though not proof to the intermediacy proposal; further work is planned by one of the authors (WCB).

Branch and Jones[31] have attempted to show that the brominium ion and not hypobromous acid is the intermediate in the bromination of aromatic ethers, but they have neglected to take all possible explanations into consideration and their logic is therefore inconclusive.

In discussion of reactions where there are multiple mechanistic proposals which equally and completely explain the observed data, it cannot be emphatically stated that one mechanism is exclusive; rather the reactants may be thought of as following the simplest path under the immediate conditions. It is only appropriate to think of the most probable reaction pathway rather than an exclusive mechanism.

It is suggested that this uncertainty in the evaluation of the pathway of a chemical reaction may be referred to as the *principle of mechanistic indeterminancy.* A forthcoming publication on the periodate–glycol reaction will discuss this in more detail. Systems of this type appear to be very common; in fact, it is an exceptional reaction to which this idea cannot be applied. The only qualification is that a simple equilibrium must be associated with the reaction under consideration. A complete evaluation of the mechanism of any reaction cannot be made until all plausible mechanisms are assembled and are assumed to be contributors of varying importance to the over-all system.

Acknowledgments.—The authors wish to express their appreciation to Mr. Walter Sampson, Glassblower, and Mr. John S. Heiser, Instrument Maker, for the many helpful suggestions and for their excellent work in the construction of the stirred flow apparatus.

[31] S. J. Branch and B. Jones, *J. Chem. Soc.*, 2317 (1954); 2921 (1955).

[CONTRIBUTION FROM THE UNIVERSITY OF WASHINGTON, SEATTLE 5, WASHINGTON]

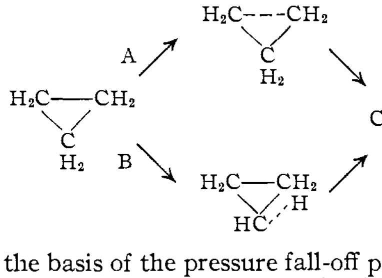
Kinetics of the Thermal Unimolecular Isomerization Reactions of Cyclopropane-d_2[1]

BY E. W. SCHLAG[2] AND B. S. RABINOVITCH

RECEIVED MARCH 15, 1960

The structural and geometric thermal unimolecular isomerization of cyclopropane-d_2 has been studied at 718°K. over a pressure range. The fall-off behavior was found to be the same as that of light cyclopropane at this temperature, a fact difficult to interpret by the Slater theory. A value of $n = 14$ fits both isomerization processes. Activation energies were measured at several pressures in the fall-off regions. Relevant reaction mechanisms are discussed in light of the findings. Comparison to previous data for light cyclopropane at 773°K. is made. An improved method for graphically determining k_∞ is suggested.

An important example of a unimolecular reaction is the isomerization of cyclopropane to propylene.[3] This reaction has gained particular prominence as the first to which the theory of Slater has been applied in detail.[4,5] Two mechanisms for this reaction proposed by Chambers and Kistiakowsky[3] have been the most important:



On the basis of the pressure fall-off predicted by the Slater analysis for the two mechanisms ($n = 13$ for mechanism B, $n = 3$ for mechanism A), it has been concluded that "hydrogen transfer" as in mechanism B accorded best with the experimental findings.[4–6]

If, however, the reaction coördinate for "ring opening" by mechanism A were not a highly symmetrical coördinate as was used[4] but was instead a more complex coördinate,[7] this would increase the theoretically predicted value of n, and then ring enlargement[8] is not necessarily excluded. In fact, "ring opening" by mechanism A could result in the geo-

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[1] Abstracted in part from a Ph.D. thesis by E. W. S., University of Washington, 1958. This work was supported by a grant from the National Science Foundation.

[2] Department of Chemistry, Northwestern University, Evanston, Illinois.

[3] T. S. Chambers and G. B. Kistiakowsky, THIS JOURNAL, **56**, 399 (1934).

[4] N. B. Slater, *Proc. Roy. Soc.* (*London*), **A218**, 224 (1953).

[5] H. O. Pritchard, R. G. Sowden, A. F. Trotman-Dickenson, *ibid.*, **A217**, 563 (1953).

[6] This conclusion contained the implicit, though reasonable, assumption that "ring opening" as in mechanism A is not characterized by a bond dissociation energy significantly less than the 65 kcal. observed value for isomerization; an energy below 65 kcal. for ring opening has been proposed by many investigators.

[7] B. S. Rabinovitch and K.-W. Michel, THIS JOURNAL, **81**, 5065, (1959). (It should be noted that the values of k_∞ and of n for cyclobutane, given in this reference, were based on an unfortunate error in transcription of the literature rate data and are incorrect.)

[8] The terminology "trimethylene biradical" and "ring opening" has been employed to describe an intermediate species in mechanism A. This name and description must not be taken too literally since the opening ends of the cyclopropane structure would not be removed from each other's sphere of influence, nor are they in trimethylene. The exact nature of this expanded ring is open to discussion; *cf.* our previous note[9] and Smith.[10]

NOTE ADDED IN PROOF.—M. C. Flowers and H. M. Frey [*J. Chem. Soc.*, 2758 (1960)] have concluded recently, on the basis of certain experimental tests, that the occurrence of a biradical intermediate in the thermal isomerization of cyclopropane is ruled out. We believe that these tests are intrinsically incapable of providing the criterion alleged. In addition, their results actually may be interpreted as being suggestive of the existence of an appreciable reorganization energy upon ring opening and, hence, suggestive of the existence of an appreciable barrier to recyclization of a singlet trimethylene biradical. If this were to be confirmed by further experimental tests which can be performed, then it would indeed be quite meaningful to speak of the existence of a singlet biradical as an entity with operational significance. B. S. R. thanks Dr. Frey for a preprint of this paper.

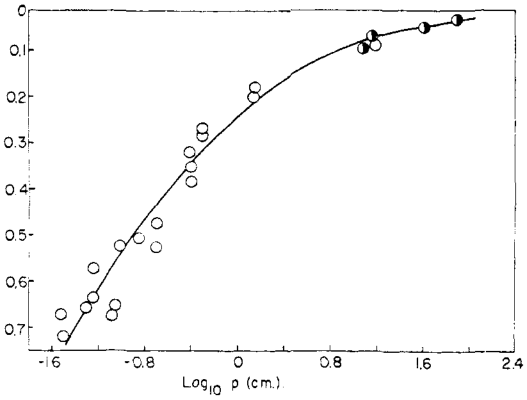

Fig. 1.—Fall-off plot for geometrical isomerization of cyclopropane-d_2, 718°; ⊙, pure gas; ◑, H_2 inert.

metric *cis–trans* isomerization which we have reported in a preliminary account of incomplete results of this study with cyclopropane-d_2[9]; although this finding still leaves indeterminate a positive choice between the two mechanisms.[10] In the present paper are presented the complete results of our work on the thermal unimolecular isomerization of cyclopropane-d_2.

Experimental

Materials.—*cis*- and *trans*-Cyclopropane-d_2 were prepared by the reduction of cyclopropene by methods analogous to those used previously for acetylenic stereospecific reductions.[11] The compounds were purified by means of gas chromatography.[12] The *trans*-cyclopropane-d_2 contained about 6% cyclopropane-d_1 and 8% *cis*-cyclopropane-d_2. Correction for these was made in the calculations. The *cis*-cyclopropane-d_2 was of similar composition.

Light cyclopropane, Matheson tank-grade quality, was purified similarly.

Apparatus.—A standard vacuum apparatus was employed with two reactors; one was a 175 cc. fused silica vessel, and the other was a 4.2 l. Pyrex vessel. The temperature uniformity in the large furnace was ±0.6° and in the small furnace was ±0.1°. Temperature fluctuation during a run was ~0.2°. Temperature was measured with chromel–alumel thermocouples calibrated against a standard Pt–10% Rh couple. The limit of accuracy of the determination of the temperature is estimated to be >0.5°.

Procedure.—*trans*-Cyclopropane-d_2 was used as starting material for most runs. The reaction sample was removed from the furnace at periodic intervals and was analyzed for geometric isomerization. Small samples were also taken for gas chromatographic analysis. Only in runs at extremely low pressures was a substantial part of the sample consumed in chromatographic analysis, and at the lowest pressure used each time point corresponded to a separate run. Runs were carried to 25–30% *cis* and 6–10% propylene formation. The *cis-trans* equilibrium ratio is unity within experimental error.

Analysis.—Propylene analysis was made by gas chromatography. The absolute error was ~0.2%. The geometric isomers were analyzed with a Beckman IR-2 spectrometer at 11.83 μ, a very intense *cis* band. The infrared spectra are given elsewhere.[12] Empirical Beer–Lambert law constants were obtained for the mixtures. Calibration was made in terms of optical density per unit pressure Γ, a value that was independent of the total pressure up to a pressure of 1.5 cm. The absolute accuracy of this analysis was ~0.5%.

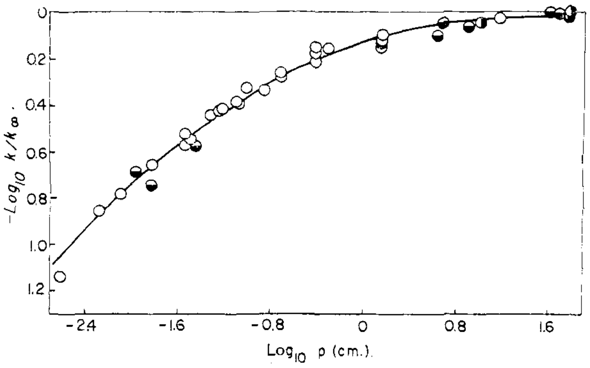

Fig. 2.—Fall-off plot for structural isomerization: cyclopropane-d_2, ⊙, pure gas; ◑ H_2, inert; cyclopropane, ◒.

Results

Heterogeneity.—After initial seasoning with cyclopropane, no increase in rate was noted with packed vessels having a ten-fold higher surface/volume ratio. A reproducible reaction rate could always be attained without difficulty, the rate being identical for seasoned quartz and Pyrex vessels.

Effect of Oxygen.—As much as 0.2 mm. pressure of air had no effect on the rate constants for geometric and structural isomerization.

Pressure Fall-off.—Rate constants for geometric and structural isomerization, k_g and k_p as defined below, are presented in Figs. 1 and 2, respectively, as a function of pressure at 718.0°K. The theoretical Slater fall-off curves for $n = 14$ are drawn in. These curves give good fit, although the accuracy is such that $n = 13$[4,5] must be considered equally valid. To obtain the theoretical curves, Slater's table[13,14] of $I_n(\theta)$ was extended by calculation on an IBM 650 digital computer.[12] The fall-off can be equally well fitted by the classical Kassel expression with $s = 11$.

The pressure ranges covered for the geometric and structural isomerizations correspond to factors of 3×10^3 and 2×10^4, respectively. The values of $k_{p\infty} = 1.57 \times 10^{-5}$ sec.$^{-1}$ and $k_{g\infty} = 4.0 \times 10^{-4}$ sec.$^{-1}$ at 718°K. were employed. The fall-off for the structural isomerization of light cyclopropane is seen to be identical, within experimental error, to that for cyclopropane-d_2 (Fig. 2). Experimental values of the constant, $\gamma = p/\theta$, were computed from the data of Figs. 1 and 2 and are $\log \gamma = -5.85$ for k_g, and $\log \gamma = -6.32$ for k_p; for $n = 13$, $\log \gamma = -5.73$ for k_p.

Inert Gas.—In order to conserve deuterated reactant, hydrogen was used to approach the high pressure region. Relative efficiencies of 0.2 for k_p and 0.3 for k_g, on a pressure for pressure basis, were established. These numbers were determined near the high pressure region; the different efficiencies for the two processes is probably due in large part to

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(9) B. S. Rabinovitch, E. W. Schlag and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(10) F. T. Smith, *ibid.*, **29**, 235 (1958), and private communication. An internal rotation analog of the hydrogen transfer mechanism for geometric isomerization has been pointed out by Smith. Inasmuch as we have already postulated[9] onset of hindered internal rotation in the activated complex for ring opening and Smith has later amplified his proposal to include ring expansion, the distinction between the two mechanisms, although real, becomes somewhat less drastic and more semantic than might first appear and is responsible for the difficulty in making a positive operational distinction; however, see ref. 8.

(11) B. S. Rabinovitch and F. S. Looney, THIS JOURNAL, **75**, 2652 (1953). The trimethyl cyclopropyl ammonium iodide precursor was obtained through the courtesy of Professor K. B. Wiberg.

(12) E. W. Schlag, Ph.D. thesis, University of Washington, 1958.

(13) N. B. Slater, *Phil. Trans. Roy. Soc.* (*London*), **A246**, 57 (1953).

(14) N. B. Slater, "The Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959.

TABLE I

ARRHENIUS PARAMETERS FOR STRUCTURAL AND GEOMETRIC ISOMERIZATION OF CYCLOPROPANES

	p (718.0°K.), cm.	log A_g	E_g, kcal. mole	log A_p	E_p, kcal./mole
cyclo-$C_3H_4D_2$	0.03	14.0	59.5 ± 2.6^a	13.3	61.4 ± 1.4^a
	1.5	14.6	59.6 ± 1.3	14.3	63.0 ± 0.5
	~76 (3 atm. H_2)	16.41	65.1 ± 0.5		
	~56 (3 atm. H_2)			15.12	65.4 ± 1.1
cyclo-C_3H_6	76.5			15.26	65.9 ± 0.4

[a] Probable error.

the experimental error attendant on the determination of inert gas efficiencies in this region. The relative efficiency of hydrogen reported previously[5] for light cyclopropane was 0.24.

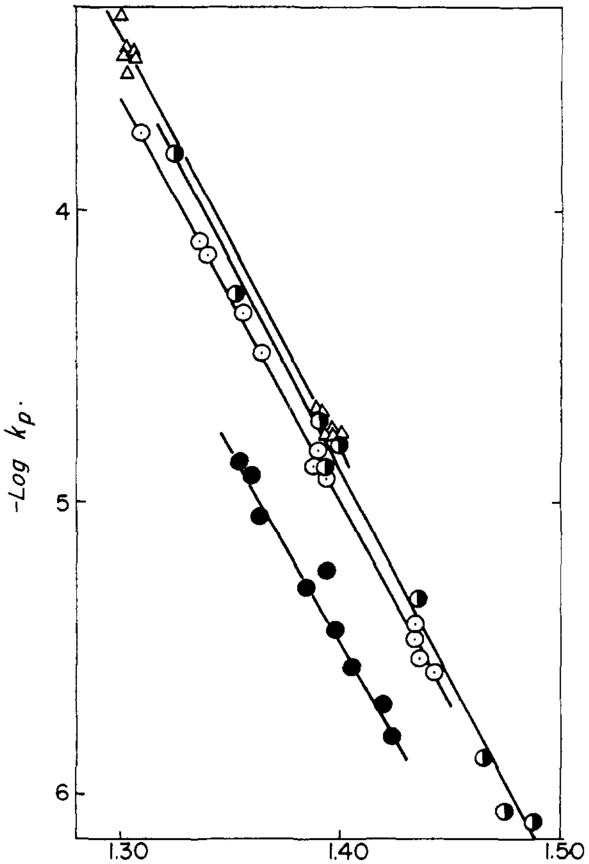

Fig. 3.—Plot of log k_p *vs.* $1/T$: cyclopropane-d_2, ◑, 3 atm. H_2; ⊙, 1.5 cm.; ●, 0.03 cm.; cyclopropane, △ 76 cm.

Effect of Temperature.—The temperature dependence of rate was investigated at three pressures for both structural and geometric isomerizations; light cyclopropane was studied as well (Figs. 3 and 4). The Arrhenius parameters fitted by least squares are summarized in Table I. The decline of E with pressure is expected in theory, while the greater decline for E_g relative to E_p is consistent with the fact that the geometric isomerization is farther into the fall-off region than is the structural isomerization, at the same pressure.

Although the difference between E_p and E_g for cyclopropane-d_2 at $p = \infty$ is given as only 0.3 kcal., it is evident from inspection of activation energies at lower pressures in Table I, as well as from the slight inversion of the magnitudes of E_p as between light and deuterated species, that there is experimental error here: that for $p = \infty$, E_p is quite likely at least 1 kcal. greater than E_g and that the ratio of A factors is probably a little less than stated.

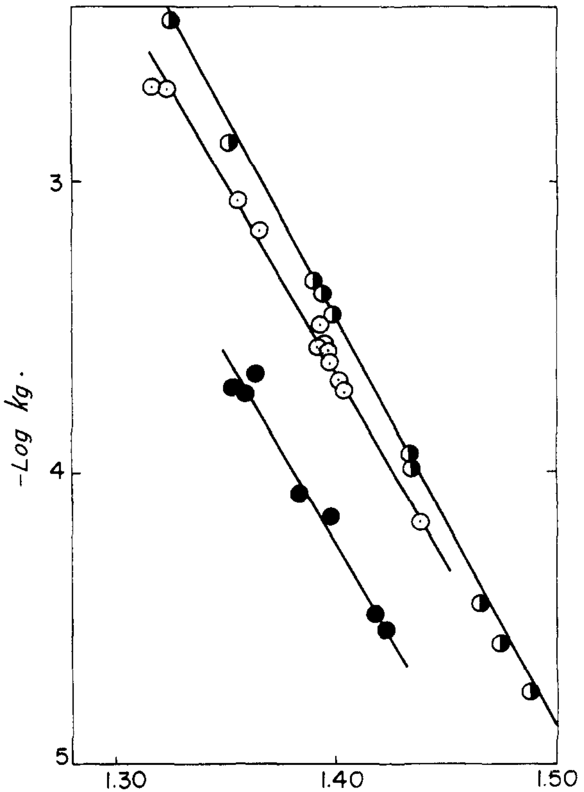

Fig. 4.—Plot of log k_g *vs.* $1/T$ for cyclopropane-d_2; ◑, 3 atm. H_2; ⊙, 1.5 cm.; ●, 0.03 cm.

Exchange Reactions.—The occurrence of inter- or intra-molecular exchange processes was ruled out by mass spectrometric analysis of the product cyclopropanes. Cyclopropane-d_1 or -d_3 would be formed by an intermolecular process and 1,1-cyclopropane-d_2 by an intramolecular process if these occurred; the relevant peaks were absent in the products.

Discussion

Mechanism of the Reaction.—Consider the scheme

$$\begin{tikzcd}
T \arrow[r, shift left, "k_aM"] & T^* \arrow[l, shift left, "k_dM"] \arrow[r, shift left, "k_1"] \arrow[dr, "k_4"'] & b \arrow[l, shift left, "k_2"] \arrow[r, shift left, "k_2"] \arrow[d, "k_3"] & C^* \arrow[l, shift left, "k_1"] \arrow[r, shift left, "k_dM"] \arrow[dl, "k_4"] & C \arrow[l, shift left, "k_aM"] \\
& & P & &
\end{tikzcd}$$

in which T* and C* refer to particular states of collisionally energized *trans-* and *cis*-cyclopropane-d_2, b is an enlarged ring intermediate and P is propylene. Define the observed rate constants

$$k_g = -\frac{1}{(T - C)}\frac{d(T - C)}{dt},\ k_p = \frac{1}{(T + C)}\frac{dP}{dt}$$

where k_g is defined in this way partly for reasons of convenience.

In mechanism A($k_4 = 0$), k_g is a pure measure of ring expansion. Various postulates may be appropriate to the microscopic processes involved at each internal energy quantum state of reacting molecules. For the well-known model of Kassel, the observed rate constants may be adequately formulated, with use of the steady-state method applied to the above reaction scheme, as a single summation or integration of Lindemann terms over relevant energies[15]

$$k_g = \sum \frac{k_a k_1 M}{k_d M + k_1};\quad k_p = \sum \frac{k_a k_1 M}{k_d M(2k_2/k_3 + 1) + k_2}$$

where k_dM is the average collision frequency per molecule, while k_aM includes the energy distribution function factor.[16]

It can be seen that in mechanism A, the fall-off displayed by the two constants will be *roughly* similar except for a modified collision frequency in the case of k_p.[17] This will have the effect of shifting the curves on the pressure axis if the ratio k_2/k_3 is virtually independent of energy, as seems to be indicated by our previous work in which the decomposition of vibrationally highly excited cyclopropane was studied.[18] The similarity in the observed fall-off shapes and activation energies found here is thus explicable in this mechanism. Explanation of the data by mechanism B is also made in terms of the postulated similarity in the nature of the two transition states,[10] and the frequency factor difference is included *post hoc* by an assumed entropy difference.

It seems worthwhile to make a few additional remarks concerning these mechanisms; however, in view of the indecisiveness of choice we refer elsewhere[12] for elaboration: (1) for geometric isomerization to occur by mechanism A, internal rotation in the "biradical" must be rapid. It can be shown from statistical calculations of rate constants on the Marcus model that this seems indeed the case. (2) The observed value of the pre-exponential factor for k_g (Table I) can be encompassed in mechanism A by an enhanced entropy of activation in the processs leading to biradical formation. As pointed out before,[9] the observed entropy of activation is explained by a loosened ring having hindered internal rotation. The enhanced frequency factor $\sim 10^{16}$ seems more difficult to envisage for mechanism B,[10] notwithstanding the increased reaction path degeneracy in this mechanism. (3) Failure to find an experimental effect due to radical inhibitors or to find a C_6 dimer is not an argument against "ring opening" by mechanism A. Statistical calculations reveal that this equilibrium lies well over on the side of excited cyclopropane molecules and collision processes are not of importance.

Extrapolation to k_∞.—In order to evaluate n as in the fall-off plots of Figs. 1 and 2, it is first necessary to obtain k_∞. This is often done by a straight line extrapolation of a plot of k^{-1} *vs.* p^{-1}. Since there is neither theoretical nor practical justification for this plot, it seems better to employ a plot that may be extrapolated to k_∞ with less curvature. An improvement is effected[12] by a plot of k^{-1} *vs.* $p^{-1/2}$, and this has been used here. A further example of application of this plot has been given elsewhere.[7]

The Propylene Pressure Shift with Temperature.—Slater has suggested that a useful test of his theory is the temperature dependence of fall-off behavior.[13] A comparison of the data of this study with the data for light cyclopropane (for which they give $n = 13$) obtained by Pritchard, Sowden and Trotman-Dickenson[5] as corrected to $773°K$.[19] may be made since $I_n(\theta)$ is found here to be the same for both light and deuterated cyclopropane (Fig. 2). The pressure shift with temperature predicted by Slater theory is $\Delta \log p = n/2 \log T_2/T_1 = 0.2$ for $n = 13$–14. The value of $\gamma = p/\theta$ is $10^{-5.73}$ for $n = 13$ at 718°K. and $10^{-5.20}$ from the work of Pritchard, *et al.*, for $n = 13$ at 773°K., whence $\Delta \log p_{\text{expt.}} = 0.53$ for this intra-process pressure shift. Although the data may be adjusted somewhat by choosing values of k_∞ in both cases so as to give a smaller experimental pressure shift with temperature, the large discrepancy cannot be bridged. The quantum model of Slater occasions an even larger discrepancy ($\Delta \log p = 0.10$ is predicted).[20] Hence it appears that for these data the theoretical relation is not borne out.

The Pressure Shift between Structural and Geometric Isomerization.—The experimental shift between the two fall-off curves (Figs. 1 and 2) is $\Delta \log p = 0.47$ (for $\Delta n = 0$). As mentioned above,

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(15) H. S. Johnston, *J. Chem. Phys.*, **20**, 1103 (1952). It is implicit in this formulation that the unimolecular rate constants k_1, k_2, k_3 and k_4 may be represented at a particular total vibrational energy by average values characteristic of the total energy. Explicit experimental support for this view is found in the recent work of J. N. Butler and G. B. Kistiakowky [THIS JOURNAL, **82**, 759 (1960)] on the equivalence of the reaction ability of methyl cyclopropanes which have been energized by different activation processes, by our own similar results with cyclopropane-d_2 (ref. 18) and by the equivalence of the rates of decomposition of *sec*-butyl radicals formed at the same total vibrational energy by different chemical reactions (R. E. Harrington, B. S. Rabinovitch and H. M. Frey, *J. Chem. Phys.*, in press). The more general cases of inefficient collisional energy transfer and of pressure-dependent specific decomposition probabilities have been examined recently by Buff and Wilson [F. P. Buff and D. J. Wilson, *J. Chem. Phys.*, **32**, 677 (1960); D. J. Wilson, *J. Phys. Chem.*, **64**, 323 (1960)].

(16) If mechanism B applies ($k_3 = 0$, and b is then an activated complex), there would be a small contribution to k_g from the structural isomerization process (*ca.* 4%) *i.e.* one has expressions of form, $k_a M(k_1 + k_4)/(k_d M + (k_1 + k_4))$; while for k_p these are of form $k_a M k_4/(k_d M + k_4)$. In either mechanism k_g is substantially, if not rigorously, to be identified with geometric isomerization. For a detailed formulation of the kinetic schemes, ref. 12 may be consulted.

(17) In this and the following discussion, the different regions of energy involved in the equations for k_g and k_p may be kept in mind and tend to complicate detailed interpretation of the experimental findings.

(18) B. S. Rabinovitch, E. Tschuikow-Roux and E. W. Schlag, THIS JOURNAL, **81**, 1081 (1959).

(19) H. S. Johnston and J. R. White, *J. Chem. Phys.*, **22**, 1969 (1954).

(20) N. B. Slater, *Proc. Roy. Soc.* (*Edinburgh*), **A64**, 161 (1955). It may be noted that the pressure shift with temperature seems a more powerful test between Slater's classical and quantum models than is the change of activation energy with temperatures predicted in the quantum model.

the main source of a pressure shift at constant temperature between these two processes for the same fall-off parameter n lies in mechanism A in the modification of the collision constant by the factor $(2k_2/k_3 + 1)$. It should be remembered that the summations in equations 1 and 2 are over different energy regions and the factor cited is not given by the ratio of observed rate constants.

The Kinetic Isotope Effect.—An average ratio of observed rate constants of 1.22 was found for structural isomerization of light and deuterated cyclopropane at 718°K., which gives a value of $k_H/k_D = 2.18$ after correction for the hydrogen in propylene-d_2.[21] This is a reasonable order of magnitude. Over the range of pressures studied, comparison of the fall-off for light and heavy cyclopropane reveals no change in the ratio (Fig. 2). This indicates that for this range of pressure and the comparatively small region of fall-off covered the value of k_H/k_D underwent no change outside of experimental error. However, accurate determination of the isotopic rate ratio should be based on an internal comparison method; our data do not provide a proper basis for further discussion, except the remark that they do not support the results of a previous isotope rate study.[21a] The isotope effect would not be expected to disappear entirely at the low pressure limit.

Average Rate Constant.—The high pressure average rate constant of the reacting molecule, for geometric isomerization, may be represented in the manner of Johnston and White[19] as

$$<k_E>^T_\infty = k_d M(k_{g\infty}/k_g - 1)$$

The value of this quantity obtained from the data of Fig. 1 is 2.27×10^7 sec.$^{-1}$. This magnitude is adequately encompassed by a modified expression of the form

$$k_{\bar{E}} = A \left\{ \frac{\bar{E} - E_0 + E'_z}{\bar{E} + E_z} \right\}^{s-1}$$

used earlier by us elsewhere,[18] where $s = 20$–21, and the other quantities have their usual significance. A value of $s \simeq 20$ is much greater than the value obtained from the classical expression for $k_{\bar{E}}$ and contrasts also with the value of $s = 11$ obtained for fit of the fall-off with the classical Kassel expression; the value of s needed to fit experimental data on a quantum model is considerably larger than that obtained from a classical calculation; a detailed quantum calculation of the fall-off behavior by Marcus[22] indicates that a value of $s = 21$ gives a fit of the data for structural isomerization.

The Value of n.—From this study of cyclopropane and cyclopropane-d_2, the value of n determined from the fall-off of k_p by an application of the classical Slater theory is 13–14; this is the same as the value found previously for light cyclopropane.[5] In Slater's theory, $n = 14$ is the highest value which n can assume for light cyclopropane, which has seven doubly degenerate vibrational modes. For the cyclopropane-d_2 molecule, for which only twofold symmetry operations are possible, there are no degenerate vibrations, and according to the theory this should result in an increase in the value of n toward 20 or 21. This is not found here to be the case. This invariance of n in cyclopropane-d_2, as found from the fall-off, or non-equilibrium behavior, of the system, may be the most unequivocal test to date of the postulates of the theory.

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(21) (a) R. E. Weston, *J. Chem. Phys.*, **23**, 988 (1955); **26**, 975 (1957); (b) J. Bigeleisen and M. Wolfsberg, *Adv. Chem. Phys.*, **1**, 15 (1958).

(22) R. A. Marcus, private communication. We thank Prof. Marcus for permission to quote these unpublished results.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS COMPANY, SOUTH CHARLESTON, WEST VIRGINIA]

Polymerization of Styrene by *n*-Butyllithium. II. Effect of Lewis Acids and Bases[1]

BY F. J. WELCH

RECEIVED APRIL 25, 1960

The rate of polymerization of styrene initiated by *n*-butyllithium is greatly accelerated by small quantities of Lewis bases, such as ethers or amines, and retarded by Lewis acids, such as zinc or aluminum alkyls. From the dependence of rate on acid and base concentration information was obtained concerning the nature of the interaction of these additives with lithium alkyls. Evidence is presented which confirms that acids form complexes of the type RLi·A with lithium alkyls, whereas bases form complexes of the type RLi·2B. Equilibrium constants for complex formation have been calculated from the rate data. The strength of the complexes with bases decreases in the order tetrahydrofuran > 2,5-dimethyltetrahydrofuran > ethyl ether, triethylamine. With acids the order is triisobutylaluminum > di-*n*-butylzinc. Ethyl sulfide, tri-*n*-butylphosphine, di-*n*-butylmercury and alkyl halides do not form strong complexes with lithium alkyls in benzene solution.

Introduction

In the presence of small quantities of lithium alkyls styrene polymerizes by a mechanism involving the successive additions of lithium alkyl to the double-bond of the monomer forming a new lithium alkyl.[2] For *n*-butyllithium concentrations <0.020 *M* polymerization in hydrocarbon solvents obeys the simple rate law

$$\frac{-d(M)}{dt} = k\,(RLi)\,(M)$$

However, the addition of small quantities of ethers, particularly tetrahydrofuran, or tertiary amines causes a large increase in the rate of polymerization.[2,3] Lewis bases of this type also have a marked effect on the stereospecificity[4-6] and rate[6] of diene

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(1) Presented in part at the 135th Meeting of the American Chemical Society, Boston, April, 1959

(2) F. J. Welch, THIS JOURNAL, **81**, 1345 (1959).

(3) K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Sci.*, **35**, 259 (1959).

(4) H. Morita and A. V. Tobolsky, THIS JOURNAL, **79**, 5853 (1957); A. V. Tobolsky and C. E. Rogers, *J. Polymer Sci.*, **40**, 73 (1959).