conclusively by the experimental result that collisional deactivation was achieved at much lower pressure here than in the ketene–ethylene system.[9] Also, the average lifetime of the vibrationally excited cyclopropane was of the order of 10^{-7} sec, which is about three orders of magnitude lower than that obtained in the former system. However, the lower lifetime value is in accord with the value obtained in the thermal isomerization of cyclopropane[16] at 445°.

In summary, it should be pointed out that, although there is no direct evidence for the existence of a diradical in the tetrahydrofuran system, it was necessary to postulate such a species from the nature of the decomposition products. The initial diradical is formed with excess vibrational energy, and its decomposition path is dependent on the total pressure in the system. At least one product, cyclopropane, exhibited a behavior of "hot" molecule. However, its energy content appears to be significantly less than that obtained in the methylene–ethylene system, and the lifetime is similar to that in the thermal decomposition of cyclopropane. Further study of the photodecomposition of other members of the cyclic ether system are under way and may help in establishing conclusively the importance of a diradical mechanism.

[16] B. S. Rabinovitch, *et al.*, *J. Am. Chem. Soc.*, **81**, 1981 (1959).

Thermal Isomerization of 1-Methylcyclobutene at Low Pressures[1]

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Contribution from the Department of Chemistry, The University of Rochester, Rochester, New York. *Received June 9, 1969*

Abstract: The homogeneous, gas-phase, thermal isomerization of 1-methylcyclobutene to 2-methyl-1,3-butadiene has been studied in a 12-l. vessel at 150° for initial pressures from 1.1 to 0.004 mm and from 1.0 to 0.001 mm at 175°. In this pressure range the first-order rate constant decreases as the initial pressure is lowered: at 0.024 mm, the rate constant at 175° has decreased to about one-half the rate constant at 1 mm, and at 150° to approximately four-sevenths the value at 1 mm. At 175° the rate constant for 0.0015 mm has decreased to about one-sixth that at 1 mm. The decrease in rate constant for 1-methylcyclobutene at 175° occurs about $^1/_{20}$th to $^1/_{25}$th the pressure observed by Hauser for a comparable decrease of the cyclobutene rate constant at 150.4°. The curve showing the relative falloff of the rate constant with decreasing initial pressure of 1-methylcyclobutene at 175° lies close to the curve for the results of Frey and Marshall for 3-methylcyclobutene at 123.5°. The present results are compared with the predicted dependence of the rate constant for 1-methylcyclobutene on pressure, calculated by Elliott and Frey using RRKM theory.

The thermal isomerizations of cyclobutene and its alkyl derivatives into the corresponding 1,3-butadienes have been found to occur in the vapor phase at 130–200° as homogeneous unimolecular processes suitable for rate studies.[3–6] Moreover, the steric aspects of the isomerization and the kinetics of the liquid phase reactions of various cyclobutenes have been considered in a number of recent publications.[7]

The kinetics of the isomerization of cyclobutene in the gas phase have been investigated in the first-order region[3,8] and at lower pressures where the rate constant falls off.[3,9] The effect of methyl substitution upon the Arrhenius parameters of the reaction at moderate pressures has been studied by Frey and his coworkers.[4–6] A slight increase in the activation energy (~2.5 kcal/mole) and a lowering of the rate constant are produced by substitution of a methyl group in the 1 position,[4] and an effect in the opposite direction was observed for a 3-methyl group.[5] Over the pressure range of 5–150 mm the first-order rate constant for the isomerization of 1-methylcyclobutene into 2-methyl-1,3-butadiene underwent no change with pressure.[4] It was of interest to study the reaction at lower pressures and to compare the behavior of 1-methylcyclobutene with the results for related compounds. For 3-methylcyclobutene the decrease in the first-order rate constant with decreasing initial pressure has been determined in the region 45–0.01 mm.[10] Elliott and Frey[11] have calculated falloff curves for cyclobutene, 3-methylcyclobutene, and 1-methylcyclobutene by the use of the Marcus modification of the Rice–Ramsperger–Kassel theory and have compared the calculated curves with the existing experimental data for cyclobutene and 3-methylcyclobutene. Thus, the present study of the isomerization of 1-methylcyclobutene can provide a

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[1] (a) This work was supported by a grant from the National Science Foundation; (b) taken in part from the Ph.D. thesis of Margaret A. Karlsson, 1966.

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[3] W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958).

[4] H. M. Frey, *Trans. Faraday Soc.*, **58**, 957 (1962).

[5] H. M. Frey, *ibid.*, **60**, 83 (1964).

[6] H. M. Frey, *ibid.*, **59**, 1619 (1963); G. R. Branton, H. M. Frey, and R. F. Skinner, *ibid.*, **62**, 1546 (1966); H. M. Frey, B. M. Pope, and R. F. Skinner, *ibid.*, **63**, 1166 (1967); H. M. Frey, D. C. Marshall, and R. F. Skinner, *ibid.*, **61**, 861 (1965); H. M. Frey and R. F. Skinner, *ibid.*, **61**, 1918 (1965).

[7] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, and H. A. Brune, *Chem. Ber.*, **98**, 2339 (1965); H. M. Frey, D. C. Montague, and I. D. R. Stevens, *Trans. Faraday Soc.*, **63**, 372 (1967).

[8] R. W. Carr, Jr., and W. D. Walters, *J. Phys. Chem.*, **69**, 1073 (1965).

[9] W. P. Hauser and W. D. Walters, *ibid.*, **67**, 1328 (1963).

[10] H. M. Frey and D. C. Marshall, *Trans. Faraday Soc.*, **61**, 1715 (1965).

[11] C. S. Elliott and H. M. Frey, *ibid.*, **62**, 895 (1966).

comparison of experimental results with the predicted curve.

Experimental Section

Materials. 1-Methylcyclobutene was prepared according to the method of Gil-Av and Herling.[12] Methylenecyclobutane was isomerized over a sodium-on-alumina catalyst and the reaction was driven toward completion by the removal of 1-methylcyclobutene in a continuing distillation (36.6° at 748 mm) through a spinning-band column. For the distillate, the infrared spectra of the vapor and a solution in CCl_4 agreed satisfactorily with those in the literature.[13]

The sample was purified gas chromatographically over a Perkin-Elmer RX column (poly(propylene glycol) as the liquid phase) in series with a column containing silver nitrate–diethylene glycol as the partitioning agent (H column) to remove methylenecyclobutane (less than 1%) and other trace impurities. The purified sample (II) was dried over different desiccants and distilled trap-to-trap at various temperatures to obtain 1-methylcyclobutene samples IIA, IIB, and IIC, all of which were more than 99.9% pure. Sample IID contained portions subjected to a partial pyrolysis followed by gas chromatographic purification. Similar kinetic behavior was observed for the samples treated in different ways.

The sample of 2-methyl-1,3-butadiene (isoprene) used in this work was found to be least 99.8% pure in several gas chromatographic analyses with different columns and detectors. Mass spectrometric analyses showed no detectable higher molecular weight impurities. The ultraviolet absorption spectrum agreed satisfactorily with that shown in the literature.[14]

Apparatus and Kinetic Procedures. For most phases of this study the reaction vessel was a 12-l. spherical Pyrex glass flask contained in an electrically heated furnace.[15] For the measurement of the temperature, platinum—platinum-13% rhodium thermocouples (standardized at the melting points of NBS zinc and tin) were placed at four places on the surface of the vessel and at its center. The portion of the high-vacuum system used in the kinetic procedures was kept grease-free by the use of mercury-sealed, ground-glass float valves instead of stopcocks. Before each experiment the system was evacuated until the pressure of any gas other than mercury was less than 10^{-6} mm. A known amount of degassed 1-methylcyclobutene was introduced into the reaction vessel and after a suitable reaction time the entire reaction mixture was removed by condensation in a trap at $-196°$. The extent of isomerization was determined by ultraviolet spectrophotometry and also by gas chromatography, in some cases. Corrections for the time of removal were determined by the use of simulated reaction mixtures under various reaction conditions.

As a result of the kinetic procedures, the pressure of mercury in the reaction vessel may have been appreciably lower than its vapor pressure at room temperature. To minimize the inert gas effect of mercury upon the observed rate constant, however, steps were taken in some experiments to further reduce the pressure of mercury, mainly by cooling the mercury float valve adjacent to the reaction vessel (float valve M) to 0 to $-15°$.

Analyses. The reaction mixtures were analyzed primarily by the use of a Beckman DU spectrophotometer, equipped with a photomultiplier, hydrogen lamp, and stabilized power supply. Ultraviolet absorption analyses were performed for 14 of the early experiments in the analytical system used in previous work[16] and, for all other experiments, in a low-volume spectrophotometric section joined by a float valve to the system used for introduction and removal of samples from the reaction vessel. Where practicable, the isoprene pressure was determined from measurements made at both 216 and 222.6 $m\mu$. Results at the two wavelengths differed by less than 0.8% (average) in the pressure of isoprene. Calibrations were obtained using known pressures of isoprene; corrections were made, where necessary, for the small absorption of 1-methylcyclobutene.

In addition to spectrophotometric analysis, gas chromatographic analysis was performed for some experiments. Samples of the reaction mixtures were analyzed in a Perkin-Elmer 154D gas chromatograph fitted with a thermal conductivity detector and a 3-m column (4-mm i.d.) containing tetraisobutylene on firebrick. Where multiple analyses of the same reaction mixture were made, the average deviation of the ratio of peak areas was 0.8%. Analyses of calibration mixtures of isoprene and 1-methylcyclobutene indicated that the average ratio of relative peak area to relative pressure was unity, within experimental error.

Results

Nature of the Reaction and Product Analysis. Prior to work at low pressures, an exploratory experiment (~20 mm) was carried to 80% reaction at 155° in a 330-ml Pyrex vessel packed with 9-mm tubing. Ultraviolet measurements, mass spectrometry, and gas chromatography served to identify isoprene as the only product in significant amount. In his studies above 5 mm in a silica vessel, Frey[4] observed that 1-methylcyclobutene isomerizes to isoprene without noticeable side reactions or surface catalysis. To ascertain the nature of the reaction at lower pressures in the 12-l. apparatus used in the present study, analyses were made on reaction mixtures from isomerizations performed under the following conditions (specified as millimeters of initial pressure, temperature, duration of reaction, and method of analysis): (a) 0.7 mm, 160°, 4 hr, infrared spectrum in a 1-m gas cell with a Perkin-Elmer 421 spectrometer; (b) 0.04 mm, 175°, ~80% reaction, ultraviolet spectrum at 211–230 $m\mu$ in a 1-cm gas cell with a Beckman DU instrument; (c) 0.006 mm, 150°, 79% reaction, ultraviolet spectrum at 208–400 $m\mu$ in a 2-cm gas cell with a Cary Model 11 spectrophotometer, gas chromatogram from a Perkin-Elmer Model 154D unit with a tetraisobutylene-on-Firebrick column; (d) 0.0036 mm, 175°, ~22% reaction, Cary uv gas cell; (e) 0.0038 mm, 150°, ~20% reaction, 4-m H column with flame ionization detector.[17] In these experiments isoprene was identified by comparison with a pure sample of isoprene. Unreacted 1-methylcyclobutene was the only other substance (in amounts greater than a few tenths of a per cent) detected under the conditions used. In experiments c and d mass spectrometric analysis revealed no higher molecular weight products. Even at the high percentage of reaction in c the two methods of analysis were in satisfactory agreement for the amount of reaction (uv, 78.8%; gc, 79.5%). Inspection of the chromatograms from 0.01- to 1-mm rate experiments at 150 and 175° showed less than 0.1–0.2% of detectable products other than isoprene. Comparisons of the quantity of reactant introduced into the reaction vessel with the amount of the recovered reaction mixture showed agreement within the error of the pressure measurements. No noncondensables were detected.

To determine the possibility of a reaction of isoprene in the rate experiments the following experiments with isoprene were performed in the 12-l. vessel: (1) 0.23 mm, 175°, ~30 min; and (2) 0.0011 mm, 150°, 12 hr. In the former experiment no pressure change was observed and gas chromatography gave evidence that the sample which had been heated was identical with an untreated sample of isoprene. Likewise, the extinction coefficients of the samples after treatment in experiments 1 and 2 were the same as pure isoprene at 216 and 222.6 $m\mu$. Calculations based on literature data[18] in-

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[12] E. Gil-Av and J. Herling, *Tetrahedron Lett.*, 27 (1961).

[13] F. F. Cleveland, M. J. Murray, and W. S. Galloway, *J. Chem. Phys.*, **15**, 742 (1947). The absorption at 1720 cm^{-1} for their solution in CS_2 was not evident in the CCl_4 solution spectrum.

[14] Ultraviolet Spectral Curve 50, American Petroleum Institute Research Project 44.

[15] A. F. Pataracchia, M.S. Thesis, University of Rochester, 1961; A. F. Pataracchia and W. D. Walters, *J. Phys. Chem.*, **68**, 3894 (1964).

[16] R. W. Carr, Jr., Ph.D. Thesis, University of Rochester, 1962.

[17] The H column gives good resolution of mixtures containing mono- and diolefinic C_5 hydrocarbons; see J. Shabtai, J. Herling, and E. Gil-Av, *J. Chromatog.*, **11**, 32 (1963).

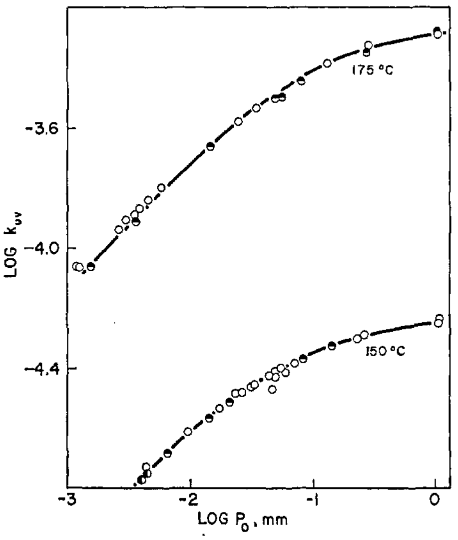

Figure 1. Pressure dependence of k_{uv}, first-order rate constant for 1-methylcyclobutene isomerization at 150 and 175°; ultraviolet spectrophotometric results.

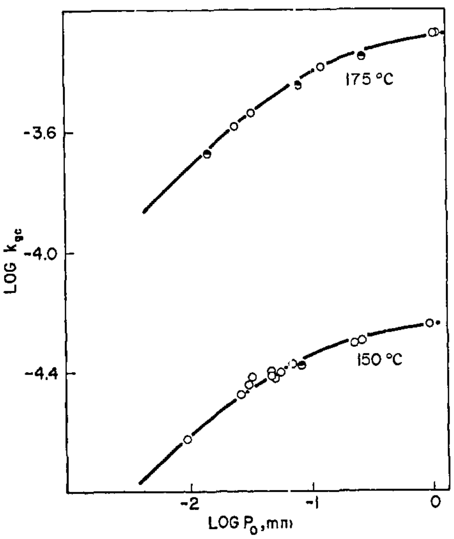

Figure 2. Pressure dependence of k_{gc}, first-order rate constant at 150 and 175°: circles, gas chromatographic results; —, k_{uv}.

dicated that any loss of isoprene *via* dimerization should be much less than 0.1% in the present work. Tests also showed that neither the time between removal and analysis nor the weak radiation from the spectrophotometer would affect the composition of the reaction mixture.

Pressure Dependence of the First-Order Rate Constant. For the study of the falloff behavior of the isomerization, the values of the first-order rate constant ($k = (1/t) \ln [P_0/(P_0 - P_I)]$ (where P_0 is the initial pressure of 1-methylcyclobutene and P_I is the pressure of isoprene formed at time t) were found from experiments at 175° for the pressure range 0.0012–1 mm and at 150° for 0.004–1 mm. In each experiment the ratio in brackets was evaluated from the spectrophotometric and pressure measurements made upon the reaction mixture after removal. The first-order rate constants are shown in Figure 1. At a pressure of 0.024 mm the first-order rate constant has decreased at 175° to about one-half the value at 1 mm and at 150° to approximately four-sevenths the value at 1 mm. For an initial pressure near 0.0015 mm at 175°, the first-order rate constant is only about one-sixth as large as it is at 1 mm. The data indicate that for experiments with approximately the same initial pressure the percentage decrease in k is somewhat greater at 175° than at 150°.

For some of the kinetic experiments, the value of the first-order rate constant was calculated from the quantities of 1-methylcyclobutene and isoprene found by gas chromatographic analysis of the reaction mixture.

In the log–log plot shown in Figure 2, each point represents a rate constant (k_{gc}) determined from gas chromatographic analysis and may be compared with the curve which was found for the ultraviolet data. The gas chromatographic data are less extensive than the ultraviolet data but show the same behavior of the rate constant at decreasing initial pressure.

In Figures 1 and 2, the half-filled circles represent experiments in which mercury pressure in the reaction vessel was decreased by changes in procedure, including cooling the mercury in the float valve M. For the higher reactant pressures, the data seem to be in good accord for the different procedures. For pressures below 0.007 mm at 175° the rate constants obtained with the lowered mercury pressure seem to lie lower and were regarded as more nearly correct for the drawing of the falloff curve.

To prepare falloff curves of log (k/k_∞) *vs.* log P_0 from the present kinetic results, one needs the values of the first-order rate constant at its high-pressure limit. For this purpose, the reciprocals of the rate constants were plotted against the corresponding reciprocals of the initial pressure and also against the reciprocals of the square root of the initial pressure.[19] Neither plot was exactly linear over the entire pressure range, but the curvatures were in opposite directions. The average of the two values for $1/k_\infty$ at one temperature was used to calculate k/k_∞. The extrapolation from the 1-mm region, although subject to some uncertainty, should be more reliable for 1-methylcyclobutene than for a simpler molecule, since for 1-methylcyclobutene the rate constant in this work seems to be approaching a limiting value and since no appreciable trend (outside the experimental error) was observed by Frey[4] over the region from 5 to 150 mm. The present values of k_∞ at 150 and 175° were 0.600×10^{-4} and 5.67×10^{-4} sec^{-1}, respectively. Values of k at 10 mm calculated from the Arrhenius expression from Frey's data would be 0.525×10^{-4} and 5.38×10^{-4} sec^{-1} at 150 and 175°, respectively.[20] An exact agreement might not be expected since the two sets of values are not calculated for the same initial pressures; moreover a 1° discrepancy in the temperature scale causes about a 10% change in rate.

Previous studies of cyclopropane,[21] cyclobutane,[22-24]

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[18] C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958).

[19] This procedure was suggested by E. W. Schlag and B. S. Rabinovitch, *ibid.*, **82**, 5996 (1960).

[20] In a private communication, Professor Frey has indicated that the rate expression is $10^{13.84} \exp\{-35035/RT\}$ in which the A factor is slightly changed from that in ref 4: H. M. Frey, Reading University, 1965.

[21] A. D. Kennedy and H. O. Pritchard, *J. Phys. Chem.*, **67**, 161 (1963).

[22] J. N. Butler and R. B. Ogawa, *J. Am. Chem. Soc.*, **85**, 3346 (1963).

[23] R. W. Vreeland and D. F. Swinehart, *ibid.*, **85**, 3349 (1963).

[24] T. F. Thomas, Ph.D. Thesis, University of Oregon, 1964.

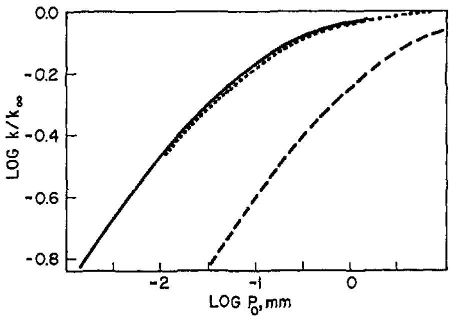

Figure 3. Comparison of the decrease in the experimental first-order rate constant for 1-methylcyclobutene at 175° with falloff data for 3-methylcyclobutene and cyclobutene: solid line, 1-methylcyclobutene; dotted line, 3-methylcyclobutene at 123.5° from ref 10; dashed line, cyclobutene at 150.4° from ref 9.

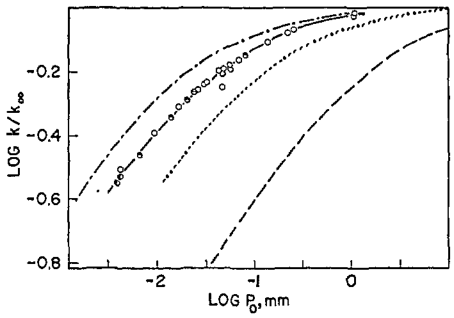

Figure 4. Comparison of the experimental and theoretical pressure dependence of the first-order rate constant for 1-methylcyclobutene at 150° with fall-off data for 3-methylcyclobutene and cyclobutene. Experimental: ○, present work, 1-methylcyclobutene, 150°; -----, 3-methylcyclobutene, 148.5°, ref 10; — —, cyclobutene, 150.4°, ref 9. RRKM theoretical: —-—, 1-methylcyclobutene, 150°, ref 11.

and methylcyclobutane[24] at 410–500° have exhibited a leveling-off of the rate constant falloff curves in the region 10^{-3} mm and below, even when 5–13-l. reaction vessels were used. In the present work no leveling-off of the falloff curve was observed for pressures of 1-methylcyclobutene in the range 0.004–0.0012 mm.

Discussion

Comparisons of the low-pressure behavior of 1-methylcyclobutene with that of cyclobutene[9] and 3-methylcyclobutene[10] may be made by inspection of Figures 3 and 4. The magnitudes of the shifts to lower pressures for the falloff curves of 1-methylcyclobutene at 150 and 175° with respect to the falloff curve of cyclobutene at 150° are about 1.54 and 1.33 log P_0 units, respectively. The displacement of the falloff curve resulting from this methyl substitution is comparable in size to that observed for replacement of H by methyl for cyclobutane (1.15–1.20 log P_0 units)[15] or cyclopropane (1.5 log P_0 units).[25] The falloff curve for 1-methylcyclobutene at 150° lies about 0.47 log P_0 unit lower than that for 3-methylcyclobutene at 148.5°. However, slightly different activation energies have been observed for reactions of cyclobutene[3,8,9] and its 1-methyl[4] and 3-methyl[5] derivatives, and Figure 3 gives a comparison of the available falloff curves at temperatures such that the values of b ($= E/RT$) are similar. For this situation, the curve for 1-methylcyclobutene at 175° almost coincides with that for 3-methylcyclobutene at 123.5° (b = 39.4 and 40.0, respectively). The similarity in the effect of methyl substitution upon the falloff curves is interesting when one considers that the cyclobutyl and cyclopropyl ring pyrolyses are characterized by much higher Arrhenius factors ($\sim 10^{15}$ sec^{-1}) and activation energies (61–65 kcal/mole) than the cyclobutene reactions ($\sim 10^{13}$ sec^{-1} and 32–36 kcal/mole, respectively), and the number and/or kinds of bonds broken are different for the three reactions. Chesick has pointed out that the magnitude of the shift in the falloff in going from cyclopropane to methylcyclopropane is in accord with the Kassel concept of intramolecular energy transfer during the lifetime of the activated molecule. The added methyl group apparently participates in the activation process as effectively as the remainder of the molecule.[25]

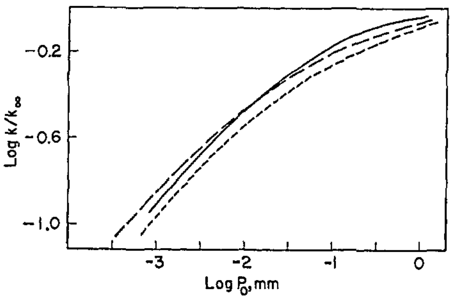

Figure 5. Comparison of the experimental data at 175.0° with the falloff curves calculated from classical Kassel theory: -----, s = 15; ———-—, s = 16; —, experimental, 1-methylcyclobutene at 175°.

The classical Kassel theory[26] of unimolecular reactions has in the past provided a convenient means for comparison of the low-pressure behavior of various molecules. Frey has performed such calculations for the 3-methylcyclobutene reaction and found that the best value of the number of effective oscillators, s, contributing to reaction was between 14 and 15.[10] The present work on 1-methylcyclobutene has also included calculation of the rate constant falloff curves using Kassel theory. Some integrations were done with a Bendix G-15 computer using the program of Schlag.[27] Other integrations, using a modification of this program by C. A. Whiteman, Jr., were performed on an IBM 650 computer. Figure 5 shows the relationship between the present data at 175° and the calculated Kassel classical falloff curves for s = 15 and 16. The theoretical curve for $s = 16$ ($E_{\text{act}} = 35.15$ kcal/mole, $\sigma = 5.9$ Å, $A = 10^{13.90}$ sec^{-1})[28] seems to offer the best fit to the experimental data, as it predicts the correct pressure region for the log k/k_∞ falloff, but is less convex than the experimental curve. A calculated curve for s = 16 at 150° gave similar agreement with the experimental results at 150° to that obtained at 175°.

For the cyclobutanes[15,23,24] and cyclopropanes,[21,25] mentioned above, the value of s (Kassel classical) is approximately 60% of the total number of vibrational de-

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[25] J. P. Chesick, *J. Am. Chem. Soc.*, 82, 3277 (1960).

[26] L. S. Kassel, "The Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., Inc., New York, N. Y., 1932, p 103.

[27] E. W. Schlag, B. S. Rabinovitch, and F. W. Schneider, *J. Chem. Phys.*, 32, 1599 (1960).

[28] Symbols are defined and used as in the standard Kassel treatment.[27] E_{act} was calculated from Frey's data by least squares, including a run done in a packed reaction vessel; A was calculated from the Arrhenius equation using E_{act} and the present experimental values of k_∞.

grees of freedom, n, while for cyclobutenes s is only about 40% of n. That the values of s for these reactions are considerably smaller than the total number of vibrational degrees of freedom is expected due to the nature of the approximations in the theory.[26,29,30]

The RRKM theory,[29] which has been formulated to take into account quantum effects and participation by all normal mode vibrations in intramolecular energy transfer, has been used by Elliott and Frey to predict the falloff in the rate constant with decreasing pressure for 1-methylcyclobutene.[11] In Figure 4, their predicted curve "B" for 1-methylcyclobutene is compared with the present experimental data for a temperature of 150°. The curvature of the experimental curve is well reproduced by that of the theoretical falloff curve, within the possible experimental error. The calculated curve for 1-methylcyclobutene lies about 0.3 log P_0 unit lower, however, with respect to pressure, than the present experimental curve. A similar difference was noted between their calculated curves and the experimental results for 3-methylcyclobutene and cyclobutene.[11,31] In both of the methylcyclobutene cases, the difference in log P_0 between the theoretical and experimental curves can be substantially reduced by the assumption of a smaller, but still reasonable, molecular diameter, *e.g.*, 5.9 Å as used in this work, instead of 7.1 Å as used by Elliott and Frey.[11]

The assumption of unit collisional deactivation efficiency may be an additional source of uncertainty in the calculated values,[11,32] even though there is much experimental evidence for highly efficient energy transfer for polyatomic molecules in some cases.[33] Frey has suggested that a collision efficiency factor for deactivation of about one-third would largely reconcile the theoretical and experimental curves for 3-methylcyclobutene[11] and cyclobutene.[11,31] A similar factor might be inferred then for the 1-methylcyclobutene.

Within the possible errors caused by the uncertainties discussed above, then, the RRKM theoretical falloff curves agree with the experimental curves for cyclobutene[34] and for the 1- and 3-methylcyclobutenes. In particular, the RRKM calculations of Elliott and Frey[11] have, within these possible errors, predicted the correct relative change in position of the falloff for cyclobutenes of different molecular complexity and for different positions of the methyl group on the cyclobutene ring by assuming all vibrational modes as active in the intramolecular transfer of energy, rather than some adjustable fraction of these (*i.e.*, s, in Kassel theory).

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(29) R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, **55**, 894 (1951); G. M. Wieder and R. A. Marcus, *J. Chem. Phys.*, **37**, 1835 (1962); R. A. Marcus, *ibid.*, **20**, 359 (1952).

(30) E. W. Schlag, *ibid.*, **35**, 2117 (1961); B. S. Rabinovitch and J. H. Current, *ibid.*, **35**, 2250 (1961); M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, *ibid.*, **37**, 1276 (1962).

(31) A recent experimental study and RRKM calculation published by Frey and Pope for perdeuteriocyclobutene gives a similar comparison between experiment and theory to that found for cyclobutene itself: H. M. Frey and B. M. Pope, *Trans. Faraday Soc.*, **65**, 441 (1969).

(32) *Cf.* J. D. Lambert, *Quart. Rev.* (London), **21**, 67 (1967).

(33) See, for example, the summary discussion in F. J. Fletcher, B. S. Rabinovitch, K. W. Watkins, and D. J. Locker, *J. Phys. Chem.*, **70**, 2823 (1966).

(34) With respect to the theoretical cyclobutene curve, some data of a preliminary nature obtained in the present study indicate that the rate constants observed for a 12-l. reaction vessel may give a slightly better curvature fit at low pressures than those found earlier for a 0.5-l. vessel. (In Figure XVIII of ref 1b, Appendix III, read [(log P_0) − 1] for log P_0.)

Radiation-Induced Interconversion of Acetone-^{14}C and 2-Propanol-^{14}C

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Abstract: The yield of 2-propanol-^{14}C (IPA*) in γ-irradiated mixtures of acetone-2-^{14}C (Ac*) and 2-propanol (IPA) is a bimolecular function of the Ac* and IPA concentrations. The maximum yield is 6.9 in an equimolar mixture of components and is the same at −196° as to 40°. The yield of Ac* in irradiated mixtures of IPA* and acetone (Ac) is also a bimolecular function of the component concentrations, with a maximum yield of 4.6 in an equimolar mixture. This conversion process is more strongly affected by temperature, and the maximum yield is lower at −196° than at 40°. Neither one of these interconversion reactions could be induced by 313-nm uv light, and the yields of γ-induced 2-butene isomerization in IPA and in Ac are relatively low. These interconversions are interpreted in terms of the various possible reactions of acetone anion (formed by electron capture) and 2-propanol cation (formed by the ionizing radiation).

Yields of hydrogen (and other products) in the radiolysis of mixtures of acetone and 2-propanol were reported some time ago;[1] the presence of small amounts of acetone (1–5 vol%) effected a marked reduction in the yield of hydrogen from the 2-propanol. At the time, this effect was interpreted in terms of hydrogen atom scavenging by the carbonyl group of the ketone.

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(1) J. D. Strong and J. G. Burr, *J. Am. Chem. Soc.*, **81**, 775 (1959).