primary spectra. In fact, it is tempting to decide that the $C_4H_6^+$ intermediate is more similar to the 1,3-butadiene or 1-butyne ions than to the other two primaries shown.

Acknowledgment.—We wish to express our appreciation to Mr. Burl L. Clark for his invaluable help in making the measurements and calculations.

BAYTOWN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Effects of Structure, Product Concentration, Oxygen, Temperature and Phase on the Radiolysis of Alkyl Iodides

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The yields of elemental iodine as a function of radiation dosage have been determined for the radiolysis with Co^{60} γ-rays of seven purified degassed alkyl iodides. Doses $>16 \times 10^{20}$ e.v./ml. were used in some cases. Although six of the iodides show linear dependence of G_{I_2} on radiation dosage at low doses, all depart from linearity at higher doses, and the G_{I_2} for isobutyl iodide decreases with increasing dose even at the start of irradiation. The linear dependence is attributed to a balanced competition between HI and I_2 for thermal radicals and, consistent with this concept, the rate of exchange with radioiodine during radiolysis is found to be dependent on the concentration of added I_2 or O_2. The dependence of G_{I_2} on the β-hydrogen content of the alkyl iodides is confirmed and ascribed to increased probability of HI formation by decomposition of excited molecules as the number of β-hydrogens per molecule increases. Added O_2 increases the initial G_{I_2} for C_2H_5I by an amount independent of the O_2 pressure from 2 to 188 mm., but as the I_2 concentration increases with increased dosage G_{I_2} returns to its degassed level at a rate inversely dependent on the oxygen pressure. With added iodine present at a concentration elevenfold greater than the dissolved oxygen, the initial G_{I_2} was the same as that in the absence of additives. G_{I_2} for four iodides tested is essentially independent of temperature in the liquid phase from 20 to $-78°$ and for C_2H_5I from 108 to $-78°$, but the G_{I_2} values for both CH_3I and C_2H_5I have a positive temperature coefficient in the crystalline solid phase.. G values for two iodides studied in both the glassy and crystalline states at $-190°$ were higher in the glassy state, a result which is tentatively ascribed to molecular orientation favoring a stereospecificity for hot radical reactions.

Introduction

The purpose of the work of this and the following paper[1] was to elucidate further[2] the mechanisms of radiolysis of the alkyl iodides. The investigations have included studies of: (1) the competitive reactions of O_2, I_2 and HI with thermal radicals produced in the radiolyses and (2) the effects of temperature, molecular structure and irradiation in the solid crystalline and glassy states on the yields of elemental iodine.

Experimental

The alkyl iodides, Eastman or Matheson best grade, were purified by passage through activated alumina, followed by distillation through a two-foot Vigreux column, the middle 50% being retained. Identical iodine yields were obtained from the irradiation of samples of ethyl iodide purified as above, and from those purified by shaking with concentrated H_2SO_4 and washing with Na_2SO_3 solution prior to distillation. The purified iodides were degassed by several cycles of freezing, pumping and thawing on a vacuum system, and then were vacuum-distilled through P_2O_5 into the irradiation vessels and sealed off.

During the irradiation, the samples (5 ml.) were contained in an annular vessel,[4] which surrounded a 40-curie Co^{60} γ-ray source.[4] The radiation intensity on the samples was 2×10^5 roentgens/hr., the absorption of energy in the alkyl iodides being at the rate of about 2×10^{19} e.v. per ml. per hr.

Iodine analyses were made with a Beckman DU spectrophotometer. A spectrophotometer cell made from square Pyrex tubing was attached to the annular vessel so that iodine analyses could be made between successive irradiations of the same sample without exposing it to the air. Concentrations were read at the absorption maximum at 478 mμ and for high concentrations at 550 and 625 mμ. The high concentration readings were checked at 478 mμ in methyl and ethyl iodide irradiations by using 0.98 and 0.95 cm. silica inserts in the analysis cells. Determinations of molar extinction coefficients were made at the three wave lengths for methyl, ethyl and *n*-propyl iodides, the values obtained being 1280, 356 and 72.8 l./mole cm., respectively. Since the extinction coefficients were the same for the three iodides, it was assumed that the same values would also be applicable to the other iodides.

To irradiate samples at -78, -123 and $-190°$, they were surrounded during the irradiation by baths of solid CO_2 and acetone, butyl chloride slush, and liquid air, respectively. A thermostatically controlled bath of mineral oil was used for the irradiations at 108°.

Oxygen of known pressure was admitted to degassed samples of ethyl iodide on a vacuum line, either from a cylinder or by heating $KClO_3$ containing MnO_2. The number of moles oxygen introduced to the sample vessel was determined from the pressure change in a known volume of the vacuum apparatus, measured with a phosphoric acid manometer. The solubility of oxygen in ethyl iodide was found to be 8×10^{-6} mole/l. per mm. pressure at 23°,[5] so that the concentration of dissolved oxygen in the samples could be determined from the gas pressure.

Iodine labeled with I^{131} was prepared from carrier-free iodine solutions by adding the desired amount of KI and oxidizing with acidified KIO_3. The iodine was transferred into the irradiation vessels by vacuum distillation through P_2O_5. A solution-type Geiger counter was used to measure

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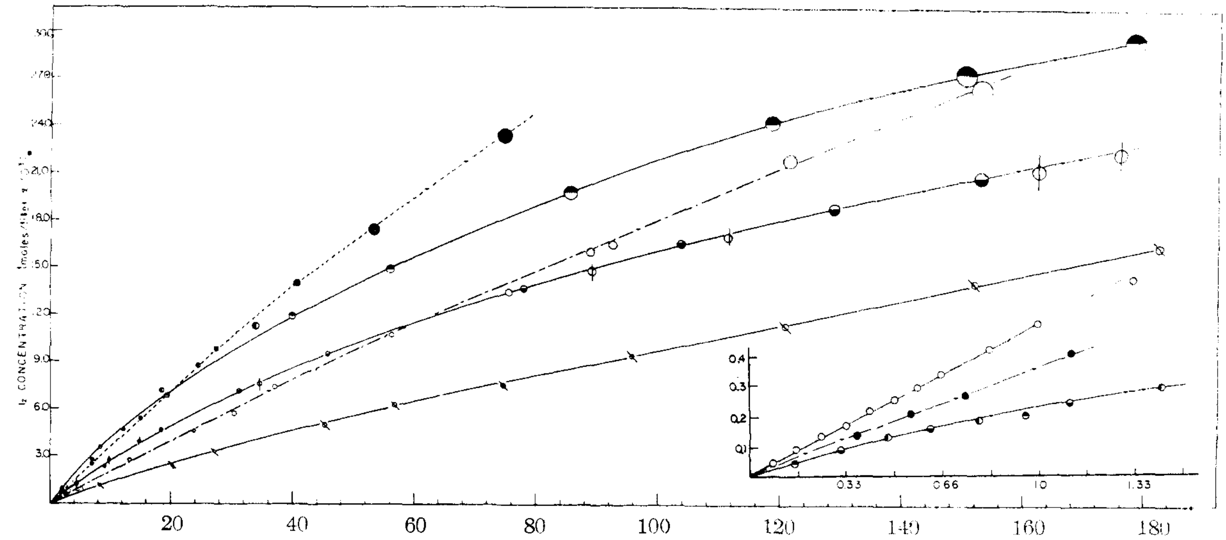
[1] R. J. Hanrahan and J. E. Willard, THIS JOURNAL, **79**, 2434 (1957).

[2] Previous investigators have determined the relative yields of I_2 from X-ray and α-particle irradiation of air-saturated ethyl iodide,[3a] from γ-irradiation of eight air-saturated alkyl iodide,[3b] from fast electron irradiation[3c] of degassed CH_3I, CH_2I_2, C_2H_5I and *n*-C_3H_7I, and from X-ray irradiation of degassed CH_3I,[3c,d] C_2H_5I,[3c,d,h] propyl[3d,h] and butyl iodides.[3d] The yields of various products from the X-ray irradiation[3e,h] and very low intensity Co^{60} γ-ray irradiation[3e] of degassed CH_3I have also been determined. Similarities and contrasts between the radiolysis and photolysis of the alkyl iodides have been considered.[3c,d,e,f] Distillation with added carriers following irradiation in the presence of radioiodine has been used to identify intermediate free radicals.[3g,h]

[3] (a) M. Lefort, P. Bonet-Maury and M. Frilley, *Compt. rend.*, **226**, 1904 (1948); (b) P. Sue and E. Saeland, *Bull. soc. chim. France*, 437 (1949); (c) R. H. Schuler and W. H. Hamill, THIS JOURNAL, **74**, 6171 (1952); (d) E. L. Cochran, W. H. Hamill and R. R. Williams, Jr., *ibid.*, **76**, 2145 (1954); (e) C. R. Petry and R. H. Schuler, *ibid.*, **75**, 3796 (1953); (f) W. H. Hamill and R. H. Schuler, *ibid.*, **73**, 3466 (1951); (g) L. H. Gevantman and R. R. Williams, Jr., *J. Phys. Chem.*, **56**, 569 (1952); (h) R. H. Schuler and R. C. Petry, THIS JOURNAL, **78**, 3957 (1956).

[4] R. F. Firestone and J. E. Willard, *Rev. Sci. Inst.*, **24**, 904 (1953).

[5] E. O. Hornig, Ph.D. thesis, University of Wisconsin, Feb. 1956, available from University Microfilms, Ann Arbor, Michigan.



Energy absorbed per ml. (e.v. × 10^{-19}).

Fig. 1.—Iodine production in the radiolysis of degassed alkyl iodides as a function of energy absorbed: ○, methyl; ●, ethyl; ◒, *n*-propyl; ◓, isopropyl; ⌽, *n*-butyl; ⍉, isobutyl; ◐, *s*-butyl.

the distribution of activity between organic and inorganic combination after radiolysis.

Results

Variation of Iodine Yields with Radiation Dosage.—Figure 1 shows the change of iodine concentration with time of irradiation for seven alkyl iodides. Six of these showed no change in slope up to radiation doses as high as 4.5 × 10^{19} e.v./ml.[6] The seventh, isobutyl iodide, gave yields which dropped from 3.36 I atoms (as $^1/_2$ I_2) produced per 100 e.v. absorbed initially to 1.89 after 0.64 × 10^{19} e.v./ml. was absorbed (see insert of Fig. 1). Identical results were obtained with each of three separately purified *i*-C_4H_9I samples. For the much higher radiation doses plotted in the main portion of Fig. 1, all of the iodides except methyl showed a region of decreasing rate of I_2 production. For those compounds which were subjected to the largest dosage (isobutyl, isopropyl, *n*-propyl) the values of $G_{^1/_2I_2}$ for increments of irradiation after the samples had been exposed to 16 × 10^{20} e.v./ml., all came to the same value of 0.95 ± 0.03. The curvature is of interest because it is indicative of competing reaction steps which change in importance with changing concentration of the radiolysis products, and because previous investigators[3c,d,e] of the radiolysis of alkyl iodides using X-rays or fast electrons and small total dosage (maximum I concentrations of about 10^{-3} mole/l.) have reported that the iodine production is linear or nearly linear[3h] with absorbed energy for all the iodides which they studied.

G **Values.**—Table I shows the values of *G* we have obtained for low radiation doses (< 1.3 × 10^{-3} mole/l. of I_2 produced), and also the literature values for similar systems. To determine the energy absorbed, $FeSO_4$ in 0.8 *N* H_2SO_4 was exposed to the source under conditions identical to those used for the alkyl iodide samples. A value of 15.6 Fe^{++} oxidized per 100 e.v. absorbed was assumed.[7] The absorption in the aqueous $FeSO_4$ solution (1.33 × 10^{19} e.v./ml. hr.) was multiplied by factors[5] to correct for the difference between its density and average atomic number and those of each of the iodides. The rates of energy absorption so obtained were 2.64 × 10^{19} e.v./ml. hr. for CH_3I, 2.26 × 10^{19} for C_2H_5I, 2.05 × 10^{19} for *n*-C_3H_7I, 2.02 × 10^{19} for *i*-C_3H_7I, 1.94 × 10^{19} for *n*-C_4H_9I, 1.92 × 10^{19} for *i*-C_4H_9I and 1.91 × 10^{19} for *s*-C_4H_9I. For four of the iodides, the *G* values for the liquids were determined on at least three separate samples from two different purifications, and several irradiations were made on each sample.[5] The results were usually reproducible to closer than ± 2%.

TABLE I

G VALUES[a] FOR IODINE PRODUCTION IN THE RADIOLYSIS OF LIQUID ALKYL IODIDES

	Present work					
	Temperatures, °C.					
	Room	108	−78	−120	−190	Other work, room temp.
CH_3I	2.52			0.94[f]	0.64[f]	3.3,[b] 2.7,[c] 2.4[d]
C_2H_5I	4.25	4.05	4.34	2.05	0.95[f] 3.05[g]	4.1,[b] 4.1,[c] 4.06[e]
n-C_3H_7I	3.20					3.5,[c] 2.88[e]
i-C_3H_7I	5.36		5.26		0.65[f]	5.3[e]
n-C_4H_9I	3.38				3.38[g]	
i-C_4H_9I	1.89[h]		1.89	3.19[f]	2.60[f]	
s-C_4H_9I	5.04		4.80		4.43[g]	

[a] The radiation yields (*G* values) are expressed as equivalents of iodine ($^1/_2$ I_2) produced per 100 e.v. absorbed. They are for irradiations at iodine concentrations of <1.3 × 10^{-3} mole/l. [b] For *ca.* 1 mev. X-radiation.[3c] [c] For 1–2 mev. electron bombardment.[3c] [d] For very low intensity Co^{60} rays.[2e,3h] [e] For 120 kvp. X-radiation.[3h] [f] Crystalline solid. [g] Glassy solid. [h] Note first paragraph under Results.

The only absolute yield for I_2 production in the radiolysis of degassed alkyl iodides by γ-rays reported in the literature, of which we are aware, is that for a five-week irradiation of CH_3I with a very low intensity (300 mc.) Co^{60} source.[3e] The value

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[6] To establish the initial linearity of the ethyl iodide plot, measurements were made at iodine concentrations as low as 10^{-6} mole/l. with the aid of a 10 cm. absorption cell.

[7] C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).

obtained after correction[3h] for $G_{Fe^{+++}} = 15.6$ is in good agreement with our result of 2.5 obtained at 550-fold higher radiation intensity. Absolute yields of iodine production from the X-ray[3c,h] and electron irradiation[3c] of CH_3I, C_2H_5I and n-C_3H_7I are in good agreement with the γ-ray yields, considering differences in dosimetric methods used.

Structure Effects.—From Fig. 1 and Table I, it may be seen that the initial values of G for the radiolysis of the iodides are related as follows: i-C_3H_7I > s-C_4H_9I > C_2H_5I > n-C_3H_7I $\cong$ n-C_4H_9I > CH_3I > i-C_4H_9I. A similar sequence of relative yields has been observed by Cochran, Hamill and Williams[3d] for the radiolysis with low energy X-rays and for photolysis with ultraviolet light and they have suggested that the order may be correlated with the fraction of the hydrogen atoms in the molecule which is in the β position to the C–I bond. Our data plotted in Fig. 2 as a function of both the fraction of hydrogen atoms in the β-position and the number of hydrogen atoms per molecule in the β-position give a smoother correlation with the latter plot. CH_3I, which has no β-hydrogen atoms, does not fall in line on either plot.

Temperature and Phase Effects.—From Table I it may be seen that the G values for liquid C_2H_5I at 108, 20 and −78° are indistinguishable and that there is likewise little or no temperature effect on the radiolysis of liquid i-C_3H_7I, i-C_4H_9I or s-C_4H_9I in going from 20 to −78°. By contrast, the three iodides for which determinations were made at two temperatures in the crystalline state, all show a higher yield at −120° than −190° (Table I and Table II).

TABLE II

EFFECT OF TEMPERATURE AND STATE ON G VALUES

	$G_{\text{liquid}}/G_{\text{cryst.}}$		$\frac{G_{\text{cryst.}}\ -120°}{G_{\text{cryst.}}\ -190°}$	$\frac{G_{\text{liquid}}}{G_{\text{glass}}\ -190°}$	$\frac{G_{\text{glass}}\ -190°}{G_{\text{cryst.}}\ -190°}$
Cpd.	Cryst. −120°	Cryst. −190°			
CH_3I	2.7	3.9	1.5		
C_2H_5I	2.0	4.3	2.3	1.35[a]	3.3
i-C_3H_7I		9.0			
n-$C_4H_{10}I$				1.0	
i-$C_4H_{10}I$			1.3	0.4	1.6

[a] The C_2H_5I glass may have crystallized before the completion of the irradiation.

Iodine yields in the solid phase irradiations were determined by spectrophotometric measurements on the liquid after melting. Identical G values were obtained for long and short solid phase irradiations and for irradiations after melting and refreezing a previously irradiated solid.

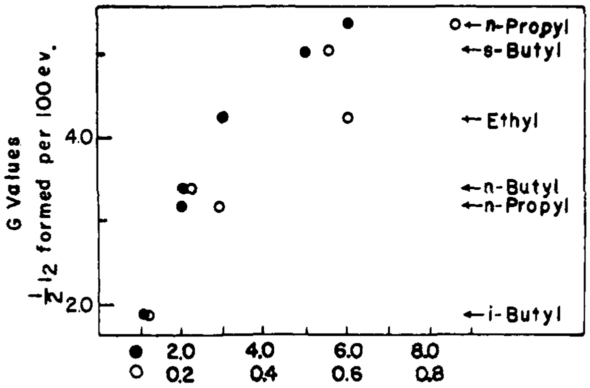

Fig. 2.—$G_{1/2 I_2}$ for the radiolysis of alkyl iodides, as a function of the β-hydrogen content: ●, number of β-hydrogen atoms per molecule; ○, fraction of hydrogen atoms in the β-position.

Of special interest is the fact that in the two cases where determinations were made both on the glassy[8] state and the crystalline states of a compound at the same temperature, the yields in the glassy state were much higher (Table II). Isobutyl iodide in the crystalline state at −190° showed a lower initial $G_{1/2 I_2}$ than the liquid but no curvature corresponding to that illustrated for the liquid in the insert on Fig. 1. After the absorption of about 8×10^{18} e.v./ml. the value for the crystals is higher than that for the liquid.

Effect of Oxygen.—The fact that iodine tagged with I^{131} exchanges with alkyl iodides undergoing radiolysis,[3c,e,h] is strong evidence for the presence of thermal alkyl radicals which return iodine to organic combination by the $R + I_2 \rightarrow RI + I$ reaction. At sufficiently high concentration, oxygen would be expected to compete with the I_2 for these radicals and thus increase the net I_2 yield. Such an increase has been demonstrated by Schuler and Petry[3h] for air-saturated and oxygen-saturated CH_3I and C_2H_5I. We have also investigated this effect with ethyl iodide using a series of different oxygen pressures ranging from 2 to 188 mm. (a variation of dissolved oxygen concentration from 1.6×10^{-5} mole/l. to 1.5×10^{-3} mole/l.). In agreement with the observations of Schuler and Petry,[3h] the *initial* rate of iodine production at all of the oxygen pressures was about 2.3 times that for degassed samples and it decreased with increasing radiation dose (Fig. 3). The higher the initial oxygen concentration the greater was the dose required to bring about a given decrease in rate toward the degassed value. This is consistent with the conclusion[3h] that the initial rate in the presence of oxygen represents the case where all

(8) When degassed samples of the alkyl iodides are cooled rapidly in liquid air, they often form transparent, glassy solids instead of opaque crystals. The glassy form is least stable for the iodides with 1, 2 and 3-carbon atoms. It is relatively easily obtained and can be indefinitely maintained at low temperatures in the cases of n-C_4H_9I and i-C_4H_9I. Similar observations on the relative stability of glasses as a function of chain length have been reported for the alkyl bromides.[9] The glasses sometime crack without crystallizing. C_2H_5I glass has been found to crystallize always when raised above about −165°.[10] It can be obtained and maintained at lower temperatures only in very clean degassed vessels with freshly annealed surfaces.

In order to be sure that the visible differences between apparently crystalline and apparently glassy samples indicate a true difference in state, we have frozen samples of n-C_4H_9I and i-C_4H_9I to the glassy state at −190° with thermocouples imbedded in them. The samples were then placed in Dewar flasks and allowed to warm slowly (15 minutes) to room temperature. During this time, the temperature of the thermocouples was recorded on a chart recorder. For both compounds the gradual slope of the warming curve changed to a vertical rise at about −125° indicating a sudden evolution of heat as a result of the conversion of the glass to the crystalline form. If, following this transition, the solid was cooled to −190° and again allowed to warm, no such heat evolution was observed, but each time the solid was melted and refrozen to the glass, the warming curves showing the crystallization process could be reproduced.[9]

(9) F. S. Rowland and W. F. Libby, *J. Chem. Phys.*, **21**, 1495 (1953).

(10) T. O. Jones and J. E. Willard, Absts. of 128th meeting of Am. Chem. Soc., Minneapolis, Minnesota, Sept. 1955, p. 35-R.

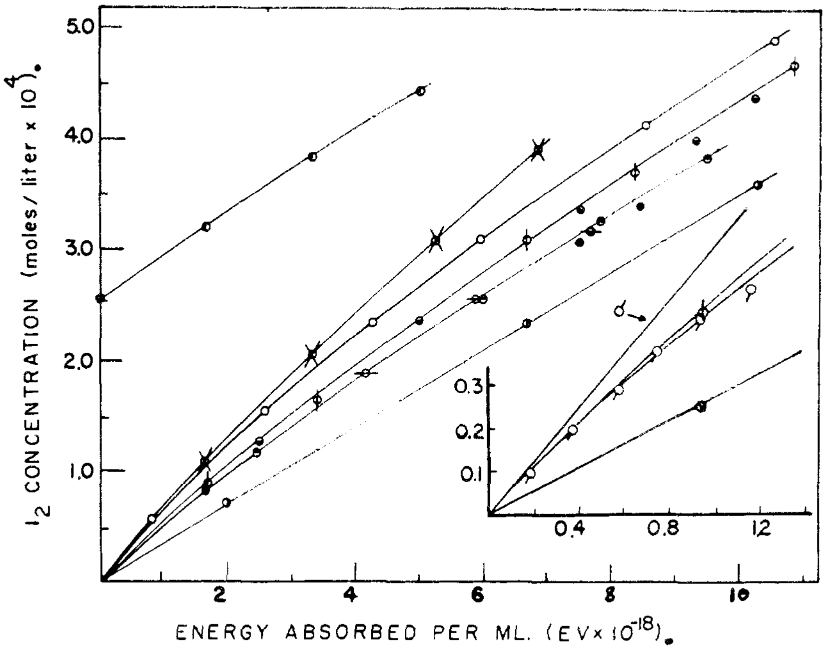

Fig. 3.—Iodine production in the radiolysis of ethyl iodide as a function of energy absorbed and of oxygen pressure. Initial oxygen pressures in mm.: ◑, degassed; ◓, 2.7; -o-, 4.7; ●, 5.6; ◒, 10.9; ϕ, 10.5; O, 18; ⊗, 42.8; ♂, 188; ◐, 7.5 (I_2 present at the start of radiolysis); ♀, 5.8, using 10 cm. light path.

thermal radicals are scavenged by the dissolved gas and none have the opportunity to return iodine to organic combination by reaction with I_2. As the I_2 concentration builds up, this species competes more and more effectively for the radicals thus reducing the rate of iodine production. The HI formed probably is oxidized by the oxygen.

The above concept of the mechanism is substantiated by the fact that the accelerating effect of O_2 can be counteracted by adding I_2 prior to irradiation (Fig. 3). At an initial mole ratio of I_2 to dissolved O_2 of 11, the rate was equal to that of degassed samples with no additives.

Estimates of the consumption of O_2 during irradiation in the experiment of Fig. 3 indicate that the decrease in its accelerating effect with time of irradiation cannot be attributed to depletion of the O_2. If it is assumed that one molecule of O_2 was consumed for each $^1/_2$ I_2 formed in excess of that formed in degassed samples, the depletion of O_2 after the rates had returned essentially to the degassed value was less than 10%. It is probable that the ratio of O_2 consumed to I_2 formed is actually less than 1/0.5, as a result of reactions of peroxy radicals to liberate I_2 from HI.

Information from Irradiation in the Presence of Radioiodine.—When it was first observed that oxygen accelerated the production of iodine from C_2H_5I and that the maximum initial rate was independent of the O_2 concentration over a wide range, it was thought that the only important reaction steps governing I_2 production were: (1) a hot radical production of $^1/_2$ I_2, such as $C_2H_5 + C_2H_5I \rightarrow C_2H_4 + C_2H_6 + I$, which was not sensitive to additives, and (2) a thermal radical step of the type $C_2H_5 + I_2 \rightarrow C_2H_5I + I$ which returned $^1/_2$ I_2 to organic combination and was sensitive to radical scavengers. According to this mechanism, the rate of exchange of radioiodine during radiolysis in the absence of oxygen should be independent of iodine concentration and should equal the increase in rate of iodine formation caused by an excess of oxygen. Also, the ratio of the *G* value for exchange to that for I_2 production should be constant, in the absence of oxygen.

Experiments designed to test these predictions gave the data of Table III which indicate that there must be another species in addition to iodine which competes for the thermal radicals in degassed samples. It may be seen that (1) the *G* value for exchange with both C_2H_5I and *i*-C_3H_7I increases with increasing initial iodine concentration, (2) the *G*

TABLE III

EFFECT OF I_2 AND O_2 CONCENTRATIONS ON EXCHANGE[a] OF I^{131} BETWEEN I_2 AND RI DURING RADIOLYSIS

Cpd. irradiated	I_2 added, mole/l. × 10^3	Time of irradn., min.	*G* of exchange	$\frac{G_{ex}{}^{d}}{(G^{1}/_{2}I_2)}$	$\frac{G_{ex}{}^{e}}{(G^{1}/_{2}I_2)}$ pure
C_2H_5I	0.30	10	4	1.24	0.93
	0.51	10	4.3	1.36	1.02
	2.1	10	6.2	2.03	1.45
[b]	0.63	7.5	2.2	0.34	0.51
[c]	0.31	5	0.4	0.08	0.14
i-C_4H_9I	0.49	15	5.1	3.22	2.76
i-C_3H_7I	0.29	6	6.1	1.70	1.14
	0.11	5	4.2	1.00	0.79

[a] "Exchange" as used here includes transfer of iodine from I_2 or HI to all organic forms. It has been shown by Gevantman and Williams[3g] and Schuler and Petry[3h] that exchange occurs predominantly into the parent compound. [b] C_2H_5I + 1 atm. of O_2 to give a dissolved O_2 concn. of *ca.* 6 × 10^{-3} mole/l. [c] C_2H_5I + 550 mm. of O_2 to give a dissolved O_2 concn. of *ca.* 4 × 10^{-3} mole/l. [d] Comparison of *G* exchange with $G^1/_2I_2$ in the same sample containing initially added I_2 at the concn. of column 2. [e] Comparison of *G* exchange for the samples with added iodine, with $G^1/_2I_2$ for degassed samples with no I_2 initially present.

value for I_2 production decreases with increasing initial iodine concentration, and (3) the ratio of the *G* value for exchange to that for iodine production in degassed samples increases with increasing concentration of initially added iodine.

Below we report evidence that HI is a radiolysis product of the alkyl iodides. In the following paper it will be shown that the effect of initial I_2 concentration on the *G* values for iodine production and exchange may be quantitatively explained on the basis of a competition between HI and I_2 for alkyl radicals, similar to the competition which has been shown to occur in the photolysis[11] of ethyl iodide.

Evidence That HI is a Product.—In order to determine HI production, samples of alkyl halides which had been irradiated in the presence of radioiodine were frozen with liquid air before breaking the vacuum, and were then shaken with a mixture of CCl_4 and H_2O. The HI dissolved in the water while the I_2 stayed predominantly in the CCl_4. The water was washed three times with fresh aliquots of CCl_4 and counted, the ratio of its activity to the total inorganic activity indicating the fraction of the latter which was HI. Ratios of HI/I_2 formed ranging from less than unity for C_2H_5I and *i*-C_4H_9I to considerably higher for *i*-C_3H_7I were found. In view of present knowledge of the role of HI in the mechanism[1] these would be expected to vary with the initial iodine concentration and the duration of the irradiation.

Discussion

The evidence presented above advances our knowledge of the radiolysis of alkyl iodides in several respects.

1. **Competitive Radical Reactions.**—By showing (Fig. 3, Table III) that the rate of iodine production and the rate of exchange of radioiodine are dependent on the ratio of oxygen concentration to iodine concentration and also on the ratio of iodine concentration to some other product (shown later to be HI), the results indicate that the yields, both with and without oxygen present, are determined by competitive reactions which consume thermal radicals.

2. **Absence of Intensity Effect.**—The fact that the *G* values for iodine production (Table I) are the same for irradiation at 2×10^5 r./hr. with a 40 c. Co^{60} source as at 350 r./hr. with a 300 mc. source[3e] confirms the fact that the radiolysis is independent of the intensity of γ-radiation. This is consistent with the conclusion, which may be reached from a consideration[12] of relative concentrations of radicals and iodine scavenger molecules, that there is no interaction between radicals produced in different tracks.

3. **Structure Effects.**—The fact, reported by Cochran, Hamill and Williams,[3d] that $G_{1/2\,I_2}$ for the radiolysis of alkyl iodides increases as a function of the hydrogen atoms on the carbon atoms adjacent to the one containing the iodine has also been observed in our work (Fig. 1). A smoother relationship is obtained (Fig. 1) if the yield is plotted against the number of hydrogens in the β-position than against the fraction of the hydrogens in this position. If the yield were dependent on the fraction rather than the number of hydrogen atoms in the β-position, it would suggest a hot radical mechanism in which the radicals could react equally well with any hydrogen atom but only reaction with β hydrogens could lead to iodine production, for example: (1) $\underline{R} + CH_3CH_2CH_2I \rightarrow RH + CH_2CH_2CH_2I$; (2) $\underline{R} + CH_3CH_2CH_2I \rightarrow RH + CH_3CHCH_2I$. Reaction 2 might be expected to lead to production of $^1/_2\ I_2$ by (3) $CH_3CHCH_2I \rightarrow CH_3CH{=}CH_2 + I$, but the product of (1) could not form a double bond by elimination of I and would probably react by (4) $CH_2CH_2CH_2I + I_2 \rightarrow CH_2ICH_2CH_2I + I$. Evidence from characterization experiments[3g,h] with radioiodine indicates little or no diiodide formation and so argues against the sequence of reactions 1 and 4 which would be expected to be prominent if the suggested hot radical hypothesis were responsible for the β-hydrogen effect.

In view of the evidence[1] that a large portion of the iodine produced in the radiolysis of ethyl iodide results from the step $C_2H_5 + HI \rightarrow C_2H_6 + I$ in competition with $C_2H_5 + I_2 \rightarrow C_2H_5I + I$, it may be speculated that the increase in rate of iodine production with increase in the number of β-hydrogen atoms is a result of an increase in the probability that *excited molecules* can eliminate HI and thus increase the ratio of HI to I_2 in the system. This could be a one-step process such as $CH_3CHICH_3 \rightarrow CH_2{=}CHCH_3 + HI$. As noted above, we have found that the yield of HI from *i*-C_3H_7I is considerably greater than from C_2H_5I and *i*-C_4H_9I.

4. **Non-linear Dependence of Yield on Energy Input.**—Figure 1 shows that all of the iodides except *i*-butyl show a linear increase in iodine concentration with absorbed energy up to about 10^{-3} *M*, in accordance with previous observations,[3] but that all of these show a curvature in the direction of lower *G* values if the irradiation is continued to 10^{-2} *M* I_2 or higher. It appears[1] that in the linear region, iodine production is the result of a hot reaction, plus a competition between I_2 and HI for thermal radicals, with the fraction of radicals which are used up by each path in the competition remaining constant because the ratio of HI produced to I_2 produced remains constant. It would appear that the most probable cause of deviation from linearity, at concentrations where direct energy absorption by the reaction products is negligible, is a reaction between HI and some other reaction product to decrease the rate of HI accumulation and hence favor the reaction $R + I_2 \rightarrow RI + I$ over that of $R + HI \rightarrow RH + I$. If olefins are produced which can react with HI ($C_2H_4 + HI \rightarrow C_2H_5I$) this process, being bimolecular, might become apparent only after these reactants had built up appreciably in concentration. Scavenging of radicals by a product other than I_2 or HI is not a satisfactory explanation of the curvature since such a species would be in constant ratio

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[11] (a) D. Bunbury, R. R. Williams, Jr., and W. H. Hamill, Abstracts 128th Meeting, Am. Chem. Soc., Minneapolis, Sept. 1955, p. 36R; (b) D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **78**, 6228 (1956).

[12] G. Levey and J. E. Willard, *ibid.*, **74**, 6161 (1952).

to the HI and I_2 throughout an experiment. It is possible that electron attachment or charge transfer processes which can lead to the net removal of HI or increased return of I_2 to organic combination become more important as the I_2 and HI concentrations increase.

Temperature and Phase Effects.—The fact that samples of the same solid alkyl iodide at the same temperature give different G values for I_2 production when they are in the glassy state than when they are in the crystalline state seems to indicate that the orientation of the molecules with respect to each other at the time energy is absorbed is an important factor in determining the chemical consequences of the energy absorption. In the ordered arrangement of a crystal hot C_2H_5 radicals formed from C_2H_5I may preferentially attack certain parts of adjacent C_2H_5I molecules, while in the random arrangement of a glass there can be no such specificity. Such preferential attack or various other sterically sensitive hot reactions may account for the difference in the G_{I_2} values in the different states.

For reactions activated by radiative neutron capture[12–14] the "organic yield" has been observed to increase, decrease or remain essentially unchanged with change of phase, depending on the compound, but with no obvious correlation with the molecular structure or the density.[12–14] In view of the contrast between the iodine yields for the glass and the crystalline phases in the present work, it seems plausible that the primary factor in determining the effect of freezing on the organic yields of activation by nuclear processes may be the orientation of the molecules in the crystal lattice.

The absence of a temperature effect in the radiolysis of liquid C_2H_5I from −78 to 108° suggests that the pattern of radical recombination reactions which occurs is not governed by the ease of diffusion of the radicals. This behavior is in contrast to that of CCl_3Br where G_{Br_2} is temperature sensitive, the apparent activation energy being about 3 kcal./mole.[15]

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MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Quantitative Treatment of the Elementary Processes in the Radiolysis of Alkyl Iodides by γ-Rays

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The mechanism of radiolysis of alkyl iodides with Co^{60} γ-rays includes the production of HI, I_2, alkyl radicals and hydrocarbons within the "hot spots" of the radiation tracks, and reaction of the thermalized radicals outside the tracks with HI and I_2 to abstract H and I, respectively. From the effects of added HI and I_2 on the rates of I_2 production and radioiodine exchange, it is possible to deduce the rates of the elementary reactions. For ethyl iodide, integrated rate equations which predict the rates of I_2 and HI production and of exchange have been obtained. The predicted rates are in agreement with the experimental results.

Introduction

The yield of iodine per unit of energy absorbed in the radiolysis of degassed ethyl iodide[1] is independent of the concentration of iodine built up during the radiolysis[1,2] and is independent of the temperature from −78 to 108°.[2] It has been thought that the iodine yield is independent of initially added iodine[3,4] although the data presented might be interpreted to indicate a small decrease for such addition.[3] These facts have led to the assumption that iodine production does not occur by any reaction involving the thermalized radicals, *i.e.*, occurs only by hot processes.

In the present work a careful re-examination of the effect of I_2 added prior to radiolysis has shown that it reduces the initial rate of iodine production by nearly 50%. This, together with the observation that HI is a product of the radiolysis,[2] has indicated that an important part of the mechanism is a reaction in which thermal alkyl radicals abstract hydrogen from HI, as it is in the photolysis of ethyl iodide reported by Bunbury, Williams and Hamill.[5] A quantitative study has therefore been made of the role played by HI and I_2 in competing for thermalized radicals.

Experimental

The methods of purification and irradiation of alkyl iodides were similar to those described in the preceding paper.[2] Mallinckrodt reagent grade iodine was used without further purification. All reaction mixtures were degassed by vacuum line techniques.

Dry HI was prepared from a 55% aqueous solution of HI (Merck) from which the free iodine was removed with red phosphorus. The water was removed by covering the frozen solution with P_2O_5, and allowing it to melt after evacuation. The HI gas was then passed through more

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(1) A review and bibliography of the subject is given in the preceding paper.[2]

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