for cyclobutene than cyclobutane, but the difference in the energies of activation for the reactions of cyclobutene and cyclobutane is much larger than the resonance energy of butadiene.

In a consideration of the isomerization of cyclobutene, the simplicity of the over-all process, the first-order character, and the lack of effect of nitric oxide or propylene would be in agreement with a unimolecular mechanism. Likewise the frequency factor is of the magnitude expected for a unimolecular reaction.[22] By a comparison of the expression $\kappa e(kT/h)e^{\Delta S^{\ddagger}/R}$ with the observed frequency factor,[22a] the entropy of activation $\Delta S^{\ddagger}$ at 150° can be estimated when a value of κ, the transmission coefficient, is assumed. For $\kappa = 1$ the calculated entropy of activation is -1.4 cal./deg. mole and for $\kappa = 0.5$ the entropy of activation is essentially zero. A negative value of the entropy of activation does not appear likely for the reaction. In view of the possibility of an uncertainty in κ or an inaccuracy in the frequency factor due to a small error in the activation energy, the numerical values estimated as above may be somewhat incorrect. However, the results seem to indicate that the entropy of activation is relatively small in contrast to the value of +8–9 cal./deg. mole found for cyclobutane, methylcyclobutane and ethylcyclobutane. In this connection it is of interest to note that from the data reported in the literature the increase in the entropy of 1,3-butadiene[23] over that for cyclobutene[24] at 127° is + 4.5 cal./deg. mole. On this basis the apparent smallness of the entropy of activation for the isomerization of cyclobutene does not appear unreasonable.

Acknowledgment.—The authors wish to express their appreciation to the National Science Foundation and the Celanese Corporation of America for financial support during various phases of this study. They also wish to thank Dr. R. C. Lord for a sample of cyclobutene, Mr. R. C. Wilkerson for mass spectrometric analyses, and Mr. Carl Whiteman for the infrared measurements.

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[22] (a) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 26, 295–296; (b) N. B. Slater, *Trans. Roy. Soc.* (*London*), **246A**, 57 (1953).

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[24] A. Danti, *ibid.*, **27**, 1227 (1957).

Rochester, N. Y.

[Contribution from the Department of Chemistry, University of Notre Dame]

Diffusion and Hot Radical Kinetics in the Photolysis of Methyl Iodide in Cyclohexane[1]

By Roswell F. Pottie, William H. Hamill and Russell R. Williams, Jr.

Received February 24, 1958

Solutions of methyl iodide in cyclohexane have been photolyzed at 2537 Å. Products and their quantum yields were: methane 0.190, cyclohexyl iodide 0.085, cyclohexene 0.057, iodine 0.048, hydrogen iodide 0.009. Methane is attributed to reaction of hot methyl radicals with solvent and to reaction of thermal methyl radicals with hydrogen iodide. Cyclohexene is attributed to a diffusion controlled reaction between cyclohexyl radicals and iodine atoms which remain in proximity after the hot reaction. Hydrogen iodide is twice as effective as iodine in reacting with methyl radicals. Recombination of methyl radical–iodine atom pairs following dissociation varies exponentially with the square root of hydrogen iodide concentration, indicating a diffusion-controlled process.

Introduction

The present study is based upon, and extends, recently reported work.[2,3] In particular it attempts to illustrate further the kinetic peculiarities of reactions of atoms and free radicals in the liquid state which depend largely upon diffusion-controlled processes. Such effects can be recognized and isolated since their kinetic behavior differs notably from reactions occurring in the steady state, to which the more familiar methods of gas kinetics apply. Insofar as steady-state processes occur in liquids, the same type of approach may be expected to apply.

The system methyl iodide–cyclohexane was chosen for study because Schuler's[2] preliminary observations identified or indicated the products of photolysis as iodine, hydrogen iodide, methane, cyclohexene and cyclohexyl iodide. Of these, hydrogen iodide and cyclohexene could not then be accounted for. Subsequently Bunbury[3] showed that the photolysis of ethyl iodide in the liquid phase produced ethylene and hydrogen iodide by reaction of iodine atoms with ethyl radicals. It would be expected that cyclohexyl radicals and iodine atoms might behave analogously. Two such reactants must be originally juxtaposed, and this condition is met by a prior reaction of hot methyl radical with cyclohexane. Furthermore, thermal encounters between CH_3–I or C_6H_{11}–I, yielding CH_3I, $C_6H_{11}I$ or C_6H_{10} and HI, are expected to be diffusion-controlled. Such encounters in the steady state are impossible for the light flux used in the presence of even minute concentrations of molecular iodine because of its very efficient scavenging action.

Experimental

Materials.—Methyl iodide was purified by passage through a 25 cm. column of activated silica gel, followed by distillation in a 4 ft. column packed with 1/8 in. glass helices at a reflux ratio of 10:1. The middle one-third was re-

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[1] This article is based on a dissertation submitted by R. F. P. in partial fulfillment of the requirements for the Ph.D. degree. The work was carried out under the auspices of the Radiation Project, Department of Chemistry, University of Notre Dame, supported in part by the U. S. Atomic Energy Commission under contract AT(11-1)-38 and Navy Department loan contract Nonr-06900. Presented at the 132nd meeting of the American Chemical Society, New York, N. Y., 1957.

[2] R. H. Schuler and W. H. Hamill, This Journal, **73**, 3466 (1951).

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

tained and stored in a brown bottle over copper wire. The refractive index, n^{25}D 1.5281 was constant and the samples remained water-white for periods as long as one year.

Cyclohexane was purified by various methods, depending on the initial purity. Technical grade cyclohexane was washed with fuming sulfuric acid, dilute base and water, dried and fractionally distilled. In some cases the distillate was passed through a column of activated silica gel. Spectral grade cyclohexane (Eastman Organic Chemicals) was either used as received after proving that peroxides were absent and checking the ultraviolet transmission, or further purified by refluxing over lithium aluminum hydride, distilling and passing through a column of silica gel. Phillips research grade or a C.P. grade of cyclohexane was treated with fuming sulfuric acid, etc., and then passed through several successive columns of silica gel until the ultraviolet spectrum approximated that of the best spectral grade sample. In all cases the purity was tested by the optical transmission and by refractive index. Several samples were further tested by determination of the mass spectrum of both total liquid and a vapor fraction in order to check for other hydrocarbon impurities. Cyclohexene (Eastman Organic Chemicals) was washed with successive portions of dilute acidified ferrous sulfate. The product was washed with distilled water, dried over calcium chloride and fractionally distilled. Samples were withdrawn from a constant boiling middle one-third fraction and introduced into small Pyrex ampoules. These samples were degassed by repeating freezing and pumping and were sealed under vacuum. The ampoules were opened as required to recalibrate the method devised to analyze for cyclohexene. Iodine (Rascher and Betzold C.P. resublimed) was used without further purification. Hydrogen iodide was prepared from phosphoric acid and potassium iodide. Neopentane (Phillips research grade) was transferred on the vacuum line directly into a cell for photolysis. Paraffin oil (Nujol) was used as received. Sodium–biphenyl reagent was prepared[4] for analysis of organic iodides.

Apparatus.—The source of illumination was a Hanovia SC-2537A low pressure mercury discharge tube in the form of a helical grid. The lamp was housed in a ventilated box and the light intensity was controlled by manual adjustment of the input Variac. The lamp was maintained at a temperature of 45 ± 2° by a stream of air circulating through the housing. Samples could be photolyzed either inside the helix or at a window in the lamp housing. Cylindrical Vycor cells joined to Pyrex through graded seals were used. The vapor space above the liquid sample was shielded with black tape. The light absorbed by methyl iodide was thus confined to 2537 Å. since Vycor (Corning 7910) cuts off above 1849 Å. The remainder of the light emitted by the lamp is in the visible spectrum.

Preparation of Samples.—The cells for photolysis were provided with two side arms equipped with break-offs. The central stem was joined to the vacuum-line through a capillary constriction.

A prepared solution of methyl iodide and cyclohexane was dried over phosphorus pentoxide and partially degassed by several cycles of freezing, pumping and thawing. The sample was then distilled twice trap-to-trap while pumping. and then by distillation into the cell. Contamination by air was reduced to the point where its contribution to the mass spectrum of product gases was indistinguishable from the normal background. In some experiments iodine was added to the solution before degassing and was distilled simultaneously into the reaction cell. If hydrogen iodide were to be added the central stem of the reaction cell was fitted with a stopcock and the measured volume of gas immediately condensed into the cell. The solution for photolysis then was introduced. These precautions were necessary in order to avoid loss of hydrogen iodide by absorption in stopcock grease or by reaction with mercury. The results of several tests demonstrated that both iodine and hydrogen iodide were introduced quantitatively into the reaction cell. Solutions of methyl iodide in neopentane were introduced into the reaction cell by the same technique. In experiments using Nujol it was added directly to the cell before sealing to the vacuum line and degassed at 100°. Previously degassed methyl iodide was then distilled into the cell.

The light flux was determined for both positions using ethyl iodide as an actinometer and taking the value 0.13 as the quantum yield for production of I_2.[5] All runs of methyl iodide in cyclohexane were monitored by simultaneous photolysis of ethyl iodide.

Analysis.—No adequate method for analysis of cyclohexene could be found in the literature so the following technique was devised. Cyclohexene and iodine were known[6] to undergo a reversible atom-catalyzed addition. Reaction is *ca.* 90% complete under practical experimental conditions and a bright tungsten light must be used to accelerate attainment of equilibrium. By calibrating under carefully standardized conditions the method becomes quantitative. Our procedure involved (a) adding a considerable excess of iodine to the exposed sample, (b) equilibrating at 0°, (c) removing excess iodine by washing with a solution of sodium thiosulfate, then with water, (d) destroying the diiodide at some higher temperature and then determination of the iodine released. A 1 *M* solution of iodine in methyl iodide was prepared for estimation of relatively large amounts (*ca.* 50 micromoles) of cyclohexene, while 0.15 *M* iodine in chloroform was used for smaller concentrations. The method was calibrated with solutions of known concentration of cyclohexene and factors were determined relating iodine released to cyclohexene added. The sample for analysis was made up of 5 ml. of the solution of cyclohexene in cyclohexane, 7 ml. of carbon tetrachloride, 5 ml. of the iodine solution. Equilibration was performed with the test-tube containing the sample immersed in an ice–water-bath under illumination of a tungsten lamp. One hour sufficed for equilibration. Following elimination of excess iodine, the diiodide was decomposed by placing the sample a few centimeters above a lamp and titrating iodine until no further release occurred. Under these conditions the factor for converting iodine uptake to cyclohexene is 1.173 for the methyl iodide solution and 1.168 for the chloroform solution. It is estimated that cyclohexene can be determined within 1% for 50 micromoles, and within 5% for 10 micromoles.

Following illumination the cell was sealed to the vacuum line *via* capillary constriction and break-off, cooled to −196° and gaseous product collected, measured and reserved for mass analysis. Degassed water was distilled into the cell, the contents frozen and the cell sealed and removed from the line. After shaking the warmed cell to extract hydrogen iodide into the aqueous phase the contents were again frozen, sealed to the vacuum line *via* the second break-off and residual gas collected as before. If more than a few micromoles of gas was collected, the operation was repeated.

The mixture in the reaction cell was poured into a separatory funnel along with additional distilled water and carbon tetrachloride used to rinse the cell. The phases were separated; the aqueous phase was washed with carbon tetrachloride to remove iodine. If cyclohexene were to be determined, the washings were added to the organic phase to a total volume of 7.0 ml. of carbon tetrachloride. Any additional carbon tetrachloride washings were added to a separate flask. Otherwise all washings, regardless of amount, were added to the organic phase. The aqueous phase was titrated to determine hydrogen iodide. To obtain clear end-points with brom cresol purple, it was necessary to bubble carbon dioxide-free air through the solution during titration. Concentrated aqueous potassium iodide was added to the organic phase and the iodine was titrated with standard thiosulfate. The phases were separated once more and the organic layer was analyzed for cyclohexene as described above.

In several runs, after iodine had been estimated, the organic layer was run into a semi-micro still. A few ml. of normal hexane was added and methyl iodide distilled over. After approximately half of the *n*-hexane had been collected, the residue in the still pot was analyzed for organic iodide by means of sodium–biphenyl reagent, and then potentiometric titration with silver nitrate.[4] Complete removal of methyl iodide was checked by analysis of the last distillate. The method was further checked with a known solution of *n*-amyl iodide in cyclohexane and *n*-hexane. After a few ml. of *n*-hexane was removed by distillation, analysis of the residue showed quantitative retention of the iodide. Since

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[4] F. L. Benton and W. H. Hamill, *Anal. Chem.*, **20**, 269 (1948); L. M. Liggett, *ibid.*, **26**, 748 (1954).

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

[6] R. J. Birkenhauer, Ph.D. dissertation, Univ. of Notre Dame 1941.

the boiling point of cyclohexyl iodide is more than 30° above that of *n*-amyl iodide, the method is suitable for quantitative determination of cyclohexyl iodide.

Runs were performed in which the gases were removed at the temperature of ethyl bromide mush (−119°) or toluene mush (−95°) to ascertain if gases other than methane were photolytic products. In some instances traces of ethane were found, but never in any appreciable amount. In all cases the composition of gas averaged about 98% methane, the remainder consisting of hydrogen, air, solvent and methyl iodide.

Results

I. Methyl Iodide in Cyclohexane.—Preliminary runs indicated that the products were methane, iodine, cyclohexene, cyclohexyl iodide and hydrogen iodide. In several instances hydrogen iodide was estimated first by titration with standard base, and then acidification with dilute nitric acid and determination of the iodide by potentiometric titration. The concentration of iodide ion was equal to the hydrogen ion concentration within experimental error. No evidence was found for carbon-to-carbon bonds formed with the solvent, nor was there any indication that other iodides were produced. These conclusions are based on a prolonged photolysis followed by mass spectrometric analysis. A peak at $m/e = 210$ corresponds to cyclohexyl iodide. No diiodides were present nor could any other iodide peak be found except that of methyl iodide. There was no evidence of any hydrocarbon peaks for masses greater than that of cyclohexane.

The results of a series of runs, corrected to the same integrated light flux, are presented in Fig. 1. The samples for these and the experiments below consisted of 4.875 ml. of cyclohexane and 0.125 ml. of methyl iodide. Quantum yields obtained from Fig. 1 are:

$$\Phi_{CH_4} = 0.190, \Phi_{C_6H_{10}} = 0.057, \Phi_{I_2} = 0.048, \Phi_{HI} = 0.009.$$

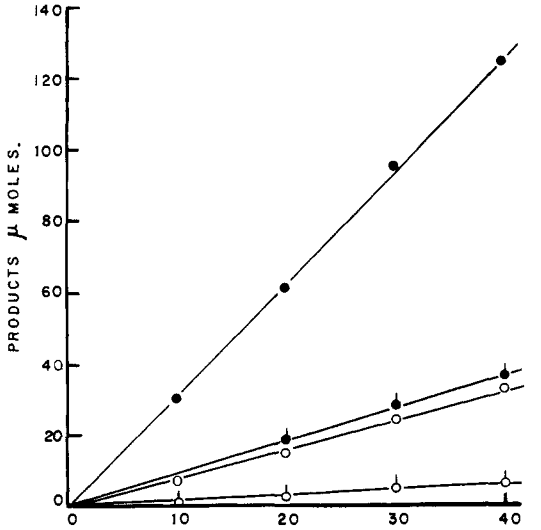

Fig. 1.—Production of methane, ●; cyclohexene, ●̇; iodine, ○; and hydrogen iodide, ♁ : *vs.* photolysis time.

II. Methyl Iodide in Cyclohexane with Added Water and Iodine.—Solutions of iodine and methyl iodide in cyclohexane were combined with 0.1 ml. of water. The samples were introduced into the reaction cell by the normal procedure. Irradiations were performed by illuminating the cell for two-minute intervals, followed by one minute of vigorous shaking. This procedure was devised to prevent reaction of hydrogen iodide with methyl, etc., free radicals. Total photolysis time was the same for all experiments. The results appear in Table I and in Fig. 2.

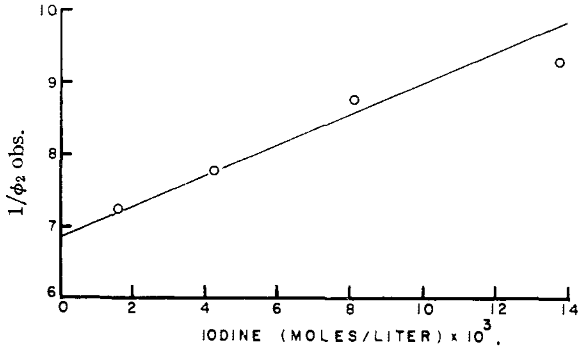

Fig. 2.—Quantum yield of hot methane against added iodine.

III. Methyl Iodide in Cyclohexane with Added Iodine and Hydrogen Iodide.—Bunbury[3] found that when iodine and hydrogen iodide are added to a similar system in which both diffusion-controlled and steady-state reactions occur, there is no significant interference with diffusion processes if the concentration of scavenger is less than 10^{-3} mole fraction, and it can be considered that the scavenger removes only free radicals in the steady state. Thus, quantum yields for methane were determined as a function of the before-after average ratio of iodine to hydrogen iodide, as indicated in Fig. 3.

Table I

Photolysis of Methyl Iodide in Cyclohexane with Added Iodine and Water

Iodine added (μmoles)	7.3	21.1	40.8	69.0
Products, μmoles				
Methane	114.2	105.5	93.73	88.91
Cyclohexene	40.6	36.4	31.8	31.2
Hydrogen iodide	40.3	37.2	33.5	32.4
Final iodine	8.7	21.2	40.2	68.1
Average iodine	8.0	21.2	40.5	68.6
Light correction factor	1.19	1.11	1.09	1.05
Methane/cyclohexene	2.81	2.90	2.95	2.85

IV. Methyl Iodide in Cyclohexane with Added Hydrogen Iodide.—One run was performed in which hydrogen iodide was added before photolysis in an amount sufficient to scavenge all steady-state radicals at the beginning of the photolysis but insufficient to interfere significantly with diffusion-recombination processes. The reaction cell was fitted with an optical cell and the production of iodine *vs.* time of photolysis was determined spectrophotometrically. The initial rate of production of iodine was calculated from the limiting slope and corresponded to a quantum yield of 0.312 for I_2. The decreasing rate with increasing time of photolysis presumably is due to reaction of steady-state radicals with iodine.

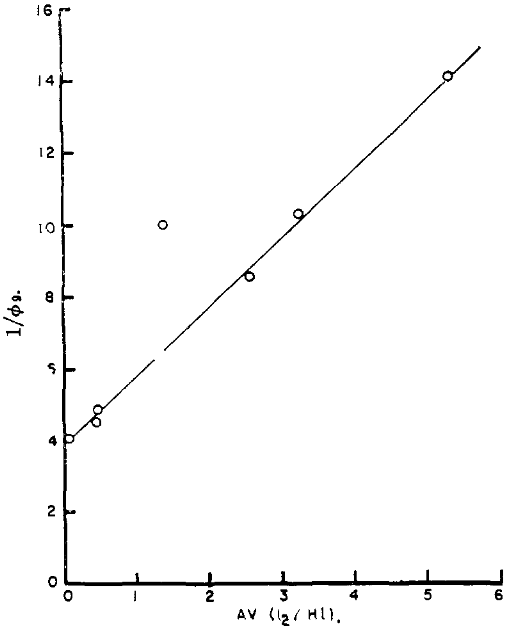

Fig. 3.—Steady-state methane *vs.* the ratio of iodine to hydrogen iodide.

A series of runs was performed in which hydrogen iodide was added in quantities sufficient not only to scavenge all steady-state radicals but also to interfere partially with diffusion-controlled processes. Hydrogen iodide was measured before and after photolysis and the average concentration was used. Considerable production of hydrogen occurred, presumably as a result of partial absorption of light by hydrogen iodide. Quantum yields of methane were corrected to conditions of total light absorption by methyl iodide by assuming that the quantum yield of hydrogen production from hydrogen iodide is unity. This was verified by determining the extinction coefficient of hydrogen iodide in cyclohexane at 2537 Å. The extinction coefficient was approximately 90, in good agreement with that calculated from the above assumption. The results of this series appear in Fig. 4. The average error in the yield of methane is taken to be 0.3 micromoles corresponding to an uncertainty in the quantum yield of 0.01. It can be seen that one point is well outside the experimental error and no weight was given to it.

V. Methyl Iodide in Other Solvents.—Solutions of methyl iodide in Nujol were photolyzed with an L-shape cell immersed in liquid nitrogen in a wide mouth dewar flask. A faint yellow color appeared at the surface of the cell soon after the beginning of photolysis. This color became deeper as photolysis progressed. Analysis of the gases collected at −95° comprised 87% of methane with the remainder being mostly hydrogen. A second run with iodine and air dissolved in solution gave the same amount of methane as before, with a slight increase in hydrogen. Methane was the chief product of photolysis at room temperature, the rate of production being increased about sevenfold. The approximate quantum yields for products at room temperature were $\Phi_{CH_4} = 0.17$, $\Phi_{I_2} = 0.032$.

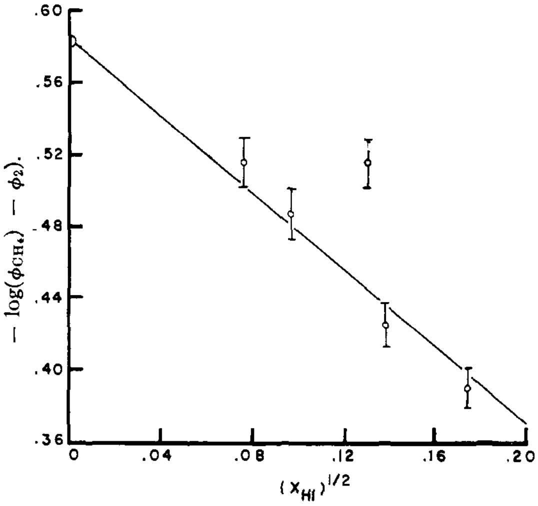

Fig. 4.—Diffusion analysis of methane quantum yield *vs.* added hydrogen iodide.

Several solutions of methyl iodide in neopentane were photolyzed intermittently with iodine determined spectrophotometrically after each period of illumination. The production of iodine was linear with time and the chief gaseous product was methane. Minor amounts (less than 3%) of isobutane, propane and ethane were present in the gases collected at −119°. Quantum yields for methane and iodine were: $\Phi_{CH_4} = 0.039$, $\Phi_{I_2} = 0.0045$.

Discussion

The mechanism is postulated

$$
\begin{array}{lll}
CH_3I + C_6H_{12} + h\nu \longrightarrow & (\boldsymbol{CH_3} + I + C_6H_{12}) & \phi\, I_a \\
(\boldsymbol{CH_3} + I + C_6H_{12}) \longrightarrow & CH_4 + (C_6H_{11} + I) & \Phi_2 I_a \\
\longrightarrow & (CH_3 + I) + C_6H_{12} & (\phi_1 - \Phi_2) I_a \\
\longrightarrow & CH_3 + I + C_6H_{12} & \Phi_4 I_a \\
(CH_3 + I) \longrightarrow & CH_3I & \Phi_5 I_a \\
(C_6H_{11} + I) \longrightarrow & C_6H_{10} + HI & \Phi_6 I_a \\
\longrightarrow & C_6H_{11}I & \Phi_7 I_a \\
\longrightarrow & C_6H_{11} + I & \Phi_8 I_a \\
CH_3 + HI \longrightarrow & CH_4 + I & k_9(CH_3)(HI) \\
CH_3 + I_2 \longrightarrow & CH_3I + I & k_{10}(CH_3)(I_2) \\
C_6H_{11} + HI \longrightarrow & C_6H_{12} + I & k_{11}(C_6H_{11})(HI) \\
C_6H_{11} + I_2 \longrightarrow & C_6H_{11}I + I & k_{12}(C_6H_{11})(I_2) \\
I + I \longrightarrow & I_2 & k_{13}(I)^2
\end{array}
$$

Parentheses indicate substances which may react before reaching the stationary state and $\boldsymbol{CH_3}$ denotes a hot methyl radical. The pair $(CH_3 + I)$ have a common parent and may have a re-encounter resulting in geminate recombination. The pair $(C_6H_{11} + I)$ do not have a common parent but are postulated to be formed in approximate juxtaposition. Such partners are further postulated to obey the equations of diffusion-recombinations as developed by Noyes[7] and by Roy, Williams and Hamill.[8]

The first eight reactions are essentially direct effects of light absorption by methyl iodide since none of the products can interfere with any of the subsequent processes unless they are present in considerable quantity. They are accordingly rep-

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(7) R. M. Noyes, THIS JOURNAL, **77**, 2042 (1955).

(8) J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **76**, 3274 (1954); **77**, 2953 (1955).

resented by their respective quantum yields rather than by rate constants. The last five reactions are considered to be controlled by stationary state kinetics. Methyl and cyclohexyl radicals which escape from diffusion-controlled processes compete for hydrogen iodide and iodine. It follows that for steps 9, 10

$$\frac{1}{\Phi_9} = \frac{1}{\Phi_4} + \frac{k_{10}(I_2)}{\Phi_4 k_9(\mathrm{HI})}$$

where Φ_9 is the quantum yield of methane produced by step 9. Experimentally it is the difference between Φ_{CH_4} observed and Φ_2. Correspondingly, Φ_4 is the yield of thermal methyl radicals in the stationary state. An appropriate graph (Fig. 3) leads to values of the parameters.

However, it is first necessary to determine Φ_2, the quantum yield for hot methane. It is evident that if only steps 2 and 9 are responsible for production of methane, elimination of reaction 9 would permit direct measurement of Φ_2. In experiments with added iodine, water removes hydrogen iodide before it can react with steady-state radicals. Iodine gives additional protection to hydrogen iodide by scavenging these radicals. Short photolysis periods with vigorous intermittent agitation also contribute to this protection. However, a complicating factor arises because of absorption of light by the iodine–methyl iodide and iodine–cyclohexane complexes. The observed quantum yield for methane (all hot methane in this case) must be corrected to conditions of total absorption of light by methyl iodide. This is done as

$$\Phi_{CH_4} = \frac{\Phi_2\,\epsilon_{CH_3I}\,(CH_3I)}{\epsilon_{CH_3I}(CH_3I) + \epsilon_X(X) + \epsilon_{I_2}(I_2)}$$

Φ_{CH_4} is the observed quantum yield of methane, ϵ_X is the molar extinction coefficient of the iodine–methyl iodide complex X, (X) is the concentration of the complex in moles/liter, ϵ_{CH_3I}, (CH_3I) and ϵ_{I_2}, (I_2) are the corresponding quantities for methyl iodide and iodine. It is considered that light absorbed by the complex has no effect other than reduction of the light absorbed by methyl iodide. This conclusion is based on previous work.[5] Combining the above equation and the equilibrium constant of the complex gives

$$\Phi_{CH_4}^{-1} = \Phi_2^{-1} + \frac{\epsilon_{I_2} + \dfrac{K(CH_3I)\epsilon_X}{1 + K(CH_3I)}}{\epsilon_{CH_3I}(CH_3I)}\,\frac{(I_2)}{\Phi_2}$$

In Fig. 2, Φ_2 is plotted against (I_2) for the experiments with added iodine and water. The graphical slope and intercept are consistent with $\epsilon_X = 2.6 \times 10^4$, $\epsilon_{CH_3I} = 400$, $\epsilon_{I_2} = 1920$, $K = 0.22$, and $\Phi_2 = 0.15$. The equilibrium constant K was taken from the data of Keefer and Andrews.[9] The extinction coefficient of iodine in cyclohexane was determined in the present study. Cochran[5] observed that the extinction coefficient of the iodine complex in liquid methyl iodide is 1.5×10^4. The above value agrees with this result when one considers the rather approximate nature of the present treatment, as well as the possible effect of different environments on absorption of light by the complex. The value for ϵ_{I_2} is in good agreement with that reported.[10]

A more nearly accurate determination of Φ_2 may be obtained by taking the average ratio of methane to cyclohexene from the water–iodine runs in which there was no net production of iodine and calculating the yield for hot methane from the quantum yield of cyclohexene as given by Fig. 1. This ratio should be independent of variation in light flux and should be unaffected by the presence of iodine. The quantum yield obtained for hot methane by this method is 0.165, in satisfactory agreement with the value calculated from Fig. 2.

In experiments with added iodine and hydrogen iodide the difference between the quantum yield for total methane and that for hot methane equals the yield of methane which results from steady-state reaction of methyl radicals with hydrogen iodide. In Fig. 3 the reciprocal of this difference is plotted against $(I_2)/(\mathrm{HI})$. The values found for the parameters are $k_9/k_{10} = 2.0$ and $\Phi_4 = 0.26$.

In the experiment with a small concentration of hydrogen iodide before photolysis the initial quantum yield for iodine is 0.312. According to the mechanism this yield is the sum of Φ_4 and Φ_8 since at the beginning of photolysis all steady-state radicals are being scavenged by hydrogen iodide. This leads to a value of 0.051 for Φ_8 which is the quantum yield of cyclohexyl radicals that have escaped diffusion recombination. Because Φ_2 is equal to the sum of Φ_6, Φ_7, Φ_8, the value of Φ_7 is

$$\Phi_7 = 0.165 - 0.057 - 0.051 = 0.057$$

Steps 3 and 4 of the mechanism are diffusion-controlled. Roy, Williams and Hamill[8] proposed the following equation for the amount of recombination in such a system.

$$\log(1 - W) = \log(1 - W_0) - P_1(5.75\gamma\rho_0)^{-1} + P_1P_2^{1/2}(3.24\gamma^2)^{-1}X^{1/2}$$

In this equation W is the probability of recombination of two free radicals modified by a scavenger at mole fraction X competing for one of the radicals; P_1 is the probability of recombination per encounter of the radicals; P_2 is the probability of reaction between one of the fragments and scavenger upon encounter; $\gamma = L/d$ and $\rho_0 = \bar{R}_0/d$ where L is the mean free path, d the collision diameter and $\bar{R}_0$ the initial mean separation of the fragments.

In this work the added reactive scavenger was hydrogen iodide. It is unlikely that reactions of hot methyl radicals are affected by the scavenger since the hot radical reaction must take place within a few collisions. In the present treatment $(1 - W)$ is $(\Phi_{CH_4} - \Phi_2)/(1 - \Phi_2)$. If primary recombination does not occur the final form of the diffusion equation becomes

$$\log(\Phi\,CH_4 - \Phi_2) = \log(1 - \Phi_2) - P_1(5.75\gamma\rho_0)^{-1} + P_1P_2^{1/2}(3.24\gamma^2)^{-1}X^{1/2}$$

It is further assumed in accordance with previous work that $P_1 = P_2 = 1$. Thus, from the parameters of the graph in Fig. 4 we obtain: $\gamma = 0.54$ and $\rho_0 = 0.64$. In previous work Bunbury[3] found $\gamma = 0.33$ and $\rho_0 = 0.57$ for the photolysis of ethyl iodide in cyclohexane. Both of these num-

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(9) R. M. Keefer and L. J. Andrews, This Journal, **74**, 1891 (1952).

(10) S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, *ibid.*, **75**, 2900 (1953).

bers are consistent with the above results since the alkyl radicals are similar. $\gamma = 0.43$ and $\rho_0 = 2.3$ when the results of Levey and Willard[11] on neutron capture in liquid methyl iodide are analyzed by diffusion kinetics.[8] It would be expected that the value of γ might approximate ours since the mean free path of the methyl radical is involved in both cases although in different media. No meaningful comparison can be made of the values for ρ_0 because of the different modes of dissociation.

By our mechanism the quantum yield for cyclohexene should equal the sum of the yields for iodine and hydrogen iodide. The experimental results in Fig. 1 and Table I adequately meet this condition. In Table I the yield for cyclohexene should equal the yield for hydrogen iodide since there is no net production of iodine. The mechanism also requires

$$\Phi_{CH_4} = \Phi_{C_6H_{10}} + \Phi_{I_2} + \Phi_{C_6H_{11}I}$$

This relation was tested in an experiment in which methane, iodine and cyclohexyl iodide were determined. Cyclohexene was not measured in the same run but was calculated from the yield of methane and the ratio of quantum yields for methane to cyclohexene in Fig. 1. The total production of cyclohexene, iodine and cyclohexyl iodide was 131 micromoles, while methane amounted to 147 micromoles. Considering that six independent analyses are involved (two for actinometry) the agreement is adequate.

A critical step in the mechanism is the second which postulates that the solvent is attacked by a hot methyl radical with the formation of methane. *All net chemical reaction is contained in or follows from this step.* This reaction is plausible because of the high energy of the methyl radical. The chemical evidence obtained in this study for such solvent participation in the kinetics is based on the identification and estimation of methane, cyclohexene and cyclohexyl iodide as ultimate products of these reactions. The hot radical nature of the process was tested by adding water and iodine to the solution before photolysis. When correction was made for absorption of light by species other than methyl iodide, the quantum yield for methane was found to be independent of the concentration of scavenger (iodine). Since reaction of thermal methyl radicals with hydrogen iodide was impossible, it followed that all methane resulted from processes involving interaction between the solvent and a very reactive methyl radical. Additional support for this postulate was found when glassed solutions of methyl iodide in Nujol were photolyzed at 77°K. The yield of methane was independent of the concentration of added oxygen and iodine (which is soluble in the glass) both of which would be expected to react with steady state radicals and reduce the amount of methane if it resulted from such radical–solvent interaction. When Cochran[5] photolyzed ethyl iodide in partially deuterated *n*-hexane, a significant portion of the ethane contained deuterium. When ethyl iodide was photolyzed in cyclohexane,[3] some 30% of the ethane resulted from hot-radical processes. Evidence supporting a similar reaction in liquid *n*-hexane has been reported.[12] Evidence for hot methyl reactions in the vapor phase is clear although quantum yields are very small.[13] These results support our proposal that a hot methyl radical extracts hydrogen from the solvent.

It was expected that when methyl iodide was photolyzed in neopentane there would be no net production of iodine, since the iodine atom should be unable to abstract hydrogen from the neopentyl radical which is produced by methyl attack on the solvent. However, the constant rate of production of iodine suggests that the neopentyl radical may rearrange or decompose.[14] The activation energy for such a process might be supplied by the attacking hot methyl radical. It would seem to be necessary to postulate further that a free radical species so produced reacts with the adjacent iodine atom to produce hydrogen iodide and an olefin. Iodine then remains when the preponderant methyl radicals react with hydrogen iodide.

Analysis of the experiments with added hydrogen iodide establishes that the reaction between the methyl radical and the iodine atom, immediately following bond rupture, is a diffusion-controlled process, and that the third and fourth steps of the mechanism are in agreement with the experimental results. Reactions 6, 7 and 8 previously have been postulated[3] for the photolysis of ethyl iodide in cyclohexane. In this work the yield of cyclohexene was independent of added iodine up to 10^{-3} mole fraction. This shows that cyclohexene is not a product of a steady-state process. No conventional mechanism seems capable of accounting for the facts. The analogy with the diffusion-controlled reaction between ethyl radicals and iodine atoms suggests a corresponding mechanism in the present system. The necessary precursors, cyclohexyl radicals and iodine atoms, are present in the system. As products of a hot radical reaction they are presumably within diffusion distance. Taking the combined quantum yields of cyclohexene and cyclohexyl iodide at low iodine concentrations as a measure of "recombination" and the value of Φ_{CH_4} as measuring the number of primary events, then $W = (\Phi_6 + \Phi_7)/\Phi_2 = 0.7$. This is approximately the value expected if cyclohexyl iodide were to be photolyzed. For comparison, consider the probability of recombination of CH_3 and I in step 5. $\Phi_5 = 1 - \Phi_2 - \Phi_4 = 0.57$ and the corresponding probability of recombination is given by $W = \Phi_5/(\phi_1 - \Phi_2) = 0.68$ when $\phi_1 = 1$. If we accept the diffusion mechanism, it may be concluded that the hot methyl radical reacts within *ca.* one molecular diameter or not at all.

Reactions 8 through 11 follow as a consequence of the previous reactions. It is of interest that the ratio of rate constants for reaction of ethyl radicals with hydrogen iodide and iodine in liquid ethyl iodide is 2.97.[3] The corresponding ratio is 2.38 in cyclohexane. These compare with $k_9/k_{10} = 2.00$ found in this work for similar reactions of methyl

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radicals. Ogg and Williams[15] measured the competition between hydrogen iodide and iodine for methyl radicals in the gas phase. In contrast to the values above for liquid phase, iodine was found to be considerably more reactive than was hydrogen iodide. It is possible that the relative effectiveness of these radical scavengers was reversed by complexing of iodine with methyl iodide and cyclohexane[10] in the liquid phase.

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[CONTRIBUTION FROM THE CHEMICALS RESEARCH DIVISION, ESSO RESEARCH AND ENGINEERING COMPANY]

The Dipole Moment of the Carbon–Carbon Bond

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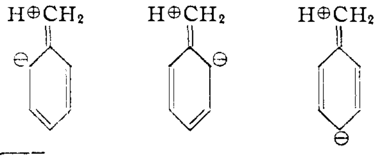
RECEIVED MARCH 14, 1958

A simple vector model, based on the postulate that the covalent single bond between two differently hybridized carbon atoms is polarized, has been developed for predicting the dipole moments of certain molecules. Experimental evidence leading to this postulate is reviewed. Bond moments for the H–C bonds occurring in methane, ethylene and acetylene, taken from infrared dispersion measurements, have been used to calculate a limited number of bond moments involving the differently hybridized states of carbon. Omission of a non-zero bond moment for the $C(sp^3)–C(sp^2)$, $C(sp^2)–C(sp)$ and $C(sp^3)–C(sp)$ bonds has been shown to be inadequate for calculating molecular moments. Inclusion of the C–C moments in the vector model yields results in excellent agreement with observed values. The limits of applicability of this approach are given.

Introduction

The point of view that a molecular dipole moment is the vector sum of the various bond moments in a molecule has led to the successful elucidation of many molecular structures. In the development of this approach, bonds between atoms of the same element have been considered to have a zero moment. The purpose of this paper is to show that the dipole moments of certain molecules can be predicted simply and accurately by postulating a non-zero moment for the covalent single bond formed between two carbon atoms of different hybridization.

Hyperconjugation and Dipole Moments.—The symmetrical tetrahedral structure of methane, in which the four non-zero H–C bond moments are opposed, precludes a molecular dipole moment. Whereas substitution of one hydrogen atom in methane by a tetrahedral methyl group does not give rise to a dipolar molecule,[1] similar substitution by a phenyl group yields toluene which has a moment of 0.37 *D*.[2] Similar results are found in the cases of propene[2] and propyne,[3] for example. The geometry of the toluene molecule does not permit a resultant moment as long as all of the H–C bond moments are assumed equal. The theory of hyperconjugation[4] has, therefore, been resorted to in order to explain this apparently anomalous value. On this basis, the following polar structures have been written[5] for toluene



each of the three forms being triply degenerate because of the indistinguishability of the three hydrogen atoms of the methyl group, there being nine such structures possible. The observed moment was then ascribed to very small contributions from each of these highly polar structures. Indeed, molecular orbital methods of calculation[6,7] have yielded moments in close agreement with the observed although, significantly, the two approaches have given quite different charge distributions in the toluene molecule.

The advent of nuclear magnetic resonance spectral analysis has served to shed new light on the problem. Since chemical shifts observed in proton resonances reflect differences in electron distribution about chemically non-equivalent protons, the n.m.r. spectrum of toluene should show splitting of the two proton lines corresponding to the ring and methyl group protons.

Corio and Dailey[8] determined the n.m.r. spectra of a number of monosubstituted benzenes and found the substances investigated to fall into two groups. One group consisted of those molecules which showed no splitting of the absorption line of the ring protons, *i.e.*, chemically equivalent protons. In this group were listed the substituents, CH_3, C_2H_5, Br, Cl, OH, OCH_3, CH_2Cl, $CHCl_2$, CN, CH_2OH and CH_2NH_2. In the second group were listed those substances which showed splitting of the ring proton absorption line and included the substituents NO_2, CHO, COCl, COOH, NH_2, I, and others. It must, therefore, be concluded that structures such as those pictured above (or a hybrid thereof) have no real existence when the substituent is one of those listed in the first group and that the explanation of the non-zero dipole moment of toluene must be sought elsewhere.

The Carbon–Hydrogen Bond Moment.—The magnitude and direction of the moment of the

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