[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Isomerization of Cyclobutene[1,2]

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Cyclobutene has been observed to isomerize into 1,3-butadiene at temperatures near 150°. The rate was measured by means of ultraviolet spectrophotometric analyses for butadiene. Packing the reaction vessel with Pyrex glass or quartz tubes did not alter the rate. The calculated first-order constants have been found to remain unchanged over the pressure range from 50 to 5 mm. at 150°. Addition of propylene or nitric oxide produced no inhibition. From experiments with initial pressures of 8–14 mm. at temperatures from 130 to 175° an activation energy of 32.5 kcal./mole was obtained. The observed first-order rate constant could be expressed as $k = 1.2 \times 10^{13} e^{-32500/RT}$ sec.$^{-1}$.

Cyclobutane[3] and related compounds[4] have been found to decompose in the gas-phase at temperatures near 400–450°. The reactions obey first-order kinetics and the products are the result of a simple ring cleavage which does not appear to involve free radical chain processes. Earlier results obtained in this Laboratory indicated that at 420° cyclobutene probably yields considerable 1,3-butadiene,[5] but at this temperature a subsequent dimerization of the butadiene also occurs. The present study was undertaken to ascertain whether under less drastic conditions cyclobutene might undergo a simple reaction without the occurrence of secondary reactions.[6] In this case the kinetics of the reaction might be studied and compared with the pyrolyses of other four-membered ring compounds.

Experimental

Materials. The first sample of cyclobutene was prepared by Dr. F. Kern from the reaction of cyclobutyl bromide with trimethylamine, the treatment of the quaternary salt with silver oxide, and the subsequent transformation of the quaternary base into cyclobutene.[7] This material was twice distilled in a Podbielniak low-temperature fractionating column and yielded a sample (I) with a boiling point of 3° at 763 mm. Mass spectrometric analyses[8] indicated that it was not quite pure, probably containing several per cent. of another C_4 hydrocarbon.

The methods of Heisig,[9] Willstätter,[6,10] and Roberts and Sauer[7] with slight modifications were used in the preparation of most of the cyclobutene from cyclobutanecarboxylic acid. The cyclobutyltrimethylammonium iodide after recrystallization from absolute ethyl alcohol was converted into the quaternary base by the use of an anion exchange resin (Amberlite IRA-400-OH).[11] The cyclobutene was distilled in a Podbielniak column with Heligrid packing and the following fractions were selected for the majority of the kinetic experiments: a center cut (II), a second center cut (III), and two end cuts which were combined as sample (IV). All of these samples had the same boiling point, 1.6° at 743 mm. compared with a calculated literature value of 1.8° at 743 mm.[9] Another sample (V) was prepared in the same manner but without distillation in the Podbielniak column. The sample was treated with anhydrous copper sulfate. Its infrared absorption curve compared favorably with that given in the literature[12] and with the infrared spectra of samples II, IIc and III which were essentially identical. The designation (IIc) means sample II treated with anhydrous copper sulfate. At −79.5 to −79° samples II, III and IV had vapor pressures in the region from 7.8 to 8.1 mm. which may be compared with the values of 7.9–8.2 mm. calculated for this temperature range from Heisig's equation.[9] Sample V had a vapor pressure of 8.2 mm. at about −78°.

Sample VI[13] was given to us by Dr. R. C. Lord who stated that it contained butadiene as an impurity. A small amount of an impurity with an absorption at 13.7 μ was removed completely by refluxing over silver oxide. The ultraviolet absorption spectrum of sample VI indicated the presence of 5% 1,3-butadiene (or an impurity with a similar absorption). In the calculation of the rates the appropriate corrections were made for this impurity.

In other tests of purity of samples mass spectrometric analyses[8] showed that sample II was purer than I or V; sample V was almost identical with II but contained about 0.3% of an impurity which might be dimethyl ether. None of the samples used except VI had an appreciable absorption in the region 203–230 mμ.

For calibration purposes 1,3-butadiene (Matheson, 99%) was dried over anhydrous calcium sulfate and subjected to a low temperature trap-to-trap distillation only the center fraction being used. Nitric oxide (Matheson, >98.7%) was twice distilled from −158 to −196°. The propylene (Ohio Chemical Co.) was 99.5% pure.

Apparatus.—Most of the experiments were performed in a cylindrical Pyrex vessel designated as A (0.53 liter, 7.5 cm. diameter) which was surrounded by three concentric tubes of aluminum to provide temperature uniformity. The furnace and its temperature control were similar to those used earlier.[14] To test for heterogeneity a 0.44 liter Pyrex glass reaction vessel B was packed with thin-walled Pyrex tubes to increase the surface-to-volume ratio 34-fold. Another Pyrex glass reaction bulb C (0.4 liter) which was packed with 6 mm. i.d. quartz tubing had a 10-fold greater surface-to-volume ratio than the unpacked vessel. The measurement of the temperature at the center of the reaction vessel was made with a platinum, platinum–13% rhodium thermocouple (B and S gauge 24) connected to a Leeds and Northrup type K-2 potentiometer. The thermocouple which was generally used with the reaction bulbs described above was standardized at the melting points of zinc (419.5°) and tin (231.9°). On the basis of the tests of the thermocouples and the estimated uniformity of the temperature throughout the reaction zone, the over-all uncertainty should not exceed a few tenths of a degree. The pressure of cyclobutene in the reaction vessel was measured with a 10 mm. di-

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(2) Abstracted from the Ph.D. thesis submitted by Walter Cooper.

(3) C. T. Genaux, F. Kern and W. D. Walters, THIS JOURNAL, **75**, 6196 (1953).

(4) (a) R. E. Wellman and W. D. Walters, *ibid.*, **79**, 1542 (1957); (b) M. N. Das, F. Kern, T. D. Coyle and W. D. Walters, *ibid.*, **76**, 6271 (1954).

(5) Results of F. Kern mentioned in footnote 21 of ref. 3.

(6) The formation of butadiene had been observed in earlier work with certain cyclobutyl compounds. R. Willstätter and W. v. Schmaedel, *Ber.*, **38B**, 1994 (1905), reported that some butadiene was formed in the decomposition of cyclobutyltrimethylammonium hydroxide at higher temperature and also in the reaction of quinoline and cyclobutene dibromide. Roberts and Sauer in ref. 7 found that in the pyrolysis of O-cyclobutyl S-methyl xanthate at about 250° butadiene was formed. Vogel (see ref. 18) has isomerized substituted cyclobutenes into derivatives of butadiene.

(7) J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

(8) (a) Performed by the Consolidated Electrodynamics Corp.; (b) by R. C. Wilkerson of the Celanese Corporation of America.

(9) G. B. Heisig, THIS JOURNAL, **63**, 1698 (1941).

(10) R. Willstätter, *Ann.*, **317**, 220 (1891).

(11) The procedure with the resin was similar to that of V. Boekelheide, J. Weinstock, M. F. Grundon, G. L. Sauvage and E. J. Agnello, THIS JOURNAL, **75**, 2556 (1953).

(12) J. D. Roberts and C. W. Sauer, *ibid.*, **74**, 3192 (1952).

(13) Prepared by the procedure described by A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, *ibid.*, **74**, 4867 (1952).

(14) D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948)

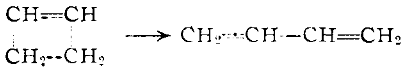
ameter (o.d.) mercury manometer which was read with a Gaertner M930–300 cathetometer.

Experiments were performed also in a small cylindrical quartz reaction vessel (22 ml., 2.4 cm. diam., 5 cm. light path) which was situated between the monochromator and the phototube compartment of a Beckman DU spectrophotometer. In the course of the work two different vessels D and E were used for following the reaction *in situ*. Suitable electrical heating, thermal insulation, and temperature regulation were provided.

Reaction Products.—The major product of the reaction at 150° was identified initially in two ways. Several experiments at pressures of 7–15 mm. cyclobutene were allowed to proceed for 90 min. The reaction mixtures were condensed at −196° and then volatilized into a one-meter gas cell for analysis in a Perkin–Elmer Infrared Spectrometer Model 12AB. In addition to the smaller peaks due to the unreacted cyclobutene, there were marked absorption peaks at 5.5, 6.3, 7.3, 9.8 and 11.0 μ which corresponded to the absorption regions of 1,3-butadiene as verified with a pure sample on the same instrument and by comparison with the literature curves.[15] The mixture from a 9 mm. experiment with a reaction time of 86 min. at 150° was expanded into a Beckman 2560-S10 cell (1 cm. light path) and the ultraviolet absorption measured from 202 to 220 mμ in a Beckman DU spectrophotometer. The shape of the absorption curve for the mixture agreed closely with that for a similarly measured sample of pure 1,3-butadiene and with a published curve.[15] Maxima were observed at 204, 209.5 and 216 mμ.

Since it was found in the early experiments at 150° that the reaction proceeds in a constant volume system essentially without a pressure change, it appeared that an isomerization was occurring. There was, however, the possibility that the major reaction might be accompanied by both pressure-increasing and pressure-decreasing reactions which as a result of a fortuitous balancing produced no pressure change. That non-condensable gases do not constitute a significant portion of the products was observed in the following manner. In six experiments with 4–15 mm. initial pressure at 150° carried to more than 60% conversion, it was possible to condense, on an average, in the cold finger (−196°) adjacent to the reaction vessel 99.3 ± 0.3% of the reaction mixture. Likewise two other experiments at 150° gave no indication of appreciable quantities of gases volatile at −139°.

A mass spectrometric analysis[8a] of the reaction mixture from a 9.8 mm. experiment after 42 min. at 150° was as follows: cyclobutene, 62.6%; 1,3-butadiene, 36.7%; hydrogen, 0.7%. No higher molecular weight compounds were reported. Further work will be needed to ascertain whether hydrogen is present to the extent indicated by this single analysis. In an experiment conducted in reaction vessel D for a time corresponding to approximately six half-times it was found by ultraviolet absorption measurements that about 4.7 mm. 1,3-butadiene had been formed from 4.7 mm. cyclobutene initially present. The ratio of the final pressure to the initial pressure was 1.00. On the basis of the analytical data the reaction seems to occur according to the equation



$$\begin{array}{c} CH{=}CH \\ | \quad\quad | \\ CH_2{-}CH_2 \end{array} \longrightarrow CH_2{=}CH{-}CH{=}CH_2 \qquad (1)$$

Rate Measurements.—In the experiments in vessels A, B and C samples of the reaction mixture were removed after definite time intervals and analyzed spectrophotometrically for 1,3-butadiene. Prior to the taking of the sample several small portions of the reaction mixture were removed rapidly in order to flush out the connecting tubing. A portion of the sample was expanded into an evacuated 1-cm. gas cell and the optical density was measured at selected wave lengths from 205.5 to 220 mμ with the Beckman DU spectrophotometer. From the data the pressure of 1,3-butadiene in the cell could be determined since the optical densities had been measured for a number of pressures of 1,3-butadiene. The 1,3-butadiene pressure was compared with the total pressure of the reaction mixture in order to obtain the percentage of reaction. Since the quantity of the sample removed for analysis was small and since the total amount of material remaining in the reaction zone could be determined by pressure measurements, it was possible to take samples at three or four successive intervals during the course of the reaction.

In a number of experiments a large amount (24–83%) of the reaction mixture was removed before a sample was taken for spectrophotometric analysis. This procedure was used to test whether the samples obtained in the previous experiments were representative of the reaction mixture. In the study of the rate of isomerization of cyclobutene at initial pressures of 1 mm. or less another technique was used. At a given time all of the material in the reaction bulb was condensed into a finger at −196°. The gases were then volatilized into the 1-cm. gas cell for analysis.

By the use of reaction vessel D or E the rate of formation of 1,3-butadiene was measured *in situ*. Measurements of the change in optical density with time were made for various wave lengths from 214 to 230 mμ. For calibration purposes the optical densities of known pressures of butadiene were measured at the reaction temperature. In special experiments it was found that the ultraviolet radiation from the Beckman DU spectrophotometer did not produce photochemical effects upon the reaction mixture to a detectable extent under the conditions used.

Results and Discussion

Preliminary Considerations.—In a series of experiments conducted at 150° in the small quartz cell D the optical density of the reaction mixture was measured *in situ* near the start of the isomerization (1–8% conversion). Plots of the optical density against time extrapolated to zero time and showed that the initial slope is a maximum indicating the absence of an induction period. To determine whether the isomerization is homogeneous, experiments were performed in reaction vessels A (unpacked), B (Pyrex glass packing) and C (quartz packing). The results from experiments in the packed vessels were compared with the data from experiments in the unpacked vessel similar (whenever possible) with respect to initial pressure, % conversion, cyclobutene sample, etc. For this comparison the ratios of the first-order rate constants are shown in the last column of Table I. Since the values in the last column are close to unity, the data indicate that the rate of the thermal reaction is not affected by an increase in surface to volume ratio or by a change in the nature of the surface from Pyrex glass to quartz. These results give evidence that under the conditions used

TABLE I

EFFECT OF SURFACE UPON THE RATE OF ISOMERIZATION OF CYCLOBUTANE

Temp., °C.	Init. press., mm.	Packed vessel	% Reaction	$k_{\text{packed}}/k_{\text{unpacke}}$
150	6	B	21	1.05[a]
150	9	B	23	0.99
150	11	B	23	1.07[b]
150	21	B	19–61	0.98[c]
150	8	C	24–53	0.99[c]
150	12	C	27–40	1.01[c,d]
150	15	C	26	0.97
140	7	B	13–32	0.94[c,d]

[a] Average of two experiments for the packed and unpacked bulbs, measured in a 5 cm. absorption cell. Analyses for the other experiments in the 1 cm. absorption cell. [b] Average of two experiments compared with a 9 mm. experiment in the unpacked vessel. [c] Average of ratios (k_p/k_u) determined several times during the reaction. [d] Compared with an unpacked experiment with 3 mm. higher initial pressure.

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[15] Spectral Data, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pennsylvania: Infrared Curves 42, 379, and 917; Ultraviolet Curve 65.

in the present study the isomerization of cyclobutene occurs predominantly in the vapor phase.

Order of the Reaction.—At 150° the rate of isomerization was measured in reaction vessel A at different initial pressures. In the experiments shown in Table II samples were withdrawn for analysis as the reaction proceeded and the values of the first-order rate constants, shown in the fourth column, were calculated from the observed % butadiene formed and the time elapsed since the start of the reaction. For each rate constant there is shown in the third column the extent to which the reaction has progressed. The initial pressure for each experiment is given in the second column, but for each successive reaction interval the pressure ordinarily will be about 3% lower due to the withdrawal of material in the sampling procedure. The results in Table II show that the the first-order rate constant remains essentially the same over the pressure range from 50 to 5 mm., thereby giving evidence for the first-order character of the isomerization. The data in Table II also indicate that the value of k remains almost constant at increasing percentages of reaction. Moreover, it was observed that for experiments at 25 to 4 mm. in the temperature range 150–175° the value of the first-order rate constant (calculated as in Table II) for reactions carried to 60–70% averaged not more than 5% lower than the value after 20–45% reaction.

TABLE II

RATE OF ISOMERIZATION OF CYCLOBUTENE AT 150° WITH DIFFERENT INITIAL PRESSURES

(Reaction vessel A)

Sample and treatment[a]	Initial pressure, mm.	Reaction, %	$10^4 k$, sec.$^{-1}$
II(c)	50	22	2.0
		44	1.9
I	24.9	23	2.0
		39	2.0
II(c)	15.7	23	2.1
		40	2.0
VI(b,d)	12.3[g]	22[e]	2.0
		39[e]	2.0
		50[f]	1.9
II	8.9	25	1.98
		49	1.91
II	8.7	23	2.05
II(a)	7.6	22	1.96
		39	1.98
II(c)	7.2	23	2.05
		40	2.04
		51	1.99
II	4.5	38	1.90

[a] Letters in parentheses indicate the treatments of cyclobutene prior to reaction: (a) 1 N HCl; (b) freshly distilled sodium; (c) anhydrous $CuSO_4$; (d) Ag_2O. [e] 28% of reaction mixture removed before sample was taken. [f] 36% of reaction mixture removed before sample was taken. [g] In this case the pressure in the subsequent stages was considerably lower than this value as a result of the large amount of mixture removed before each sampling.

Preliminary experiments were performed at initial pressures of 0.7–0.1 mm. to find out whether the rate constant eventually would fall off, as would be expected for a unimolecular reaction. The results indicated that at a pressure near 0.5 mm. a decrease in rate constant of about 25–30% has occurred and for a 0.2 mm. initial pressure the rate constant is probably about one-half of the value shown in Table II. For the investigation of this behavior additional experiments are planned.

In two of the early experiments performed in quartz vessel D with initial pressures of 5 and 11 mm. at a constant temperature in the neighborhood of 180–185°, the pressure of butadiene was measured spectrophotometrically *in situ* during the course of the reaction. The percentage of unreacted cyclobutene was calculated on the basis that the reaction mixture consists only of cyclobutene and butadiene. Plots of log (% unreacted cyclobutene) against reaction time were linear until at least 70% reaction, confirming the first-order nature of the isomerization over the major portion of the reaction. Subsequently nine experiments were performed in quartz vessel E at 150° with initial pressures of 6–10 mm. Absorbancy readings were made *in situ* at definite times until 16–34% reaction had occurred. The results obtained at different initial pressures and during the course of the isomerization were in accord with the behavior expected for a first-order reaction. However, the rate constants calculated after 5 and 21 minutes of reaction *in situ* were found to be approximately 18–20% lower than those obtained after 21 minutes in the large reaction vessel at comparable initial pressures. Due to the small size of reaction vessel E the connecting tubing adjoining (above) the reaction cell, but not at the reaction temperature, amounted to 17% of the total volume. Since this "dead space" was at a lower temperature, it was estimated that about 22% of the molecules were not in the reaction cell. Therefore, appreciable amounts of butadiene may have been transported by convection and diffusion into a region where little or no reaction was occurring, thus lowering the concentration of butadiene in the reaction cell. Under these circumstances the rates measured *in situ* seem to be in relatively satisfactory agreement with those obtained in the large reaction bulb by the discontinuous sampling technique.

Activation Energy.—For the determination of the variation of the rate of the reaction with temperature, experiments were performed at temperatures from 130 to 175° in reaction vessel A at initial pressures in the range 8–14 mm. In the first series of experiments the ordinary procedure for flushing the connecting tubing was used, but in the second series a large percentage (20–50%) of the reaction mixture was removed in the flushing operation before a sample was taken for analysis. For each series of experiments the logarithm of the first-order rate constant was plotted against $1/T$. For these plots the rate constants were ordinarily calculated from experiments involving reaction times longer than 10 minutes but with percentages of reaction less than 50%. From the slope of each line the activation energy of the isomerization of cyclobutene was computed. An activation energy of 32.5 kcal./mole (expressed to the nearest 0.5 kcal.) was obtained from these experiments with no significant difference in the values for the two series of experiments. With this activation energy the data from both series were used for the calculation of an average value of the frequency factor which appears in the following rate expression for the isomerization of cyclobutene: $k = 1.2 \times 10^{13} \cdot e^{-32500/RT}$ sec.$^{-1}$ The results from the two series of experiments are summarized on a single plot shown as Fig. 1.

Effect of Added Substances.—In order to obtain additional information with respect to the mechanism of the isomerization, experiments were performed in the presence of substances[16] which are known to inhibit many free radical chain reactions. Table III gives the results of experiments with added nitric oxide or propylene. In the last column values are listed for the ratio of the rate constant in the presence of added substance ($k_{\text{A.S.}}$) to the rate constant for cyclobutene alone (k). The ratio in every case is almost one so that there is no indication that the isomerization proceeds by way of a free radical mechanism. Since 1,3-butadiene, which is the main product, appears to react readily with free radicals,[17] it might be expected that if radicals of sufficient reactivity are present during the isomerization, a reaction with butadiene might occur yielding other products. No evidence for the formation of products of this type at longer reaction times has been obtained.

TABLE III

INFLUENCE OF ADDED SUBSTANCES UPON THE RATE OF ISOMERIZATION OF CYCLOBUTENE AT 150°

P_0, mm.	Added substance	$P_{\text{A.S.}}$, mm.	% Reaction	$k_{\text{A.S.}}/k^a$
10.3	Nitric oxide	0.1	22–39	1.02
8.6	Nitric oxide	.26	21–36	0.96
10.4	Nitric oxide	.27	21–37	1.03
9.8	Propylene	4.9	23–39	1.06
9.1	Propylene	5.2	22–38	1.02

[a] $k_{\text{A.S.}}$ denotes the rate constant in the presence of the added substance. In each case the value given is an average of the ratio ($k_{\text{A.S.}}/k$) determined after approximately 22% and 38% reaction. For each percentage of reaction the rate constant k was an average value from three experiments (7 to 24 mm.) without added substances. Sample I was used for all the experiments.

Discussion.—From the findings of the present study it appears that in the neighborhood of 150° cyclobutene undergoes a homogeneous isomerization into 1,3-butadiene. The over-all reaction of cyclobutene in opening only one bond to form an isomer is different from the pyrolytic reactions which have been observed for several other four-membered ring compounds without a double bond in the ring.[3,4] With the latter compounds the over-all process involved a split of the ring into two molecular fragments Furthermore the activation energy for the isomerization of cyclobutene is considerably smaller than those observed for the decompositions of cyclobutane[3] and cyclobutanone.[4b] This smaller activation energy permits the isomerization to proceed at a temperature considerably below that required for the pyrolyses of the other compounds. It is not surprising that the opening of the cyclobutene ring should not be difficult. In discussing the formation of derivatives of butadiene from substituted cyclobutenes Vogel[18] has suggested that the lability of the ring is due to (a) a weakening of the C–C bond in the 3-4 position (Staudinger–Schmidt rule) as a result of the influence of the double bond, (b) ring strain, and (c) the energetically unfavorable constellation of the hydrogen atoms (or substituents) on carbon atoms 3 and 4. Examination of models indicates a greater ring strain for cyclobutene than cyclobutane. Various recent observations have been taken as indicative of strain in the cyclobutene ring. In an electron diffraction study of cyclobutene Goldish, Hedberg and Schomaker[19] have suggested that the greater angle stress at <C–C=C (over that of <C–C–C) results in the lengthening of the single bond in the 3-4 position. The unusually low frequency observed for C=C has been ascribed by Lord and Rea[20] to a decrease in the force constant as a consequence of the strain in the four-membered ring. The fact that the 1,3-butadiene being formed will be stabilized to some extent by resonance[21] may tend to make the ring opening somewhat easier

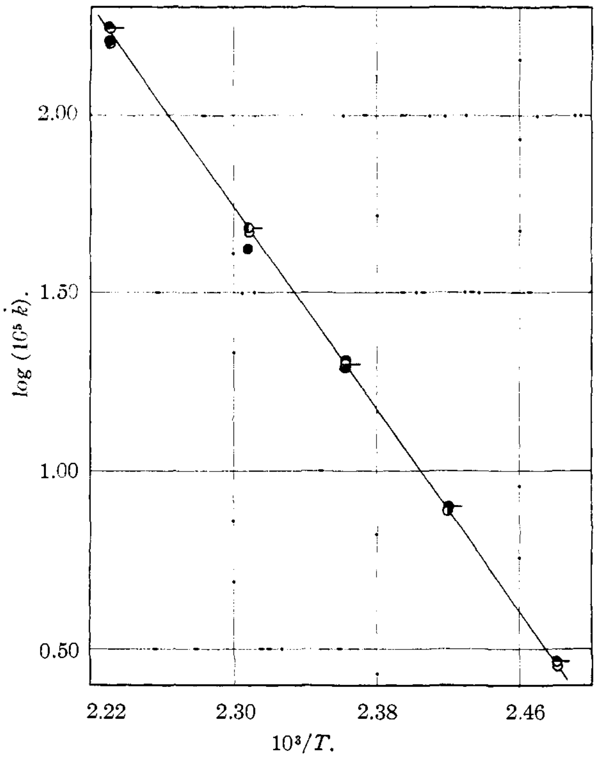

Fig. 1.—Change in the rate of isomerization of cyclobutene with temperature. Samples: I, ○; II, ●; III, ◐; IV, ◑; V, ◓; VI, ◒. Points with horizontal lines represent experiments in which a large amount of reaction mixture was removed before the sample was taken. For coincident values of two samples, only one sample is shown.

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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.

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

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

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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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[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).