

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND.]

## The Mechanism of Hydrogen Formation in the Radiolysis of Cyclohexane and Other Hydrocarbons<sup>1</sup>

BY SAM Z. TOMA AND WILLIAM H. HAMILL

RECEIVED OCTOBER 11, 1963

The  $\gamma$ -radiolyses of liquid alkanes with and without added iodine and methyl iodide or olefins have been investigated. The systems and yields were:  $G(\text{H}_2)$ ,  $G(\text{CH}_4)$ , and  $G(\text{HI})$  in cyclopentane, *n*-hexane, 3-methylpentane, and 2,4-dimethylpentane, each containing  $2 \times 10^{-2} M$  iodine and up to 0.8 *M* methyl iodide;  $G(\text{c-C}_6\text{H}_8)$  and  $G(\text{c-C}_6\text{H}_9\text{I})$  in cyclopentane-methyl iodide;  $G(\text{c-C}_6\text{H}_{10})$ ,  $G(\text{c-C}_6\text{H}_{11}\text{I})$ , and  $G(\text{C}_{12}\text{H}_{22})$  in cyclohexane-methyl iodide-iodine;  $G(\text{H}_2)$ ,  $G(\text{HD})$ , and  $G(\text{D}_2)$  for 1% cyclohexene-*d*<sub>10</sub> in cyclohexane and 1.5% cyclohexene-*d*<sub>10</sub> in cyclopentane. Ultraviolet absorption of products was measured *in vacuo* for cyclohexane, cyclopentane, *n*-hexane, 0.05 *M* cyclohexene in cyclohexane, and 0.05 *M* cyclopentene in *n*-hexane at 20°, and for 0.1 *M* cyclohexene and 0.1 *M* cyclopentene in 3-methylpentane glass at -196°. The results are interpreted in terms of electron attachment and charge transfer as well as free-radical reactions. A yield of 0.5 molecule/100 e.v. or greater has been found in cyclohexane for an organic product not previously reported.

### Introduction

It has been commonly assumed that the yields of hydrogen from radiolysis of liquid saturated hydrocarbons can be accounted for by two types of process. The H atom component has been identified with the apparent limiting decrease in  $G(\text{H}_2)$  caused by certain additives, including iodine, several halides, and various unsaturates. The mechanism responsible for the observed effect has often been assumed to be simple scavenging of H atoms, with little or no supporting chemical evidence. The molecular hydrogen component has been established by complementarity.<sup>2-5</sup> It is unfortunately true that free radical scavengers can usually interfere in ionic processes by electron attachment, protonation, or simple positive charge exchange. In order to avoid complications, Jenkinson and Dyne used mixtures of cyclohexane-*d*<sub>12</sub> with several hydrocarbons.<sup>6</sup> The extrapolated  $G(\text{D}_2)$  from dilute solutions was always much less than  $G(\text{HD})$  and in  $\text{C}_6\text{H}_{12}$ - $\text{C}_6\text{D}_{12}$  systems iodine and benzene depressed both yields nearly proportionately. These facts do not fit the usual views of atomic and molecular yields of hydrogen.

Radiolysis of liquid cyclohexane has been studied extensively, but only Dyne and Stone<sup>7</sup> have reported a material balance, their achievement consisting of finding a larger  $G(\text{C}_6\text{H}_{10})$  than other investigators had reported.<sup>8</sup> Recent work<sup>9</sup> indicates that one or more organic products in significant yield have never been detected in the radiolysis of pure cyclohexane since post-irradiative addition of iodine produces  $G(\text{HI}) > 0.4$ .

These facts and recent advances in detecting ionic processes have induced us to re-examine the radiolysis of cyclohexane and to include examination of other hydrocarbons for comparison.

(1) This article is based on a thesis submitted by Sam Z. Toma in partial fulfillment of the requirements for the Ph.D. degree in the University of Notre Dame, June, 1963. The work was supported in part by the Radiation Laboratory of the University of Notre Dame, operated under contract with the United States Atomic Energy Commission.

(2) T. J. Hardwick, *J. Phys. Chem.*, **65**, 101 (1961).

(3) L. J. Forrestal and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 1535 (1961).

(4) J. R. Nash and W. H. Hamill, *J. Phys. Chem.*, **66**, 1097 (1962).

(5) R. H. Schuler, *ibid.*, **61**, 1472 (1957).

(6) W. M. Jenkinson and P. J. Dyne, *Can. J. Chem.*, **38**, 539 (1960); **39**, 2163 (1961).

(7) J. A. Stone and P. J. Dyne, *ibid.*, **39**, 2381 (1961).

(8) They reported  $G(\text{H}_2) = 5.5$ ,  $G(\text{C}_6\text{H}_{10}) \approx 3.27$ ,  $G(\text{C}_{12}\text{H}_{22}) \approx 1.95$ ,  $G(\text{cyclohexylhexene-1}) = 0.27$ .

(9) J. R. Roberts and W. H. Hamill, *J. Phys. Chem.*, **67**, 2446 (1963).

### Experimental

Only procedures differing from those reported previously<sup>3</sup> are described here.

**Materials.**—Saturated hydrocarbons were purified by one of the following methods: (i) Phillips pure grade reagents were scrubbed with sulfuric acid (97%) and passed through silica gel. (ii) Fisher spectrograde reagents were passed through a 5-ft. column (20 mm. i.d.) of silica gel and the first 200 ml. retained. (iii) Matheson Coleman and Bell spectral grade reagents were passed through silica gel. (iv) Matheson Coleman and Bell spectral grade reagents were treated with bromine and passed through silica gel. (v) Phillips research grade reagents were used as received.

Baker analyzed reagent grade methyl iodide was purified by distilling through a 60-cm. column packed with glass helices; the middle third fraction was retained. After distillation it was passed through a column packed with silica gel and stored over copper wire in the dark. Cyclohexyl and cyclopentyl iodides from K and K Laboratories were used as received.

K and K Laboratories research grade cyclohexene was passed through a column packed with aluminum oxide (top) and silica gel (bottom). The purity was checked by v.p.c. Eastman White Label grade cyclohexene was passed through silica gel column. Matheson Coleman and Bell cyclopentene was distilled from sodium mirror and passed through silica gel. Rascher and Betzold C.P. grade resublimed iodine was used as received.

Distilled water was passed through an ion exchange column. After brief boiling the water had a pH of 7.

**Sample Preparation.**—Samples of 20 ml. were used. When iodine was added, 0.5% of water was always included to prevent loss of hydrogen iodide by reaction with intermediates or products. The degassing procedure was identical with that for gas collection described below. The  $\gamma$ -radiation source has been described elsewhere.<sup>10</sup>

**Ultraviolet Absorption.**—Spectra of  $\gamma$ -irradiated samples (without exposure to air) were measured in a rectangular cell of fused silica using a Cary Model 14 spectrophotometer. The silica cell was connected through a graded seal with the Pyrex cell which was exposed to  $\gamma$ -radiation.

**Product Analysis.**—The measurement of hydrogen iodide in the radiolysis of saturated hydrocarbons containing dissolved iodine was performed with particular care. The procedure<sup>3</sup> was standardized to minimize random errors and to yield reliable measurements for the several micromoles of acid formed in the radiolysis of systems of interest.  $\text{CO}_2$  was eliminated by boiling before all titrations. The over-all reproducibility was better than 1%.

The microstill used for gas collection has been modified slightly. The condenser temperature was controlled by air passed through a cooled copper coil. Three pumping cycles at most were necessary to remove gases, which were analyzed by mass spectrometry. Analyses for all runs with one hydrocarbon were performed consecutively on the same day. Hydrogen and methane standards were used before and after each series. When  $\text{D}_2$  and HD were

(10) C. J. Hochandel, J. A. Ghormley, and M. Burton, *Nucleonics*, **13**, 74 (1955).

present, H<sub>2</sub> and D<sub>2</sub> standards were run before and after each analysis and HD sensitivity was taken as mean of the two.

### Results

Systems consisting of alkane with methyl iodide and dilute iodine are described in Tables I-III.<sup>11,12</sup> The results are qualitatively very similar for corresponding products. There are three striking regularities. Yields of hydrogen are nearly the same for all hydro-

TABLE I

RADIOLYSIS OF ALKANE-METHYL IODIDE-IODINE<sup>a</sup>

CH <sub>3</sub> I, mole/l.	G(H <sub>2</sub> )	G(CH <sub>4</sub> )	G(HI)	G(CH <sub>4</sub> + HI)
<i>n</i> -Hexane				
0	2.90 <sup>b</sup>	0.09	2.24	2.33
0.081	2.21	.33	1.78	2.11
.32	1.69	.50	1.70	2.20
.81	1.36	.59	1.53	2.11
3-Methylpentane				
0	2.44 <sup>c</sup>	0.15	2.00	2.15
0.081	1.70	.35	1.92	2.27
.32	1.39	.54	1.76	2.30
.81	1.13	.64	1.71	2.35
2,4-Dimethylpentane				
0	2.37 <sup>d</sup>	0.26	2.21	2.47
0.081	1.65	.49	2.15	2.64
.32	1.30	.60	1.92	2.52
.81	0.99	.68	1.81	2.49

<sup>a</sup> Dose =  $2.9 \times 10^{22}$  e.v./l. All solutions contain 0.02 M I<sub>2</sub>.

<sup>b</sup> Reported yields of H<sub>2</sub> for pure *n*-hexane are 5.1 ( $5.0 \times 10^{22}$  e.v./l.),<sup>11</sup> 5.0 ( $1.7 \times 10^{23}$  e.v./l.),<sup>12</sup> and 5.3 mol./100 e.v. ( $1.5 \times 10^{21}$  e.v./l.).<sup>2</sup> <sup>c</sup> In pure 3-methylpentane hydrogen yields of 3.4 ( $1.7 \times 10^{23}$  e.v./l.)<sup>12</sup> and 4.56 mol./100 e.v. ( $1.5 \times 10^{21}$  e.v./l.)<sup>2</sup> have been reported. In this work  $G(\text{H}_2)$  was 3.90 for pure hydrocarbon. <sup>d</sup> For pure 2,4-dimethylpentane hydrogen yields of 4.9 ( $1.7 \times 10^{23}$  e.v./l.)<sup>12</sup> and 4.19 ( $1.5 \times 10^{21}$  e.v./l.)<sup>2</sup> have been reported.

TABLE II

RADIOLYSIS OF CYCLOPENTANE<sup>a</sup>-METHYL IODIDE-IODINE<sup>b</sup>

CH <sub>3</sub> I, mole/l.	G(H <sub>2</sub> )	G(CH <sub>4</sub> )	G(HI)	G(C <sub>5</sub> H <sub>8</sub> )	G(C <sub>5</sub> H <sub>9</sub> I)	G(CH <sub>4</sub> + HI) <sup>c</sup>
0	5.25			2.92		
0	3.74	0.01	2.19	1.64	2.96	2.20
0.081	2.50	.28	1.84	1.23	2.23	2.12
.32	1.83	.45	1.82	1.07	1.85	2.27
.81	1.65	.59	1.68	0.93	1.60	2.27

<sup>a</sup> Phillips research grade cyclopentane was used for runs in which  $G(\text{C}_5\text{H}_8)$  and  $G(\text{C}_5\text{H}_9\text{I})$  alone were measured. For all others, cyclopentane was purified by method (i). <sup>b</sup> Solutions contain 0.02 M I<sub>2</sub> except for the first run. Dose was  $8.3 \times 10^{22}$  e.v./l. for  $G(\text{C}_5\text{H}_8)$  in pure cyclopentane,  $1.1 \times 10^{23}$  e.v./l. for separate runs in which only  $G(\text{C}_5\text{H}_8)$  and  $G(\text{C}_5\text{H}_9\text{I})$  were measured, and  $2.2 \times 10^{22}$  e.v./l. for all others. <sup>c</sup> The yield of "thermal H atoms" has been reported<sup>2</sup> as 3.06/100 e.v.

TABLE III

RADIOLYSIS<sup>a</sup> OF CYCLOHEXANE<sup>b</sup>-METHYL IODIDE-IODINE

CH <sub>3</sub> I, mole/l.	G(H <sub>2</sub> ) <sup>c</sup>	G(C <sub>6</sub> H <sub>10</sub> )	G(C <sub>12</sub> H <sub>22</sub> )	G(C <sub>6</sub> H <sub>11</sub> I)
0	5.44	2.69	1.61	
0	3.47	1.51	0.31	3.92
0.081	2.60	1.01	.21	2.82
.32	2.05	0.85	.14	2.37
.81	1.40	0.71	.08	1.97

<sup>a</sup> Dose was  $3.1 \times 10^{22}$  e.v./l. for the first run and  $5 \times 10^{22}$  e.v./l. for all others. Except for the first run, solutions contain  $6 \times 10^{-3}$  mole/l. of I<sub>2</sub>. <sup>b</sup> Cyclohexane was purified by method (ii). <sup>c</sup> Interpolated from Forrestal's measurements normalized to give  $G(\text{H}_2) = 5.44$  for pure cyclohexane (cf. ref. 3).

(11) J. Denhartog and P. J. Dyne, *Can. J. Chem.*, **40**, 1616 (1962).

(12) H. A. Dewhurst, *J. Phys. Chem.*, **62**, 15 (1958); *J. Am. Chem. Soc.*, **80**, 5607 (1958).

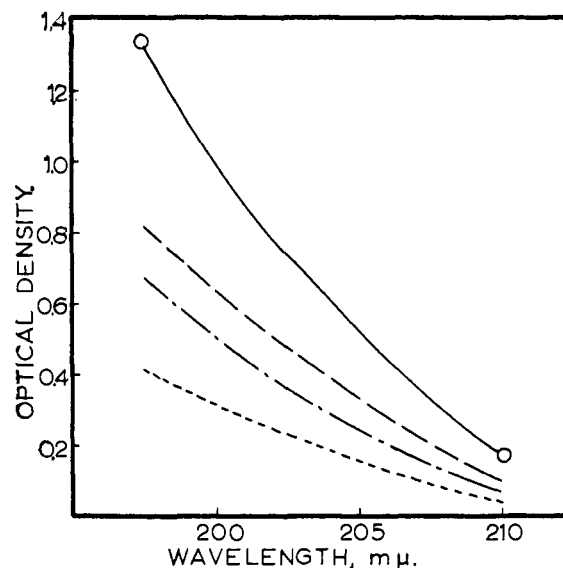


Fig. 1.—Ultraviolet absorption spectrum: —, observed of cyclohexane after a dose of  $9 \times 10^{21}$  e.v./l.; ---, calculated spectrum of cyclohexane due to a dose of  $9 \times 10^{21}$  e.v./l. in cyclohexane using v.p.c. analysis and previously determined extinction coefficients; - · - · -, observed spectrum of cyclohexane after a dose of  $4.5 \times 10^{21}$  e.v./l.; · · · · ·, calculated spectrum of cyclohexane due to a dose of  $4.5 \times 10^{21}$  e.v./l. in cyclohexane using v.p.c. analysis and previously determined extinction coefficients.

carbons at each concentration of methyl iodide when normalized to  $G(\text{H}_2)$  in 0.02 M iodine. Values of combined  $G(\text{CH}_4 + \text{HI})$  are all substantially equal to 2.2 at all concentrations of methyl iodide. The ratio of the yields of cycloolefin to cycloalkyl iodide is approximately the same for all solutions in cyclopentane (*ca.* 0.56) and for all solutions in cyclohexane (*ca.* 0.36).

Unsaturated hydrocarbons are often difficult to analyze by v.p.c. Thus, it was not possible to interpret readily the v.p.c. results for radiolysis of pure cyclopentane using silver nitrate-diethylene glycol and  $\beta,\beta$ -oxydipropionitrile columns, although it was evident that several products besides cyclopentene and bicyclopentyl were present with combined yields totaling about one. On the other hand, ultraviolet spectra of unsaturates are characterized by very large extinction coefficients at *ca.* 250 m $\mu$  for conjugated and  $< 210$  m $\mu$  for nonconjugated olefins.<sup>13</sup>

As nearly as could be determined by v.p.c. the radiolysis of pure cyclohexane (dose =  $4.6 \times 10^{22}$  e.v./l.) produced neither 1,3- nor 1,4-cyclohexadiene. Neither was there any ultraviolet absorption in the 250 m $\mu$  region although as little as  $10^{-5}$  M conjugated unsaturation could have been detected. The molar extinction coefficient of 1,4-cyclohexadiene is negligible in this spectral region<sup>13</sup> and a different approach was used. Addition of iodine following irradiation produced no benzene, while 1,4-cyclohexadiene was oxidized to benzene with 20% efficiency under similar conditions. The ultraviolet spectrum of irradiated cyclohexane maintained under vacuum appears in Fig. 1 where it can be seen that there is no conjugated diene absorption between 220–360 m $\mu$ . Vapor phase chromatographic analysis of this sample for cyclohexene demonstrated that much of the absorption in the 210 m $\mu$  region must be attributed to another unsaturate. These measure-

(13) A. Polgar and J. L. Jungnickel, "Organic Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1956.

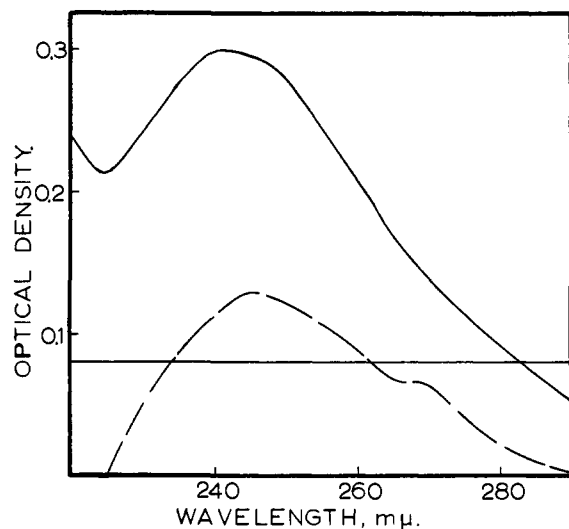


Fig. 2.—Spectra: —, observed spectrum of irradiated 0.05 *M* cyclohexene in cyclohexane after a dose of  $4.5 \times 10^{22}$  e.v./l.; ---, the observed spectrum on photobleaching the electron band formed in radiolysis of 0.1 *M* cyclohexene in 3-methylpentane glass at  $-196^\circ$ ; dose  $6.0 \times 10^{21}$  e.v./l.

ments were confirmed by v.p.c. and ultraviolet analysis of  $10^{-3}$  *M* cyclohexene in *n*-hexane. It is plausible to suppose that the extra unsaturation may be responsible for post-irradiation reaction with iodine.

When solutions of iodine in cyclohexane were irradiated and then extracted with aqueous thiosulfate solution, the organic layer absorbed strongly at 266 mμ. The anticipated absorption of cyclohexyl iodide in this region is much smaller than the observed value because of a small extinction coefficient (*ca.* 400 l./mole cm.).

Post-irradiative addition of iodine to pure cyclohexane liberates hydrogen iodide<sup>9</sup> and produces a new product with  $\lambda_{\max} \cong 270$  mμ. This absorption cannot be due to vicinal diiodides since they are easily decomposed and have small extinction coefficients. Conjugated olefins absorb in this region and have very large extinction coefficients ( $\sim 10^4$ ); 1,4- or 1,5-hexadiene were plausible products which could have been responsible for the observed effects. However, radiolysis of cyclohexane yielded a product with  $G \geq 0.5$  and a retention time (10-ft. silicic grease column at  $40^\circ$ ) between those of authentic 1,5- and 1,4-hexadiene. Bromine removes this product.

To determine whether radiolysis of cyclohexene or cyclopentene gives rise to conjugated unsaturation and to allow examination of the mechanism in some detail, alkane-alkene mixtures were irradiated and subsequently examined spectrophotometrically. The result for radiolysis of 0.05 *M* cyclohexene in cyclohexane at laboratory temperature after a dose of  $4.5 \times 10^{22}$  e.v./l. appears in Fig. 2. The result for radiolysis of 0.1 *M* cyclohexene in 3-methylpentane at  $-196^\circ$  is reported in full elsewhere.<sup>14,15</sup> In the low temperature run electrons were trapped by olefin producing a band with  $\lambda_{\max}$  1800 mμ; positive holes were partly trapped by olefin giving a second band with  $\lambda_{\max}$  725 mμ. Optical bleaching of trapped electrons destroyed cations to enhance the yield of species absorbing at  $\lambda_{\max}$  245 mμ. This band resembles that obtained by radiolysis

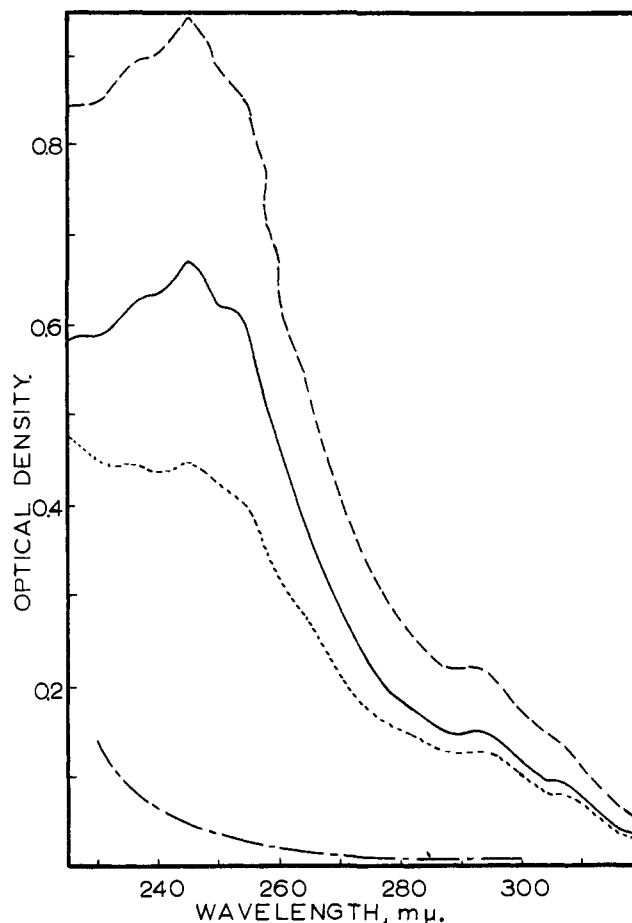


Fig. 3.—Ultraviolet absorption spectrum of irradiated cyclopentene in *n*-hexane: —, 0.1 *M* after a dose of  $5.6 \times 10^{22}$  e.v./l.; ---, 0.05 *M* after a dose of  $4.2 \times 10^{22}$  e.v./l.; ·····, 0.1 *M* after a dose of  $2.8 \times 10^{22}$  e.v./l.; - · - ·, pure *n*-hexane after a dose of  $5 \times 10^{22}$  e.v./l.

of the cyclohexane-cyclohexene solution at laboratory temperature and provides fairly direct evidence for the origin of the conjugated olefinic product.

Solutions of cyclopentene in *n*-hexane were irradiated at laboratory temperature and the ultraviolet absorption compared with irradiated pure *n*-hexane in Fig. 3. The large band approximates the spectrum of cyclopentadiene.<sup>13</sup>

The spectrum of 0.1 *M* cyclopentene in 3-methylpentane irradiated at laboratory temperature and a dose of  $4 \times 10^{22}$  e.v./l. appears in Fig. 4. The spectrum is substantially the same at  $-196^\circ$ . When a solution of the same composition was irradiated at  $-196^\circ$  there appeared bands at  $\lambda_{\max}$  1800 mμ due to solvated electrons and at  $\lambda_{\max}$  700 mμ due to olefin cations as well as a band at 230–250 mμ typical of conjugated unsaturation.<sup>14,15</sup> When the electron band was optically bleached, the 700 mμ band also disappeared by ion recombination and the 230–250 mμ absorption markedly increased. The increased absorption produced in this manner is represented by the lower curve of Fig. 4.

Irradiation of 0.1 *M* cyclohexene-*d*<sub>10</sub> in cyclohexane at  $6 \times 10^{22}$  e.v./l. gave  $G(\text{H}_2) = 3.44$ ,  $G(\text{HD}) = 0.29$ ,  $G(\text{D}_2) = 0.011$ . For 0.15 *M* cyclohexene-*d*<sub>10</sub> in cyclopentane,  $G(\text{H}_2) = 3.86$ ,  $G(\text{HD}) = 0.23$ , and  $G(\text{D}_2) = 0.008$ .

#### Discussion

The proposal that the component of  $G(\text{H}_2)$  not strongly suppressed by iodine in cyclohexane may be

(14) J. P. Guarino and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 777 (1964).

(15) We are indebted to Dr. J. P. Guarino for performing the low temperature experiments.

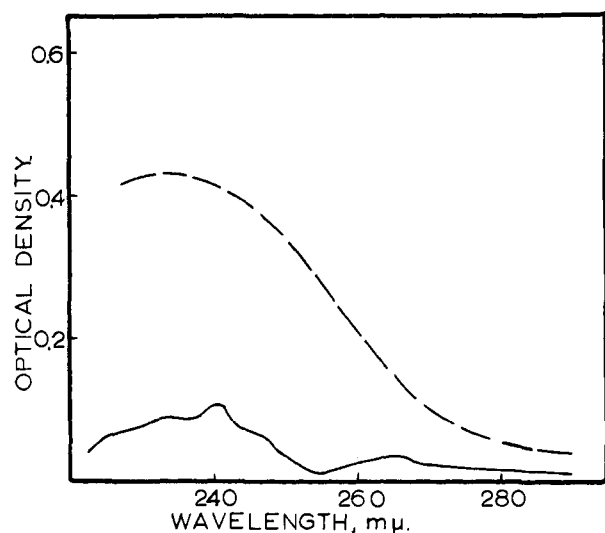
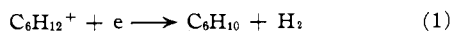
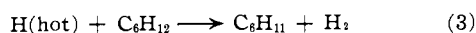
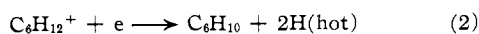


Fig. 4.—Ultraviolet spectrum of irradiated 3-methylpentane with 0.1 *M* cyclopentene: — — —, observed spectrum at room temperature after a dose, at room temperature, of  $3.8 \times 10^{22}$  e.v./l.; — — —, observed spectrum due to photobleaching of the electron band at liquid nitrogen temperature after a dose, at liquid nitrogen temperature, of  $6 \times 10^{21}$  e.v./l.

attributed to molecular elimination of hydrogen,<sup>3</sup> possibly following ion recombination, is clearly incon-

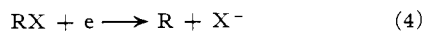


sistent with the small  $\text{D}_2/\text{HD}$  observed by Jenkinson and Dyne from  $\text{C}_6\text{D}_{12}$  in light hydrocarbons.<sup>6</sup> The quantitative relationship,  $-2\Delta G(\text{cycloolefin}) = -\Delta G(\text{cycloalkyl iodide})$ , which applies to the results in Tables II and III, in conjunction with the work cited, can be accounted for by a mechanism of the type



A completely parallel description evidently applies to the results for cyclopentane.

When the thermal component of  $G(\text{H}_2)$  in cyclohexane is suppressed by *ca.*  $10^{-2}$  *M* iodine, further addition of cyclohexene<sup>9</sup> continues to suppress  $G(\text{H}_2)$  while addition of methyl iodide (Table III and ref. 3) continues to depress the somewhat correlated  $G(\text{H}_2)$ ,  $G(\text{C}_6\text{H}_{10})$ , and  $G(\text{C}_{16}\text{H}_{11}\text{I})$  by removing a common precursor of these products.<sup>16</sup> We account for the effect of cyclohexene or benzene<sup>17</sup> in cyclohexane upon  $G(\text{H}_2)$  by positive charge exchange as well as H-atom scavenging. In rigid alkane media<sup>14</sup> containing cyclohexene or benzene both  $\text{C}_6\text{H}_{10}^+$  and  $\text{C}_6\text{H}_6^+$  are produced efficiently at solute concentrations of 0.1 mole % or more with a concentration dependence resembling that found in the present work. The effect of various alkyl halides to depress  $G(\text{H}_2)$  in excess of that due to H-atom scavenging has already been attributed to such processes<sup>8,9,17</sup> as



and this has now been confirmed in rigid media by observation of  $\text{I}^-$  from  $\text{CH}_3\text{I}$ ,<sup>18</sup> of  $(\text{C}_6\text{H}_5)_3\text{C}$  from triphenylmethyl chloride, and of  $\text{C}_6\text{H}_5\text{CH}_2$  from benzyl halides or acetate.<sup>19</sup> The dissipation of potential energy

(16) A related explanation was offered by Dyne and Jenkinson<sup>8</sup> to account for somewhat comparable effects of 6 mole % benzene and of  $5 \times 10^{-2}$  *M* iodine upon  $G(\text{H}_2)$ ,  $G(\text{HD})$ , and  $G(\text{D}_2)$  in  $\text{C}_6\text{D}_{12}$ - $\text{C}_6\text{H}_{12}$  mixtures.

(17) W. Van Dusen and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 1535 (1961).

(18) E. P. Bertin and W. H. Hamill, *ibid.*, **86**, 1301 (1964).

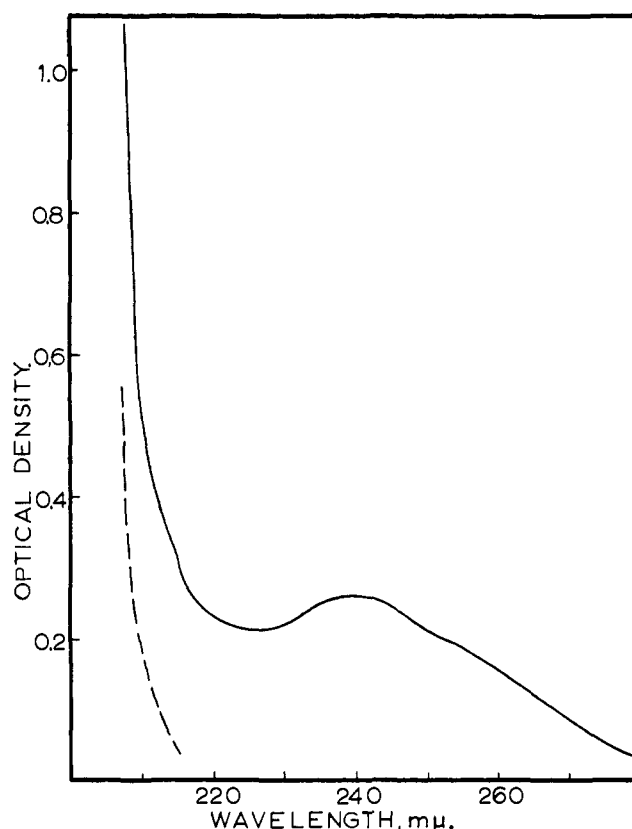
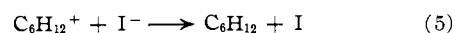


Fig. 5.—Ultraviolet absorption spectrum of irradiated cyclopentane: — — —, observed spectrum; — — —, calculated spectrum of cyclopentene from v.p.c. analysis and previously determined extinction coefficients.

following electron attachment due to the electron affinity of X, together with the depression of charge recombination energy arising from polarization of the liquid dielectric, totaling 5–6 e.v.,<sup>20</sup> apparently suffice to prevent decomposition by ion recombination,<sup>21</sup> *i.e.*



There is an additional effect to be considered. Positive ions produced by electron impact *in vacuo* are frequently excited.<sup>22</sup> When ion–electron recombination occurs within  $10^{-13}$  sec.,<sup>23</sup> the process will then be particularly exothermic. Attachment of the electron would be expected to increase the recombination time to more than  $10^{-10}$  sec., permitting electronic and vibrational relaxation and providing opportunity for ion–molecule reactions to occur.

Another consequence of formation of positive ions in excited states is to promote positive charge exchange which could not occur for an ion in its ground state. Resonance charge exchange between molecular species  $\text{M}^+$  and  $\text{M}$  is very improbable because of Franck–Condon restrictions.<sup>24</sup> Between different species, even with a qualitatively favorable but small difference of ionization potentials, charge exchange cannot occur from the ion in its ground state because of these entropy effects. Excitation of the ion can increase its free energy enough to supply this deficit.

(19) J. Ward, M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *Discussions Faraday Soc.*, in press.

(20) D. R. Kearns and M. J. Calvin, *J. Chem. Phys.*, **34**, 2026 (1960).

(21) P. R. Geissler and J. E. Willard, *J. Am. Chem. Soc.*, **84**, 4627 (1962).

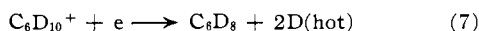
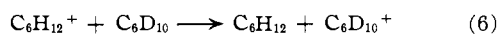
(22) C. E. Melton and W. H. Hamill, unpublished results.

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

(24) W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

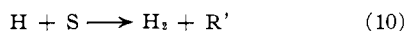
If positive charge exchange occurs in liquid mixtures, whether from an excited or ground state ion, and if reaction 2 describes correctly the fate of  $C_6H_{12}^+$ , then in mixtures of cyclopentane ( $I = 10.53$  e.v.)<sup>25</sup> and cyclohexane ( $I = 9.88$  e.v.) it must be expected that  $G(H_2, \text{hot})/G(C_6H_{10}) = 2$ . The extrapolated yield of HD, taken as a measure of hot hydrogen, for  $C_6D_{12}$ - $C_6H_{10}$  mixtures, was 10 molecules/100 e.v.<sup>11</sup> In the present work a similar extrapolation based upon measurement of  $G(C_6H_{10})$  from 10.4 electron % cyclohexane in cyclopentane ( $G_{\text{extrap}} = G_{\text{obsd}}/\text{electron fraction } C_6H_{12}$ ) gave 4.8 molecules/100 e.v. From 4.9 electron % cyclohexane in cyclopentane containing  $10^{-2} M$  iodine  $G(c-C_6H_{10})_{\text{extrap}}$  was 4.2.

It may be expected that positive charge exchange will occur between alkane and alkene. Radiolysis of dilute cyclohexene- $d_{10}$  in cyclohexane or cyclopentane produced much more HD than  $D_2$ . Solutions were too dilute to warrant extrapolation to pure cyclohexene- $d_{10}$ , but values of  $G(HD)$  were much larger than corresponds to direct effects. The results in Fig. 2 show that a conjugated unsaturate is produced under the conditions of these experiments, and the run at  $-196^\circ$  (Fig. 2) shows that the same, or a very similar, product arises from cyclohexene cation-electron recombination. Combining both sets of experiments indicates that



followed by reaction 3. The radiolysis of dilute solutions of cyclopentene ( $I = 9.01$  e.v.) in *n*-hexane ( $I = 10.08$  e.v.) also shows the formation of a conjugated unsaturate presumed to be cyclopentadiene since the spectra agree<sup>26</sup> (*cf.* Fig. 3). Based upon the reported extinction coefficient of cyclopentadiene (2500 l./mole cm. at 244  $m\mu$ ),  $G(C_5H_6) = 0.6$  in 0.05 *M* cyclopentene. Again it has been shown that cyclopentene in 3-methylpentane glass at  $-196^\circ$  forms both anions and cations and that photodetached electrons react with cations to product a product having an optical absorption similar to that found for runs at room temperature.<sup>14,15</sup>

Hardwick<sup>2,27</sup> has employed alkenes as scavengers (S) for H-atoms in alkanes (RH), assuming that the only significant reactions were



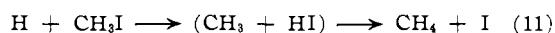
Yields of atomic and molecular hydrogen were then deduced by conventional kinetic analysis. The unimportance of step 10 for olefins as scavengers has been shown by several investigators for ethylene, propylene, butylene, and several other olefins.<sup>28-31</sup> It must be concluded that reaction 10 is unimportant. The formation of HD from cyclohexene- $d_{10}$  as solute in the present work is therefore to be interpreted as due almost entirely to the consequence of charge exchange proc-

esses which do not lend themselves to stationary-state kinetics.

For solutions of iodine in cyclohexane it had appeared from previous work<sup>3</sup> that  $G(H_2)$  and  $G(HI)$  were complementary. The limiting  $G(HI)$  served as a measure of the yield of thermal H atoms. Since it is now clear that a significant part of  $G(HI)$  arises from a post-irradiative reaction, the problem requires re-examination. For an analogous system, 0.02 *M* iodine in cyclopentane was found in this work to depress  $G(H_2)$  from 5.25 to 3.74 while  $G(HI)$  was 2.19. From other work<sup>4</sup> it may be estimated that in 0.02 *M* iodine  $G(I^-)$  will be about 0.5. According to analogs of reactions 2 and 3 this will prevent the formation of one molecule of hydrogen per 100 e.v. The adjusted  $G(H_2)$  for thermal hydrogen becomes  $1.51-1.0 \cong 0.5$ , and any correspondence with  $G(HI)$  is entirely lost. In a similar way, 0.02 *M* iodine produced a decrease of 1.46 in  $G(H_2)$  and a value of 2.00 for  $G(HI)$  in 3-methylpentane. Allowing for the effect of  $G(I^-) \cong 0.5$  gives an estimated  $G(H_2, \text{thermal}) = 0.46$ .

When increasing amounts of methyl iodide are added to any of these hydrocarbon solutions,  $G(CH_4)$  increases at first and then becomes constant while  $G(HI)$  decreases and also becomes constant. The sum of the two yields is constant over a range of solute concentration within any one system. If  $\Delta G(CH_4)$  relative to the solution of iodine alone is combined with  $G(HI)$ , this sum is *ca.* 2.2 for all hydrocarbons studied in this work and also for cyclohexane.<sup>3</sup>

The diffusion controlled reaction



leading to  $CH_4$  has been described<sup>8</sup> and is completely consistent with present results. It appears that  $I_2$  and  $CH_3I$  are approximately equally reactive toward H atoms<sup>5,32</sup> and it follows that in solutions containing 0.02 *M* iodine and 0.81 *M* methyl iodide, substantially all H atoms react with the latter. We know from photochemical studies of diffusion-controlled reactions between radical pairs that geminate recombination or re-encounter is *ca.* 80% probable (for  $C_2H_5I$ ) even after an energetic primary dissociative act.<sup>33</sup> Using the same efficiency for reaction 11 we obtain a tentative value of  $G(H, \text{thermal})$  in cyclopentane  $0.59/0.80 = 0.7$ . Data for other paraffins lead to comparable values. The discrepancy between these low values of thermal H-atom yields and the higher values deduced from  $G(HI)$  using iodine may be due in part to post-irradiative reactions and in part to reactions of iodine with reactive intermediates. Thus, reaction of iodine with alkyl radical to give alkene and hydrogen iodide is slightly endothermic and does not occur,<sup>33</sup> but reaction with an allylic radical to yield conjugated diene may be exothermic and efficient.

Reliable measurement of  $G(H, \text{thermal})$  is a more difficult task than it first appeared to be. Of the various reagents which have been tested, ethylene seems to be least objectionable since it neither attaches electrons<sup>14</sup> nor is it likely to undergo positive charge exchange. In addition it reacts with H atoms almost exclusively by addition in the gas phase.<sup>30,31</sup> Holroyd<sup>34</sup>

(25) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1962).

(26) E. D. Bergmann, "Organic Electronic Spectral Data," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1960, p. 47.

(27) T. J. Hardwick, *J. Phys. Chem.*, **66**, 291 (1962).

(28) H. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **14**, 57 (1946).

(29) K. R. Jennings and R. J. Cvetanovic, *ibid.*, **35**, 1233 (1961).

(30) H. Okabe and J. McNeisby, *ibid.*, **36**, 601 (1962).

(31) K. Yang, *J. Am. Chem. Soc.*, **84**, 719 (1962).

(32) H. A. Gillis, R. R. Williams, and W. H. Hamill, *ibid.*, **83**, 17 (1961).

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

used ethylene in liquid cyclopentane and  $G(\text{H}_2)$  decreased from 5.2 in pure cyclopentane without reaching a well-defined lower limit. Assuming simple competition between ethylene and cyclopentane to yield ethane (*via*  $\text{C}_2\text{H}_5 + \text{RH} \rightarrow \text{C}_2\text{H}_6 + \text{R}$ ) or hydrogen we obtain by conventional stationary-state kinetics from Holroyd's results limiting values of  $G(\text{C}_2\text{H}_6)$  approximating 1.0, 0.80, and 0.9 at 28, 15, and 0°, respectively. Since  $G(\text{H}_2) + G(\text{C}_2\text{H}_6)$  is constant at each temperature, one may conclude that  $G(\text{H}, \text{thermal}) \cong 0.9$ . This supports the low yield of thermal H atoms based upon our own measurements.<sup>35</sup>

The correlation between the yields  $2\Delta G(\text{C}_5\text{H}_8) \approx \Delta G(\text{C}_5\text{H}_9\text{I})$  for cyclopentane suggests interdependent mechanisms for the formation of these products. The substantial constancy of  $G(\text{HI}) + G(\text{CH}_4)$  indicates that the organic counterparts of these products are not

(34) R. A. Holroyd, *J. Phys. Chem.*, **66**, 730 (1962).

(35) Holroyd did not draw the same conclusion. He assumed that his  $G(\text{H}_2) = 5.2$  for pure cyclopentane was low because of H-atom scavenging by product cyclopentene, for which the final concentration approximated  $10^{-4} M$ . This same concentration of ethylene, however, produced no detectable effect. The value of  $G(\text{H}_2)$  in Table II for pure cyclopentane agrees with Holroyd's value.

included among those reported. In cyclohexane it is also clear that  $G(\text{H}_2)$ ,  $G(\text{C}_6\text{H}_{10})$ , and  $G(\text{C}_6\text{H}_{11}\text{I})$  behave qualitatively the same with respect to concentration of methyl iodide while again  $G(\text{HI}) + G(\text{CH}_4)$  is constant and requires other conjugate organic products and an independence of the ion recombination process.

According to Dyne and Stone<sup>7</sup> the only organic products from  $\gamma$ -radiolysis are cyclohexene and bicyclohexyl- and cyclohexylhexene-1, and the yields of these hydrogen-deficient products accounted for 99% of  $G(\text{H}_2)$ . These products cannot account for the large absorption in the 200 m $\mu$  regions observed in the present work in excess of that required for  $G(\text{C}_6\text{H}_{10})$  determined by v.p.c. analysis in irradiated pure cyclohexane. It appears to be a nonconjugated olefinic product and our results show that this excess absorption can be accounted for, at least in part, by an olefin boiling around 65° and resulting from C-C bond rupture since it is neither 1,3- nor 1,4-cyclohexadiene. Finally, it would have been very remarkable if no C-C bonds were broken by radiolysis of cycloalkanes since it is a rather efficient process in linear and branched alkanes.<sup>12,21</sup>

[CONTRIBUTION FROM THE MELLON INSTITUTE RADIATION RESEARCH LABORATORIES, PITTSBURGH, PA.]

## The Radiolysis of Deaerated Aqueous Solutions of 2-Propanol Containing Nitrous Oxide<sup>1</sup>

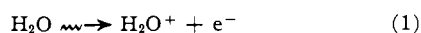
BY J. T. ALLAN AND C. M. BECK

RECEIVED OCTOBER 23, 1963

Deaerated aqueous solutions of 2-propanol containing nitrous oxide were irradiated with 2.5 Mev. electrons and the yields of nitrogen, hydrogen, acetone, and hydrogen peroxide measured as a function of pH, solute concentration, and radiation dose rate. The effects of additional solutes on the product yields were also investigated. The results have been interpreted on the basis of the primary formation of two reducing species in irradiated water—the hydrated electron and a species which behaves as a hydrogen atom. The yields, reactivity, and possible modes of formation of these species have been discussed.

### Introduction

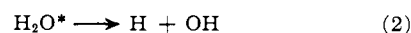
In general the radical species formed in the radiation-induced decomposition of water have been referred to as "H" and "OH." The radicals were assumed to result from reactions between water molecules and the charged intermediates<sup>2</sup> produced according to



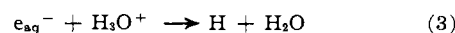
or from excited water molecules formed by recombination of the electrons and the positively charged parent ions.<sup>3</sup> Later studies<sup>4-9</sup> indicated the existence of two different forms of reducing species in aqueous systems, which led to a re-evaluation of previous considerations concerning reactions of the charged intermediates with suitable acceptors.<sup>10</sup> Chemical<sup>4-9,11,12</sup> and physical<sup>13,14</sup>

investigations have now established that radiation-produced electrons constitute the major portion of the so-called "H" radicals in aqueous media and that these may give rise to hydrogen atoms by reaction with  $\text{H}_3\text{O}^+$ . The charged reducing species (hydrated electron or negative polaron<sup>15</sup>) is referred to here as  $e_{\text{aq}}^-$ .

Allan and Scholes<sup>7</sup> showed that, in addition to hydrated electrons, another reducing species was produced independently in a yield of  $G \sim 0.6$ . This was presumed to be a hydrogen atom and to be formed by the decomposition of an excited water molecule according to



$\text{H}_2\text{O}^*$  could presumably result from direct excitation or from ion recombination.<sup>3</sup> To distinguish this independently formed species from the hydrogen atom produced in the reaction



it will be referred to as  $\text{H}^\alpha$ . The existence of  $\text{H}^\alpha$  has since been confirmed by other workers using different aqueous organic systems.<sup>11,16</sup> For  $^{60}\text{Co}$ - $\gamma$  and electron

(1) This work is supported, in part, by the U. S. Atomic Energy Commission.

(2) D. E. Lea, "Actions of Radiations on Living Cells," Cambridge University Press, 1946.

(3) M. Burton, J. L. Magee, and A. H. Samuel, *J. Chem. Phys.*, **20**, 760 (1952); H. A. Samuel and J. L. Magee, *ibid.*, **21**, 1080 (1953).

(4) E. Hayon and J. Weiss, *Proc. Intern. Conf. Peaceful Uses At. Energy*, **29**, 80 (1958).

(5) J. H. Baxendale and G. Hughes, *Z. physik. Chem.*, **14**, 306 (1958).

(6) N. F. Barr and A. O. Allen, *J. Phys. Chem.*, **63**, 928 (1959).

(7) J. T. Allan and G. Scholes, *Nature*, **187**, 218 (1960).

(8) F. S. Dainton and D. B. Peterson, *ibid.*, **186**, 878 (1960).

(9) P. Kelly and M. Smith, *J. Chem. Soc.*, 1487 (1961).

(10) (a) G. Stein, *Discussions Faraday Soc.*, **12**, 227, 289 (1952); (b) H. Frohlich and R. L. Platzman, *Phys. Rev.*, **92**, 1152 (1953); (c) J. Weiss, *Nature*, **174**, 78 (1954); (d) R. L. Platzman, *Radiation Res.*, **2**, 1 (1955); (e) J. Weiss, *Experientia*, **12**, 7, 280 (1956).

(11) E. Hayon and A. O. Allen, *J. Phys. Chem.*, **65**, 2181 (1961).

(12) G. Czapski and H. A. Schwarz, *ibid.*, **66**, 471 (1962).

(13) E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962).

(14) J. P. Keene, *Nature*, **197**, 47 (1963).

(15) J. Weiss, *ibid.*, **186**, 751 (1960).

(16) (a) J. Rabani, *J. Am. Chem. Soc.*, **84**, 868 (1962); (b) J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 1865 (1962).