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Temperature and Phase Effects on the Photolysis of Ethyl Iodide

BY RAY H. LUEBBE, JR., AND JOHN E. WILLARD

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The photolysis of ethyl iodide by 2537 Å. light has been studied in the liquid at 25° and −70° and in the glass at −180°. The quantum yields for elementary processes in the reaction mechanism have been deduced to be as follows: (a) for the thermal ethyl radicals which escape caging or diffusive recombination with the parent partner, 0.32 at 25°, 0.08 at −70° and (by extrapolation) 5×10^{-4} at −180°; (b) for production of iodine by processes independent of caging effects (probably $C_2H_5 + C_2H_5I \rightarrow C_2H_6 + C_2H_4 + I$) *ca.* 0.038; (c) for production of HI by $C_2H_5I \rightarrow C_2H_4 + HI$, or other hot process, 0.17 at 25°, 0.18 at −70° and 0.22 at −180°. The results are in agreement with earlier work by Bunbury, Williams and Hamill on the photolysis of ethyl iodide in showing a competition between HI and I_2 for thermal ethyl radicals but indicate that about 18% (rather than <3%) of the net iodine production at 25° is by a hot process. The ratio of the rate constants for reaction of thermal ethyl radicals with HI and I_2 (k_{I_2}/k_{HI}) at 25° is found to be close to unity in agreement with the results obtained from a study of the radiolysis but in contrast to the value of 0.34 from the earlier photochemical studies. This ratio increases to 2.5 at −70° indicating a difference of 1 kcal./mole in activation energy of the two reactions. An activation energy of 1.8 kcal./mole is indicated for escape of the ethyl radicals from the I atoms with which they are combined before absorbing a photon. Integrated rate equations for the production of HI, I_2 and exchange of radioiodine at room temperature have been derived in a manner similar to that used in treating the results of the radiolysis of ethyl iodide. The same types of elementary reaction steps seem able to explain the results of both the radiolysis and photolysis. Electron paramagnetic resonance spectra of glassy ethyl iodide photolyzed at −180° indicate that the quantum yield of trapped-in ethyl radicals is less than 10^{-5}, whereas the 100 e.v. yield for such radicals produced by Co^{60} γ-radiation is of the order of unity for the glass and 0.01 for the polycrystalline solid.

Introduction

Bunbury, Williams and Hamill[1] have shown that the mechanism of the photolysis of liquid ethyl iodide by 2537 Å. light at room temperature includes a competition between hydrogen iodide and iodine for thermalized C_2H_5 radicals. In studies of the radiolysis[2] of liquid ethyl iodide at room temperature it has been possible to analyze quantitatively such competing elementary reaction steps and to obtain integrated rate equations for HI and I_2 production and for exchange with radioiodine. This was done by the technique of determining limiting initial rates of iodine production in the presence of added iodine and of added hydrogen iodide. In the present work we have analyzed the elementary steps of the photolysis of liquid ethyl iodide in the same way, both at 25 and −70°, with the aim of obtaining information on the activation energies of competing elementary reactions. Exploratory investigations also have been made of the effects of additives on the photolysis of glassy ethyl iodide at −180°, and evidence for formation of trapped radicals during the photolysis and radiolysis of the solid has been sought by electron paramagnetic resonance measurements.

Experimental[3]

Cryostat.—All samples were illuminated in a cryostat described earlier.[4] It consists of a coolant reservoir, to the bottom of which is soldered a heavy walled copper tube with a cell compartment at the lower end. Provision is made for insulating the cell compartment and maintaining all windows free of condensation and passing a beam of light through the cell while it is kept at the desired temperature. In the present work three temperatures were used: room temperature; −70 ± 2°, which was maintained by the use of pulverized Dry Ice in the reservoir; and about −180°, maintained with liquid air in the reservoir.

Illumination.—Two Hanovia SC 2537, 110 ma., low pressure mercury vapor lamps were used, one facing each of the two diametrically opposite windows of the cryostat. The spectral and intensity characteristics and the operation of these lamps have been described earlier.[5] To minimize intensity fluctuations a milliameter was used in series with each lamp, and the current was adjusted manually with a

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[1] D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **78**, 6228 (1956).

[2] R. J. Hanrahan and J. E. Willard, *ibid.*, **79**, 2434 (1957).

[3] Additional details are given in the Ph.D. thesis of Ray H. Luebbe, Jr., University of Wisconsin, 1958, available from University Microfilms, Ann Arbor, Michigan.

[4] T. O. Jones and J. E. Willard, *Rev. Sci. Inst.*, **27**, 1037 (1956).

[5] G. M. Harris and J. E. Willard, THIS JOURNAL, **75**, 4678 (1954).

variable resistance when it drifted as a result of changes in the line voltage. Except for the end window the lamps were wrapped in asbestos and operated without cooling. A few turns of electrically heated nichrome wire around the end near the window served to prevent condensation of mercury on the window. A series of tests showed that the rate of iodine production in the photolysis of ethyl iodide was directly proportional to the current through the lamps. This indicated that the light output is proportional to the current since it is known that the quantum yield of the photolysis is independent of the light intensity.[1] Vycor filters and Vycor reaction cells were used to exclude light of wave lengths less than 2400 Å. from the reaction mixtures. If the quantum efficiency of the photolysis of liquid ethyl iodide at 25° is 0.26[6] equivalent of iodine produced per quantum absorbed, the rate of light absorption by ethyl iodide in the 10 mm. i.d. tubular cells used in the present work was 2.5×10^{-6} einstein/hr.

Sample Preparation.—All samples for photolysis were prepared on a vacuum line from Eastman Kodak Co. white label ethyl iodide which had been further purified by passage through activated alumina and fractional distillation on a Todd column. They were degassed and dried with P_2O_5, on the vacuum line. For those samples which were to be analyzed spectrophotometrically 3 ml. of liquid ethyl iodide was sealed in a vessel which consisted of a 10 mm. i.d. Vycor tube 4 cm. long attached through a graded seal and 6 mm. i.d. tubing to a square Pyrex cell 1 cm. on a side and about 4 cm. long. The entire assembly was about 28 cm. long. The square Pyrex end was used when analyzing the solutions for iodine on a Beckman spectrophotometer. The round Vycor end was used as the reaction cell during photolysis. The round Vycor tubing was much more resistant to cracking when samples were frozen than was square silica tubing which was used early in the work. For the experiments at −70° the cells were chilled for 10 minutes in chopped Dry Ice, before insertion in the prechilled cryostat. Freezing of the ethyl iodide to a glass for the runs at −180° was accomplished by first immersing the cell in liquid air to a depth almost even with the top of the liquid, for 30 seconds (to allow the vapor to condense without forming seed crystals on the walls), and then completely immersing the cell. Since the glasses tended to crack with prolonged photolysis they normally were melted and refrozen after each hour of illumination.

Hydrogen iodide gas was prepared from Merck Analytical Grade hydriodic acid, 55% aqueous solution, by reaction of the water with P_2O_5, and was metered into the reaction vessels by use of a calibrated volume and a mercury manometer. The amounts of HI calculated from the metering agreed within a few per cent. with analyses made by the oxidation method described earlier.[7]

Analysis.—I_2 concentrations were determined with a Beckman DU spectrophotometer equipped with a photomultiplier detector. When employed with compensator cells of suitable concentration, and an interference filter with maximum transmission at 4780 Å. to cut out the small amount of light at wave lengths other than that used for analysis, this allowed the determination of absorbancies as high as 5. The absorbancy index of iodine in ethyl iodide at 4780 Å. is 1.28×10^3 l. mole^{-1} cm.$^{-1}$.[8] When the 28 cm. cells were used, they and the cell compartment were covered with a wooden box to exclude room light. HI concentrations at the end of the experiments were determined by oxidation of the HI to I_2.[7]

The molar ratios of ethylene to ethane produced by the photolysis of ethyl iodide were determined by gas chromatography. For these experiments 0.3-ml. samples of ethyl iodide were used, and the photolysis cells consisted of 7 cm. tubes of 4 mm. i.d. silica tubing with a thin bulb blown at one end to facilitate breaking in the gas stream. During illumination the cells were mounted in the light path through the cryostat by means of a positioning block designed for the purpose. To produce sufficient products for analysis the samples usually were illuminated for 24 hr. During irradiations of the glass at −180° the samples were melted and refrozen every hour to lessen the cumulative buildup of product concentration at the interface where the light was absorbed. Following illumination the sample tube was placed in a piece of polyethylene tubing through which helium flowed and carried the contents on to the chromatographic column when the tube was broken. The desired separation of ethylene and ethane was accomplished by an 8 foot long column of 30–60 mesh firebrick coated with a solution of silver nitrate in propylene glycol and maintained at about 0°, which retards olefins with respect to alkanes. This column was preceded by a fourteen foot column of firebrick coated with Dow-Corning 200 silicone oil and maintained at room temperature. The silicone oil column served to prevent the ethyl iodide, iodine and hydrogen iodide from getting to the second column where they would react with the silver nitrate.[7a] Detection was by Gow–Mac thermal conductivity cells and a chart recorder. Calibration runs showed that the peak areas per mole were the same for ethylene and ethane within an experimental uncertainty of about 4%.

Exchange Reactions.—Ethyl iodide containing iodine tagged with I^{131} was prepared by adding a few microliters of aqueous carrier-free I^{131} iodide solution to 3 ml. of 8×10^{-4} *M* iodine in ethyl iodide. Following addition of P_2O_5 to remove the water the solution was degassed and distilled into the reaction vessel on the vacuum line. Analysis of the illuminated solutions was carried out by freezing with liquid air, breaking open the cell, adding water, separating the organic layer from the water in a separatory funnel and making a second extraction of the organic layer with aqueous sulfite solution. Carbon tetrachloride was added to dilute the organic layer to the desired volume prior to extraction. The water extract which contained the HI, the sulfite solution which had extracted the I_2 and the organic layer which contained the iodine which had entered organic combination, were each counted with a well-type scintillation counter. Corrections were applied for an average 2.7% exchange and an apparent HI production (a concentration of about 5 mole % relative to the tagged iodine initially added) which were found to occur regularly during the tagging and sample preparation but before illumination.

Results

Products and Product Yields.—The products we have observed in the photolysis of ethyl iodide are I_2, HI, C_2H_6 and C_2H_4. These were found at all three temperatures investigated, 25, −70 and −180°. No other products were found, although C_3H_8 and C_4H_{10} would have been detected if present as only 5% of the ethane. Alkyl iodides such as CH_3I and C_3H_7I would not have been detected by our methods.

Spectrophotometric measurements made at intervals during the photolysis showed that the iodine concentration increases linearly with time of illumination over the range studied, when no additives are present (Fig. 1) and analysis for HI at the end of illumination showed that the HI/I_2 ratio is constant for runs at a single temperature (Table I). The ratio of C_2H_4/C_2H_6 was likewise independent of the extent of photolysis (Table II).

If the data of Table I for increase in absorbancy per hour are used together with the literature value[6] of 0.26 equivalent of iodine produced per quantum in liquid C_2H_5I at room temperature, the quantum yields for iodine and HI production in the present work can be estimated. They, together with certain product ratios and quantum yields of elementary processes to be discussed below, are summarized in Table III. For the estimates for −180° the run in which the sample was melted after each minute of photolysis was used, in order to minimize the influence of the accumulated products in the volume where photolysis occurs. The increase

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[6] B. L. Cochran, W. H. Hamill and R. R. Williams, Jr., THIS JOURNAL, **76**, 2145 (1954).

[7] (a) R. J. Hanrahan, Ph.D. thesis, University of Wisconsin, 1957, available from University Microfilms, Ann Arbor, Michigan; (b) T. O. Jones, R. H. Luebbe, Jr., J. R. Wilson and J. E. Willard, *J. Phys. Chem.*, **62**, 9 (1958).

[8] E. O. Hornig and J. E. Willard, THIS JOURNAL, **79**, 2429 (1957).

TABLE I

I_2 AND HI PRODUCTION IN THE PHOTOLYSIS OF C_2H_5I

Temp., °C.	Length of photolysis, hr.	Δ log I_0/I[a] per hr., before oxidation	Δ log I_0/I[a,b] per hr., after oxidation	(HI)/(I_2)
25(liq.)	6.5	0.151	0.192	0.56
	5.9	.175[c]	.225[c]	.58
	7.0	.143		
	7.3	.142	.181	.54
	6.0	.140	.180	.57
	Average	.14	.18	.56
− 70(liq.)	8.1	0.063	0.137	2.36
	7.8	.077	.169	2.40
	6.0	.060	.126	2.22
	9.0	.063	.136	2.24
	Average	.066	.14	2.3
−180(glass)	8.25	0.048	0.15	4.2
	4.25	.047	.155	4.6
	7.25	.041	.13	4.5
	9.80	.048	.18	5.3
	Average	.046	.15	4.6
−180(glass)[d]	3.0[d]	0.016	0.13	15

[a] Absorbance at 4780 Å. [b] The difference between the absorbancies listed in this column and those in the preceding column is due to the oxidation of the HI which yields one mole of I_2 for every two moles of HI present before oxidation.[7] [c] Not included in average. [d] Glass melted and refrozen after each minute of radiolysis rather than after each hour as in the other runs at −180°.

TABLE II

RATIO OF C_2H_4 TO C_2H_6 PRODUCED IN THE PHOTOLYSIS OF ETHYL IODIDE

Temp., °C.	C_2H_4/C_2H_6 Individual runs[a]	Av.
25(liq.)	1.6, 1.4, 1.6	1.5
− 70(liq.)	3.3, 3.1	3.2
−180(glass)	5.1, 7.7, 6.1, 6.6, 6.3	6.4

[a] At both 25 and −180° the total illumination periods for the runs listed varied by a factor of about 5.

in the quantum yield of HI with decreasing temperature compensates for the decrease in the I_2 yield to such an extent that the combined yield of the two (expressed as equivalents of iodine) decreases only slightly with temperature. An analogous but less pronounced increase in HI/I_2 ratio with decreasing temperature has been observed in the photolysis of n-C_3H_7I.[9]

The ratio of C_2H_4/C_2H_6 which we have found at 25° is in exact agreement with that found by Bunbury, Williams and Hamill[1] while our value and theirs for the HI/I_2 ratio are in fair agreement, being 0.56 and 0.47, respectively. The values are in good agreement with the relationship C_2H_4/C_2H_6 = HI/I_2 + 1, which is required by stoichiometry.

Effects of Added I_2 and HI on the Quantum Yield of Iodine Production.—The production of iodine as a function of time of photolysis at 25° when HI and I_2 were added prior to illumination is shown in Fig. 1. The points represent experimental data; the curves were drawn from equations which will be discussed later. All the runs with added HI gave the same initial rate (maximum rate); likewise both the runs with added I_2 gave the same initial rate (minimum rate); when these experiments were repeated at −70°[3] the same qualitative behavior was observed, though the maximum rate was considerably lower. At −180° it was found that there was no effect of additives either on the rate of I_2 production or on the ratio of HI/I_2 produced during the photolysis. The rate of I_2 production was constant, as it was in the absence of additives.

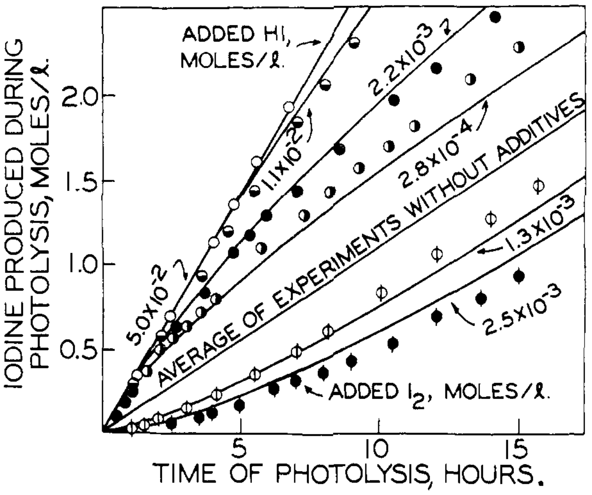

Fig. 1.—Effect of added HI and I_2 on the photolysis of ethyl iodide at 25°. Points are from experimental data; curves are calculated.

TABLE III

SUMMARY OF QUANTUM YIELDS[e] AND RATIOS OF HI/I_2, C_2H_4/C_2H_6 AND k_{12}/k_{HI} IN THE PHOTOLYSIS OF C_2H_5I

	25°	−70°	−180°(glass)	BWH[h] values
$\Phi_{1/2 I_2}$	0.26[e]	0.12	0.030	
			.086[f]	
Φ_{HI}	.073	.14	.22	0.061
			.20[f]	
$\Phi_{HI + 1/2 I_2}$	.33	.26	.25	.32
			.28[f]	
(HI)/(I_2)	.56	2.3	15	.47
			4.6[f]	
(C_2H_4)/(C_2H_6)	1.5	3.2	6.4	1.5
Φ_A[a]	0.32	0.08	0.00045[f,g]	0.21
Φ_B[b]	.36	.13	.030	
Φ_C[c]	.17	.18	.22	.19
k_{12}/k_{HI}[d]	1	2.5		.34

[a] Quantum yield for escape of thermal C_2H_5 radicals from primary or diffusive recombination with parent iodine atom. [b] Quantum yield in equivalents per einstein for production of 1/2 I_2, by reactions 3b and 4 listed later in text. [c] Quantum yield of processes which produce HI, *i.e.*, reactions 2a and/or 3a given later in text. [d] Ratio of rate constant for the reaction $C_2H_5 + I_2 \rightarrow C_2H_5I + I$ to that for $C_2H_5 + HI \rightarrow C_2H_6 + I$. [e] Calculated as equivalents/einstein assuming as an actinometric standard that $\Phi_{1/2 I_2} = 0.26$ at 25°.[6] [f] These values for −180° are from the experiment in which the glass was melted and refrozen following each minute of illumination. One hour periods of illumination without melting were used in the other runs at −180°. [g] Calculated from the activation energy estimated from the values at 25 and −70°. [h] Bunbury, Williams and Hamill[1] used a temperature of 37° in some experiments and "room temperature" in others.

As in the radiolysis experiments,[2] it appears that the initial rate with added HI represents the rate when all C_2H_5 radicals which escape diffusion

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(9) C. E. McCauley and T. J. Hilsdorf, THIS JOURNAL, **80**, 5101 (1958).

controlled recombination with their original I atom partner react with HI by the process $C_2H_5 + HI \rightarrow C_2H_6 + I$. The initial rate with added I_2 represents the case where all such radicals react by $C_2H_5 + I_2 \rightarrow C_2H_5I + I$.

Plots of the average rate observed up to time, *t*, *vs*. *t* extrapolated to $t = 0$ were used to determine the limiting initial rates. Values obtained in this way are shown in Table IV.

Table IV

Initial Rates for the Production of I_2 in the Photolysis of C_2H_5I with and without Added HI and I_2

Temp., °C.	Additive	No. of runs	Initial rate, µmoles/hr./3 ml.
25(liq.)	None	4	0.33 ± 0.03
	HI	3	.87 ± .03
	I_2	2	.06 ± .01
− 70(liq.)	None	4	.15 ± .01
	HI	4	.26 ± .03
	I_2	2	.06 ± .01
−180(glass)	None	4	.11 ± .01
	None	1	.037[a]
	HI	2	.10 ± .01
	I_2	2	.10 ± .01

[a] The C_2H_5I in this run was melted and refrozen after each minute of illumination whereas the other samples at −180° were melted each hour. Three hours total illumination was given in each case.

Table IV shows that within experimental error the rate of I_2 production in the glass at −180° is unaffected by the presence of additives, though it is decidedly affected by the frequency of melting.

Results of Exchange Experiments.—The results of the exchange experiments are shown in Fig. 2.

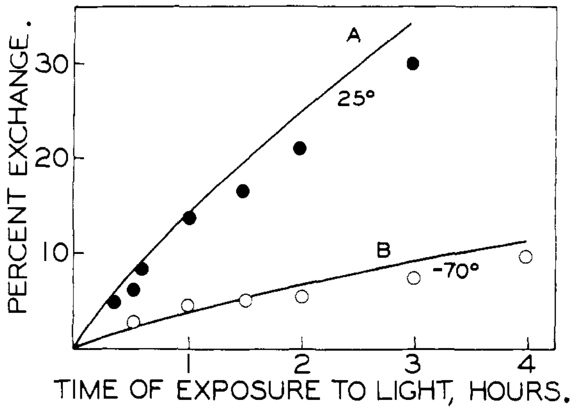

Fig. 2.—Photochemical exchange between I_2 containing I^{131} and C_2H_5I. Points are from experimental data; curves are calculated.

As in Fig. 1, the points represent the experimental data and the curves were drawn from equations which will be described. Curve A represents the per cent. of I^{131} activity found in organic form as a function of the time of exposure to the light (after correction for the 2.7% dark exchange induced by the tagging procedure) at 25°. Curve B represents the photochemical exchange at −70°. The percentage exchange varies with time in a manner which is dependent on the fraction of the activity remaining in inorganic combination, on the progressive dilution of the activity by the increase in I_2 and HI concentration in the solution caused by the photolysis and on the increasing HI/I_2 ratio as photolysis proceeds. It can be seen that the quantum yield of exchange, like that of iodine production, is considerably lower at −70° than at 25°. At −180° no photochemical exchange was found in photolyses as long as 8 hr. (with melting and refreezing every hour).

Electron Paramagnetic Resonance Measurements on Photolyzed and Radiolyzed Solid C_2H_5I.—Electron paramagnetic resonance spectra[10] of both photolyzed[11] and radiolyzed[12] solid ethyl iodide have been run. They showed no evidence of trapped radicals in any of the photolysis experiments with either glassy or polycrystalline ethyl iodide. Ethyl iodide glass which had been irradiated with Co^{60} γ-rays showed however, a clear six-line spectrum (Fig. 3), with a 130 gauss spread, which was ascribed to the ethyl radicals.[13b] From the intensity of the absorption, it could be estimated that about 5×10^{16} trapped ethyl radicals had been produced. This would indicate a G-value (trapped radicals produced per 100 e.v. absorbed) of the order of unity. Slight absorption by H atoms (not shown in Fig. 3) was also detected, though the intensity indicated that they were present in a concentration 50–70 fold lower than the ethyl radicals. The e.p.r. spectrum of the sample of radiolyzed polycrystalline ethyl iodide gave absorption which could be ascribed to the ethyl radical, though the intensity indicated a concentra-

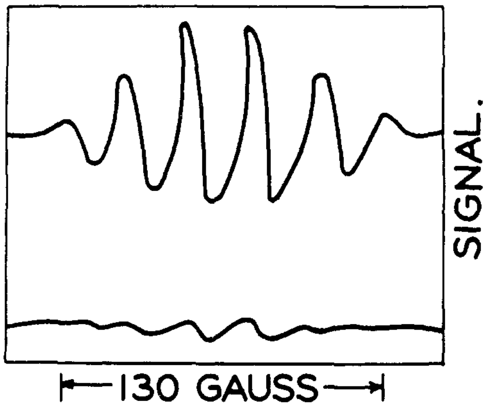

Fig. 3.—Electron paramagnetic resonance spectrum of glassy (top) and polycrystalline (bottom) ethyl iodide at −180°. The spectrum of the latter is shown at 6-fold greater sensitivity than the spectrum of the former.

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(10) Preliminary tests with photolyzed samples were carried out with the aid of Prof. R. N. Dexter in his Laboratory in the Physics Department of the University of Wisconsin. The later experiments were done in the laboratory of Dr. Max Matheson of the Argonne National Laboratory with his assistance, the resonance spectra being run by Dr. William Hayes.

(11) Three hours photolysis in the cryostat using the two lamps and cells of the type described for the gas chromatographic analysis. In addition both glassy and polycrystalline ethyl iodide were photolyzed at pumped liquid nitrogen temperature for 1 hr. using the equipment described by Smaller and Matheson.[13a] It is estimated that about 10^{17} quanta of 2537 Å. light entered the sample tubes during these latter photolyses.

(12) The radiolyses were made at liquid nitrogen temperature for 20 min. at a dose rate of about 1.6×10^{17} e.v. $g.^{-1}$ $min.^{-1}$ using the Argonne Co^{60} source as described by Smaller and Matheson.[13a]

(13) (a) B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958); (b) W. Gordy and C. G. McCormick, This Journal, **78**, 3243 (1956).

tion 30–40 fold lower than the concentration of ethyl radicals in the γ-irradiated glass. No H atom absorption was detected in the polycrystalline sample.

Discussion

Elementary Reaction Steps in the Photolysis.—The above observations on the photolysis of ethyl iodide, including the effects of added HI and I_2, the evidence for "hot" HI and I_2 production which is not affected by additives and the temperature coefficients, can be explained by the reaction steps

$$C_2H_5I + h\nu \longrightarrow \underline{C_2H_5I} \qquad (1)$$

$$\underline{C_2H_5I} \longrightarrow C_2H_4 + HI \qquad (2a)$$

and/or

$$\underline{C_2H_5I} \longrightarrow (\underline{C_2H_5}\cdot + I\cdot) \qquad (2b)$$

$$(\underline{C_2H_5}\cdot + I\cdot) \longrightarrow C_2H_4 + HI \qquad (3a)$$

and/or

$$(\underline{C_2H_5}\cdot + I\cdot) \longrightarrow \underline{C_2H_5}\cdot + I\cdot \qquad (3b)$$

$$(\underline{C_2H_5}\cdot + I\cdot) + M \longrightarrow C_2H_5I + M \qquad (3c)$$

$$\underline{C_2H_5}\cdot + C_2H_5I \longrightarrow C_2H_4 + C_2H_6 + I\cdot \qquad (4)$$

$$\underline{C_2H_5}\cdot + M \longrightarrow C_2H_5\cdot + M \qquad (5)$$

$$I\cdot + I\cdot \longrightarrow I_2 \qquad (6)$$

$$C_2H_5\cdot + I_2 \xrightarrow{k_{I_2}} C_2H_5I + I\cdot \qquad (7)$$

$$C_2H_5\cdot + HI \xrightarrow{k_{HI}} C_2H_6 + I\cdot \qquad (8)$$

The notation of enclosing fragment species in parentheses, ( ), indicates that they have not yet escaped the possibility of diffusive recombination. Underlining a species indicates that it still possesses energy given it by the photon in excess of average thermal energies. Presumably both reactions 3a and 3b may occur with thermalized ethyl radicals as well as with those of higher energy.

These reaction steps are similar to those proposed earlier for the photolysis[1] and radiolysis of liquid C_2H_5I at room temperature but include steps for the production of $^1/_2$ I_2 by the attack of energetic C_2H_5 radicals on C_2H_5I (4) and the production of HI by direct elimination from C_2H_5I (2a), which were not included in discussion of the earlier photochemical work. These are required because we find the initial rate of I_2 production in the presence of added I_2 to be about 18% of the rate in the absence of additive; and because the gross production of HI(Φ_c) does not increase with decreasing temperature as much as might be expected if it were all formed by reaction (3a). This will be discussed in more detail in a later section.

The elementary reactions proposed above do not include the reaction $I + C_2H_5I \rightarrow C_2H_4 + HI + I$ recently reported by McMillan and Noyes.[14] Their data indicate that the quantum yield is *ca.* 0.002. Assuming the same quantum yield under our conditions, the contribution of this reaction to the yield of HI which we have observed would be very small (Table III).

Rate Equations and Absolute Rates of Elementary Processes.—Using the data on initial rates of I_2 production with and without additives (Fig. 1) and the treatment applied earlier to the radiolysis of C_2H_5I,[2] it is possible to derive integrated rate equations for the production of HI and I_2 as well as an equation which will predict the rate of photochemical exchange of I^{131} between I_2 and C_2H_5I for any concentrations of HI and I_2 in C_2H_5I. Let

A = rate of production of thermal ethyl radicals (reaction 5)
B = total rate of production of I_2 by "hot" processes (reactions 3b and 4, but not reaction 8)
C = rate of HI production *via* reaction(s) 2a and/or 3a.

A, B and C are constant if the light intensity is constant and if the concentration of products in the reaction zone does not build up too much, *i.e.*, to give absorption of light by products or to provide molecules other than C_2H_5I for attack by energetic C_2H_5 radicals (as in reaction 4). Most of the incident light is absorbed within a small fraction of a millimeter at the face of the cell, since the molar absorbancy index of ethyl iodide is 400 at 2537 Å.[15] For this reason the thermalized ethyl radicals would not be expected to distribute themselves homogeneously throughout the cell. However, the absence of butane formation indicates that their local concentration does not build up enough for radical–radical reactions between them to take place. Their fate is then governed solely by the HI/I_2 ratio since they are removed by the competitive reactions 7 and 8.

Using the values of the initial rates with and without additives from Table III, it is possible to derive the value of the constants A and B at both 25 and −70°. In order to evaluate C it is necessary to make an assumption about the ratio k_{I_2}/k_{HI}. The results on the radiolysis of ethyl iodide indicate that this ratio is very close to 1 at room temperature.[2] Substitution of values of the minimum, maximum and normal rates from Table IV into equation 21[16] of reference 2 (which should be equally valid for the photolysis as for the radiolysis) yields a predicted ratio of HI/I_2 of 0.50 at 25° *if* it is assumed that $k_{I_2}/k_{HI} = 1$. The experimentally determined ratio of 0.56 indicates that this is a reasonably good assumption. The indicated experimental value for k_{I_2}/k_{HI} would be 1.12. Within experimental error this agrees with the value found from the radiolysis studies and is much different from the value of 0.34 reported by Bunbury, Williams and Hamill.[1] Assuming, then, that the value of $k_{I_2}/k_{HI} = 1$ and that the ratio HI/I_2 = 0.50, it is possible to evaluate C at 25°. The values of the constants at 25° are: $A = 0.810$ μmole/hr., $B = 0.462$ μmole/hr. and $C = 0.435$ μmole/hr. Using the normal rate of I_2 production at 25° of 0.328 μmole/hr. together with the reported quantum efficiency of 0.26 equivalent/einstein at 25°,[6] it can be calculated that the rate of light input to the cell is 2.52 microeinsteins/hr. The constants A, B and C can then be expressed in terms of quantum efficiencies. These values are shown in Table III.

The rate equations for the photolysis at 25° (assuming $k_{I_2}/k_{HI} = 1$ and expressing all concentra-

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(14) G. R. McMillan and W. A. Noyes, Jr., THIS JOURNAL, **80**, 2108 (1958).

(15) R. N. Haszeldine, *J. Chem. Soc.*, 1764 (1953).

(16) There is a misprint in equation 21 of reference 2. It should read

$$\left(\frac{(HI)}{(I_2)}\right)_{\text{normal}} = \frac{k_{I_2}\,(\text{normal rate-minimum rate})}{k_{HI}\,(\text{maximum rate-normal rate})} \qquad (21)$$

A similar correction is needed in footnote *f* of Table II of reference 2.

tions in moles/liter) are

$$d(I_2)/dt = 0.867 - 0.810(I_2)/[(HI) + (I_2)] \quad (23)$$

$$d(HI)/dt = -0.375 + 0.810(I_2)/[(HI) + (I_2)] \quad (24)$$

$$d(HI + I_2)/dt = 0.492 \quad (25)$$

$$d(C_2H_5I)_{exch}/dt = 0.810(I_2)/[(HI) + (I_2)] \quad (26)$$

Equation 25 can be integrated directly to give equation 29. Equation 29 can then be used to substitute for $[(HI) + (I_2)]$ in terms of time t in equations 23, 24 and 26. These equations may then be integrated directly to give equations 27, 28, and 30, respectively.

$$(I_2)_t = 0.328t + 0.666[(HI)_0 + (I_2)_0] + [0.334(I_2)_0 - 0.666(HI)_0]\left[1 + \frac{0.492t}{(HI)_0 + (I_2)_0}\right]^{-1.65} \quad (27)$$

$$(HI)_t = 0.164t + 0.334[(HI)_0 + (I_2)_0] + [0.666(HI)_0 - 0.334(I_2)_0]\left[1 + \frac{0.492t}{(HI)_0 + (I_2)_0}\right]^{-1.65} \quad (28)$$

$$(HI + I_2)_t = 0.492t + (HI)_0 + (I_2)_0 \quad (29)$$

$$(C_2H_5I)_{exch} = 0.540t + [0.33(I_2)_0 - 0.664(HI)_0]\left[1 - \left(1 + \frac{0.492t}{(HI)_0 + (I_2)_0}\right)^{-1.65}\right] \quad (30)^{17}$$

The constants, A and B, can be calculated at −70° in the same manner as at 25°, since no assumptions about the ratio k_{I_2}/k_{HI} are needed. This is not true of the constant C for the calculation of which it was assumed that $k_{I_2}/k_{HI} = 1$. Substitution of the minimum, maximum and normal rates at −70° (Table IV) into equation 21 yields a predicted ratio for HI/I_2 of 0.92 if it is assumed that $k_{I_2}/k_{HI} = 1$. The experimentally determined ratio of 2.3 indicates that this is not a valid assumption at −70°. The value of k_{I_2}/k_{HI} in equation 21 which is required to fit the experimental data for the other quantities is 2.5. The constant C can be evaluated using the experimentally determined ratios of $HI/I_2 = 2.3$ and $k_{I_2}/k_{HI} = 2.5$. The values of the three constants at −70° are: $A = 0.200$ μmole/hr., $B = 0.158$ μmole/hr. and $C = 0.450$ μmole/hr. The rate equations at −70° are (using $k_{I_2}/k_{HI} = 2.5$)

$$d(I_2)/dt = 0.258 - [0.200(I_2)]/[0.4(HI) + (I_2)] \quad (23')$$

$$d(HI)/dt = 0.250 + [0.200(I_2)]/[0.4(HI) + (I_2)] \quad (24')$$

$$d(HI + I_2)/dt = 0.508 \quad (25')$$

$$d(C_2H_5I)_{exch}/dt = [0.200(I_2)]/[0.4(HI) + I_2] \quad (26')$$

Equations 23′, 24′ and 26′ cannot be integrated by standard techniques, since there is no expression available for $[0.4(HI)+(I_2)]$ in terms of time t. When equation 25′ is integrated it yields

$$(HI + I_2) = 0.508t + (HI)_0 + (I_2)_0 \quad (28')$$

Comparison of Experimental Results with Yields Predicted by Equations.—The solid lines of Fig. 1 show the iodine production as a function of time as predicted from equation 27 for the initial concentrations of I_2 and HI used in the experiments. They are in semi-quantitative agreement with the experimental points. The deviations may result from errors in determining the initial rates with and without additives (the accuracy of these determinations depends on the reproducibility of the light intensity) and in the assumption that the ratio k_{I_2}/k_{HI} at 25° is exactly unity.

In the exchange experiments using I^{131}, ratios of HI/I_2 were determined by comparing the counting rate of the water extract (HI) with that of the sulfite extract (I_2). These ratios agreed well with those calculated using equations 27 and 28.

Curve A, Fig. 2 for the predicted photochemical exchange of I_2 with C_2H_5I at 25° was obtained with the aid of equations 26, 27 and 28, using the method of iterative calculations described earlier.[2] The calculations allow for the dilution of the radioiodine by the I_2 and HI produced during the photolysis. Unlike the radiolysis results,[2] which showed a 20% higher observed rate of exchange than that predicted from the equations, the observed and predicted photolysis results are in fair agreement, such discrepancy as there is being in the opposite direction to that for the radiolysis. The better agreement may perhaps be explained by the fact that while the energetic electrons in the radiation system may excite ethyl iodide molecules to electronic states which may undergo exchange with I_2 molecules, the photons of 2537 Å. light may not be able to excite the molecules to such states.

Curve B in Fig. 2, which represents the predicted photochemical exchange at −70°, was calculated in essentially the same way as was curve A, except that equation 26′ was used and, since integrated rate equations were not available, the concentrations of I_2 were obtained from spectrophotometric readings at half-hour intervals and the HI concentrations were determined from the counting rates of the fractions containing the HI and I_2 together with the spectrophotometrically determined I_2 concentration.

The quantum efficiency for the photochemical exchange of I^{131} between I_2 and C_2H_5I depends on the ratio HI/I_2. The "limiting" quantum efficiency (*i.e.*, the quantum efficiency when there is a large excess of I_2 present) is the same as the quantum efficiency for the production of thermal ethyl radicals, 0.810 μmole hr.$^{-1}$/2.52 microeinsteins hr.$^{-1}$ = 0.32, at 25°. This is somewhat lower than the average value of 0.42[18] reported earlier for a series of experiments on the exchange in which the individual results showed wide variation from the average.

Effect of Temperature on Caging Effectiveness and on k_{I_2}/k_{HI} Ratio.—The rate of production of thermal ethyl radicals which do not recombine with their original I atom partner (designated above by the constant A) is 0.81 μmole hr.$^{-1}$ at 25° and 0.20 μmole hr.$^{-1}$ at −70°. Expressed as an activation energy this difference represents 1.8 kcal./mole for the escape of the ethyl radical from its partner iodine atom after absorption of a 2537 Å. photon by a C_2H_5I molecule. The temperature may affect both the penetrability of the cage walls for the freshly born fragments which carry the excess energy from the photon and also the probability

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[17] There is an error in equation 30 of reference 2. That equation should read

$$(C_2H_5I)_{exch} = 0.1017t + (0.228[I_2]_0 - 0.772[HI]_0)\left[1 - \left(1 + \frac{0.847t}{(HI)_0 + (I_2)_0}\right)^{-1.55}\right]$$

[18] W. H. Hamill and R. H. Schuler, THIS JOURNAL, **73**, 3466 (1951). We have corrected the value of 0.64 found by these authors for the fact that in their actinometric calculations they used 0.4 rather than 0.26[5] as the quantum yield of $^1/_2I_2$.

that the fragments will diffuse away from each other after thermalization. The value of 1.8 kcal./mole is similar to the 2.1 kcal./mole attributed by Firestone[19] to the escape of Br atoms from cages of CCl_3Br molecules in the radiolysis of CCl_3Br. It would be expected from the data at 25 and −70° that the value of *A* at −180° would be negligibly small but no experiments on the exchange or effect of added I_2 at this temperature have been done under conditions suitable for determining *A*.

The rates of iodine production by processes which are not affected by scavengers at the concentrations of Fig. 1 at 25°, −70° and −180° are 0.46, 0.16 and 0.038 μmole hr.$^{-1}$, respectively. This iodine production (designated by the constant *B*) is attributed to the reactions $(\underline{C_2H_5} + I) \rightarrow \underline{C_2H_5} + I$(3b) and $\underline{C_2H_5} + C_2H_5I \rightarrow C_2H_4 + C_2H_6 + I$ (4). The rates at 25 and −70° indicate an over-all activation energy of 1.4 kcal./mole, for the production of $^1/_2I_2$ by these two processes. From this the predicted value of *B* at −180° would be 3.2×10^{-3} μmole/hr. or one-tenth as large as observed. It is probable that the observed yield at −180° is due entirely to a temperature independent reaction such as (4) while most of the yield at the higher temperatures is due to the radical escape reaction 3b. If the value of *B* at −180° (0.038) is subtracted from the measured values of *B* at 25 and −70° the new values become 0.424 and 0.120 μmole hr.$^{-1}$, which give an activation energy of 1.6 kcal./mole, *i.e.*, very nearly the same as the activation energy for the constant *A* which is the rate of escape of thermal ethyl radicals and iodine atoms from recombination.

The constant *C* which represents the rate of HI production *via* the reaction $\underline{C_2H_5I} \rightarrow C_2H_4 + HI$ (2a) and/or $(C_2H_5 + I) \rightarrow C_2H_4 + HI$ (3a) is 0.44 μmole hr.$^{-1}$ at 25° and 0.45 μmole hr.$^{-1}$ at −70°. The identity of these two values suggests that HI production occurs predominantly by (2a)[20] or some other reaction which does not require reencounter of a C_2H_5 radical with its iodine atom partner, rather than by 3a, since the escape of C_2H_5 radicals from diffusive recombination and other reactions at the site of formation is decreased to one-fourth (0.81 to 0.20 μmole hr.$^{-1}$) in going from 25 to −70°, but HI production did not increase.[22] The rate of HI production in the glass at −180° for the last run shown in Table I was 0.55 μmole hr.$^{-1}$, which is a change of only 22% from the 0.45 value for *C* at −70°. It may be assumed that the observed rate of HI production at −180° is equal to the primary rate because thermal radical reactions are essentially stopped.

From the fact that the ratio of k_{I_2}/k_{HI} increases from about 1.1 at 25° to 2.5 at −70°, it follows that the activation energy for the reaction $C_2H_5 + HI \rightarrow C_2H_6 + I$ is about 1 kcal. per mole higher than for the reaction $C_2H_5 + I_2 \rightarrow C_2H_5I + I$. Both reactions are known to have very low activation energies. The increase in the observed HI/I_2 ratio with decrease in temperature results from the activation energy difference, a difference which is so small that determinations at low temperatures are required to show experimentally distinguishable differences in rate.

Absence of Scavenger Effect and Exchange in Solid State.—The fact that no exchange with radioiodine occurred and that added HI and I_2 did not affect the photolysis rate in solid C_2H_5I glass at −180° proves that thermal ethyl radicals were not formed or that if formed they did not have opportunity to interact with the additives.[23] From the decrease in A (the rate of production of thermal ethyl radicals) in going from 25 to −70°, it can be estimated that the quantum yield for the escape of C_2H_5 radicals from recombination with their I atom partners is only 4.5×10^{-4} at −180° (Table III). Since this is trivial compared to the observed yield of product formation, virtually all reaction must occur close to the site of photon absorption and reactions 7 and 8 would not be expected to contribute appreciably.

Another feature of these experiments would preclude reaction of radicals with additives. This is the fact that the half thickness for absorption of the incident light by the C_2H_5I is only 6×10^{-5} cm., as a consequence of which the concentration of products in the region of light absorption became as high as 2 moles/l. in the usual hour of illumination. In the solid state the local concentration in the region of light absorption is not reduced by diffusion and mixing with the rest of the sample in the cell, as it is in the liquid. Therefore the concentration of additives was small compared to the local concentration of products and any ethyl radicals which escaped primary or diffusive recombination would always react with product molecules rather than additives.

Effect of 1 Minute Illumination as Compared to 1 Hour Illumination.—In order to explore the influence of high local product concentration on the I_2 and HI production rates, one experiment was done in which each of the four faces of the reaction

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[19] R. F. Firestone, Ph.D. Thesis, University of Wisconsin, 1954.

[20] If reaction 2a is possible it might occur in the gas phase, whereas this would be impossible for 3a under normal photolysis conditions where C_2H_5 radicals would encounter I_2 much more frequently than I. Exploratory experiments by T. Gover in our laboratory indicate that the quantum yield of HI from the irradiation of gaseous C_2H_5I at 150 mm. pressure with 2537 Å. light is less than 10^{-4}. This suggests that if reaction 2a is important it may require that the absorbing molecules be in a liquid environment. Thrush[21] has reported a transient spectrum of HI following the flash photolysis of gaseous C_2H_5I and has attributed it to the reaction $C_2H_5I \xrightarrow{h\nu} C_2H_4 + HI$. The evidence does not, however, require this reaction 2a as compared to (3a), since the concentration of atoms and radicals produced by the flash was probably high enough to provide encounters between them. The reaction $I + C_2H_5I \rightarrow C_2H_4 + HI + I$[14] could also occur under these conditions. The transient nature of the HI spectrum may have resulted from the occurrence of reaction 8.

[21] B. A. Thrush, *Proc. Roy. Soc.* (*London*), **A243**, 555 (1958).

[22] McCauley and Hilsdorf[9] have suggested that the caging effect on a reaction analogous to (3a) accounts for the higher HI/I_2 ratio at −60 than 25° which they have observed for the photolysis of *n*-propyl iodide. The present work suggests that this change in ratio may be due to a higher activation energy for reaction of C_3H_7 radicals with HI than with I_2.

[23] There is of course question as to whether the additives remained in homogeneous molecular distribution in the glassy solvent. In view of the rapid freezing to the glassy state and the clear transparent appearance of the glass, it is not improbable that they did. Milman[24] has demonstrated that dissolved Br_2 shows a typical scavenger effect on the organic yield of the (n,γ) process in solid C_2H_5Br when the liquid solution is frozen fairly rapidly, but not when it is frozen very slowly.

[24] (a) M. Milman, THIS JOURNAL, **79**, 5581 (1957); (b) **80**, 5592 (1958).

cell containing C_2H_5I glass at −180° was irradiated for only one minute, following which the C_2H_5I was melted, mixed, refrozen and illuminated again in the same way. This sequence was repeated until the accumulated illumination time totaled 3 hr. A second cell was illuminated as a control for 1 hr. intervals, totalling 3 hr., at periods interspersed with the 1 minute illuminations. Expressed as increase in absorbancy hr.$^{-1}$ due to I_2 formed by irradiation and to I_2 formed by oxidation of the HI in the analysis procedure, respectively, the run with 1 hr. illuminations gave 0.037 and 0.093 and that with 1 minute illuminations 0.016 and 0.118. The HI/I_2 ratio for these runs was 5.0 for the former and 15 for the latter.

It is possible that the lower HI/I_2 ratio from the longer irradiation resulted from absorption of light by the HI or an HI–C_2H_5I complex built up to high concentration at the interface where the light entered the cell. The absorbancy index of HI under these conditions is not known. If it were the same as that for gaseous HI,[25] only about 2% of the incident light would have been absorbed by HI[3] in these experiments. If the I_2–C_2H_5I complex considered earlier[6] can form at liquid air temperature, it is probable that it absorbed an appreciable fraction of the light in the experiments with 1 hour illumination at this temperature.

It is probable that in the experiments with one hour illuminations the average local concentration of HI in the region where the light was absorbed was high enough for it to compete for C_2H_5 radicals which otherwise would undergo primary recombination or hot radical reactions with C_2H_5I. It seems likely that this competition accounts for at least part of the increased I_2 yield and lowered HI yield for the experiments with a one hour illumination period as compared to those with one minute illumination intervals.

Bunbury, Williams and Hamill[1] found that concentrations of HI of the order of 1 mole % added to ethyl iodide before photolysis (I_2 was also added at a concentration of 0.1 mole %) at 25° gave an anomalously low ratio of C_2H_4/C_2H_6 (and also presumably of HI/I_2, though this was not measured). They attributed this effect to competition of HI with a diffusion-controlled back reaction between ethyl radicals and iodine atoms (such as 3a). The effect of this would be to decrease the rate of C_2H_4 and HI production and increase the rate of C_2H_6 and I_2 production thus giving lower C_2H_4/C_2H_6 and HI/I_2 production ratios than would be observed with the same ratio of HI/I_2 present at concentrations of HI and I_2 so low that they would not interfere with reaction 3a.

Regardless of the reason for the differences between the runs with long and short illumination at −180°, it appears that the run with short illuminations offers the better basis for evaluating temperature and phase effects in making comparisons with the liquid phase runs.

Test for Trapped Radicals.—The fact that no butane was found as a product of the photolyses at −180° suggested that the yield of trapped C_2H_5 radicals in the solid must be low compared to the localized 2 *M* concentration achieved by other products, since at this concentration appreciable bimolecular radical combination would have been expected at the time of the warming and melting process. The absence of frozen-in radicals in excess of about 10^{-7} *M* in terms of the whole solution or 10^{-3} *M* in terms of the local volume element where light absorption occurred, seems to be confirmed by the absence of any electron paramagnetic resonance absorption such as that which gave pronounced peaks ascribed to trapped C_2H_5 when radiolyzed C_2H_5I was tested at −180° (Fig. 3).

One possible explanation for the existence of trapped radicals in the radiolysis of C_2H_5I glass at −180° and not in the photolysis is that the dissociating C_2H_5I molecules have more energy for escaping from the parent cage when activated by ionizing radiation than when activated by light. However, the rate of production of ethyl radicals at −180° as estimated from the rates at 25 and −70° is 0.0012 μmole/hr., or 2×10^{15} radicals produced in the 3 hr. photolysis, a number easily detected by the resonance equipment. Assuming that this many radicals were formed during the photolysis they must have been consumed before the resonance measurement. This may be due to the heating effect discussed below.

If no heat were dissipated from the small volume element where the light is absorbed in the photolysis studies the heating rate during illumination would be of the order of 100°/minute. Undoubtedly the heat is dissipated fairly rapidly through the cell, but it is probable that the volume element in which the light was absorbed was at an appreciably higher temperature than the coolant—possibly enough higher to permit the diffusion of radicals, which would otherwise have been trapped, to points where they could react with I, HI or I_2. Norman and Porter[26] have reported evidence for the production of trapped radicals in the photolysis of dilute (10^{-3} *M*) ethyl iodide solutions in hydrocarbon glasses. In the case of such dilute solutions the energy of the light would be absorbed throughout the bulk of the medium and the heating effects would not be nearly so pronounced. Localized heating effects would not occur when glassy C_2H_5I is irradiated with Co^{60} γ-rays and that may be why trapped radicals were observed in the γ-irradiated samples.

The explanation for the much higher *G*-value of trapped radical production in glassy compared to polycrystalline ethyl iodide is not obvious. The results are in accord, however, with observations of Livingston[27] on the electron paramagnetic resonance spectra of γ-irradiated H_2O–H_2SO_4 systems. He found that the *G*-value for trapped H atom production was much higher for the amorphous state than for the polycrystalline state. A possible explanation for the difference in results between the crystalline and the glassy state is that the crystal lattice organization of the molecules in the former makes it more difficult for the radicals to escape from the parent cage. Another possibility is that

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(25) C. F. Goodeve and A. W. C. Taylor, *Proc. Roy. Soc.* (*London*), **154**, 181 (1936).

(26) I. Norman and G. Porter, *ibid.*, **A230**, 399 (1955).

(27) R. Livingston, abstracts of the symposium, "The Formation and Stabilization of Free Radicals," National Bureau of Standards. Washington, D. C., September, 1957, p. L 1.

the particular orientation of adjacent molecules in the crystal favors a hot reaction which competes with cage escape and thermalization. This difference in G-value for trapped ethyl radical production between the crystalline and glassy solid undoubtedly has some relation to the observation[28] that the G-value for iodine production in the radiolysis of solid ethyl iodide at −190° was 3.05 for the glass but only 0.95 for the crystal. Other related observations on the effect of phase and temperature on reactions activated by light, ionizing radiation and nuclear processes have been summarized earlier.[7b]

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MADISON, WISCONSIN

(28) E. O. Hornig and J. E. Willard, THIS JOURNAL, **79**, 2429 (1957).

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

A Study of the Methyl–Oxygen and the Methyl–Nitric Oxide Reactions by Flash Photolysis[1]

BY WILLIAM C. SLEPPY AND JACK G. CALVERT

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The flash photolysis of azomethane was studied in experiments with added inert gases and oxygen or nitric oxide. The data from the O_2- and NO-free systems indicate that a fraction of the methyl radicals formed in the flash photolysis of azomethane are energy rich and abstract hydrogen rapidly unless they are thermally equilibrated by inert gas. The unimportance of the possible transient species CH_3N_2 in this system is indicated. From the experiments with added oxygen the reaction, $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$ (1). is shown to be third order and the rate constant for 25° is derived: $k_1 = 1.0_4 \times 10^{-31}$ (cc./molec.)^2 sec.$^{-1}$. The analogous reaction with nitric oxide, $CH_3 + NO \rightarrow CH_3NO$ (2), is found to be second order in the same pressure region (150–280 mm. of neopentane): at 25° $k_2 = 1.0_5 \times 10^{-12}$ cc./molec-sec. It is suggested that the difference in the order observed in the reactions 1 and 2 and analogous reaction, $CH_3 + CO \rightarrow COCH_3$, for the similar pressures and a given M, is related to the difference in the exothermicities of these reactions.

The detailed mechanism of the oxidation of organic free radicals remains one of the major unsolved problems in chemistry. Good qualitative descriptions of possible reactions have been offered for years, but very few attempts have been made to obtain quantitative data related to the individual steps in the suggested mechanisms. In this work we have attempted to derive quantitative rate data for the initial step in the oxidation of the methyl free radical. Although there can be little doubt that the first steps in the reactions of methyl radicals with oxygen and nitric oxide are (1) and (2), respectively

$$CH_3 + O_2\,(+M) \longrightarrow CH_3O_2\,(+M) \qquad (1)$$

$$CH_3 + NO\,(+M) \longrightarrow CH_3NO\,(+M) \qquad (2)$$

quantitative data concerning these reactions are meager. The estimates of the rate constant k_1 made from photochemical experiments at low intensities are derived[2–4] from the experimentally determined ratios k_1/k_3 and $k_3/k_4^{1/2}$, assuming k_4

$$CH_3 + RH \longrightarrow CH_4 + R \qquad (3)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (4)$$

equal the collision number. RH indicates acetone[2] or azomethane.[3] It appeared to us that the determination of the rate constants k_1 and k_2 compared directly to k_4 was highly desirable. This was impossible or very difficult in the usual low intensity photochemical experiments, since the concentration of methyl radicals was so low that (1) or (2) occurred to the practical exclusion of (4). In our work this direct comparison was made by producing very high methyl radical concentrations through flash photolysis of azomethane mixtures. The data are used in conjunction with Shepp's value[5] for k_4 to derive rate constants for the reactions 1 and 2 and to test the suggestion of the participation of the third body M in these reactions.[4,6]

Experimental

Apparatus.—The flash system was similar to those described by Porter[7] and by Ramsay[8] except that provision was made for product analysis. The flash system consisted of a quartz photolysis cell, one meter in length and 315 cc. in volume, which was connected in series with a trap and an all glass circulating pump. The photolysis system, the sample storage system, the Ward still and the Toepler pump for product removal were all isolated from stopcocks by mercury valves. A quartz initiating flash tube, one meter long, paralleled the reaction cell. It was filled with krypton at a pressure of 5.7 cm. The photolysis cell and flash tube were enclosed in a stainless steel reflector to increase the effective intensity in the cell.

In the usual experiment a capacitance bank of 600 µf. was charged to 4000 v. Upon discharge through the flash tube a 4800 joule flash of about 1 msec. duration was produced. The intensity of the flash was very reproducible; this can be seen in the smallness of the scatter of the data

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(1) Presented before the Division of Physical and Inorganic Chemistry, 133rd Meeting of the American Chemical Society, San Francisco, April, 1958.

(2) F. B. Marcotte and W. A. Noyes, Jr., *Disc. Faraday Soc.*, **10**, 236 (1951).

(3) G. R. Hoey and K. O. Kutschke, *Can. J. Chem.*, **33**, 496 (1953).

(4) D. E. Hoare and A. D. Walsh, *Trans. Faraday Soc.*, **53**, 1102 (1957).

(5) A. Shepp, *J. Chem. Phys.*, **24**, 939 (1956).

(6) M. I. Christie, *Proc. Roy. Soc.* (*London*), **A224**, 411 (1958).

(7) G. Porter, *ibid.*, **A200**, 284 (1950).

(8) D. A. Ramsay, *J. Chem. Phys.*, **20**, 1920 (1952).