

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Diffusion and Hot Radical Kinetics in the Photolysis of Liquid Ethyl Iodide¹

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Air-free ethyl iodide has been photolyzed both in the pure liquid state and in cyclohexane solution, using light of 2537 Å. The composition of the product mixture was independent of the extent of photolysis and in the case of pure ethyl iodide was found to be: C₂H₄, 38.8; C₂H₆, 26.0; I₂, 24.2; HI, 11.3; H₂, 0.03 mole %. By the use of initially added HI and I₂ it has been shown that the ratio C₂H₄/C₂H₆ is a linear function of I₂/HI. When HI exceeded 3×10^{-3} mole fraction, the ratio C₂H₄/C₂H₆ was depressed below the value predicted by the linear function, due to decrease in the C₂H₄ yield, which is constant at lower HI concentrations. A mechanism has been proposed and tested in which the primary act is dissociation of the C-I bond. It is further proposed that diffusion-controlled reactions occur between the ethyl radicals and iodine atoms yielding for recombination $\phi_3 = 0.60$, for ethylene and for hydrogen iodide $\phi_2 = 0.19$, and for diffusion apart into the steady state $\phi_3 = 0.21$. The effect of high concentrations of hydrogen iodide is to diminish ϕ_1 and ϕ_2 by intervention in the diffusion-controlled processes.

Introduction

The quantum yield for production of iodine in photolysis of pure liquid ethyl iodide at 2537 Å. is 0.26² gram atom. Many previous investigations have considered iodine to be the only significant iodine-containing product, and have therefore taken this quantum yield to be equal to that for decomposition of ethyl iodide. Studies of the absorption spectrum³ have indicated that the primary process is the rupture of the C-I bond. By use of dissolved iodine tagged with I¹³¹, Hamill and Schuler⁴ demonstrated that the quantum yield for iodine exchange with ethyl iodide is approximately 0.64, thus confirming the dissociative nature of the primary act and the efficiency of the reaction of ethyl radicals with molecular iodine. In that work, the forward process was attributed to hot radical reaction of ethyl radicals with ethyl iodide.

Unfortunately, the fact of the inequality of ethylene and ethane and the suggestion that hydrogen iodide may be involved in the reaction, as originally proposed by Emschwiler,⁵ were not given due regard in later studies of the system. The present investigation began with the confirmation of the fact that $\phi_{C_2H_4} > \phi_{C_2H_6} = \phi_{I_2}$ which in turn requires the production of hydrogen iodide. This was sought and found in appropriate amounts. These results have required a complete reconsideration of the mechanism of the photolysis.

Experimental

Materials.—Ethyl iodide was purified by passage through a column of silica gel and then by fractional distillation. A middle cut boiling at 72.2° (760 mm.) was water-white and was stored in a brown bottle over copper wire; n_D^{20} 1.5106.

Cyclohexane, technical grade, was washed with fuming sulfuric acid, dilute base, water, dried and then fractionally distilled, retaining a middle cut.

(1) This article is based on a thesis submitted by D. L. B. in partial fulfillment of the requirements for the Ph.D. degree. The work was carried out under the auspices of the Radiation Project, Department of Chemistry, University of Notre Dame, supported in part by the U. S. Atomic Energy Commission under contract AT(11-1)-38 and Navy Department loan contract Nonr-06900. Presented at the 128th meeting of the American Chemical Society, Minneapolis, Minnesota, September, 1955.

(2) E. Cochran, W. H. Hamill and R. R. Williams, Jr., *THIS JOURNAL*, **76**, 2145 (1954).

(3) T. Iredale, *et al.*, *Phil. Mag.*, **78**, 1093 (1929); *J. Phys. Chem.*, **33**, 290 (1929); *Nature*, **126**, 604 (1930); *Proc. Roy. Soc. (London)*, **A133**, 430 (1931).

(4) W. H. Hamill and R. Schuler, *THIS JOURNAL*, **73**, 3466 (1952).

(5) G. Emschwiler, *Compt. rend.*, **192**, 799 (1931).

Iodine was resublimed after grinding with potassium iodide.

Hydrogen iodide was prepared by reaction of phosphoric acid with potassium iodide. The product vapors were passed through a trap cooled with Dry Ice and condensed at liquid air temperature. The hydrogen iodide was further distilled twice from bulb to bulb, using Dry Ice and liquid air and distilled once from phosphorus pentoxide. The product was stored at the temperature of Dry Ice.

Pyridine, Coleman and Bell C.P. grade was dried with potassium hydroxide before use.

Deuterium iodide, containing 85-95 atom % D was prepared by catalytic reaction of deuterium⁶ with iodine (courtesy of Dr. R. Carter).

Carbon tetrachloride, technical grade, was chlorinated, washed with aqueous thiosulfate and bicarbonate and water. It was dried over calcium chloride and filtered.

Cyclohexene, from Eastman Kodak Co., was washed with dilute ferrous sulfate slightly acidified with sulfuric acid, with water, dried over calcium chloride, and fractionally distilled, retaining the middle third.

Radioactive iodine¹³¹ in carrier-free solution⁷ was evaporated to dryness in a small glass tube and the residue heated with crystalline iodine to effect exchange.

Ethylene, Phillips Research Grade, was used as received.

Apparatus.—The light source was a Hanovia SC2537 low pressure mercury resonance lamp of helical shape, stated by the manufacturer to emit 85% of its radiant energy in the non-reversed 2537 Å. line. Most of the remaining energy is in the visible spectrum, with an unknown contribution from the 1849 Å. mercury line. The latter component was removed by use of reaction vessels fabricated from Vycor (Corning 7910) which cuts off at ca. 2400 Å. The resonance lamp was operated at constant voltage and current and was continuously ventilated by an air stream to keep its temperature at $37 \pm 3^\circ$.

The experiments were carried out in cylindrical Vycor cells 1.3×25 cm. joined to Pyrex through a graded seal. A constriction for sealing off the reaction system and a break-off for re-entry were provided. All cells were cleaned with nitric acid and thoroughly outgassed by heating and pumping before use.

Most of the experiments were performed with the system held in a reproducible position with respect to the lamp, at a distance of about 4 cm. In some experiments, as noted, the system was placed in the center of the lamp helix at 37° and in others at distances greater than 4 cm. from the lamp at room temperature. In this manner light intensity variations greater than $100 \times$ could be obtained. In all exposures the vapor space above the liquid sample was shielded with black tape.

Procedure.—Samples of ethyl iodide were distilled *in vacuo* from phosphorus pentoxide to the reaction cell cooled in liquid air after several cycles of thawing, freezing and pumping. Iodine, when used, was added to the ethyl iodide before distillation and distilled into the reaction cell simultaneously. Hydrogen iodide was measured as the gas on the vacuum line and condensed into the reaction cell after

(6) Deuterium obtained from the Stuart Oxygen Co. by authorization of the U. S. Atomic Energy Commission.

(7) Obtained from the Oak Ridge National Laboratory by authorization of the U. S. Atomic Energy Commission.

the ethyl iodide. For solutions of ethyl iodide in cyclohexane the drying agent was magnesium oxide since it was found that phosphorus pentoxide liberated small amounts of carbon dioxide from cyclohexane. The reaction cell with sample was sealed off from the vacuum line for illumination.

After a measured exposure the reaction cell was sealed to the column of a simple microstill. This consisted of a 20 cm. length of 8 mm. glass tubing with a concentric glass rod, allowing about 1 mm. clearance in the annular space. The top of this column was attached to the outer member of a cold finger about 10 cm. in diameter and 15 cm. in height. A stopcock for evacuation and sample removal was attached to the cold finger near its upper rim.

About one ml. of water was placed above the break-off and frozen on the cold finger with Dry Ice. The still was evacuated and the break-off opened to admit the sample, which was then refluxed. The Dry Ice in the condenser was allowed to evaporate, so that the ice melted, absorbing the hydrogen iodide. Dry Ice was again added to the condenser to freeze the water and refluxing continued in order to remove product gases from the sample with high efficiency. These gases were withdrawn for measurement of total pressure and volume in a modified Saunders-Taylor apparatus. A Consolidated 21-103A mass spectrometer was used for analysis of the gaseous products (chiefly ethane and ethylene with a little ethyl iodide).

The efficiency of the micro-still may be illustrated by the following result. In a blank distillation of ten ml. of nominally pure ethyl iodide, two successive samples of the residual vapor (chiefly ethyl iodide) were collected and analyzed. The first contained 8.2% methyl iodide, and the second 0.8% methyl iodide. Mass spectrometric analysis of the original liquid sample indicated less than 0.1% methyl iodide. This amount will not interfere with the experiments but is efficiently collected by the still. Ethane and ethylene should be even more efficiently removed.

After removal of gases, five ml. of deaerated distilled water was added to the ethyl iodide in the reaction cell and both organic and aqueous phases were placed in a separatory funnel. The phases were separated; the aqueous phase was washed with carbon tetrachloride to remove iodine and these washings were added to the organic phase. To this phase was added concentrated aqueous potassium iodide and the iodine was titrated with standard thiosulfate. The aqueous phase was titrated with standard base, using brom cresol purple indicator, to determine hydrogen iodide.

Results

Ethyl Iodide.—Pure liquid ethyl iodide was photolyzed at several light intensities and for varying times with the results shown in Table I. The amounts of products agree only semi-quantitatively from one run to another, but the relative yields are evidently independent of the intensity and length of exposure.

Taking the significant products to be C_2H_4 , C_2H_6 , I_2 and HI, stoichiometry requires that for hydrogen balance the mole numbers N are related by

$$N_{C_2H_4} - N_{C_2H_6} = N_{HI}$$

For iodine balance

$$N_{HI} + 2N_{I_2} = N_{C_2H_4} + N_{C_2H_6}$$

which yields

$$N_{C_2H_6} = N_{I_2}$$

To a satisfactory approximation these requirements are met by the results shown in Table I.

Some photolyses were carried out with cyclohexene initially added to the system in the expectation that this reagent would consume hydrogen iodide. The results of these experiments appear in Table II. The effect upon hydrogen iodide production and on the ethylene-ethane ratio is evident, but even at the highest concentration of

cyclohexene, the removal of hydrogen iodide is not complete.

TABLE I
PHOTOLYSIS OF ETHYL IODIDE AT 2537 Å.

Expt. no.	I-1	I-2	I-3	I-4	I-5	I-6
Approx. relative light flux	1	1	0.1	0.01	1	1
Photolysis time (min.)	15	7	120	1200	7	20
Gas anal. (%)						
C_2H_4	57.32	51.29	51.44	54.47	55.27	50.54
C_2H_6	38.34	34.99	34.94	37.36	39.13	32.69
EtI	1.72	4.10	7.17	7.91	4.70	1.87
MeI	0.13	6.19	0.57	0.09	0.45	0.09
H_2	2.21 ^a	2.66 ^a	.04	.00	.00	.00
C_4H_{10}	0.0	0.12 ^d	.0	.00	.00	.00
Air			5.07 ^c	.00	.00	14.52 ^c
CO_2	0.28	0.65	0.57	.17	.45	0.28
Yield (μmoles)						
C_2H_4			134.1	318.7	80.7	115.4
C_2H_6			91.1	218.6	52.7	74.7
I_2		44.5	85.0	206.7	^b	82.0
HI			39.6	73.5	^b	93.1
C_2H_4/C_2H_6	1.49	1.47	1.47	1.46	1.41	1.54

^a Water not used in the still to absorb HI. Mercury in the Saunders-Taylor became filmed, presumably due to formation of mercury iodides. ^b Cell cracked on warming. HI and I_2 lost. ^c It is presumed that air entered after the photolysis. ^d This result was obtained by taking a second gas fraction with the condenser at 0° to enhance butane collection.

TABLE II
EFFECT OF ADDED CYCLOHEXENE, PYRIDINE AND IODINE ON PHOTOLYSIS OF ETHYL IODIDE

Expt. no.	Reagent added	Vol., %	C_2H_4 moles ^b	$\frac{HI}{C_2H_4}$	$\frac{C_2H_4}{C_2H_6}$
II-1	C_6H_{12}	0.25	1.58
II-2	C_6H_{12}	1.0	..	0.10	1.70
II-3	C_6H_{12}	5.0	..	.02	2.76
II-4	None	..	8.63	.88	1.50
II-5	C_5H_5N	0.20 ^a	5.15	..	30
II-6	C_5H_5N	.19	7.66	..	26
II-7	C_5H_5N	.48	5.31	..	21
II-8	C_5H_5N	.79	7.14	..	20
II-9	I_2	1 mole %	7.45	.63	3.62
II-10	I_2	9.9 mole %	5.40	.64	13.6

^a Iodine, 0.2 mole %, added initially. ^b Corrected approximately to constant exposure.

Pyridine proved to be more successful in removing hydrogen iodide, but with this reagent a thermal reaction occurs with ethyl iodide. Preliminary tests showed that this could be reduced to a negligible amount by carrying out the experiment with short exposure at 5°. The results of these experiments are given in Table II. The trend in the ratio C_2H_4/C_2H_6 with increasing pyridine is not considered significant.

The effect of added iodine on the relative amounts of products is also shown in Table II.

The results of the experiments described in Table II lead to the conclusion that while the ethylene yield remains approximately constant, the ethane yield is strongly dependent on the hydrogen iodide-iodine ratio in the sense expected if it is formed by reaction of ethyl radicals reacting

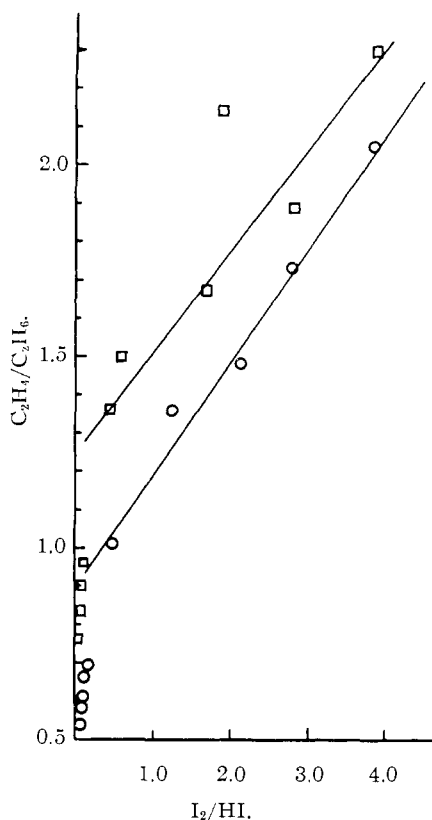


Fig. 1.—Dependence of C_2H_4/C_2H_6 on I_2/HI : a, in pure C_2H_5I (O); b, in C_6H_{12} solutions (\square).

with hydrogen iodide in competition with iodine. This was further examined by introducing various amounts of iodine and hydrogen iodide into the system before photolysis and observing the ratio C_2H_4/C_2H_6 in the products. The concentration of iodine which could be used was severely limited by the necessity of avoiding significant light absorption by the iodine-ethyl iodide complex.² The principal variable was therefore the hydrogen iodide concentration, which varied from 0.0215 to 0.943 mole %. Iodine concentration remained fairly constant at about 0.1 mole %. The results of these experiments are shown in Fig. 1a and the choice of variables is discussed in the next section. One point on the graph corresponds to the "natural" ratios I_2/HI and C_2H_4/C_2H_6 found in the photolysis of pure ethyl iodide.

As a further test of the supposition that ethane arises from reaction of ethyl radicals with hydrogen iodide, three experiments were carried out with deuterium iodide added before photolysis. Considerable isotopic dilution of this reagent occurred during introduction, presumably by exchange with adsorbed water in the glass manifold. The successive experiments represented increasing efforts to reduce this loss of deuterium and the ethane/ethane-*d* ratios found were 14.7, 6.1 and 2.3. These experiments qualitatively confirm the supposition as to the source of ethane.

Solutions of Ethyl Iodide in Cyclohexane.—Ethyl iodide at 2.5–5 volume % solution in cyclohexane was photolyzed in the usual manner and

the products obtained are shown in Table III. Note that the hydrogen iodide found is greater than the difference between ethylene and ethane. Since photolysis of methyl iodide in cyclohexane produces cyclohexyl iodide and cyclohexene,⁴ we may expect analogous reactions which would account for the deficit.

TABLE III

PHOTOLYSIS OF CYCLOHEXANE SOLUTION OF ETHYL IODIDE

Expt. no.	III-1	III-2	III-3
Relative light flux	1	0.01	1
Vol. % C_2H_5I	2.5	2.5	5.0
Photolysis time (min.)	20	960	10
Gas anal. (%)			
C_2H_4	57.73	59.99	58.82
C_2H_6	39.44	36.95	38.23
C_2H_5I	0.59	0.97	1.43
CH_3I	0.00	0.00	0.00
H_2	1.60	1.29	0.42
C_4H_{10}	0.05	0.05	.05
C_6H_{12}	.32	.43	.79
CO_2	.27	.32	.26
Air	.00	.00	.00
Yield of products (μ moles)			
C_2H_4	145.7	120.2	75.6
C_2H_6	99.5	74.0	49.2
I_2	65.5	41.8	30.3
HI	58.5	51.0	33.0
H_2	4.0	2.6	0.54
C_2H_4/C_2H_6	1.46	1.62	1.54

The effect of pyridine on the products of the photolysis in solution was examined as before, after preliminary tests which showed that the rate of the thermal reaction in solution is negligible at room temperature. The addition of pyridine in a mole ratio of 0.026 to ethyl iodide increased the C_2H_4/C_2H_6 ratio to 4.0 in two experiments. This change is not as large as that observed in the pure liquid and shows that in solution a substantial part of the ethane does not arise from reaction with hydrogen iodide.

The effect of initially added iodine and hydrogen iodide was also examined in solution, with the results shown in Fig. 1b. Again, one of the points corresponds to the "natural" ratios I_2/HI and C_2H_4/C_2H_6 .

Test of Addition of Hydrogen Iodide to Ethylene.

—It was considered possible that the sharp decrease in the C_2H_4/C_2H_6 ratio at high concentrations of hydrogen iodide (see Fig. 1) could be due to thermal addition of hydrogen iodide to ethylene and therefore the extent of this reaction under our experimental conditions was observed. Iodine containing I^{131} was dissolved in cyclohexane together with hydrogen iodide and ethylene in amounts comparable to those encountered in the photolyses. This sample was evacuated and irradiated in the usual fashion, except that a Corning 5562 filter was used. This filter transmits 0% at 3360 Å. and 49% at 4060 Å. Transmission in the visible spectrum approaches 100%. The irradiation was about three times as long as the usual

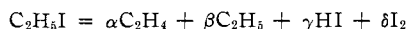
photolysis. After irradiation the cell contents were placed in a separatory funnel, and the organic layer was washed with aqueous sodium bisulfite, aqueous potassium iodide and water. The separate phases, including appropriate washings, were counted in a jacketed G-M counter of standard design. A blank experiment omitting hydrogen iodide, ethylene and the illumination, showed that only 0.4% of the activity remained in the organic phase after separation. In the test experiment 1.65% of the activity was found in the organic phase. With correction for the blank, we estimate that not more than 10% of the hydrogen iodide adds to ethylene in the photolysis experiments. No correction was applied.

Conclusions

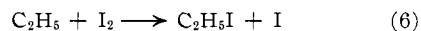
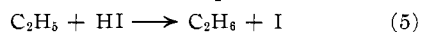
The experimental results of this work require a substantially new view of the mechanism of photolysis of liquid ethyl iodide. The important facts previously established are⁸: (a) $\phi_{C_2H_6} = 1.5 \phi_{C_2H_5}$; (b) ϕ_{I_2} decreases with increasing wave length; (c) ϕ_{I_2} is independent of temperature; (d) ϕ_{I_2} is independent of extent of photolysis; (e) ϕ_{I_2} is independent of light flux; (f) addition of iodine-131 produces $C_2H_5I^{131}$ and $\phi_{exchange} = 0.45$.⁹

The present work confirms items (a), (d), (e) and adds the following: (g) $\phi_{HI} = \phi_{C_2H_4} - \phi_{C_2H_6}$; (h) $\phi_{C_2H_6} = \phi_{I_2}$; (i) $\phi_{C_2H_6}$ greatly decreases with addition of pyridine; (j) addition of DI produces C_2H_5D ; (k) $\phi_{C_2H_6}$ is a function of $(I_2)/(HI)$; (l) $\phi_{C_2H_6}$ is constant at small (HI) and decreases at $>10^{-2}M$.

From the preceding we conclude, in part, that ethyl radicals are produced and that they react either with iodine or with hydrogen iodide. *Stoichiometrically* we have



We postulate the mechanistic equations



A straightforward steady-state treatment of this mechanism yields

$$\frac{C_2H_4}{C_2H_6} = \frac{\phi_\alpha}{\phi_\beta} + \frac{\phi_\alpha k_6}{\phi_\beta k_5} \times \frac{(I_2)}{(HI)}$$

This relation is demonstrated in Fig. 1a except at high concentrations hydrogen iodide. Since pyridine depresses the ethane yield 20-fold it appears that most of the ethane arises from reaction 5 with a small contribution from a hot radical reaction. From the slope and intercept of the curve in Fig. 1 we find

$$\frac{\phi_\alpha}{\phi_\beta} = 0.89 \text{ and } \frac{k_6}{k_5} = 0.34$$

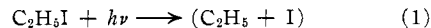
The partial mechanism proposed evidently accounts for items (f) through (k) above and also largely accounts for (c) since both reactions 5 and 6 presumably have very small activation energies

(8) For the pertinent literature see refs. 3, 5, and also G. K. Rollefson and M. Burton "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1939.

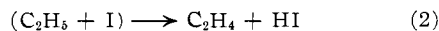
(9) The value originally reported⁴ has been corrected for a revised value² of ϕ_{I_2} from liquid ethyl iodide which was used as an actinometer.

and ΔE_{act} , which largely governs ϕ_{I_2} , is necessarily quite small.

The important problem now is to account for the formation of ethyl radicals, required by (f) and (j), and also for hydrogen iodide. In consideration of (l) we reject a branching primary photolytic act, producing either C_2H_5 and I or C_2H_4 and HI , and postulate instead a single, conventional primary act



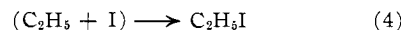
with the qualification that the primary products are subject to a *diffusion-controlled* disproportionation



where parentheses enclose particles subject to interaction by diffusion.

This proposal is suggested by recent repeated demonstrations of such effects,¹⁰ by the evident exothermicity of the reaction and by its inherent plausibility. Step 2 accounts for (1) above since $\phi_{C_2H_5}$ is expected to be constant when little or no radical scavenger is present. At higher concentration of scavenger, *viz.*, iodine or hydrogen iodide, ethyl radicals capable of undergoing diffusion-controlled reaction are removed prior to occurrence of step 2. This decrease in $\phi_{C_2H_5}$ is anomalous from the viewpoint of conventional stationary-state kinetics alone. Appreciable deviations from the stationary state relation given above were actually found and are evident in Fig. 1 at relatively large concentrations of hydrogen iodide.

Step 2 logically requires the alternative competitive processes



where step 3 represents the transition from diffusion kinetics to stationary state kinetics. Step 4 corresponds to Franck-Rabinowitch recombination. It is of interest that this effect has often been invoked to account for a decrease in quantum yield for liquid phase photolyses relative to their gas phase counterparts. According to the present proposal it has quite the reverse effect since step 2 largely controls net decomposition but is as much subject to "cage effects" as is step 4. In the subsequent discussion the combined contributions of steps 2 and 4 comprise "recombination."

It can be seen that the proposed mechanism requires all quantum yields to be independent of the extent of photolysis in the absence of added iodine and hydrogen iodide, as required by (d).

When ethyl iodide is photolyzed without added iodine or hydrogen iodide, the quantum yield of molecular iodine is 0.13.² Under these conditions, the ethylene-ethane ratio is 1.48. Therefore, since

$$\phi_{I_2} = \phi_{C_2H_6} = 0.13$$

and the yield of ethylene is constant, determined by reaction 2 at low hydrogen iodide concentration, it follows that¹¹

$$\phi_2 = 1.48 \times 0.13 = 0.19$$

(10) For appropriate references see J.-C. Roy, J. R. Nash, R. R. Williams, Jr., and W. H. Hamill, *THIS JOURNAL*, **78**, 519 (1956).

(11) If it is assumed that the minimum value of $\phi_{C_2H_6}$ with pyridine present represents a hot radical reaction, then its value is ca. 0.13/30 (from ϕ_2 and Table II).

From the intercept of Fig. 1 and the stationary-state relation above we find

$$\phi_3 = \frac{\phi_2}{0.89} = 0.21$$

Assuming that $\phi_2 + \phi_3 + \phi_4 = 1$ we find

$$\phi_4 = 0.60$$

The effect of high concentrations of hydrogen iodide is to interfere with the diffusion-controlled reaction, producing more ethane and less ethylene than expected from the simple steady-state treatment. This effect can be treated quantitatively by use of a semi-empirical equation developed previously.¹⁰ That equation may be stated in the form

$$-\log(1 - W) = \frac{P_1}{5.75\gamma\rho_0} - \frac{P_1P_2^{1/2}}{3.24\gamma^2} X^{1/2}$$

where

W = probability of recombination of reaction 2, 4

P_1 = probability of recombination or reaction upon encounter

P_2 = probability of reaction of C_2H_5 with scavenger (HI) upon encounter

γ = mean free path of diffusion in units of molecular diameter

ρ_0 = initial separation in units of molecular diameter

X = mole fraction of scavenger (HI)

In the present experiments at high hydrogen iodide concentrations practically all ethyl radicals which escape their original partners (reaction 3) react with hydrogen iodide (reaction 5) to produce ethane. Therefore the measure of non-recombination ($1 - W$) is the quantum yield of ethane $\phi_{C_2H_6}$, which increases with increasing hydrogen iodide concentration. The quantum yields for reactions 2, 3 and 4 are no longer fixed, but vary from their "natural" values ϕ_2° , ϕ_3° , ϕ_4° , given above, due to action of hydrogen iodide to produce ethane. The ratio R of ethylene to ethane will be given by

$$R = \frac{\phi_2^\circ - \Delta\phi_2}{\phi_3^\circ + \Delta\phi_2 + \Delta\phi_4}$$

The $\Delta\phi$'s are changes resulting from diffusion-controlled reactions with scavenger. $\Delta\phi_2$ represents the fraction of primary events which yield ethane instead of ethylene and $\Delta\phi_4$ represents the fraction of primary events which yield ethane instead of recombination. We assume that

$$\frac{\Delta\phi_4}{\Delta\phi_2} = \frac{\phi_4^\circ}{\phi_2^\circ} = \frac{0.60}{0.19} = 3.2$$

and solve for

$$\Delta\phi_2 = \frac{\phi_2^\circ - R\phi_3^\circ}{1 + 4.15R}$$

The quantum yield of ethane under these conditions is

$$\phi_{C_2H_6} = \phi_3^\circ + \Delta\phi_2 + \Delta\phi_4$$

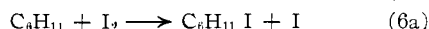
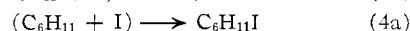
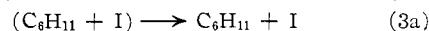
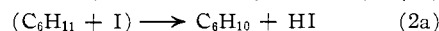
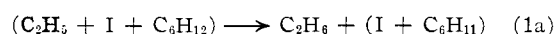
which becomes

$$\phi_{C_2H_6} = \phi_3^\circ \left[1 + \frac{3.7 - 4.2R}{1 + 4.2R} \right]$$

To test the diffusion hypothesis we plot $\log \phi_{C_2H_6}$ versus $(X_{HI})^{1/2}$ as shown in Fig. 2a. Assuming $P_1 = P_2 = 1$ the slope and intercept of the line shown yield $\rho_0 = 0.69$ and $\gamma = 0.35$. It is not to

be expected that values of ρ_0 for nuclear recoil and for photolysis would agree, except by chance. If both processes are governed by diffusion kinetics, however, then it is to be expected that the parameter γ shall exhibit a common value. The results obtained from the earlier Szilard-Chalmers studies¹⁰ yielded $\rho_0 = 3.6$ and $\gamma = 0.35$. We believe that the present results lend considerable support, in principle, to the earlier proposal.

The photolysis in solutions has nearly the same features as that in the pure liquid, except that pyridine does not produce as large a decrease in $\phi_{C_2H_6}$. We take this to be evidence that some ethane is produced by a hot radical reaction of ethyl radical on cyclohexane. This would leave a cyclohexyl radical to undergo a diffusion-controlled reaction with the neighboring iodine atom, producing cyclohexene or cyclohexyl iodide, which have been previously detected in the system cyclohexane-methyl iodide.⁴ Therefore, in addition to reactions 1-7, the mechanism in solution apparently includes the following reactions, which are correspondingly numbered



This mechanism corresponds directly to that for liquid ethyl iodide except for the formation of ethane by reaction of hot ethyl radicals (represented by C_2H_5) in step 1a. In all other respects it is what we would expect for the photolysis of cyclohexyl iodide.

The graph of these results in Fig. 1b cannot be expected to be linear, as was the case for pure liquid ethyl iodide, since there is a constant contribution from step 1a. The non-linearity may, of course, be less than experimental error. Extrapolation of these results to very large concentrations of hydrogen iodide gives

$$\frac{\phi_2}{\phi_3 + \phi_{1a}} = 1.25$$

The ethylene-ethane ratio with added pyridine gives

$$\phi_2/\phi_{1a} = 4$$

and therefore

$$\phi_3/\phi_2 = 0.55$$

It is known from previous work² that $\phi_{I_2} = 0.11$ in cyclohexane solution without added iodine or hydrogen iodide. Under similar conditions we find $\phi_{C_2H_6}/\phi_{I_2} = 2.5$ and therefore

$$\phi_2 = 2.5 \phi_{I_2} = 0.27$$

Since $\phi_2 + \phi_3 + \phi_4 + \phi_{1a} = 1$, we find

$$\phi_{1a} = 0.07$$

$$\phi_2 = 0.27$$

$$\phi_3 = 0.15$$

$$\phi_4 = 0.51$$

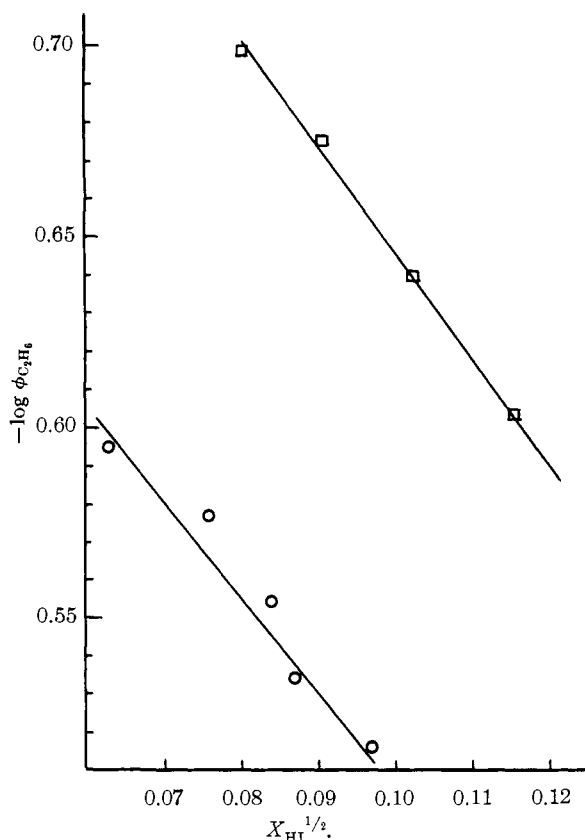


Fig. 2.—Test of diffusion equation: a, in pure C_2H_5I (O); b, in C_6H_{12} solutions (\square).

The relatively large contribution of the hot radical reaction in solution can be attributed to an identity reaction in the pure liquid



The ratio of ethylene to ethane for photolyses in solution, except at high hydrogen iodide concentrations, is found by steady-state treatment to be

$$\frac{C_2H_4}{C_2H_6} = R = \frac{\phi_2}{\phi_3 \frac{k_5(HI)}{k_5(HI) + k_6(I_2)} + \phi_{1a}}$$

which may be rearranged to

$$\frac{1}{R} \frac{\phi_2}{\phi_3} - \frac{\phi_{1a}}{\phi_3} = 1 + \frac{k_6(I_2)}{k_5(HI)}$$

A test of this function, using $\phi_2/\phi_3 = 1.8$ and $\phi_{1a}/\phi_3 = 0.45$ is shown in Fig. 3. The intercept is unity, as should be the case, and the slope gives

$$\frac{k_6}{k_5} = 0.41$$

which is comparable to the value obtained for liquid ethyl iodide. The difference may be due to complexing of iodine in ethyl iodide.²

Photolysis in solution also shows, at high concentrations of hydrogen iodide, effects which we attribute to a diffusion-controlled process and we ap-

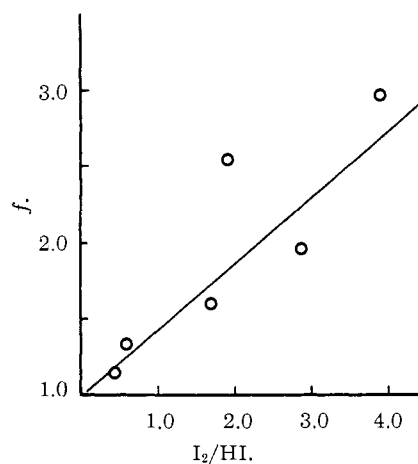


Fig. 3.—Steady-state treatment in solutions $f = 1/[1/R)(\phi_2/\phi_3) - \phi_{1a}/\phi_3]$

ply the same test. In this case, the measure of non-recombination is $\phi_{C_2H_6} - \phi_{1a}$ and by a treatment similar to that used above, this may be given as

$$\phi_{C_2H_6} - \phi_{1a} = \phi_3 \left[1 + \frac{5.3 - 4.2R}{1 + 2.9R} \right]$$

In Fig. 2b $\log(\phi_{C_2H_6} - \phi_{1a})$ is plotted *versus* $(X_{HI})^{1/2}$. The slope and intercept of the line shown give $\rho_0 = 0.57$ and $\gamma = 0.33$.

We believe that this new mechanism for the photolysis of ethyl iodide in the pure liquid and in solution should apply to other alkyl halides (except methyl iodide) as well. In the course of an investigation of the isomerization of propyl iodide during photolysis¹² hydrogen iodide had been proposed as an intermediate, but was not found among the products. Indeed, it would not be expected, since propane and propylene are equal in that system. Evidently hydrogen iodide adds to propylene much more readily than to ethylene.

In a previous investigation² a correlation between the structure of an alkyl iodide and the quantum yield for iodine production was observed. This correlation, that ϕ_{I_2} increases with increasing fraction of beta hydrogens in the alkyl iodide, fits the present mechanism since reaction 2 can occur only with beta hydrogen and this reaction is the key to the formation of all products. Since a similar correlation was found in the radiolysis of alkyl iodides, we conclude that the present mechanism in its entirety is involved in the radiolysis of ethyl iodide although the nature of the primary process is not as readily conceived. It is quite likely that contributions from additional steps are also involved although they can scarcely be predicted. Further work along this line has been initiated and hydrogen iodide, iodine, ethane and ethylene have been identified as major products.

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(12) C. F. McCauley, W. H. Hamill and R. R. Williams, Jr., *THIS JOURNAL*, **76**, 6263 (1954).