicates that the 3950-A peak ("390 mμ") must be assigned to I_2^-, RI_2^-, or some other negative complex, rather than to I^-, because it always grows in intensity after irradiation, indicating that it is formed from two species by diffusion or reorientation following irradiation.

Implications from Transparency of RI–MTHF Glasses. The fact that alkyl iodides with well-defined absorption maxima in 3-MP glass (Figure 4) are transparent following similar irradiation in the polar glass MTHF implies either: (1) shifts of up to several thousand angstroms in the absorption maxima of the species observed in 3-MP, or (2) major differences in the yields of the trapped absorbing species, or both. It seems improbable that spectral shifts can account for the transparency. However, differences in the products of radiolysis in the two systems could arise because positive charge is less mobile in MTHF than in 3-MP,[9] or because there is less aggregation of the halide molecules into clumps in the more polar MTHF. Immobility of the positive charge would lessen the probability of forming RI^+. Monomolecular dispersion of the RI would minimize the possibility of conversion of RI^+ monomers to $(RI)_n^+$ aggregates, of ion–molecule reactions such as $RI^+ + RI \rightarrow R_2I^+ + I$,[10] and of forming negative complex ions such as I_2^- and RI_2^-. Complex species such as these appear to be necessary to explain spectra such as those of Figure 4.

There is convincing evidence that radiolysis of solutions of RI in MTHF leads to electron capture by the RI.[9,11] Esr studies show that part or all of this is dissociative capture.[12] Thus the transparency of the radiolyzed glass indicates that I^- does not absorb in the region examined (3000–10,000 A) in MTHF.

Processes in γ-Irradiated RI–3-MP Glass. The post-irradiation decay and growth relations of the absorption peaks produced in experiments such as those illustrated in Figure 4 indicate that each maximum represents a different species, all of which are unstable at temperatures above 163°K. The post-irradiation reactions may include transfer of negative and positive charge, neutralization, reorientation of solvent molecules around the charged species, ion–molecule reactions, and formation of complexes such as I_2^-, $RI \cdot I^-$, $HI \cdot I^-$, $RI \cdot I$, $RI \cdot HI$, and $RI \cdot I_2$. Changes in viscosity, energy requirements for diffusion, and activation energies cause the rates of these processes to vary with temperature and illumination.

If the fraction of collisions having the energy E required for reaction is $e^{-E/RT}$, then at 77°K, 10^{-3E} of all collisions will have the requisite energy for reaction (for E in kcal/mole). Thus, if a particle undergoes 10^{12} collisions/sec with reaction partners and the frequency factor for reaction is unity, its average lifetime will be about 1 sec if $E = 4$ kcal/mole, or about 1 month if $E = 6$ kcal/mole. Such estimates preclude the possibility that abstraction of hydrogen

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(10) H. A. Gilles, R. R. Williams, and W. H. Hamill, *J. Am. Chem. Soc.*, 83, 17 (1961).

(11) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussions Faraday Soc.*, 36, 169 (1963).

(12) We have observed the esr signal of CH_3 radicals in solutions of CH_3Cl in MTHF, in which electrons have been produced by photoionization of tetramethyl-p-phenylenediamine (as previously observed in 3-MP[4]), and alkyl radical esr spectra in γ-irradiated MTHF glass containing 1×10^{-2} mf alkyl halides.

from the 3-MP by neutral atoms or radicals is one of the processes observed at 77°K, but do not exclude association and charge transfer.

Reaction of radiolytic fragments from one RI molecule with those from another, or with another RI molecule, rather than with the solvent, seems necessary to explain the observed spectra. In 3-MP at 77°K (viscosity = 10^{12} poise[13]), diffusion must be very slow. Purely random distribution of 10^{-2} mf RI would give an average distribution of 6% of the molecules as nearest neighbors.[14] Since the polar RI molecules are present in a nonpolar medium, more extensive clumping seems probable, and this can account for the occurrence of intramolecular reactions on a time scale faster than allowed by diffusion.

Assignment of Absorption Peaks. A definitive assignment of each of the six absorption peaks of Figure 4, plus the rising absorption at the low wavelength side of the plot (and of the related peaks in Figure 5), is clearly impossible as yet. Steps toward such assignments have, however, been made.

The 3950-A peak must be a negative species, or be formed from one, since it is greatly decreased by electron scavengers. It is not a primary product of radiolysis, since it grows following irradiation. The rate of growth in the 3-MP matrix appears to be first order, as in pure alkyl iodides.[3] If it is assumed, as seems necessary, that the species contains two iodine atoms (*e.g.*, I_2^- or RI_2^-), the first-order growth implies that the species is formed in a dimer or clump of RI molecules, rather than by random combination of fragments produced in separated parts of the system. The absorption spectrum is consistent[3] with that to be expected for I_2^-.

On warming to 103°K the 3950-A peak disappears and is replaced by a peak at 3650 A. This peak is in the position of the absorption of I_3^- and could result from the reaction $I_2^- + I_2^- \rightarrow I_3^- + I^-$. The existence and stability of I_3^- in 3-MP, up to 163°K where the matrix is quite liquid, raises the question of the stabilization of charged species in nonpolar solutions. If the I_3^- is present, then cations must also be present up to 163°K where recombination by diffusion must become rapid.[15]

By contrast with the 3950-A peak, the positions of the other peaks observable at 80°K vary from one alkyl iodide to another, and these peaks are not produced in the HI–3-MP glass. It may be concluded, therefore, that each of them represents a species which includes the alkyl group.

Assignment of the peak in the 4400–4800-A region to RI^+, as has been proposed for CH_3I,[2] is plausible. As found by Bertin and Hamill[2] for radiolyzed CH_3I in 3-MP glass, we have found, for n-C_4H_9I as the solute, that electron scavenging additives increase the initial absorption at this peak, implying that the species responsible is either positively charged or formed from a positively charged precursor by a neutralization process. Consistent with this conclusion is the fact that 2-MP-1, which immobilizes positive charge, reduces the peak.

The symmetry of the growth of the 7600-A peak (as measured by the absorption at 7000 A), relative to the decay of the 4550-A peak for n-C_4H_9I (Figure 4), suggests that the 7600-A absorption is due to a positive species or is formed by the neutralization of a positive species responsible for the 4550-A peak. The only other region of the spectrum in which there is initial decay is at 3500 A. If neutralization is involved in the decay at 4550 A, the negative species must either be that which absorbs at 3500 A or be transparent in the region examined. The negative species cannot be weakly trapped electrons because these are precluded by the electron scavenging action of the RI present.

Neutralization of RI^+ by RI^- seems improbable. For these species to be in close proximity electrons and positive charge from the 3-MP would have to migrate to the same RI clump. Also, the possible products of neutralization of RI^+ by RI^- would not be expected to absorb in the 7600-A region. If the 7600-A peak is due to a positive species, it may be RI_2^+ formed by the ion–molecule reaction $RI^+ + RI \rightarrow R_2I^+ + I$,[10] or be caused by an aggregate[2] of the type $(RI)_n^+$ formed by polarized reorganization of the molecules within a clump. It is of interest to note that the yield of the 4550-A peak from the radiolysis of n-C_4H_9I in 3-MP passes through a maximum at about 10^{-2} mf n-C_4H_9I, while the yield of the 7600-A peak continues to increase up to much higher concentrations (Figure 7). This may reflect the influence of increasing clumping probability as the concentration is increased.

The intensity of absorption at 5400 A grows on standing following irradiation, in parallel with the decay of absorption at 4450 A and the growth at 7600 A; it then decays in parallel with the decay at 7600 A. Electron scavengers reduce the intensity achieved by the 5400-A peak, suggesting that it may be a negative species that disappears by neutralization of the species responsible for the 7600-A peak, leading to formation of a neutral complex responsible for the 5000-A peak.

The experiments on the photolysis of n-C_4H_9I and of HI in 3-MP glass (Figures 1 and 3) indicate production of an uncharged species which absorbs at 4400 A and which grows in concentration after photolysis.[16] The most probable species to account for the 4400-A photolytic peak seems to be RI·I. It is known[18] that iodine atoms are produced by the photolysis of alkyl iodides. There is also evidence[19] that RI is formed when HI is photolyzed in 3-MP glass. The growth of a second peak in the photolyzed HI–3-MP glass, in the 3950-A region (Figure 1), must be due to a second neutral complex involving some combination of two or more of the species RI, I_2, HI, and I. As would be expected for neutral species, the spectra of Figures 1 and 3 are not affected by the presence of concentrations of CCl_4 which en-

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(13) J. R. Lombardi, J. W. Raymonda, and A. C. Albrecht, *J. Chem. Phys.*, **40**, 1148 (1964).

(14) M. M. Kreitman and D. L. Barnett, *ibid.*, **43**, 364 (1965).

(15) Independent evidence for the persistence of charged species up to this temperature and higher in 3-MP–RX glasses in which such species have been produced by radiation at 77°K, is given by measurements of the electrical conductivity during warm-up: B. Wiseall and J. E. Willard, unpublished.

(16) Timm has reported and discussed the spectra of more dilute solutions of HI in a 2-methylbutane–3-MP matrix at 77°K before and after a larger radiation dose than used here,[17a] and also the spectrum of C_2H_5I before and after photolysis in a similar mixed solvent.[17b]

(17) (a) D. Timm, *Acta Chim. Scand.*, 16, 1455 (1962); (b) in press.

(18) See, for example: R. H. Luebbe, Jr., and J. E. Willard, *J. Am. Chem. Soc.*, **81**, 761 (1959).

(19) S. Aditya and J. E. Willard, *ibid.*, **88**, 229 (1966).

hance the 4400-A peak and reduce the 3950-A peak in radiolyzed solutions.

It is notable that the 3950-A peak produced by the γ irradiation of HI–3-MP glass is not affected by the presence of 1.4×10^{-2} mf CCl_4, in contrast to the peak in RI solutions. This appears to mean either that HI is a more efficient electron scavenger than CCl_4 or that the peak observed in the radiolyzed HI solution is due to the neutral species produced in the photolyzed HI solution rather than to a species such as I_2^-.

$G(I_2)$ Yield at Low RI Concentration. Among the observations of interest in this work is the fact that a positive value of $G(I_2)$ ($G = 0.06$) is found for solutions of n-C_4H_9I in 3-MP glass at a concentration as low as 3×10^{-4} mf, whereas, in a liquid alkyl iodide–hydrocarbon solution (C_2H_5I in n-C_5H_{12}), iodine production was not observable at 4.8×10^{-2} mf.[20] One interpretation of this phenomenon is that the butyl iodide exists as clumps of molecules in the glass and that charge or energy or both are efficiently transferred from the 3-MP to these domains of concentrated iodide.

(20) (a) P. R. Geissler and J. E. Willard, *J. Am. Chem. Soc.*, **84**, 4627 (1962); (b) also see G. Westmorland, T. S. Croft, W. C. Blaskey, and R. J. Hanrahan, Division of Physical Chemistry, 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961, Paper 119.

γ Radiolysis of Oleic Acid[1]

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Abstract: Exposure of oleic acid in the absence of air to Co^{60} γ rays (in agreement with findings in earlier investigations involving other types of ionizing radiation) results in polymerization, *cis–trans* isomerization, decarboxylation, and hydrogenation, in order of decreasing extensiveness. Hydrocarbons resulting from decarboxylation are primarily of chain length C_{17}; others of higher molecular weight are believed to be derived from dimers by secondary reaction. Contrary to conclusions reached in earlier work, the major hydrocarbon is *cis*-8-heptadecene, the "straightforward" decarboxylation product of oleic acid. Decarboxylation, which occurs independently of concurrent events (hydrogenation and isomerization) affecting the center of unsaturation, is believed to be initiated by loss of an electron from the carboxyl group, followed by events in which the hydrogen-bonded association dimers of the acid play an important role. Dimers, apparently largely doubly unsaturated and cross-linked at carbon atoms adjacent to the double bonds, are believed to arise largely *via* coupling of allylic radicals produced both by hydrogen-atom abstraction and by C–H bond homolysis. Higher polymers are produced by secondary reactions.

Except insofar as hydrocarbons, by virtue of their low polarity, may be included in the class, little intensive study has been devoted to the effects of ionizing radiation on lipids, although interest in possible genesis of petroleum *via* interaction of natural radioactivity with lipids of organic matter in sedimentary deposits stimulated investigation of radiolysis of fatty acids (*i.e.*, long straight-chain carboxylic acids) early in the still rather short history of such studies. This research[2] established, for example, that decarboxylation of saturated fatty acids (to yield hydrocarbon RH from acid RCOOH) occurs under these circumstances and that, in addition to carbon dioxide, hydrogen is an important constituent of the mixture of gaseous products; smaller amounts of carbon monoxide and water are also formed.[3] With the possible exception of carbon dioxide, these volatile products arise *via* processes which remain vaguely understood.

Oleic acid (*cis*-9-octadecenoic, the most abundant fatty acid involved in lipids of historic living organisms) was shown[4] to undergo extensive polymerization, hydrogenation (to stearic acid), and decarboxylation to 8-heptadecene, which was, curiously, believed[5] to have the *trans* configuration.[6]

As part of a program[7] designed to enhance understanding of alteration of lipids *in vivo* induced by penetrating radiation, oleic acid has now been exposed to a wide range of doses of γ radiation and detailed analysis of the resulting mixtures used to deduce probable mechanisms of radiolysis of this key substance.

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(1) This paper is based on work performed under Contract AT(04-1)-GEN-12 between the Atomic Energy Commission and the University of California, Los Angeles, Calif.

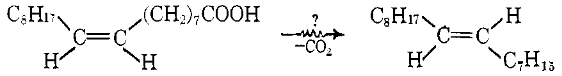
(2) C. W. Sheppard and V. L. Burton, *J. Am. Chem. Soc.*, **68**, 1636 (1946).

(3) W. L. Whitehead, C. Goodman, and I. A. Breger, *J. Chim. Phys.*, **48**, 184 (1951).

(4) V. L. Burton, *J. Am. Chem. Soc.*, 71, 4117 (1949).

(5) V. L. Burton and I. A. Breger, *Science*, 116, 477 (1952); identification of *trans*-8-heptadecene was based primarily on an infrared spectrum interpretation which would be regarded today as insufficiently appreciative of the high intensity of the 10.3-μ absorption of *trans* unsaturation and of the location and moderate intensity of the 14.3-μ absorption of *cis;* the significance of absorption at 3.35 μ (*cis*) and at 10.1 and 11.0 μ (terminal or "vinyl" unsaturation) in their spectra was also overlooked.

(6) The obvious implication that *cis–trans* isomerization of the carbon–carbon double bond and decarboxylation are concomitant processes is clearly of fundamental importance from the mechanism standpoint.



cis *trans*

(7) See D. R. Howton, *Radiation Res.*, 20, 161 (1963).