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## Effects of Ionic and Free Radical Processes in the Radiolysis of Organic Liquid Mixtures<sup>1</sup>

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The gamma-radiolyses of liquid cyclohexane, its dilute iodine-containing solutions and various binary liquid mixtures over the complete range of composition have been investigated. The systems and yields measured were:  $G(\text{H}_2)$  and  $G(\text{C}_6\text{H}_{10})$  in cyclohexane;  $G(\text{H}_2)$ ,  $G(\text{C}_6\text{H}_{10})$ ,  $G(\text{C}_6\text{H}_{11}\text{I})$  and  $G(\text{HI})$  in cyclohexane-iodine;  $G(\text{H}_2)$ ,  $G(\text{CH}_4)$ ,  $G(\text{C}_6\text{H}_{10})$  and  $G(\text{HI})$  in cyclohexane-methyl iodide- $10^{-2}$   $M$  iodine;  $G(\text{H}_2)$  and  $G(\text{CH}_4)$  in cyclohexane-methyl iodide- $10^{-2}$   $M$  hydrogen iodide;  $G(\text{H}_2)$  and  $G(\text{HCl})$  in cyclohexane-chloroform;  $G(\text{H}_2)$  and  $G(\text{HCl})$  in cyclohexane-*n*-propyl chloride;  $G(\text{H}_2)$ ,  $G(\text{CO}_2)$  and  $G(\text{CH}_4)$  in cyclohexane-benzyl acetate. The results are interpreted in terms of electron attachment and charge transfer as well as free radical reactions and energy transfer.

### Introduction

The radiolysis of liquid cyclohexane has been studied repeatedly in the pure state,<sup>2-4</sup> in binary mixtures<sup>2,5,6</sup> and with small concentrations of solute.<sup>7-10</sup> The emphasis in these studies, as in almost all studies of the radiation chemistry of liquids, has been directed to energy transfer and free radical processes, with one exception.<sup>7</sup> In this instance an attempt to find evidence for electron attachment (or "capture") by organic halides and other solutes at *ca.* 0.1  $M$  now appears to have miscarried because of a well known difficulty to distinguish between electrons and H-atoms in liquids. Since that time evidence has accumulated that  $G(\text{H-atoms})$  in gamma-irradiated liquid cyclohexane is approximately 2.0, although such evidence as the formation of hydrogen iodide from added iodine has been attributed to reaction between  $\text{C}_6\text{H}_{12}^+$  with  $\text{I}^-$  or an excited molecule  $\text{C}_6\text{H}_{12}^*$  with  $\text{I}_2$ .<sup>11</sup>

The present study was undertaken in the expectation that by examining irradiated mixtures of cyclohexane with various additives, over the entire range of composition, it should be possible to distinguish free radical effects from other phenomena. In particular it was expected that organic halides would yield evidence for electron attachment as well as for scavenging of H-atoms.

### Experimental

**Materials.**—Cyclohexane of spectral grade was passed through a 50 cm. column of silica gel and used without further purification. Ultraviolet transmission of the purified material was practically 100% to below 250  $\mu$ . Vapor phase chromatography showed a small impurity peak tentatively identified as 2,4-dimethylpentane.

(1) This article is based on a thesis submitted by L. J. F. in partial fulfillment of the requirements for the Ph.D. degree in the University of Notre Dame, January, 1959. This work was performed under the auspices of the Radiation Laboratory, 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.

(2) G. R. Freeman, *J. Chem. Phys.*, **33**, 71 (1960); *Can. J. Chem.*, **38**, 1043 (1960).

(3) H. A. Dewhurst, *J. Phys. Chem.*, **63**, 813 (1959).

(4) A. C. Nixon and R. E. Thorpe, *J. Chem. Phys.*, **28**, 1004 (1958).

(5) A. MacLachlan, *J. Am. Chem. Soc.*, **82**, 3309 (1960).

(6) J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).

(7) R. R. Williams, Jr., and W. H. Hamill, *Radiation Research*, **1**, 158 (1954).

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

(9) M. Burton, J. Chang, S. Lipsky and M. P. Reddy, *Radiation Research*, **8**, 203 (1958).

(10) G. Meshitsuka and M. Burton, *ibid.*, **10**, 499 (1959).

(11) M. Burton and J. Chang, private communication.

Methyl iodide was distilled through a two-foot, glass helix-packed column at 10:1. The fraction collected at 42.0-42.5° and 745 mm. was retained.

Chloroform of C.P. grade was shaken with water, dried over calcium chloride and distilled as above. The center cut boiling at 60.5° and 750 mm. was retained.

Propyl chloride and benzyl acetate were Eastman red label grade, used as received.

Iodine of C.P. grade was resublimed. Hydrogen iodide was prepared from potassium iodide and phosphoric acid.

**Sample Preparation.**—Liquid mixtures were measured volumetrically. Concentrations of iodine were determined by titration with thiosulfate. Hydrogen iodide was measured ( $P-V-T$ ) on the vacuum line and condensed into the irradiation cell. Sealed Pyrex cells were used for irradiation.

**Radiation.**—Two  $\text{Co}^{60}$  sources were employed. On the basis of Fricke dosimetry, dose rates were approximately  $2 \times 10^{19}$  and  $8 \times 10^{20}$  e.v. l.<sup>-1</sup> min.<sup>-1</sup>. Doses ranged from  $10^{22}$  to  $10^{23}$  e.v. l.<sup>-1</sup>. Radiation temperature approximated 20°.

**Analysis.**—The irradiated cell was connected to the vacuum line through a breakseal. Gaseous products were separated by vacuum fractional distillation on a 30 cm.  $\times$  1.4 cm. column with a cold finger on top. Accumulated gas was removed intermittently from the top of the column and the  $P-V-T$  measured. Samples were analyzed in a CEC 21-103A mass spectrometer.

Acid was measured by titration, using brom cresol purple. In all runs for which the yield of hydrogen halide is reported, the solution to be irradiated was saturated with water. The yield of hydrogen halide is otherwise low and irreproducible. Except when specified, samples were dry.

Cyclohexene was measured as its diiodide by a procedure previously described.<sup>12</sup>

Cyclohexyl and *n*-hexyl iodides from irradiated solutions of cyclohexane-iodine were determined with a Perkin-Elmer vapor Fractometer. Retention times were established by authentic samples. Irradiated materials were first shaken with aqueous sodium thiosulfate, then exposed to tungsten light to decompose  $\text{C}_6\text{H}_{10}\text{I}_2$ , again treated with thiosulfate, then dried. Most of the cyclohexane was removed on a small distilling column prior to analysis.

### Results

**Cyclohexane.**—For doses approximating  $5 \times 10^{20}$  e.v.,  $G(\text{H}_2) = 5.85 \pm 0.08$  and  $G(\text{C}_6\text{H}_{10}) = 2.6 \pm 0.1$  as the average of seven and four runs, respectively. The measure of uncertainty in all cases is the average deviation. This value of  $G(\text{C}_6\text{H}_{10})$ , based upon an indirect method, agrees with Dewhurst's  $G(\text{C}_6\text{H}_{10}) = 2.5$  which was measured both by infrared spectrophotometry and by gas chromatography.<sup>3</sup> Burton, *et al.*,<sup>9</sup> found  $G(\text{H}_2) = 5.85$ ; Schuler<sup>8</sup> found  $G(\text{H}_2) = 5.4$ ; Freeman<sup>2</sup> reported  $G(\text{H}_2) = 5.37$  and  $G(\text{C}_6\text{H}_{10}) = 2.28$ .

**Cyclohexane-Iodine.**—The average  $G(\text{H}_2) = 3.90 \pm 0.15$  for seven runs at iodine concentrations of  $1 \times 10^{-2}$  to  $3 \times 10^{-2}$   $M$  and doses from  $2 \times 10^{22}$  to  $1 \times 10^{23}$  e.v. l.<sup>-1</sup>. Measurements of  $G(\text{H}_2)$

(12) R. F. Pottie, W. H. Hamill and R. R. Williams, Jr., *J. Am. Chem. Soc.*, **80**, 4224 (1958).

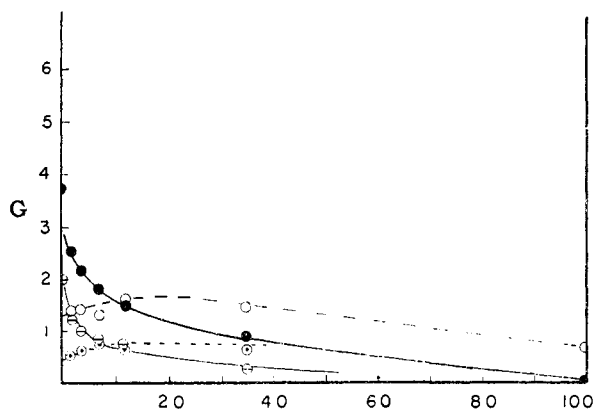


Fig. 1.—Yields per 100 e.v.: ● H<sub>2</sub>, ○ CH<sub>4</sub>, ○ HI and ○ C<sub>6</sub>H<sub>10</sub> vs. electron % methyl iodide in cyclohexane with 10<sup>-2</sup> M iodine.

at several smaller concentrations of iodine are described by the relation  $1/\Delta G(\text{H}_2) = 0.50 + 1.6 \times 10^{-3}/(\text{I}_2)$ . In water-saturated solutions of cyclohexane containing  $2 \times 10^{-2}$  and  $4 \times 10^{-2}$  M iodine,  $G(\text{HI})$  was 1.72 and 1.92, respectively. In the same runs  $G(\text{cyclo-C}_6\text{H}_{10}\text{I}) = 3.4$  and  $G(n\text{-C}_6\text{H}_{13}\text{I}) = 0.3$ . The highest value reported<sup>10</sup> for  $G(\text{HI})$ , also in water-saturated solutions, is 2.1. The average  $G(\text{C}_6\text{H}_{10}) = 1.9 \pm 0.1$  for four runs in water-saturated solutions containing iodine at concentrations approximating 10<sup>-2</sup> M.

Water is probably the least objectionable base which can be used to convert the reactive HX molecules to less soluble, less reactive solvated ionic form. There is no evident reason for water, at these low concentrations, to modify the net yields of products in any other manner. Its efficiency, even at these low concentrations which must prevail in cyclohexane-alkyl halide mixtures, was found adequate when tested by intermittent shaking of samples with a small excess of water during irradiation.

The maximum  $\Delta G(\text{H}_2)$  due to added iodine is somewhat dependent upon iodine concentration and it can only be said that our result is in fair quantitative agreement with earlier work<sup>8,9</sup> and qualitatively confirms a plateau. At 0.04 M iodine, Dewhurst<sup>8</sup> found  $G(\text{C}_6\text{H}_{10}) = 0.8$ ,  $G(\text{cyclo-C}_6\text{H}_{11}\text{I}) = 4.0$ ,  $G(n\text{-C}_6\text{H}_{13}\text{I}) = 0.3$  and  $G(\text{bicyclohexyl}) = 0.3$ . The difference between Dewhurst's  $G(\text{C}_6\text{H}_{10})$  and the present value may be due to formation of the vicinal diiodide in his work. The equilibrium constant is *ca.* 25 for  $\text{C}_6\text{H}_{10} + \text{I}_2 = \text{C}_6\text{H}_{10}\text{I}_2$  at 25° and in 0.04 M iodine about half the cyclohexene is present as the diiodide. The combined organic iodide in the present work amounts to  $G(\text{RI}) = 3.7$  whereas Fessenden and Schuler<sup>13</sup> obtained  $G(\text{RI}) = 5.6$  in the range 10<sup>-5</sup> to 5 × 10<sup>-3</sup> M iodine and the value 7.4 in 0.04 M solution. Since they also reported finding no hydrogen iodide, which is now known to undergo a back reaction, the first discrepancy,  $\Delta G(\text{RI}) = 5.6 - 3.7$ , may be due to reaction of hydrogen iodide for which  $\Delta G(\text{HI}) = 2.1$ .<sup>10</sup> The second difference,  $\Delta G(\text{RI}) = 7.4 - 5.6$  can be accounted for by cyclohexene

(13) R. W. Fessenden and R. H. Schuler, *J. Am. Chem. Soc.*, **79**, 273 (1957).

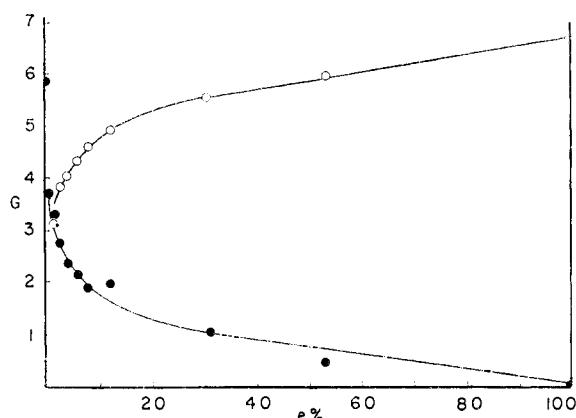


Fig. 2.—Yields per 100 e.v.: ● H<sub>2</sub> and ○ CH<sub>4</sub> vs. electron % methyl iodide in cyclohexane with 10<sup>-2</sup> M hydrogen iodide.

reacting as described above to form the diiodide. If we take *ca.* 50% reaction again and consider that there are two equivalents per mole of diiodide, we expect to find  $\Delta G(\text{RI}) = 1.9$  for our observed  $G(\text{C}_6\text{H}_{10}) = 1.9$ . Applying both corrections, amounting to  $\Delta G(\text{RI}) = 2.1 + 1.9$ , their  $G(\text{radical})$  at high concentrations of iodine becomes 3.4, in fair agreement with our combined  $G(\text{RI}) = 3.4 + 0.3$ . More important than mere agreement is plausibly accounting for an otherwise confusing anomaly in iodine scavenging.

**Cyclohexane-Hydrogen Iodide.**—As the average of two runs with 0.1 M hydrogen iodide at a dose of  $2 \times 10^{22}$  e.v.l.<sup>-1</sup>,  $G(\text{H}_2) = 6.8$ . Schuler<sup>8</sup> obtained the same value.

**Cyclohexane-Methyl Iodide.**—The yields  $G(\text{H}_2)$ ,  $G(\text{HI})$ ,  $G(\text{CH}_4)$  and  $G(\text{C}_6\text{H}_{10})$ , in solutions saturated with water and initially 0.02 M in iodine, appear in Fig. 1 as functions of the concentration of methyl iodide. The dose approximated  $8 \times 10^{22}$  e.v. l.<sup>-1</sup>. It should be noted that  $G(\text{C}_6\text{H}_{10}) \cong \frac{1}{2}G(\text{H}_2)$  and that while  $G(\text{H}_2)$  systematically decreases with increasing concentration of methyl iodide,  $G(\text{HI})$  is not greatly affected. It should be observed that  $G(\text{CH}_4) + G(\text{HI}) = 2.0$  over a range of concentration.

Results for cyclohexane-methyl iodide mixtures containing *ca.* 10<sup>-2</sup> M hydrogen iodide are reported in Fig. 2. Hydrogen iodide serves to convert methyl radicals to methane. At all concentrations of methyl iodide (excepting zero),  $G(\text{H}_2) + G(\text{CH}_4) = 6.5$ . Since methyl iodide is about as efficient as iodine for scavenging H-atoms and present at much higher concentration, it is to be expected that all thermal H-atoms, including those in the track, will initiate the reaction sequence.



In addition, methane will result from direct and other indirect effects.

**Cyclohexane-Chloroform.**—Yields of H<sub>2</sub> were measured in water-free mixtures at  $2 \times 10^{22}$  e.v. l.<sup>-1</sup> while yields of HCl were measured in water-saturated mixtures at  $4 \times 10^{22}$  to  $8 \times 10^{22}$  e.v. l.<sup>-1</sup>. Results appear in Fig. 3.  $G(\text{HCl})$  was appreciably enhanced by adding water, although hydroly-

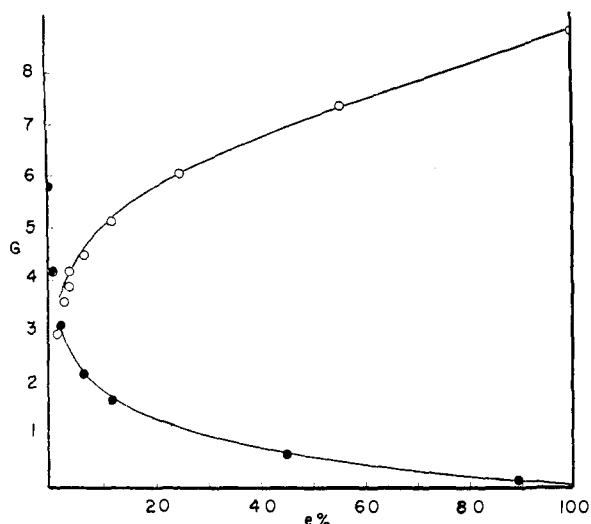


Fig. 3.—Yields per 100 e.v.: ● H<sub>2</sub> and ○ HCl vs. electron % chloroform in cyclohexane.

ysis of chloroform was shown not to occur. It is not significant to compare the effects upon  $G(\text{H}_2)$  of chloroform and of methyl iodide at small concentrations since the former proves to be a much less efficient reagent for H-atoms.

**Cyclohexane-*n*-Propyl Chloride.**—The yields  $G(\text{H}_2)$  and  $G(\text{HCl})$ , at a dose of  $4 \times 10^{22}$  e.v. l.<sup>-1</sup>, were measured in water-saturated solutions. The results appear in Fig. 4. In *n*-propyl chloride saturated with water,  $G(\text{HCl}) = 6.50$ ,  $G(\text{H}_2) = 1.20$ .

**Cyclohexane-Benzyl Acetate.**—The yields  $G(\text{H}_2)$ ,  $G(\text{CO}_2)$  and  $G(\text{CH}_4)$  at  $4 \times 10^{22}$  e.v. l.<sup>-1</sup> appear in Fig. 5. At 7.8% benzyl acetate the addition of 0.02 *M* iodine resulted in  $\Delta G(\text{H}_2) = -0.18$ ,  $\Delta G(\text{CO}_2) = -0.47$  and  $\Delta G(\text{CH}_4) = -1.48$  (or -95%). It should be noted that the limiting  $G(\text{CO}_2) = 2.0$  is attained at 4.2% benzyl acetate and that  $G(\text{H}_2)$  and  $G(\text{CO}_2)$  do not correlate as did, e.g.,  $G(\text{H}_2)$  and  $G(\text{CH}_4)$  in Fig. 2. On the other hand  $G(\text{CO}_2)/G(\text{CH}_4) = 1.3$  over the entire range of composition and presumably these products result from dissociation of acetoxy radicals. In pure benzyl acetate  $G(\text{H}_2) = 0.079$ ,  $G(\text{CO}_2) = 2.41$ ,  $G(\text{CH}_4) = 1.84$  and  $G(\text{CO}) = 0.30$ .

### Discussion

The relevant data for cyclohexane, alone or with small additions of iodine, are summarized in Table I. These results indicate three components in

TABLE I  
YIELDS OF PRODUCTS FROM IRRADIATED CYCLOHEXANE

Product	I <sub>2</sub> mole/l.	G, this work	G, lit.	Ref.
H <sub>2</sub>	0	5.85 <sup>a</sup>	5.37, 5.85	2, 9
	0.02	3.90 <sup>a</sup>	3.8	9
HI	0.02	1.8 <sup>b</sup>	2.1	10
<i>c</i> -C <sub>6</sub> H <sub>10</sub>	0	2.6 <sup>a</sup>	2.28, 2.5	2, 3
	0.03	1.9 <sup>a</sup>	0.8	3
<i>c</i> -C <sub>6</sub> H <sub>11</sub> I	0.04	3.4 <sup>c</sup>	4.0	3
C <sub>12</sub> H <sub>22</sub>	0		1.24, 2.0 <sup>a</sup>	2, 3
	0.04		0.3 <sup>a</sup>	3

<sup>a</sup> Value employed in this discussion. <sup>b</sup> The value  $G(\text{HI}) = 2.0$  will be used. <sup>c</sup> The value  $G(\textit{c}\text{-C}_6\text{H}_{11}\text{I}) = 3.7$  will be used.

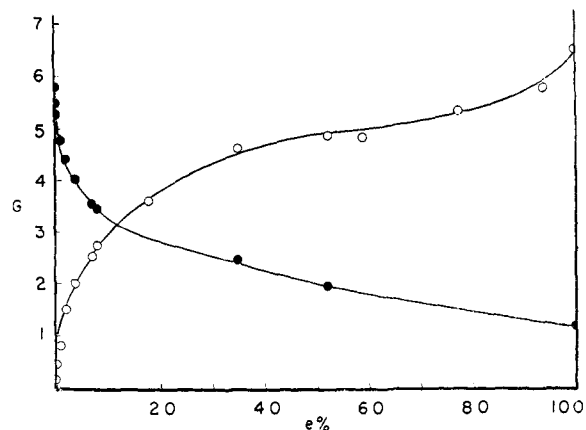


Fig. 4.—Yields per 100 e.v.: ● H<sub>2</sub> and ○ HCl vs. electron % *n*-propyl chloride in cyclohexane.

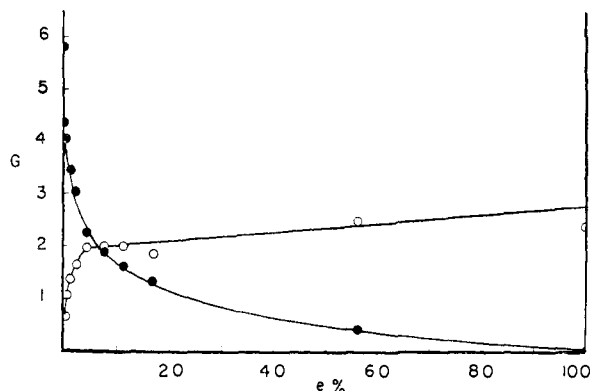


Fig. 5.—Yields per 100 e.v.: ● H<sub>2</sub> and ○ CO<sub>2</sub> vs. electron % benzyl acetate in cyclohexane.

the total  $G(\text{H}_2)$ : one due to thermal H-atoms, another due to hot H-atoms and the third molecular. The decrease  $\Delta G(\text{H}_2) = -2.0$  which results from adding iodine is matched by nearly equal  $G(\text{HI})$ . We consider this component of  $G(\text{H}_2)$  to arise by hydrogen abstraction from cyclohexane by thermal hydrogen atoms. This conclusion is supported qualitatively by decreases in both  $G(\text{C}_{12}\text{H}_{22})$  and  $G(\text{C}_6\text{H}_{10})$  caused by added iodine. The combined change in these two yields corresponds to  $\Delta G(\text{C}_6\text{H}_{11}) \cong -4.8$ , assuming that the only effect of iodine upon cyclohexyl radicals is to prevent combination-disproportionation by converting them to  $\text{C}_6\text{H}_{11}\text{I}$ . This interpretation is also supported by the observed ratio  $\Delta G(\text{C}_{12}\text{H}_{22})/\Delta G(\text{C}_6\text{H}_{10})$  which is 2.4 here and 2.2 in the vapor phase.<sup>14</sup> Cyclohexene does not form by this reaction alone, and we must use the residual  $G(\text{C}_{12}\text{H}_{22}) = 0.3$  in cyclohexane with 0.04 *M* iodine as a measure of radical reactions (within spurs) which have not been fully inhibited. By a short extrapolation, using the residual bicyclohexyl and the measured ratio of combination to disproportionation, we estimate that the unscavenged cyclohexyl radicals represent an additional 0.9  $\text{C}_6\text{H}_{11}$  per 100 e.v. or a corrected total initial yield  $G^0(\text{C}_6\text{H}_{11}) = 4.8 + 0.9 = 5.7$ . Of this amount we find part matched by  $G(\text{C}_6\text{H}_{11}\text{I}) = 3.7$ . The difference,

(14) P. W. Beck, D. V. Kniebes and H. E. Gunning, *J. Chem. Phys.*, **22**, 672 (1954).

amounting to  $5.7-3.7 = 2.0$ , matches the expected interference of iodine in reaction 3a



The empirical relation observed between  $G(\text{H}_2)$  and  $(\text{I}_2)$ , which was mentioned previously, can be attributed to the competition of reactions 3a and 3b



for which expression 4 is readily obtained

$$\frac{1}{G(\text{H}_2)} = \frac{1}{G^0(\text{H})} + \frac{k_{3a}(\text{C}_6\text{H}_{12})}{G^0(\text{H})k_{3b}(\text{I}_2)} \quad (4)$$

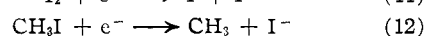
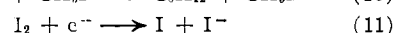
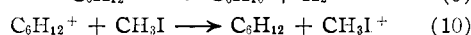
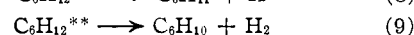
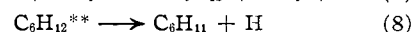
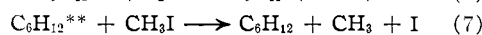
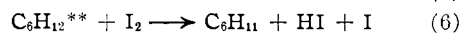
By minor rearrangement and comparison with the constants of the empirical equation we find for the initial yield  $G^0(\text{H}) = 2.0$  and  $k_{3a}/k_{3b} = 2.6 \times 10^3$ . From Schuler's observation that  $3 \times 10^{-3} M$  iodine depresses  $G(\text{H}_2)$  by 50% of the limiting decrease,  $k_{3b}/k_{3a} = 2.7 \times 10^3$ . In order to scavenge at least 99% of the available H-atoms in cyclohexane, the iodine concentration must be greater than  $0.3 M$ . This measure of  $k_{3a}$  is consistent with photochemical measurements of the photolysis of hydrogen iodide in perdeutero 3-methyl pentane for which hydrogen iodide itself served as a scavenger. Reaction of hydrogen atoms with solvent and solute were measured from yields of HD and  $\text{H}_2$ .<sup>15</sup>

The calculated  $G^0(\text{H}) = 2.0$  should match  $G(\text{HI}) = 2.0$ , as it does. The discrepancy between cyclohexyl iodide and hydrogen iodide, *viz.*  $G(\text{C}_6\text{H}_{11}\text{I}) - G(\text{HI}) = 3.7 - 2.0 = 1.7$  we are constrained to attribute to reaction of hot (*viz.* high velocity) H-atoms. The partner radical is assumed to be  $\text{C}_6\text{H}_{11}$  and another is formed by H-abstraction or  $G(\text{hot-H}) = 0.5 \times 1.7$ . The yield of molecular hydrogen resulting from the hot reaction would not be measurably affected by  $0.04 M$  iodine. The combined  $G(\text{H}_2)$  from hot and thermal H-atoms is  $2.0 + 0.85$  and the remainder is considered to be "molecular," *viz.*  $G(\text{H}_2)_{\text{total}} - G(\text{H}_2)_{\text{hot}} - G(\text{H}_2)_{\text{thermal}} = 5.85 - 2.85 = 3.0$ . The expected matching yield of cyclohexene is not observed; after correcting for incomplete inhibition of disproportionation by iodine, there remains  $G(\text{C}_6\text{H}_{10})_{\text{corr.}} = 1.9 - 0.1 = 1.8$  and a deficit of unsaturation amounting to 1.2 expressed as  $\text{C}=\text{C}$ . If we consider pure cyclohexane, the difference  $G(\text{H}_2) - G(\text{C}_{12}\text{H}_{22}) - G(\text{C}_6\text{H}_{10}) = 1.25$  is unaltered. This unsaturated hydrocarbon may be cyclohexadiene,<sup>16,17</sup> which could account for the post-irradiative disappearance of hydrogen iodide. The residual  $G(\text{HI})$  falls to 0.27 three days after irradiation,<sup>10</sup> or  $\Delta G(\text{HI}) = -1.7$ , in rough agreement with the amount of (assumed) cyclohexadiene. We have found by test that neither cyclohexene nor hexene-1 contributes to the reaction involving loss of hydrogen iodide.

Added hydrogen iodide enhances the yield of hydrogen, amounting to  $\Delta G(\text{H}_2) = 1.0$  and Schuler's interpretation that the increment arises from energy transfer<sup>8</sup> is entirely plausible. We find an analogous effect in dilute solutions of methyl iodide in cyclohexane (also  $0.02 M$  in hydrogen

iodide), for which  $G(\text{H}_2) + G(\text{CH}_4) = 6.5$ . In cyclohexane-chloroform similarly  $G(\text{H}_2) + G(\text{HCl}) = 6.5$ . These data indicate that the corresponding yield of excited states is  $G(\text{C}_6\text{H}_{12}^*) = 0.75$ . No decomposition of  $\text{C}_6\text{H}_{12}^*$  is assumed.

The other major features of the concentration-dependent yields of products from solutions of iodine and methyl iodide in cyclohexane correspond roughly to concentration intervals 0-0.1%, 0.1-10% and 10-100%. Similar effects have been observed in solutions repeatedly and are therefore general rather than unique. The nearly linear dependence in the 10-100% interval suggests a simple dilution (or direct) effect and will not be considered further. If primary processes are reflected in the final results, and we assume this to be the case, then each of the other two intervals is to be correlated with one or more of the following reactions. Double asterisks denote excited states which do not have ionic precursors and are also distinguishable from the state  $\text{C}_6\text{H}_{12}^*$  previously postulated. Positive ion-molecule reactions of cyclohexane with itself or with methyl iodide are not considered because they do not occur to a measurable extent in the mass spectrometer.<sup>18</sup>



Reaction 5 is inconsistent with this and previous work<sup>8</sup> if the unquenched molecule decomposes by either 8 or 9. Reaction 6 cannot be important since  $G(\text{C}_6\text{H}_{11})$  was shown to be unaffected by addition of iodine. The effect of iodine on  $G(\text{H}_2)$  was fully accounted for by reaction with thermal H-atoms and, *over the same region of concentration*, the effect of methyl iodide was likewise explained, eliminating reactions 7 and 12 in the 0-0.1% range. The similarity of reactions 11 and 12 in the mass spectrometer (no activation energy and appreciable cross sections<sup>19,20</sup>) indicates that 11 is not involved either, nor would the observed formation of hydrogen iodide be expected as a consequence of this reaction. Reaction 10 would be allowed from a consideration of ionization potentials<sup>21</sup> alone. Considering, however, the marked similarity in the 0-0.1% range of methyl bromide and methyl iodide in depressing  $G(\text{H}_2)$  for cyclohexane and the impossibility of charge exchange between  $\text{C}_6\text{H}_{12}^+$  and  $\text{CH}_3\text{Br}^{21}$ , we eliminate reaction 10 in dilute solutions. Reaction 8 is not inconsistent with any of the available data in the 0-0.1% range of solute concentration and we postulate that  $G(\text{thermal H}) = 2.0$  and  $G(\text{hot H}) = 0.85$  are both associated with this step. It is plausible

(18) We are indebted to Drs. R. P. Pottier and L. P. Theard for these observations.

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

(20) M. A. Biondi and R. E. Fox, *Phys. Rev.*, **109**, 2012 (1958).

(21) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

(15) J. R. Nash, R. R. Williams, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **82**, 5974 (1960).

(16) A. C. Nixon and R. E. Thorpe, *J. Chem. Phys.*, **28**, 1004 (1958).

(17) L. S. Polak, *Doklady Akad. Nauk S.S.S.R.*, **119**, 117 (1958).

that the excited state is repulsive since even large concentrations of methyl iodide have little or no effect on the corresponding  $G(\text{HI}) = 2.0$  (see Fig. 1). The assumed  $G(\text{hot H}) = 0.85$  must be accompanied by a rather greater yield of thermalized H-atoms.<sup>22</sup> It is quite plausible that  $G(\text{H-atom}) = 2.0$  is the thermalized component of an energetic decomposition from the repulsive state just mentioned for which the yield of excited states is  $G(\text{C}_6\text{H}_{12}^{**}) = 2.85$  and  $\text{H}_2(\text{thermal})/\text{H}_2(\text{hot}) = 2.4$ . The combined yield of excited states becomes  $G(\text{C}_6\text{H}_{12}^*) + G(\text{C}_6\text{H}_{12}^{**}) = 3.60$ .

To explain the effect upon molecular hydrogen of 0.1–10% methyl iodide only reaction 10 or 12 remains. To this we might add for generality reaction 13 to produce still another excited state with

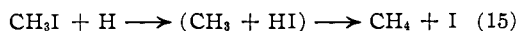


the possibility of reactions analogous to 7 and 9. Molecular hydrogen, with the accompanying cyclohexene and unidentified unsaturate, is attributed to a branching decomposition of  $\text{C}_6\text{H}_{12}^{***}$ . This appears to be required to account for the constant ratio  $G(\text{H}_2)/G(\text{C}_6\text{H}_{10})$  over a range of concentration of methyl iodide. If the two unsaturated hydrocarbons resulted from independent reactions, solutes should change them disproportionately.

Even at higher concentrations of methyl iodide, a comparison of Figs. 1 and 2 shows that hydrogen arises almost exclusively from cyclohexane and that the dependence of  $G(\text{H}_2)$  upon the concentration of methyl iodide is the same whether iodine or hydrogen iodide is the second solute. The product methane in Fig. 1 is not attributable to the stationary state reaction 14 since  $(\text{I}_2) \gg (\text{HI})$ . It



can be accounted for by the diffusion-controlled reaction 15, where parentheses enclose neighboring



particles, since  $G(\text{CH}_4)$  is unaffected by a 30-fold change in  $(\text{I}_2)$  at or below 0.1 mole %<sup>8</sup> but is decreased by somewhat higher concentrations of iodine.<sup>23</sup> The combined yield  $G(\text{HI}) + G(\text{CH}_4) = 2.0$  is almost unchanged by 2–35% of methyl iodide, and it agrees with  $G(\text{H}) = 2.0$ , as measured by iodine, which further supports reaction 15. Since the observed  $G(\text{H}_2)$  decreases markedly over the same concentration region, it is clear that the primary processes forming H and  $\text{H}_2$  are not coupled. On the other hand, Fig. 2 shows that the measured  $G(\text{H}_2)$  and  $G(\text{CH}_4)$  are precisely complementary. Such an effect in itself could arise by any of several mechanisms since the only requirement for complementarity is a one-for-one substitution of methyl iodide for cyclohexane in an ionic or excitation reaction sequence.

Our working hypothesis, mentioned previously, is that addition of organic halides to cyclohexane would provide evidence for electron attachment in irradiated mixtures. We now postulate that the effects just discussed, for the 0.1–10% interval,

(22) An efficient hot H-atom reaction producing HD results from photolysis at 2537 Å. of hydrogen iodide in liquid perdeutero-3-methylpentane for which  $\text{HD}(\text{thermal})/\text{HD}(\text{hot})$  is approximately 3; ref. 15.

(23) H. A. Gillis, R. R. Williams, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 17 (1961).

are to be correlated with reaction 12. The possibility of charge exchange by step 10 is not excluded, either as occurring independently of 12 or as being promoted by 12, since electron attachment would necessarily increase the time required for charge neutralization. An alternative consequence of 12 which can account for the observed effects is the neutralization of the ion pair



It is likely that a decrease of 3.2 e.v. in the potential energy of the ion pair, corresponding to the electron affinity of the iodine atom, together with the possibility of gradual dissipation of the diminishing potential energy of the approaching ion pair, would leave insufficient energy for decomposition or reaction of the products of neutralization.

If the effect under consideration in cyclohexane-methyl iodide is due to electron attachment, Fig. 2 indicates that  $G(e^-) = 2$  provided every event 12 ultimately yields one  $\text{CH}_4$ . It is very likely that appreciable recombination occurs between  $\text{CH}_3$  and I and the yield of electrons may easily be as great as 3. It can only be said that the permitted  $G(e^-)$  is not implausible. It is more important now to consider qualitative corroborative evidence in support of the hypothesis for electron attachment in comparable mixtures.

The irradiation of benzene-methyl iodide is of interest since the results,<sup>24</sup> under otherwise comparable conditions, are strikingly similar to those in Fig. 2. The charge exchange process 17 is not



allowed (in the gas) while electron attachment should occur as readily in one environment as the other. Also, the 2537 Å. photosensitized decomposition of ethyl iodide in benzene attains its limiting yield at much lower concentrations than does its gamma-induced decomposition.<sup>24</sup> This indicates that the effect being considered in the 0.1–10% interval is not due to energy transfer in either system.

Additional confirmation has been obtained by Dr. J. R. Nash<sup>25</sup> who observed absorption bands at 3800–3900 Å. in gamma-irradiated hydrocarbon glasses containing ~ 1% ethyl iodide or ethyl bromide but none for ethyl chloride. These absorption bands correspond to two of those reported by Grossweiner and Matheson<sup>26</sup> at 3700, 3500 and 3400 Å. from the flash photolysis of aqueous  $\text{X}^-$  which they assigned to  $\text{I}_2^-$ ,  $\text{Br}_2^-$  and  $\text{Cl}_2^-$ , respectively. Failure to find absorption in the glass containing ethyl chloride<sup>25</sup> is consistent with an appearance potential of 10 e.v. for  $\text{Cl}^-$  whereas  $\text{I}^-$  and  $\text{Br}^-$  have appearance potentials of zero, all from methyl halides.<sup>19</sup>

The results for cyclohexane-chloroform mixtures are qualitatively similar to the preceding (see Fig. 3), but the electron energy threshold for  $\text{Cl}^-$  formation is unknown. The dependence of  $G(\text{HCl})$  in this system upon halide concentration does correspond closely with results recently obtained for

(24) Mr. William Van Dusen, unpublished results, this Laboratory.

(25) Unpublished results, this Laboratory.

(26) L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, **61**, 1689 (1957).

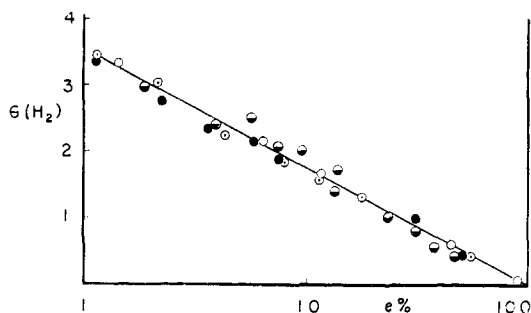
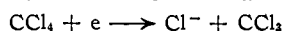


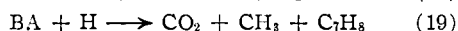
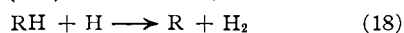
Fig. 6.—Yield per 100 e.v. of  $H_2$  vs. electron per cent. additive in cyclohexane: ●, methyl iodide; ○, chloroform; ◐, benzyl acetate; ◑, benzene.

cyclohexane-carbon tetrachloride.<sup>27</sup> The threshold for dissociative resonant electron attachment by  $CCl_4$  is 0.20 e.v.<sup>28</sup> The effect of chloroform is therefore considered to be analogous to that of methyl iodide. They differ, of course, in respect to their reactivity with H-atoms and in respect to the secondary reactions of the  $Cl^-$  and  $I^-$  atoms.



The results for cyclohexane-*n*-propyl chloride (see Fig. 4) differ somewhat from the preceding, indicating less efficient reactions. The appearance potential for  $Cl^-$  from *n*- $C_3H_7Cl$  has not been reported but for the homologous  $CH_3Cl$  it is  $10 \pm 1$  e.v.<sup>19</sup> The results are consistent with a rather inefficient dissociative electron attachment.

The results for cyclohexane-benzyl acetate (Fig. 5) resemble those of Figs. 2 and 3 as regards  $G(H_2)$  but differ as regards the products characteristic of the second component. The results suggest that  $CH_4$  and  $CO_2$  arise from the decomposition of acetoxy free radicals, which is a very efficient process.<sup>29</sup> The limiting yield  $G(CO_2) = 2$ , together with the dissimilarities relative to other systems, indicates involvement of H-atoms only. If we assume a simple competition between cyclohexane (RH) and benzyl acetate (BA) for H-atoms, then



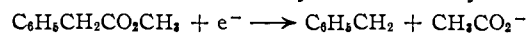
By stationary state kinetics we find the relation<sup>20</sup>

$$\frac{1}{G(CO_2)} = \frac{\text{const.}}{(BA)} + \frac{1}{G^0(H)} \quad (20)$$

where  $G^0(H)$  is the initial yield of H-atoms. The results are fully consistent with equation 20 and give  $G^0(H) = 2.0$  which further supports this interpretation. We are not committed to any detailed mechanism, but it seems more likely that the H-atom would add in *para*-position to give  $\text{H} \begin{array}{c} \text{H} \\ | \\ \text{C}_6\text{H}_4 \\ | \\ \text{H} \end{array} = \text{CH}_2$  than that it would directly displace acetoxy, giving toluene.

The preceding mechanism and the absence of complementarity between  $G(CO_2)$  and  $G(H_2)$  in Fig. 5 are consistent with the interpretation of Fig. 1 as regards the independence of  $G(H)$  and  $G(H_2)$ . The interpretations must differ with respect to dissociative electron attachment, since

the reaction would necessarily be followed by charge

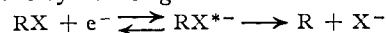


neutralization and subsequent decomposition of acetoxy radicals. Since  $G(CO_2)$  already has been fully accounted for and since  $\Delta G(H_2)$  and  $\Delta G(CO_2)$  are not coupled, the preceding reaction cannot be involved. There does appear to be another mode of decomposition since MacLachlan<sup>5</sup> found  $G(-B.A.) = 3.1$  in the 0.1 *M* solution in cyclohexane.

Any further attempt to account for the data of Fig. 5 must also take into consideration their evident similarity to the results of Burton, *et al.*,<sup>30</sup> for cyclohexane-benzene. This comparison is facilitated by plotting  $G(H_2)$  vs.  $(\log \% \text{ additive})$  in Fig. 6 and including for comparison other data from the present study. A logarithmic scale of concentration was chosen to expand the region of low concentrations; the linearity is considered to be accidental. We are forced to conclude that the similarity of results for systems with added halides to those for systems with added aromatics must also be accidental, since there is no plausible explanation. The similarity of effects on  $G(H_2)$  of added benzene and benzyl acetate is plausible and, if correct, permits us to compare these data with those of Berry and Burton<sup>31</sup> for luminescence of  $10^{-3}$  *M* *p*-terphenyl in gamma irradiated cyclohexane-benzene mixtures, for which they found a nearly linear dependence upon composition. The dissimilarity of the concentration dependences of the two phenomena suggests that they do not both involve energy transfer from cyclohexane to benzene as a controlling factor.

Whether or not energy transfer contributes to the decrease in yield of molecular hydrogen by addition of benzyl acetate or benzene to cyclohexane, it is likely that positive charge transfer will do so. Another possible example of a similar effect is shown by chloroform-benzene,<sup>32</sup> for which either  $CHCl_3^+$  or  $CHCl_2^+$  is allowed to exchange charge with  $C_6H_6$ . Additional evidence bearing on charge exchange is needed and studies are in progress.<sup>24,27</sup>

Finally, the present interpretation leads to the conclusion that if electron attachment cross-sections approximate gas kinetic cross-sections, then the electron has a very limited domain. Electron attachment then appears to occur within the first or second coordination sphere. This is rather improbable and we must consider the alternative possibility that dissociative electron attachment may be uniformly inefficient in the liquid state. Such a result might arise from a cage effect, enhanced by solvation resulting from ion-induced dipole forces. The solvent shell is contracting, rather than expanding, immediately following attachment by  $RX$  to give an excited ion



The reverse process will become impossible after a rather small initial increment in the separation of  $R - X^-$ . Considering, however, that the mean time for electron detachment in  $RX^{*-}$  may be

(27) Mr. John Roberts, work in progress, in this Laboratory.

(28) W. M. Hickham and D. Berg, *J. Chem. Phys.*, **29**, 517 (1959).

(29) J. R. Nash, W. H. Hamill and R. R. Williams, Jr., *J. Phys. Chem.*, **60**, 823 (1956).

(30) M. Burton, J. Chang, S. Lipsky and M. P. Reddy, *Radiation Research*, **8**, 203 (1958).

(31) P. J. Berry and M. Burton, *J. Chem. Phys.*, **23**, 1969 (1956).

(32) I. Bouby and A. Chapiro, *J. chim. phys.*, **52**, 645 (1955).

only  $10^{-15}$  sec., the efficiency of the forward process may be appreciably less than unity.

**Acknowledgment.**—The authors are indebted to Professor John L. Magee for helpful discussions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA]

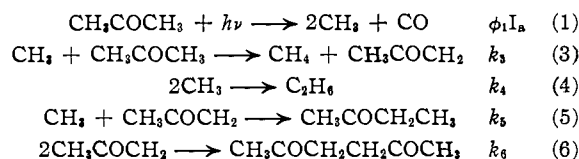
## The High Temperature Photolysis of Acetone

BY R. K. BRINTON

RECEIVED OCTOBER 6, 1960

The photolysis of acetone in the temperature range 200–475° has been investigated. Rates of formation of methane, ethane, ethylene, carbon monoxide, methyl ethyl ketone, ketene, methyl vinyl ketone and 2,5-hexanedione have been determined quantitatively. Methane formation is consistent with the mechanism  $\text{CH}_3 + \text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_4 + \text{CH}_2\text{COCH}_2$ . However, the ratio  $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}(\text{A})$  was found to be strongly dependent on acetone concentration (A) and light intensity, especially at higher temperatures which is contrary to evidence previously reported. The kinetics of another ethane reaction,  $\text{CH}_3 + \text{CH}_2\text{COCH}_2 \rightarrow \text{C}_2\text{H}_6 + \text{CO} + \text{CH}_3$  is examined as an explanation for such a behavior. The production of ketene is in agreement with the decomposition of the acetyl radical,  $\text{CH}_3\text{COCH}_2 \rightarrow \text{CH}_2\text{CO} + \text{CH}_3$ , whose activation energy is ca. 41 kcal. ( $E_7 - 1/2E_8$ ). Possible reactions responsible for ethylene formation and their correspondence to kinetic data are discussed.

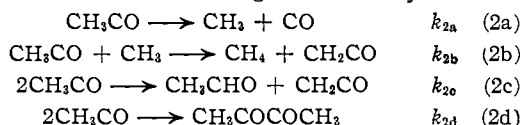
The photolysis of acetone at temperatures below 300° has been studied extensively<sup>1</sup> and in the range 100–300° may be explained satisfactorily by the mechanism.



Below 100° the simplified primary process 1 must be expanded to include the additional primary step

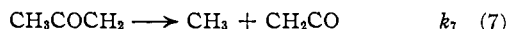


and reactions involving the acetyl radical<sup>2</sup>



account for the biacetyl, ketene and acetaldehyde found in the low temperature photolysis. The relative abundance of (1) and (1a) is certainly wavelength dependent<sup>3</sup> and perhaps temperature dependent, but above 100° the life of the acetyl radical formed by (1a) is short enough so that processes 1, 1a and 2a may be approximated quite well by (1) alone, and the reactions involving acetyl radical are no longer important.

Above 300° the photolysis is complicated by the production of ketene, probably formed by the decomposition of acetyl radical,  $\text{CH}_3\text{COCH}_2(\text{Ac})$



as well as ethylene whose mode of formation has not been satisfactorily explained. The investigations<sup>4</sup> of the photolysis above 300° are not ex-

tensive and are somewhat qualitative in nature. In the present study the rates of production of ketene (K), methyl ethyl ketone (MEK), 2,5-hexanedione ( $\text{Ac}_2$ ), ethylene, methane and ethane have been determined quantitatively in order to test the validity of the total photolysis sequence, (1) through (7), in the temperature region above 300°. Of special interest is the kinetic treatment of reactions 5, 6 and 7 which have not been examined previously in a quantitative fashion.

### Experimental

The photolyses were carried out in a 31 mm. diameter by 249 mm. long cylindrical fused silica cell (189 cm.<sup>3</sup> volume) surrounded by a 290 cm. aluminum block furnace whose ends were covered by 2 mm. thick Vycor glass plates to minimize cooling of the cell windows. The temperature of the furnace was controlled to  $\pm 0.3^\circ$  by a proportional amplifier heater control using a thermistor sensing element. In order to limit the percentage decomposition of the acetone to about 3% and yet obtain sufficient products for analysis, a one liter bulb and a 500 ml. toeppler pump were included in the photolysis system (total system volume = 1572 cm.<sup>3</sup>). At intervals during the photolysis (5–7 times) the radiation was interrupted and the total acetone in the system collected in the 1 liter bulb by use of the toeppler pump. After a mixing period the acetone was expanded into the cell and the irradiation resumed. The photolysis system and the vacuum system including gas burets and auxiliary apparatus for gas analysis was all glass with mercury check valves in all locations in contact with the products of the photolyses.

A B.T.H. ME/D 250 watt high pressure mercury arc operated on a stabilized a.c. source was used in all experiments. The Corning 9-53 Vycor plates used on the ends of the furnace, the self absorption of the lamp in the 2500 Å. region and the long wave length absorption limit of acetone restricted the effective wave length to  $\lambda\lambda$  2800–3300 Å. The light beam, which completely filled the cell in all experiments, was well collimated by use of quartz optics. Variation in the light intensity was accomplished by use of neutral density filters of chromel on fused silica plates.

The quantum yield determinations were made in the same system using acetone photolysis at 150° as an actinometer. A photolysis at the appropriate temperature was made directly preceding or following the actinometry. The amount of light absorption of the comparison experiment was made identical by adjusting the pressures so that equal percentage absorption was achieved. These percentage absorptions were previously determined by measurements with a 935 photocell and galvanometer measuring circuit. Pressures of the high temperature photolyses were always somewhat greater than the corresponding actinom-

(1) (a) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954, pp. 330–340. (b) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **18**, 1097 (1950).

(2) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 47 (1955).

(3) D. S. Herr and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **62**, 2052 (1940).

(4) (a) R. C. Ferris and W. S. Haynes, *ibid.*, **72**, 893 (1950); (b) E. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 993 (1953); (c) L. Mandelcorn and E. W. R. Steacie, *Can. J. Chem.*, **32**, 331 (1954).