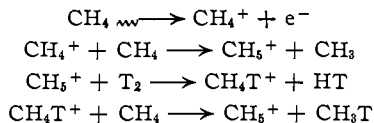


There are then at least two possible paths by which CH_2T^+ can lead to CH_3T .

(3) For the exchange of tritium with a radiation produced ion the specific sequence postulated is



(4) The general types of mechanisms as given in (1) are applicable to the exchange of T_2 with other systems. In this sense the results of this

work can be applied to T_2 exchange with other compounds to provide general mechanisms for Wilzbach labeling. However, with larger molecules the knowledge of the ions present, their state of excitation and their reactivity is so fragmentary as to make assignment of unique and detailed reaction paths for the exchange process very difficult.

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

Ionic and Free Radical Processes in the Radiolysis of Liquid Methyl and Ethyl Iodides¹

BY H. A. GILLIS, R. R. WILLIAMS, JR., AND W. H. HAMILL

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Liquid methyl and ethyl iodides have been irradiated at room temperature with a Co^{60} source at dose rates approximating 10^{19} e.v. hr.⁻¹ ml.⁻¹ in air-free samples with added HI and I_2 . In ethyl iodide, C_4H_{10} is a small but significant product; $G(\text{C}_2\text{H}_4)$ decreases at HI or I_2 concentrations $> 10^{-2} M$; $G(\text{C}_2\text{H}_6)$ increases at HI concentrations $> 10^{-2} M$ provided $\text{I}_2/\text{HI} \sim 0$; $G(\text{C}_2\text{H}_6)$ decreases at I_2 concentrations $> 10^{-2} M$ provided $\text{HI}/\text{I}_2 \sim 0$; $G(\text{C}_4\text{H}_{10})$ decreases at HI or I_2 concentrations $> 10^{-2} M$. In methyl iodide, $G(\text{CH}_4)$ increases at HI concentrations $> 10^{-2} M$, and $G(\text{C}_2\text{H}_6)$ decreases at I_2 or HI concentrations $> 10^{-2} M$. These results indicate that C_2H_5 and CH_3 are involved in diffusion-controlled reactions, as $2\text{C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_{10}$; $\text{C}_2\text{H}_5 + \text{I} \rightarrow \text{C}_2\text{H}_4 + \text{HI}$; $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$, etc., Disposition of radicals favorable to diffusion controlled reencounters may arise from track effects in general. In particular they would be favored by the pairing of alkyl radicals following charge neutralization of the products of ion-molecule reactions, as $\text{CH}_2\text{I}^+ + \text{CH}_3\text{I} \rightarrow \text{C}_2\text{H}_5\text{I}^+ + \text{I}$ and $\text{C}_2\text{H}_5\text{I}^+ + \text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_4\text{H}_{10}\text{I}^+ + \text{I}$ which have been observed in the mass spectrometer. The reaction products are qualitatively and quantitatively consistent with electron impact cracking patterns as determined by mass spectrometry.

Introduction

There are several features common to the photolysis² and radiolysis³ of ethyl iodide in the liquid phase. In particular the correlation between structure of alkyl iodides and yields of iodine in both photolysis⁴ and radiolysis^{4,5} in the liquid phase suggests that common mechanisms are involved. This correlation is that the quantum yield, or G - (100 e.v. yield), for iodine production increases with increasing number of hydrogen atoms in the β -position. The rate controlling steps are assumed to be competitive processes, e.g., $\text{C}_2\text{H}_5 + \text{I} \rightarrow \text{C}_2\text{H}_5\text{I}$ and $\text{C}_2\text{H}_5 + \text{I} \rightarrow \text{C}_2\text{H}_4 + \text{HI}$. Iodine definitely results from the reaction⁶ $\text{C}_2\text{H}_5 + \text{HI} \rightarrow \text{C}_2\text{H}_6 + \text{I}$. The relation between the number of β -hydrogens and the relative efficiency of reactions of disproportionation and dimerization is not peculiar to reactions between alkyl radicals and iodine atoms. Striking examples of the β -effect have been observed for several alkyl radicals.⁷

(1) From the Ph.D. dissertation of H. A. Gillis, University of Notre Dame, August, 1957. A contribution from the Radiation Project of the University of Notre Dame, supported in part under AEC contract AT(11-1)-38 and Navy equipment loan contract Nonr-06900.

(2) R. H. Schuler and W. H. Hamill, *THIS JOURNAL*, **73**, 3466 (1951).

(3) R. H. Schuler and W. H. Hamill, *ibid.*, **74**, 6171 (1952); R. H. S. doctoral dissertation, University of Notre Dame, June, 1949.

(4) E. L. Cochran, W. H. Hamill and R. R. Williams, Jr., *ibid.*, **76**, 2145 (1954).

(5) E. O. Hornig and J. E. Willard, *ibid.*, **79**, 2429 (1957).

(6) D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **78**, 6228 (1956).

(7) (a) J. W. Kraus and J. G. Calvert, *ibid.*, **79**, 5921 (1957); (b) A. S. Newton, *J. Phys. Chem.*, **61**, 1485 (1957).

The effect of added hydrogen iodide, over a range of concentration, upon the photolysis of ethyl iodide has been interpreted⁶ in terms of a diffusion-controlled reaction between the neighboring ethyl radical-iodine atom pair following dissociation of the C-I bond. The present work is a parallel study of evidence which might indicate diffusion-controlled processes in the radiolysis of liquid methyl and ethyl iodides from measurements of the yields of hydrocarbon products as functions of the concentrations of iodine and of hydrogen iodide.

Experimental

Materials.—Methyl and ethyl iodides were purified by the same procedure. After passing through a 60 cm. column of silica gel they were distilled through a 4 ft. glass-helix packed distilling column. The middle cut of ethyl iodide retained boiled at 72.4° (760 mm.) and n_D^{20} was 1.5138. Methyl iodide boiled at 42.5° (760 mm.) and n_D^{20} was 1.5307. Resublimed iodine was used as received. Hydrogen iodide was prepared from phosphoric acid and potassium iodide. Phosphorus pentoxide was added to 85% phosphoric acid until it dissolved only very slowly. This acid was added in vacuum to finely ground potassium iodide until evolution of gas virtually stopped. The gas was freed of most of the contaminating iodine by three distillations and then dried with phosphorus pentoxide at -45° . $n\text{-C}_4\text{D}_{10}$ was prepared by exchange between butane and deuterium over a platinum catalyst at 75° (courtesy of Dr. A. Kupperman).

Apparatus.—The 150 curie Co^{60} source has been described by Lazo.⁸ In one run X-rays from a Van de Graaff generator were used at a target current of 78 $\mu\text{amp.}$ and 1.5 m.e.v. **Procedure.**—Samples of 5 ml. in 1.6 cm. i.d. Pyrex cells were used for all gamma irradiations. They were first out-gassed by three cycles of freezing and pumping, then thaw-

(8) R. M. Lazo, Ph.D. thesis, University of Notre Dame, 1953.

ing. They were then distilled twice from trap to trap, while pumping. Finally, they were vacuum distilled into the irradiation cell. Samples received approximately 10^{21} e.v. and have been corrected, when necessary, to a common basis.

Iodine, in amounts less than 10^{-4} mole, was added to the sample before distilling into the cell. Large amounts of iodine were introduced in weighed, evacuated sealed ampoules equipped with break-off seals. Water (0.1 ml.), when used, was added to the alkyl iodide before distillation.

For runs with hydrogen iodide the cells were equipped with stopcocks as well as the usual constrictions and break-seals. Hydrogen iodide was measured into the cell of known volume and condensed with liquid nitrogen immediately. The methyl or ethyl iodide was then distilled into the cell as usual. In two tests with hydrogen iodide added in this manner, the recovery was found to be greater than 97%.

Gaseous products were recovered by distillation on the vacuum line. The cell, with breakseal, was sealed to the bottom of a 50 cm. column, 1 cm. i.d. with a coaxial glass rod and a re-entrant cold finger at top. The temperature of the cold finger was adjusted for good product recovery without excessive dilution by solvent. A stopcock in the still head was opened at intervals to a small receiver and the contents of the latter then transferred to a large holder. When water was not added to a sample prior to irradiation, it was introduced subsequently on the vacuum line to retain hydrogen iodide. One product fraction was recovered at a stillhead temperature of -120° . A second fraction, at -80 or -90° , was collected and analyzed separately. Of the product gases, only butane was present in appreciable quantity in the second fraction.

Since preliminary tests with pure ethyl iodide showed very inefficient collection of butane, an isotope dilution method was adopted. Butane- d_{10} was measured into ethyl iodide before irradiation. From the ratio of $n\text{-C}_4\text{D}_{10}$ to $n\text{-C}_4\text{H}_{10}$ in the products, the amount of butane produced during a run was obtained. In three test runs with $n\text{-C}_4\text{H}_{10}$ and $n\text{-C}_4\text{D}_{10}$ measured into ethyl iodide and then recovered as described above, it was found that the ratio of $n\text{-C}_4\text{H}_{10}$ to $n\text{-C}_4\text{D}_{10}$ in the recovered gases was 10–20% too high. It appears that some fractionation occurred since for one run three consecutive samples of gas were collected and the ratio of $n\text{-C}_4\text{H}_{10}$ to $n\text{-C}_4\text{D}_{10}$ approached the correct value as the amount of butane recovered increased. The precision of butane measurements is therefore not satisfactory. All gases were analyzed with a CEC 21-103A mass spectrometer.

After gases had been removed, the cell was opened and 5 ml. of boiled distilled water added. The aqueous phase was washed with carbon tetrachloride and the washings added to the organic phase. The iodine in the organic phase was titrated against standard thiosulfate solution. The hydrogen iodide was determined by titrating the aqueous phase with standard base using brom cresol purple as indicator.

It was considered possible that recovery of hydrogen iodide following irradiation might not be quantitative because of loss in stopcock grease or reaction with mercury. In three tests about 20 micromoles of hydrogen iodide were measured into samples of ethyl iodide and the normal gas removal operations were followed. Recovery was found to be 85–91% efficient, but this low precision does not affect the conclusions.

Results

Pure Ethyl Iodide.—The results of radiolysis of three 5 ml. samples of ethyl iodide by Co^{60} γ -rays are shown in Table I. The difference in absolute yields of the various products in the γ -ray runs may be taken as an indication of the reproducibility to be expected in all runs. The material balance of all products is indicated by their combined empirical composition C/H/I = 2.00/5.14/0.93.

Analysis for acetylene involves a large error since it is based on the 26 peak to which ethane and ethylene make large contributions. The precision of iodine analysis probably is low because of the possibility of loss during gas removal.

Values of G were based upon rate of Fe^{++} oxidation in 5 ml. samples of aqueous solutions $0.8N$

TABLE I
RADIOLYSIS OF PURE ETHYL IODIDE

Products (mole $\times 10^5$)				G^b
Ethylene	26.3	26.8	26.7	2.20
Ethane	22.7	22.9	23.7	1.92
<i>n</i> -Butane	3.96	4.11	3.83	0.33
Acetylene	1.11	1.20	1.09	.09
Methane	0.03	0.10	0.15	.01
Hydrogen	2.87	3.18	2.29	.23
Iodine	26.6	24.3	"	2.12
Hydrogen iodide	4.0	4.0	"	0.33

^a Not measured. ^b Average.

in H_2SO_4 and $5 \times 10^{-4}M$ in Fe^{++} using the same position in the cobalt source. Irradiation time was 5 min. The concentration of Fe^{+++} was determined with a Beckman DU spectrophotometer and based on an extinction coefficient of $2300 \pm 1.2\%$ at 29° . If $G(\text{Fe}^{+++})$ is taken as 15.5 ,⁹ the rate of absorption of energy by the aqueous solution was 2.93×10^{19} e.v. hr.⁻¹/5 ml. for the cell used in ethyl iodide runs and 2.90×10^{19} e.v. hr.⁻¹/5 ml. for the cell used in methyl iodide runs. The coefficients for absorption of γ -rays by photoelectric, Compton and pair production effects were estimated¹⁰ and the rates of absorption calculated to be 5.97×10^{19} e.v. hr.⁻¹/5 ml. for methyl iodide and 5.13×10^{19} e.v. hr.⁻¹/5 ml. for ethyl iodide. All yields reported are corrected for decay of Co^{60} . These yields may be slightly high from high relative absorption of weak scattered radiation by iodine.¹¹ The disagreement between the yields reported in Table I and those of Schuler and Petry¹² who found $G(\text{C}_2\text{H}_6) = 1.12$ and $G(\text{C}_2\text{H}_4) = 2.00$ exceeds the estimated maximum error of this work. The empirical composition of their total reported product is C/H/I = 2.00/4.75/1.25. Our $G(\text{I}_2)$ compares well with 2.03 found by Schuler and Petry¹² and 2.12 found by Hornig and Willard.⁵

Ethyl Iodide with Added Iodine and Hydrogen Iodide.—In order to measure the competition for ethyl radicals by hydrogen iodide and iodine, various amounts of these reagents at combined concentrations less than $0.03 M$ were dissolved in ethyl iodide before irradiation. The results of these runs are shown in Fig. 1. The average concentration of iodine was calculated on the basis that the amount of iodine produced was equal to the combined amounts of ethane plus butane. The average concentration of hydrogen iodide was calculated on the basis that the amount of hydrogen iodide produced equals the difference between the amounts of ethylene and ethane.

In order to determine how much ethane is produced by some mechanism other than reaction of ethyl radicals with hydrogen iodide in the stationary state, runs were performed with 0.1 ml. of water added to ethyl iodide, together with small amounts of iodine. The results appear in the first

(9) R. H. Schuler and A. O. Allen, *J. Chem. Phys.*, **24**, 56 (1956).

(10) C. Goodman, "The Science and Engineering of Nuclear Power," Vol. I, Addison-Wesley Press, Inc., Cambridge, Massachusetts, 1947.

(11) W. Berstein and R. H. Schuler, *Nucleonics*, **13**, No. 11, 110 (1955).

(12) R. H. Schuler and R. C. Petry, *THIS JOURNAL*, **78**, 3954 (1956).

TABLE II
RADIOLYSIS OF ETHYL IODIDE WITH ADDED IODINE AND WATER^a

I ₂ added (mole fraction × 10 ⁴)	3.7	6.3	10.5	23.3	61.5	104	148	164	232
Products (mole × 10 ⁶)									
C ₂ H ₄	28.1	27.4	28.1	26.5	25.7	22.3	23.6	23.2	23.8
C ₂ H ₆	11.3	11.0	11.1	9.76	8.63	9.31	7.20	6.79	6.74
n-C ₄ H ₁₀	3.91	4.03	3.90	3.09	2.77	2.78	2.60	2.89	2.68
C ₂ H ₂	1.42	1.30	1.29	1.19	1.29	1.35	1.32	1.34	1.40
CH ₄	0.09	0.07	0.06	0.10	0.09	0.09	0.08	0.10	0.08
H ₂	3.23	2.90	1.74	2.45	2.45	2.45	2.39	2.28	2.41
I ₂	11.4	12.2	11.9	^b	^b	^b	^b	^b	^b
HI	18.7	18.5	14.1	16.9	17.4	9.2	15.4	18.6	17.6

^a Water added in first three runs only. ^b Not measured.

three columns of Table II. The solubility of water in ethyl iodide is small, but it is sufficient to depress the steady state concentration of hydrogen iodide to a very low value. This was confirmed in one run by shaking the sample vigorously at 30 min. intervals without affecting the result. It is concluded that (HI)/(I₂) ~ 0 in ethyl iodide for these runs.

In order to test the postulate that ethyl radicals are involved in diffusion controlled reactions, large concentrations of iodine or hydrogen iodide were used with the results shown in Tables II and III. Hydrogen yields are high with added hydrogen iodide, possibly because of reaction with mercury when gases were collected for analysis.

TABLE III
RADIOLYSIS OF ETHYL IODIDE WITH ADDED HYDROGEN IODIDE

HI added (mole fraction × 10 ⁴)	32	46	97	133	281
I ₂ added (mole fraction × 10 ⁶)	0	7	0	0	0
Products (mole × 10 ⁶)					
C ₂ H ₄	25.7	20.8	24.4	23.3	21.4
C ₂ H ₆	67.6	67.1	79.6	80.0	88.3
n-C ₄ H ₁₀	3.30	2.72	2.74	2.61	1.89
C ₂ H ₂	1.26	1.35	1.30	1.31	1.14
CH ₄	0.00	0.08	0.22	0.24	0.21
H ₂	2.44	3.05	3.08	3.86	4.05

Methyl Iodide.—Results for irradiated methyl iodide appear in the first two columns of Table IV. The empirical composition of all products from pure methyl iodide was C/H/I = 1.00/2.97/1.02. Yields were $G(\text{C}_2\text{H}_6) = 1.11$; $G(\text{CH}_4) = 0.77$; $G(\text{C}_2\text{H}_4) = 0.081$; $G(\text{H}_2) = 0.060$; $G(\text{I}_2) = 1.26$; $G(\text{HI}) \cong 0.01$. As with ethyl iodide, analysis for iodine may be inaccurate because of possible loss during gas removal, but this is not indicated by the material balance. Schuler and Petry¹² reported $G(\text{C}_2\text{H}_6) = 1.05$, $G(\text{CH}_4) = 0.57$, $G(\text{I}_2) = 1.20$ and their complete product analysis corresponded to C/H/I = 1.00/3.16/0.82.

Several additional runs were performed at a later date than those in Table IV but under similar conditions. Using water-saturated samples and ca. 10⁻²M iodine, the average of 4 runs gave $G(\text{HI}) = 0.26$ with a.d. ± 0.01. For the gaseous products, the average of 2 runs in very good agreement gave $G(\text{CH}_4) = 0.60$, $G(\text{C}_2\text{H}_6) = 1.10$,

$G(\text{C}_2\text{H}_2) = 0.031$, $G(\text{C}_2\text{H}_4) = 0.082$ and $G(\text{H}_2) = 0.11$.

In order to test the postulate that methyl radicals are involved in diffusion controlled reactions, a number of runs were performed with methyl

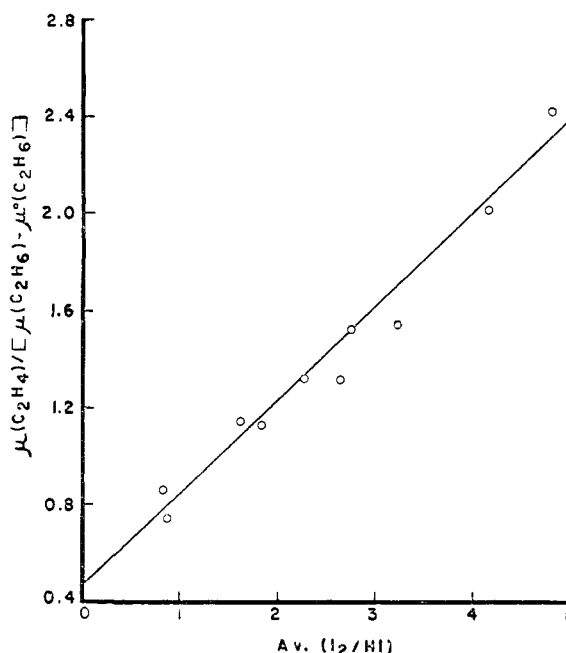


Fig. 1.—Ratio of ethylene to steady-state ethane vs. ratio of iodine to hydrogen iodide in ethyl iodide.

iodide containing a high concentration of iodine or hydrogen iodide, with the results also shown in Table IV. All yields reported are calculated to 21 hr. of radiolysis.

Discussion

Ethyl Iodide.—The facts previously established which are pertinent to the radiolysis of liquid ethyl iodide are the following. The amount of iodine produced is linear with dose to concentrations much greater than those required for effective scavenging of free radicals.^{3,5,12} Hydrogen iodide,^{3,5} ethane and ethylene¹² are also important products while hydrogen and acetylene are minor products.¹² With added radioiodine, the 100 e.v. yield of organic iodide is ca. 6³, ethyl radicals predominating.^{12,13}

(13) L. H. Cevantman and R. R. Williams, Jr., *J. Phys. Chem.*, **56**, 569 (1952).

TABLE IV
 RADIOLYSIS OF METHYL IODIDE; THE EFFECTS OF HI AND OF I₂

HI added (mole fraction × 10 ⁴)			34	75	103	21	24	42	69
I ₂ added (mole fraction × 10 ⁴)									
Products, ^a mole × 10 ⁶									
CH ₄	14.8	14.7	124	138	144	11.6	11.5	10.9	8.9
C ₂ H ₆	21.4	21.4	16.7	15.3	15.0	20.1	19.0	17.1	15.0
C ₂ H ₄	1.65	1.74	1.67	1.49	1.34				
C ₂ H ₂	0.58	0.46	0.54	0.48	0.42				
C ₃ H ₈	0.18	0.11	0.00	0.00	0.03				
H ₂	1.17	1.16	1.70	2.12	2.09				
I ₂	25.9	23.2	130	...	148				
HI	0.5	0.0							

^a Amounts of products for all runs are calculated to a common basis of 21 hr. irradiation time. Samples with added HI were actually irradiated 7 hr.

Other species contributing and their yields are $G(\text{CH}_3\text{I}^*) = 0.06$, $G(\text{CH}_2\text{I}_2^*) = 0.04$.^{12,13} $G(\text{I}_2)$ is increased by added oxygen and decreased by added iodine.^{3,5,12} The specific reaction rates of ethyl radicals with iodine and with hydrogen iodide are approximately equal. The same result has been obtained from experiments on photolysis and on radiolysis.^{6,14,15} There are marked similarities between photolysis and radiolysis of ethyl and other alkyl iodides. This similarity is related to the number of hydrogen atoms in β -position relative to iodine; their abstraction controls formation of hydrogen iodide and olefin.^{4,6}

The present work confirms and extends several of the earlier observations. Hydrogen iodide at *ca.* $10^{-2}M$ is a useful reagent for organic free radicals, establishing an upper limit $G(\text{CH}_3) \leq 0.02$ and $G(\text{C}_2\text{H}_5) \cong 7.5$ apart from reversion to alkyl iodides by reactions within spurs not susceptible to measurement. In addition it has been found that butane is a significant product and $G(\text{C}_2\text{H}_6)$ is still an important product at values of $(\text{I}_2)/(\text{HI})$ much greater than 10^2 . It is significant that $10^{-2}M$ or more of these reagents alter $G(\text{C}_2\text{H}_4)$, $G(\text{C}_2\text{H}_6)$ and $G(\text{C}_4\text{H}_{10})$ anomalously. At large concentrations either iodine or hydrogen iodide decreases butane and also ethylene while iodine decreases ethane and hydrogen iodide increases ethane. The yield of acetylene is not affected by either added iodine or hydrogen iodide. $G(\text{H}_2)$ is rather insensitive to very large concentrations of iodine and $G(\text{CH}_4)$ increases with added hydrogen iodide.

Excepting the minor products, these facts closely resemble those for photolysis and this similarity was predicted,⁶ except for butane formation. This is an important exception but it follows as an evident consequence of the mechanism adopted for photolysis when multiple events within small volumes ("spurs"), which are characteristic of radiolysis, are included as a variation of the primary act. The appreciable $G(\text{C}_4\text{H}_{10})$ for the radiolysis of liquid ethyl iodide and its dependence upon large concentrations of free radical scavengers, the absence of butane following radiolysis of ethyl iodide vapor¹⁶ or photolysis of the liquid, all strongly support the hypothesis of spurs in liquid systems.

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

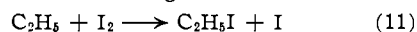
(15) R. H. Luebbe, Jr., and J. E. Willard, *ibid.*, **81**, 761 (1959)

(16) From the work of Lowell Theard in this Laboratory.

It is clear from the data reported here that butane does not arise from dimerization of ethyl radicals in the stationary state or directly from ion-molecule reactions which would be detected at least as readily in the vapor.¹⁶ It is of interest that $G(\text{C}_4\text{H}_{10}) \cong 0.04G(\text{C}_2\text{H}_5)$ for ethyl iodide and $G(\text{C}_2\text{H}_6) \cong 0.17G(\text{CH}_3)$ for methyl iodide where minimum values of $G(\text{radical})$ can be estimated from the data of Tables II and IV. These relations indicate a smaller reaction probability for recombination of ethyl radicals than for methyl radicals.

Constancy of $G(\text{I}_2)$.—The production of iodine and of hydrogen iodide is linear with dose, both in the photolysis and in the radiolysis of ethyl iodide. Since ethyl radicals react with both these products, as observed for the photolysis,^{6,15} the mechanisms must account for the constancy of Φ or G .

This aspect of the mechanism for radiolysis may be examined as follows: let the constant rates of emergence of I₂, HI and C₂H₅ from the spurs be g_1 , g_2 and g_3 . Interactions among these species occur in the steady state according to reactions



The net rates of formation of I₂ and HI are

$$\frac{d(\text{I}_2)}{dt} = g_1 + \frac{1}{2}g_3 \left[\frac{k_{12}(\text{HI})}{k_{11}(\text{I}_2) + k_{12}(\text{HI})} \right] - \frac{1}{2}g_3 \left[\frac{k_{11}(\text{I}_2)}{k_{11}(\text{I}_2) + k_{12}(\text{HI})} \right]$$

$$\frac{d(\text{HI})}{dt} = g_2 - g_3 \left[\frac{k_{12}(\text{HI})}{k_{11}(\text{I}_2) + k_{12}(\text{HI})} \right]$$

It is clear from the form of these equations that if $(\text{I}_2)/(\text{HI})$ is constant in time then both $d(\text{I}_2)/dt$ and $d(\text{HI})/dt$ are constant in time.

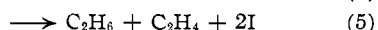
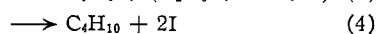
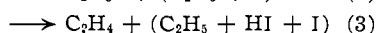
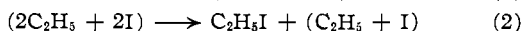
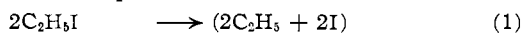
We require, then, that the ratio of differentials

$$\frac{d(\text{I}_2)}{d(\text{HI})} = \frac{k_{11}(g_1 - \frac{1}{2}g_3)(\text{I}_2) + k_{12}(g_1 + \frac{1}{2}g_3)(\text{HI})}{k_{11}g_2(\text{I}_2) + k_{12}(g_2 - g_3)(\text{HI})} = K$$

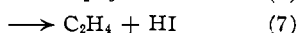
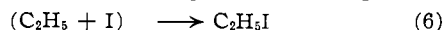
be a constant, K . In the case where $(\text{I}_2) = (\text{HI}) = 0$ at $t = 0$ we have, in addition, $(\text{I}_2) = K(\text{HI})$ which permits solution for K in terms of g_1 , g_2 , g_3 , k_{11} and k_{12} . In order to satisfy the condition $0 < K < \infty$, it is only necessary that $g_2k_{11}k_{12}(g_1 + \frac{1}{2}g_3) > 0$ and $k_{12}(g_1 + \frac{1}{2}g_3) > 0$. That is, it is only necessary that the rate constants be finite, a rather broad condition. It may be concluded that the observed constancy of $(\text{I}_2)/(\text{HI})$ is inherent in the mechanism rather than in the values of the rate constants.

The preceding considerations are equally applicable to the mechanism adopted by Hanrahan and Willard.¹⁴ With minor modifications it accounts for a constant Φ_1 in the photolysis of ethyl iodide over a wide range of (I_2) .^{2,6,15} It should be applicable to the photolysis and radiolysis of methyl iodide as well.

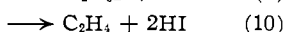
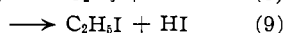
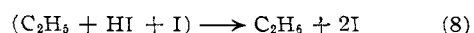
Reaction Mechanism.—As a convenient oversimplification, let us describe all spurs in terms of $(2C_2H_5, 2I)$. If the local concentrations of free radicals in spurs approximate those occurring in photolysis,⁶ for which a reencounter occurs with a probability of 0.8, then the first binary encounter among four particles has a probability of practically unity and will occur almost immediately. For the same reason, the first binary encounter will be relatively immune to interference by several mole per cent. of added free radical scavengers. We may expect then, by this approximation, to be able to describe qualitatively the diffusion kinetics involved in this system. It will be necessary to include one other feature not required for a description of the corresponding photolytic system, *viz.*, that since the first binary encounter in a spur may produce C_2H_4 and HI, the next stage of a two step spur reaction may form C_2H_6 by the diffusion-controlled reaction 8. In the following scheme, parentheses enclose free radicals in the spur which are subject to subsequent diffusion-controlled interaction. Since initial formation of I_2 in the spur should approximate that of C_4H_{10} , it can have only minor consequences and will not be included in the mechanism. The first stage of the spur reaction may therefore involve these steps



A somewhat less efficient spur reaction is still possible between remaining free radical pairs.



A very efficient reaction occurs between C_2H_5 and HI,⁶ so we must also include, as a second stage spur reaction, following step 3, the reaction step 8 as well as 9 and 10. Reaction 5 would be expected to



make only a small contribution since butane is a minor product and dimerization predominates 8:1 over disproportionation.¹⁷

Hanrahan and Willard¹⁴ accounted for C_2H_6 at large $(I_2)/(HI)$ by a hot reaction of C_2H_5 and we also previously favored such a view.² The facts reported here are inconsistent with such a hypothesis. The ratio of the lowest observed yield of C_2H_6 at high (I_2) from Table II to the highest yield of C_2H_6 at high (HI) from Table III equals 0.08,

(17) K. O. Kutschke, M. H. J. Wijnen and E. W. R. Steacie, *THIS JOURNAL*, **74**, 714 (1952).

and it establishes an approximate upper limit to the efficiency of formation of C_2H_6 from C_2H_5 by hot reaction. The actual yield of hot C_2H_6 must be still smaller since the extreme values observed are almost certainly not limiting values. Further, this hypothesis does not account for marked decreases in $G(C_2H_6)$ caused by only 0.2–2 mole % iodine (Table II).

We account for these solute effects in terms of diffusion controlled reactions, in particular 6 through 10, which are consistent with the general assumption of diffusion controlled spur reactions in irradiated liquids. In this work the systematic dependence of $G(C_2H_6)$ upon (I_2) or (HI) is fairly quantitative. That for $G(C_4H_{10})$ is at least qualitatively evident, the scatter arising from a rather difficult analysis. The cause of scatter in $G(C_2H_4)$ is not evident, but the reality of a systematic decrease with increasing (I_2) or (HI) is unmistakable. To demonstrate that this is so, combine all yields of C_2H_4 from Tables II and III, since by hypothesis I_2 and HI exert similar effects. Of the 14 runs, only one $G(C_2H_4)$ at (solute) < 0.08 mole % is equal to or less than any $G(C_2H_4)$ at (solute) > 0.08 mole %. The probability of such a result by random scatter is negligibly small. Evidence that solutes are not affecting primary processes is afforded by the constancy of the yield of C_2H_2 for the same (solute) intervals, the averages being 1.30 and 1.31 μ moles and the a. d. is $\pm 4\%$ in each case.

These facts support a bimolecular mechanism of HI formation, rather than a unimolecular mechanism. A uniform mechanism involving competition between disproportionation and combination of radical or radical-atom pairs is capable of accounting for some features of the present work as well as the previously observed correlations between yields of products and the number of H-atoms β to the free valence.^{4,5,7} The β -effect has been observed for photolysis and radiolysis, for the liquid phase and for the gas phase.

A different hypothesis was adopted by Willard and co-workers^{5,14,15} who have confirmed the β -effect⁴ for radiolysis of several liquid alkyl iodides and concluded that it represents an effect of structure upon unimolecular elimination of HI from *excited molecules*. They also interpreted the temperature independence of quantum yield of HI from ethyl iodide (25, –70, –180°) as supporting evidence, assuming the probability of reencounter between $(C_2H_5 + I)$ to decrease proportionately with decreasing probability of their mutual escape at lower temperatures. It seems to us that the sustained yield of HI in ethyl iodide glass does not require an undiminished rate of diffusion for the relative rates of reactions 6 and 7 to be maintained. It is only required that C_2H_5 acquire some rotational freedom before the inevitable reencounter with I. The infrared absorption of CH_3Br , CH_3I and CH_3CN in liquid carbon tetrachloride demonstrates rotational freedom of these molecules.¹⁸ It is, therefore, likely that an energetic C_2H_5 radical could become randomly oriented relative to its geminate I-atom in ethyl iodide glass. Finally, the results of Kraus and Calvert^{1a} with *t*-,

(18) W. J. Jones and N. Sheppard, *Trans. Faraday Soc.*, **56**, 625 (1960).

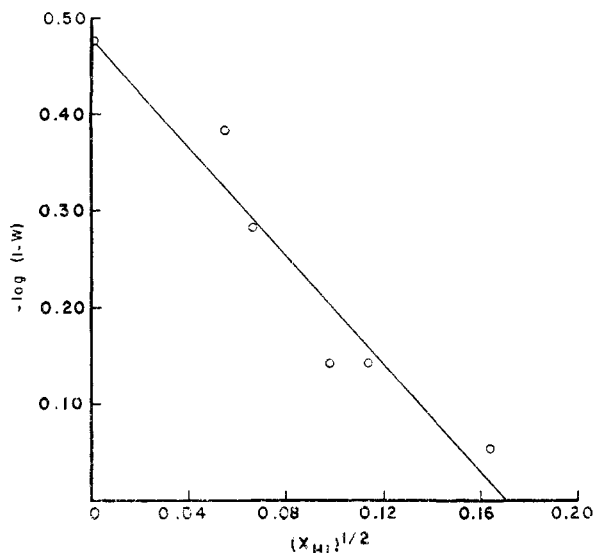


Fig. 2.—Diffusion analysis of ethane vs. hydrogen iodide in ethyl iodide.

i- and *s*-butyl radicals in the vapor phase demonstrated a β -effect for disproportionation-combination and thus support our earlier observation and interpretation.^{4,6}

A further requirement of the proposed mechanism is that $G(\text{C}_2\text{H}_4) - G(\text{C}_2\text{H}_6) = G(\text{HI})$. Considering the experimental difficulties, the data of Tables I and II meet this requirement. Ethyl radicals which escape diffusion-controlled reactions 2–10 will obey conventional stationary state kinetics. In the work described here they react with iodine or with hydrogen iodide by steps 11 and 12.

Let $G'(\text{C}_2\text{H}_6)$ be the 100 e.v. yield of ethane from non-steady state reactions, and let $G(\text{C}_2\text{H}_6)$ be the observed yield. Then

$$G(\text{C}_2\text{H}_6) = G'(\text{C}_2\text{H}_6) + G^0(\text{C}_2\text{H}_5)_s \frac{k_{12}(\text{HI})}{k_{12}(\text{HI}) + k_{11}(\text{I}_2)} \quad (13)$$

where $G^0(\text{C}_2\text{H}_5)_s$ is the initial yield of ethyl radicals which are subject to steady state kinetics. In the runs performed to test this relation, the samples were not irradiated in reproducible positions. However, at the concentrations of solutes used, $G(\text{C}_2\text{H}_4)$ and $G'(\text{C}_2\text{H}_6)$ are constant and from the first three runs in Table II, $G'(\text{C}_2\text{H}_6) = 0.40 G(\text{C}_2\text{H}_4)$. Ethylene serves as an internal dosimeter and its constant value is denoted by $G'(\text{C}_2\text{H}_4)$. Rearranging and inverting eq. 13 and multiplying both sides by $G'(\text{C}_2\text{H}_4)$ gives

$$\frac{G'(\text{C}_2\text{H}_4)}{G(\text{C}_2\text{H}_6) - G'(\text{C}_2\text{H}_6)} = \frac{G'(\text{C}_2\text{H}_4)}{G^0(\text{C}_2\text{H}_5)_s} \left(1 + \frac{k_{11}(\text{I}_2)}{k_{12}(\text{HI})} \right) \quad (14)$$

Ratios of G may be replaced by the corresponding ratios of mole numbers μ , which are employed in Fig. 1 to test eq. 14. The intercept gives $G'(\text{C}_2\text{H}_4)/G^0(\text{C}_2\text{H}_5)_s = 0.47$ which combines with $G'(\text{C}_2\text{H}_4) = 2.20$ to give $G^0(\text{C}_2\text{H}_5)_s = 4.7$. The ratio of slope to intercept gives $k_{11}/k_{12} = 0.82$. For the photolysis of ethyl iodide the corresponding function of quantum yields was incorrectly expressed in terms of the initial concentrations⁶ of hydrogen iodide. Properly calculated, the same ratio of rate constants is obtained.

Using the value of k_{11}/k_{12} we can obtain a "predicted" value of the ratio $(\text{I}_2)/(\text{HI})$ in pure ethyl iodide. For reactions in the stationary state (as distinct from spurs) where $G(\text{C}_2\text{H}_5\text{I})_s$ and G

$$G(\text{C}_2\text{H}_5\text{I})_s / G(\text{C}_2\text{H}_6)_s = k_{11}(\text{I}_2) / k_{12}(\text{HI}) \quad (15)$$

$(\text{C}_2\text{H}_6)_s$ represent yields from reactions 11 and 12. From the kinetic postulates and Fig. 1, $G(\text{C}_2\text{H}_5\text{I})_s + G(\text{C}_2\text{H}_6)_s = G(\text{C}_2\text{H}_5)_s = 4.7$. The yield of ethane from spur reactions, based on the first three runs in Table II, is 0.87 and $G(\text{C}_2\text{H}_6)_s = 1.92 - 0.87 = 1.05$ while $G(\text{C}_2\text{H}_5\text{I})_s = 4.7 - 1.05 = 3.65$. Solving equation 15 gives $(\text{I}_2)/(\text{HI}) = 4.2$. Our result, Table I, is 6.4 while Hanrahan and Willard¹⁴ found 3.4.

Diffusion Kinetics.—The mechanism of the radiation chemistry of liquid ethyl iodide is too complex to allow a fully quantitative treatment of the diffusion kinetics, as was done for the photolysis.⁶ However, by adopting the device of describing only the later stages of the diffusion in terms of a two particle spur, we can attempt a formal comparison. For this purpose the data of Table III are convenient.

Assuming reaction probability coefficients equal to unity for reaction steps 6, 7 and 12, the probability W of intervention by HI at mole fraction X (for $X_1, \sim 0$) in the diffusion controlled reactions (assumed to be 6, 7) is given by

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

The parameters γ and ρ_0 are the mean free path of diffusion and the initial separation of the atom-radical pair in units of the collision diameter.

Ethyl radicals which fail to react in the spurs by steps 6–10 will be converted to ethane by step 12. We identify the yield of ethane resulting from interference by HI with steps 6–10 as the difference between the observed yields of Table III and $G^0(\text{C}_2\text{H}_5)_s$ from Fig. 1. To convert from ΔG to W requires a normalization factor, the $G(P)$ for primary events (reaction 2 by postulate). Lacking an independent value we determine $G(P)$ by trial and error so as to maintain the value $\gamma = 0.33$ previously found to hold in liquid ethyl iodide, both for nuclear chemistry and for photochemistry.^{6,19} The best fit corresponds to $G(P) = 3.7$ and $\rho_0 = 1.1$. The adequacy of the description can be judged by Fig. 2. The former value is approximately that expected (*viz.*, three ion pairs per 100 e.v.). Also, the data indicate $-G(\text{C}_2\text{H}_5\text{I}) \sim 10$ as a limiting yield with increasing (HI) or G - (ion pairs) ~ 3.3 if $3\text{C}_2\text{H}_5\text{I}$ are consumed per ion pair (see below). The fact that $G(\text{C}_2\text{H}_5)_s$ is 4.7 while $G(P)$ is only 3.7 may be attributed to dissociative electron capture producing relatively isolated C_2H_5 , as discussed later.

The dependence of $G(\text{C}_2\text{H}_6)$ upon X_1 for ethyl iodide likewise can be described as a diffusion controlled process. Employing the value of $G(P) = 3.7$ from the preceding case we find $\gamma = 0.34$ and $\rho_0 = 0.9$. The two sets of results are therefore fairly self consistent. In both cases the value of ρ_0 , unlike that of γ , depends on the kinetic details. It somewhat exceeds that for photolysis, as might be expected, since it describes the C_2H_5 —I separa-

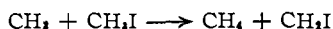
(19) J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, *THIS JOURNAL*, **76**, 3274 (1954).

tion after one stage of reaction (and some diffusion) has occurred.

Methyl Iodide.—The relevant facts previously established for the radiolysis of liquid methyl iodide are summarized. Major products are ethane, methane and iodine; minor products are hydrogen, acetylene and ethylene.²⁰ By isotopic labeling, $G(\text{CH}_3\text{I}^*) = 6$, $G(\text{C}_2\text{H}_5\text{I}^*) = 0.04$ and $G(\text{CH}_2\text{I}_2^*) = 0.16^{3,12,20}$ (assuming one labeled position). Both $G(\text{C}_2\text{H}_6)$ and $G(\text{CH}_4)$ decrease strongly with large and increasing (I_2) while $G(\text{H}_2)$ changes little.²⁰ The present work verifies the preceding, directly or indirectly, and also demonstrates a very small $G(\text{HI})$ which increases by 0.25 with addition of water, accompanied by a decrease of $G(\text{CH}_4)$ amounting to 0.17. Also $G(\text{C}_2\text{H}_4)$ is relatively sensitive to added scavenger.

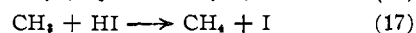
The primary reactions in methyl iodide are considered to be analogous to 1, 2, 4 and 6 for ethyl iodide.

It had appeared necessary previously, with the information then available, to postulate a hot radical reaction to account for the appearance of methane.²⁰ We conclude that most of the methane results from reaction between CH_3 and HI within the spur. Since $G(\text{CH}_2\text{I}_2^*) = 0.16$ by radioiodine labeling for one exchanging atom (while $G(\text{CH}_4) = 0.77$) the yield from the hot reaction



cannot exceed 0.16. As we shall see, it may be still less. The source of HI will be considered presently.

In order to account for the very small ratio $G(\text{HI})/G(\text{I}_2)$ in pure methyl iodide (Table IV) an approach similar to that used for ethyl iodide is appropriate. Representing the competition in the stationary state by



and the corresponding yields by $G(\text{CH}_3\text{I})_s$ and $G(\text{CH}_4)_s$ we have

$$G(\text{CH}_3\text{I}) / G(\text{CH}_4)_s = k_{16}(\text{I}_2) / k_{17}(\text{HI}) \quad (18)$$

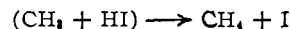
The ratio of the rate constants recently has been determined²¹ as $k_{16}/k_{17} = 0.50$. From Table IV, the difference between yields of methane from columns 3 and 6 measures $G(\text{CH}_3)_s$ in the stationary state. The difference between the average yields of methane and of ethane in columns 1, 2 and 6, 7 measures roughly $G(\text{CH}_4)_s$ and $G(\text{C}_2\text{H}_6)_s$. Finally, $G(\text{CH}_3\text{I})_s = G(\text{CH}_3)_s - G(\text{CH}_4)_s - 2G(\text{C}_2\text{H}_6)_s$ and $G(\text{I}_2) = 1.26$. Applying equation 18 gives $G(\text{HI}) = 0.02$ for pure methyl iodide, approximately that observed. The increment $\Delta G(\text{HI}) = 0.25$ or $-\Delta G(\text{CH}_4) = 0.17$ with added water measures the contribution of reaction 17 in the steady state.

The residual $G(\text{CH}_4) = 0.60$ we attribute to a spur reaction which involves H-atoms, whose possible modes of formation are itemized in Table V. It is very likely that H-atoms, however formed, would be removed efficiently by the reaction

(20) R. C. Petry and R. H. Schuler, *This Journal*, **75**, 3796 (1953).
(21) R. F. Pottier, W. H. Hamill and R. R. Williams, Jr., *ibid.*, **80**, 4224 (1958).



and that such events frequently would be followed by



Each of these reactions is diffusion controlled and thus accounts for the marked decrease in $G(\text{CH}_4)$ by added iodine (Table IV and ref. 20). A similar reaction presumably occurs in ethyl iodide but cannot be distinguished readily from other reactions which also yield C_2H_6 . These reactions also account for CH_4 from cyclohexane irradiated with dissolved CH_3I and I_2 .²²

The data of Table IV are consistent with the observation of Petry and Schuler²⁰ that C_2H_5 radicals are produced in small yield. Ethylene should result by reaction 7 and propane by a reaction analogous to 4. Further, we might expect the ratio $\text{C}_3\text{H}_8/\text{C}_2\text{H}_4$ in methyl iodide to approximate $\text{C}_4\text{H}_{10}/\text{C}_2\text{H}_4$ in ethyl iodide and the dependence of $G(\text{C}_2\text{H}_4)$ with added scavenger to be similar in the two systems, as observed.

Considerations of diffusion kinetics for the dependence of $G(\text{C}_2\text{H}_6)$ upon X_{HI} in methyl iodide lead to $\gamma = 0.40$ and $\rho_0 = 1.1$. Previous work on radiative neutron capture in liquid methyl iodide¹⁷ gave $\gamma = 0.43$.

Ionic Processes.—The relative yields of the products of radiolysis from liquid methyl iodide and from liquid ethyl iodide can be accounted for by reactions which have been observed in the mass spectrometer and by other reactions which are not inconsistent with such observations. The fates of atoms and free radicals so formed must then be treated both by diffusion kinetics for the reactions within spurs and also by conventional kinetics for reactions in the stationary state.

Table V summarizes the relative abundances P of the primary ions produced by electron impact on CH_3I and $\text{C}_2\text{H}_5\text{I}$, together with the corresponding secondary ions which have been observed in this Laboratory.²³ Species which contribute very little to ultimate products have been omitted. Neutral fragments, if well established by appearance potential measurements,²³ are listed without comment. When no such information is available, plausible species are assumed and indicated by question mark. In some instances, secondary ions have been assumed and similarly indicated.

The secondary reactions which have been assumed for CH_3^+ and C_2H_5^+ have not been observed in the mass spectrometer and would not be expected, since they involve persistent collision complexes as products of rather exothermic processes. This restriction would be much less severe in the liquid state, both because of efficient dissipation of energy and also because a much shorter time interval is involved. All ions of the type $\text{C}_n\text{H}_{2n+2}^+$ are considered to have ether-like structures. Their potential energies should be less than those of molecular alkyl iodide ions by at least the bond dissociation energy for C-I since the reaction



occurs spontaneously. The neutralization proc-

(22) R. H. Schuler, *J. Phys. Chem.*, **61**, 1472 (1957).

(23) R. F. Pottier, R. Barker and W. H. Hamill, *Radiation Research*, **10**, 664 (1959).

TABLE V
COMPARISON OF RESULTS FROM MASS SPECTROMETRY AND FROM RADIOLYSIS
Methyl iodide

<i>m/e</i>	<i>P</i>	Primary products	Secondary products	H	H ₂	HI	Final products CH ₂	CH ₃	C ₂ H ₄	C ₂ H ₅
142	100	CH ₃ I ⁺	C ₂ H ₅ I ⁺ + I					200		
141	14	CH ₂ I ⁺ + H	I ₂ ⁺ + C ₂ H ₅ ?	14						14
140	4	CHI ⁺ + 2H	CHI ₂ ⁺ + CH ₃	8				4		
139	5	CI ⁺ + H + H ₂	CI ₂ ⁺ + CH ₃	5	5			5		
128	3	HI ⁺ + CH ₂	CH ₃ I ₂ ⁺ + H	3			3	3		
127	53	I ⁺ + CH ₃	?					53		
15	28	CH ₃ ⁺ + I	C ₂ H ₅ I ⁺ ?					56		
14	4	CH ₂ ⁺ + HI				4				
13	2	CH ⁺ + 2H + I		4						
12	1	C ⁺ + 3H + I		3						
0	214	e ⁻	I ⁻ + CH ₃					214		
		Relative abundance		37	5	4	3	535		14
		Calcd. normalized relative abundance			0.9	7.7 ^a	0.6	100		3
		Obsd. normalized relative abundance			0.9	9.2 ^c	1.4 ^b	100		2 ^d
Ethyl iodide										
156	100	C ₂ H ₅ I ⁺	C ₄ H ₁₀ I ⁺ C ₄ H ₁₀ I ₂ ⁺							200
141	3	CH ₂ I ⁺ + CH ₃ ?	CH ₃ I ₂ ⁺ + C ₂ H ₄					5	3	
139	1	CI ⁺ + CH ₂ + H ₂ + H	CI ₂ ⁺ + C ₂ H ₅	1	1		1			1
128	9	HI ⁺ + C ₂ H ₄	I ₂ ⁺ + C ₂ H ₅ C ₂ H ₅ I ₂ + H	5					9	5
127	47	I ⁺ + C ₂ H ₄ + H	HI ₂ ⁺ + C ₂ H ₄	47		47			93	
29	65	C ₂ H ₅ ⁺ + I	C ₄ H ₁₀ I ⁺ ?							130
28	8	C ₂ H ₄ ⁺ + HI ?				8				
27	57	C ₂ H ₃ ⁺ + H + HI ?		57		57				
26	12	C ₂ H ₂ ⁺ + H ₂ + HI ?			12	12				
15	1	CH ₃ ⁺ + ?	C ₃ H ₅ I ⁺ + ?					1		1
13	1	CH ⁺ + ?								
12	1	C ⁺ + ?								
0	304	e ⁻	I ⁻ + C ₂ H ₅							304
		Relative abundance		110	13	124	1	6	105	640
		Calcd. normalized relative abundance			2	37 ^a	0.15	0.9	16	100
		Obsd. (corr.) normalized relative abundance			2.8	18 ^c	0.5 ^b	0.2 ^f	16	100

^a Combined H + HI. ^b By isotopic labeling, ref. 12. ^c Combined HI + CH₄. ^d Combined C₂H₄ + C₂H₅. ^e Combined HI + C₂H₆, corrected for C₂H₅ + I → C₂H₄ + HI. ^f Based upon CH₄ in Table III.

ess involving R₂I⁺ and I⁻ is therefore exothermic by less than 4 e.v. and alkyl radicals with little excess energy are to be expected. The other secondary reactions listed in Table V have been observed.

Dissociative electron attachment by methyl iodide is known to have a very low energy threshold, on the basis of mass spectrometric observation,²⁴ and the same behavior can be assumed for ethyl iodide. The process is therefore plausible in irradiated systems.²⁵ The assumption of electron capture in liquids is also consistent with the observed kinetics. The ratio of yields of ethyl radicals which enter the stationary state relative to those which react with iodine atoms to form ethylene is three times greater for radiolysis than for photolysis. Dissociative capture of an electron to yield C₂H₅ + I⁻ followed by migration of I⁻ in the coulombic field of the parent ion²⁶ would eventually leave C₂H₅ and I well separated and

thus account for the large G(C₂H₅). The products resulting from charge neutralization of all secondary ions must be assumed. Except for minor species, quite plausible assignments can be made.

Two secondary ions arise from HI⁺ in ethyl iodide and a one-to-one branching is adopted, as for the gas.²¹ Most of the primary reactions involved have been considered in recent publications.^{23,27,28} Some of these now require further consideration, as do others for which no data are available.

C₂H₄⁺.—No data are available; the reaction to form HI corresponds to recent observation of a similar decomposition for C₂H₅Br.¹⁵

C₂H₃⁺.—There are no data and two plausible sets of neutral fragments are possible, H + HI or H₂ + I. The latter would produce more H₂ than was observed and the former is therefore chosen.

C₂H₂⁺.—There are no data. This is the only mode of primary decomposition capable of produc

(24) V. H. Dibeler and R. M. Reese, *J. Res. Natl. Bur. Standards*, **54**, 127 (1955).

(25) J. L. Magee and M. Burton, *THIS JOURNAL*, **73**, 523 (1951).

(26) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

(27) A. P. Irsa, *ibid.*, **26**, 18 (1957).

(28) H. Branson and C. Smith, *THIS JOURNAL*, **75**, 4133 (1953).

ing the required yield of H₂. A similar decomposition has been observed for C₂H₅Br.¹⁵

I⁺.—The following sets of neutral fragments from C₂H₅I are energetically allowed: C₂H₃ + H₂, CH₄ + CH, CH₃ + CH₂ (all approximately thermo-neutral), C₂H₅ ($\Delta H = -58$ kcal.) and C₂H₄ + H ($\Delta H = -17$ kcal.). The first three would produce excessive amounts of measurable products. Either of the last two possibilities is acceptable. The latter was chosen.

CI⁺.—In this case, and in those which follow, the primary ion appears in the spectra of both CH₃I and of C₂H₅I. Simultaneous solution of the two thermochemical equations establishes which processes are allowed. If CH₃I⁺ → CI⁺ + H₂ + H, then from C₂H₅I either CH₃ + 2H or CH + 2H₂ or CH₂ + H₂ + H may result. The choice is not critical and the last is chosen.

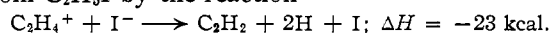
CH₂I⁺.—The appearance potentials of I⁺ and of CH₂I⁺ from CH₃I are indistinguishable and either may be the parent ion of I₂⁺ observed in the secondary spectrum. Since I⁺ does not react with C₂H₅I to yield I₂⁺ and C₂H₅, we shall assume that I⁺ and CH₃I do not form I₂⁺ and CH₃. A more compelling reason for choosing CH₂I⁺ + CH₃I → I₂⁺ + C₂H₅ is that it accounts for C₂H₅ formation. The neutral fragment accompanying primary CH₂I⁺ from C₂H₅I is somewhat uncertain because simultaneous solution of the thermochemical equations gives no thermo-neutral process. If CH₃ is produced, 38 kcal. of kinetic energy must be dissipated but smaller fragments are not allowed from the measured appearance potentials.

Insofar as ionic processes produce molecular species uniquely, the observed yields are well defined. The yield of H₂ from iodine-containing solutions may be the only example. In both systems HI forms molecularly and also by reaction between H + RI and, for ethyl iodide, C₂H₅ + I. Calculated yields of H and of HI are therefore combined in Table V. Since HI is also lost by HI + R → HR + I, the "observed"

yields of HI in Table V are based upon the sum HI + RH.

For ethyl iodide an additional, but unknown, correction should be allowed for C₂H₅ + I → HI + C₂H₄. These reactions occur to a considerable extent within spurs, for which the yields are not accurately measurable. We shall assume that $\Delta G(C_2H_4)$ and $\Delta G(HI)$ resulting from the addition of large concentrations of iodine or hydrogen iodide (Tables II and III) represented 50% of the spur reaction. The average change observed for ethylene, combining data of Tables II and III, was 5.5×10^{-6} mole. Analysis for hydrogen iodide was inaccurate but the assumed mechanism requires the same change for hydrogen iodide and for ethylene. Reaction within the spurs therefore produces roughly 10^{-5} mole of each. Observed results have been adjusted accordingly.

There is no evident source of C₂H₂ in either system, but one may speculate that it originates from C₂H₅I by the reaction



Calculated and observed abundances would be 1.2 and 1.3, respectively. All observed yields in Table V have been referred to CH₃ or C₂H₅ measured as CH₄ or C₂H₆ at high concentrations of HI.

It is difficult to assess the significance of the comparisons in Table V because of the necessity of choosing among multiple possibilities in several instances. Decompositions involving as many as three or four fragments, and presumably occurring consecutively, must be made in about four instances. For the liquid phase this may appear quite implausible. It is a fact, however, that liquid methyl iodide produces small but significant yields of H₂, C₂H₂ and C₂H₄, while liquid ethyl iodide similarly yields H₂, C₂H₂ and CH₂I₂ which imply complex decompositions. The evidence for ion-molecule reactions in the liquid phase is not strong, since the almost invariable product is the major free radical species and agreement within a factor of two must be regarded as excellent.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, NEW YORK]

Conformational Analysis of Radical Abstraction of Hydrogen Atoms from Aromatic Hydrocarbons¹

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The relative rate constants of H abstraction by methyl radicals were determined for a series of aromatic hydrocarbons. Comparison of the respective rate constants involving other radicals, such as ROO·, *t*-BuO·, CCl₃· and polystyryl, with methyl radicals reveals an extraordinarily good numerical agreement between the corresponding relative rate constants. Consideration of the interaction between the non-bonded H atoms shows that the reactivities of ethyl benzene and cumene are lower than anticipated because of the strain in the respective transition states. On the other hand, axial α C-H's in tetralin correspond to "normal" reactivities. It was shown that the ratio of reactivities of aliphatic primary:secondary:tertiary C-H's corresponds to that in the aromatic series if "normal" C-H are considered. This correlation applies also to olefinic series if the effects of strain are taken into account.

The studies of Russell on the oxidation of hydrocarbons^{2a} and of Williams, Oberright and Brooks²

(1) This work was supported by the A.C.S. Petroleum Fund.

(2) (a) G. A. Russell, *THIS JOURNAL*, **78**, 1047 (1956). (b) A. L. Williams, E. A. Oberright and J. W. Brooks, *ibid.*, **78**, 1190 (1956).

on the reactions of *t*-butoxy radicals drew our attention to an interesting observation, namely that the abstraction of hydrogen atoms by ROO· or *t*-BuO· radicals seems to proceed faster with indan or tetralin than with ethylbenzene. The reactive hydro-