

The data reported here provide no new information concerning the NH frequencies in the charged amino group. On this point we have nothing to add to the studies reported earlier.¹⁰

Recent investigations, notably those of Frank and Wen¹¹ and of Némethy and Scheraga,¹² have emphasized the importance of interactions between hydrocarbon groups and surrounding water molecules in aqueous solutions. The presence of ionic groups in such solutions also leads to reorientation and compression of water molecules around the charged groups. The transformation of a basic amine to a positively charged alkylammonium ion in aqueous solution therefore involves highly significant changes in the surrounding water structure. In our studies we cannot clearly trace just what influence the surrounding water structure may exert on the vibrational frequencies of the solute molecules, but we believe that future, more adequate treatments of these systems must take account of such interactions.

Of the compounds whose spectra are reported here, only malonic acid and the ions derived from it have, to our knowledge, been previously studied in aqueous solution.¹³ The frequencies recorded here are in good agreement with those found in the earlier study except that we now find a somewhat greater downward displacement of the C-H stretching frequencies on ioniza-

tion of the two carboxyl groups. Ethylenediamine and ethanolamine have been previously studied as the anhydrous bases, but not apparently in water solution or in the cationic form. Data on anhydrous ethanolamine were reported by Kohlrausch, *et al.*¹⁴ Our data are in excellent agreement with theirs, although we find a few additional frequencies that they did not observe. Anhydrous ethylenediamine has previously been studied by several workers.¹⁵⁻¹⁷ Here again our data are for the most part in very good agreement with the earlier work, although we have not observed some of the previously reported weak bands below 600 cm.⁻¹. The polarization data of Chauduri¹⁷ are in general accord with ours in Table I, although the numerical agreement is far from precise. This is not surprising in view of the inherent difficulties and uncertainties of such measurements.

The bending frequency ("scissors" motion) of the methylene groups in all the compounds we have studied remains almost completely unchanged by dissolving the diamines in water or by adding acid to protonate the amino groups. In all cases it is close to 1460 cm.⁻¹ and the observed variations are scarcely outside the limits of experimental error. Thus the behavior of this bending frequency offers a marked contrast to the behavior of the C-H stretching frequencies.

(14) K. W. F. Kohlrausch and G. P. Ypsilanti, *Z. physik. Chem.*, **B29**, 274 (1935); **32**, 407 (1936).

(15) K. W. F. Kohlrausch and F. Köppl, *Sitzungsber. Akad. Wiss. Wien*, **143**, 537 (1935); *Mh. Chem.*, **65**, 185 (1935).

(16) R. Ananthakrishnan, *Proc. Indian Acad. Sci.*, **5**, 285 (1937).

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(10) J. T. Edsall and H. Scheinberg, *J. Chem. Phys.*, **8**, 520 (1940).

(11) H. S. Frank and W.-Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).

(12) G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3399 (1962).

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Thermal Unimolecular Geometric and Structural Isomerization of 1,2-Dideuterio-3-methylcyclopropane¹

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The thermal geometric and structural unimolecular isomerization of methylcyclopropane and of *trans*-, *cis*-, and *cis,trans*-1,2-dideuterio-3-methylcyclopropane have been studied over a range of temperatures. Individual Arrhenius parameters have been determined for the various possible isomerization reactions. The total rate expressions are $k_{ds}(\text{struct}) = 10^{14.43} \exp(-62,300 \text{ cal./RT})$ and $k_{ds}(\text{geom. total}) = 10^{15.36} \exp(-60,500 \text{ cal./RT})$, and $k(\text{struct}) = 10^{14.61} \exp(-62,400 \text{ cal./RT})$. Isotope rate effects, including secondary effect, have been measured. The relation to other work and to the mechanisms of these reactions is discussed.

Introduction

The structural isomerization of cyclopropane to propene³ is one of the most studied examples of a unimolecular reaction. The experimental work encompasses thermal studies over a wide temperature⁴ and pressure^{5,6} range (although not a wide range of fall-off, unfortunately), the use of chemical activation techniques to produce highly vibrationally excited nearly monoenergetic cyclopropane molecules,⁷ and

the study of the magnitude of deuterium^{8,9} and tritium⁹ isotope effects. Attention has also been given to the structural isomerization reactions of substituted¹⁰⁻¹² cyclopropanes.

In addition to structural isomerization reactions, Rabinovitch, Schlag, and Wiberg¹³ discovered the reversible *cis-trans* geometric isomerization of cyclopropane-*d*₂, which they have interpreted in terms of a trimethylene *cum* expanded-ring^{6,7b,7c,14} intermediate. This discovery has initiated new discussions on the mechanism of the structural and geometric isomerization^{12,14} reactions and of the role of trimethylene.¹⁵

(8) (a) A. T. Blades, *ibid.*, **39**, 1401 (1961); (b) B. S. Rabinovitch, D. W. Setser, and F. W. Schneider, *ibid.*, **39**, 2609 (1961).

(9) (a) R. H. Lindquist and G. K. Rollefson, *J. Chem. Phys.*, **24**, 725 (1956); (b) R. E. Weston, *ibid.*, **26**, 975 (1957).

(10) (a) J. P. Chesick, *J. Am. Chem. Soc.*, **82**, 3277 (1960); (b) M. L. Halberstadt and J. P. Chesick, *ibid.*, **84**, 2688 (1962).

(11) J. N. Butler and G. B. Kistiakowsky, *ibid.*, **82**, 759 (1960); **83**, 1324 (1961).

(12) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc. (London)*, **A257**, 122 (1960); **A260**, 424 (1961); *J. Chem. Soc.*, 1157, 1689 (1962), and earlier references cited.

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

(14) F. T. Smith, *ibid.*, **29**, 235 (1958).

(1) (a) Abstracted in part from the Ph.D. thesis of D. W. S., University of Washington, 1961; (b) this work was supported by the National Science Foundation.

(2) National Science Foundation Predoctoral Fellow.

(3) T. S. Chambers and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **56**, 399 (1934).

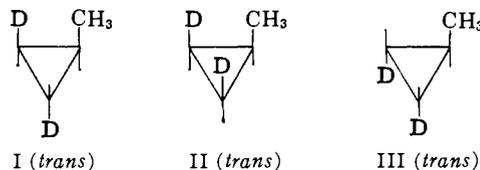
(4) W. E. Falconer, T. E. Hunter, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 609 (1961).

(5) H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc. (London)*, **A217**, 563 (1953); A. D. Kennedy and H. O. Pritchard, *J. Phys. Chem.*, **67**, 161 (1963).

(6) E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5986 (1960).

(7) (a) H. M. Frey and G. B. Kistiakowsky, *ibid.*, **79**, 6393 (1957); (b) B. S. Rabinovitch, E. Tschuikow-Roux, and E. W. Schlag, *ibid.*, **81**, 1981 (1959); (c) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

The original objective of the present work when initiated in 1958 was to provide a direct crucial test¹⁶ between the mechanism of Rabinovitch and co-workers and that of Smith¹⁴ through a kinetic study of the three geometric isomers of 1,2-dideuterio-3-methylcyclopropane: by labeling one side of the ring with



methyl, it might be possible to distinguish whether simultaneous¹³ or only consecutive¹⁴ rotation of two D bonds can occur. Unfortunately, owing largely to the difficulties encountered in the attempted preparation of pure isomers, this aim has not yet been achieved. Since useful information, including geometric and structural isomerization rate constants and isotope effects for formation of each butene product, has been obtained, it seems well not to delay publication of these data further.

Experimental

Materials.—Two isomeric mixtures (A and B) of 1,2-dideuterio-3-methylcyclopropane of the following composition were prepared and identified by previously described techniques¹⁷: (A) 48.5% of I, 48.5% of II, and 3% methylcyclopropane-*d*₁; (B) 45.5% of I, 2.3% of II, 43.2% of III, 2.9% methylcyclopropane-*d*₃, and 6.1% methylcyclopropane-*d*₁. Mixture A was used for all kinetic runs unless otherwise specified.

Light methylcyclopropane, prepared by treatment of 1,3-dibromobutane with zinc dust, was purified by g.l.p.c.

Apparatus.—All the runs were made in a spherical 315.8-cc. Pyrex vessel which was connected to a conventional gas-handling vacuum system. The dead volume was less than 0.5%. Temperature was measured by three chromel-alumel thermocouples, calibrated at the melting point of pure zinc, which were symmetrically located around the reaction vessel. The vertical and horizontal temperature gradients were ± 0.9 and $\pm 0.3^\circ$, respectively; temperature drift during a run was $\pm 0.3^\circ$. All reported temperatures are the appropriate time and geometric averages.

Analytical.—Analysis of methylcyclopropane and the four isomeric butenes was done by g.l.p.c., with use of a 20-ft. column of ethylene glycol saturated with silver nitrate. Geometric isomer analysis of I, II, and III was effected with a Beckman IR-5 infrared spectrometer equipped with specially designed cells which minimized the required sample size. Figure 1 shows the spectra of mixtures A and B. The actual composition of reacted mixtures was found by comparison with empirical calibration curves constructed from the intensities of the characteristic absorption lines of isomers I, II, and III, measured in mixtures of known composition. These calibration mixtures were prepared by combining mixture B with mixture A in desired proportions.

Procedure.—The Pyrex reaction vessel was seasoned in the same way that has proved to be satisfactory for other cyclopropane reactions.^{5,6} Since the geometric and structural isomerization rates differ by a factor of twenty, the rate constants for these simultaneous reactions were obtained from entirely different sets of runs and the procedure for each case is described below.

In the geometric isomerization study, 2 cc. of mixture A was used for each run. The sample was injected into the reaction vessel and at specific times the entire sample was rapidly and quantitatively removed from the furnace and analyzed for isomers II and III (isomer I remains constant). The entire 2-cc. sample was then degassed and returned to the reaction vessel. This was repeated four times during a run. Since the geometric isomerization reaction is considerably faster than the reaction giving butenes, it was possible to do the infrared analysis without removing the butenes, provided that the percentage of *cis-trans* isomerization was limited to less than 10%. It was shown that up to 1% of air impurity had no influence on the rate constants;

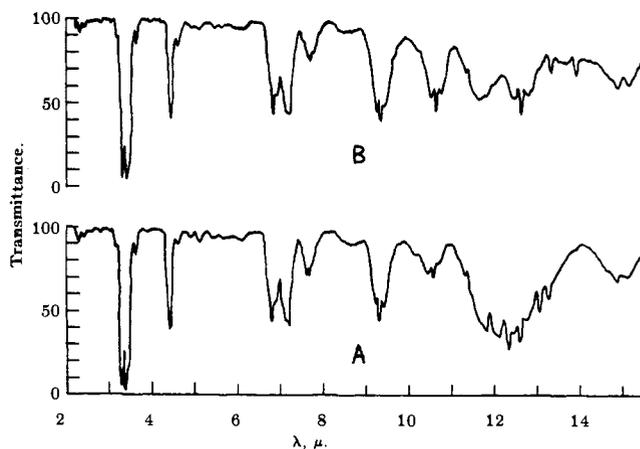


Fig. 1.—Infrared spectra of mixtures A and B measured at 7-cm. pressure, 11-cm. light path.

therefore any traces of air present as a result of the reintroduction of samples into the furnace were of no consequence.

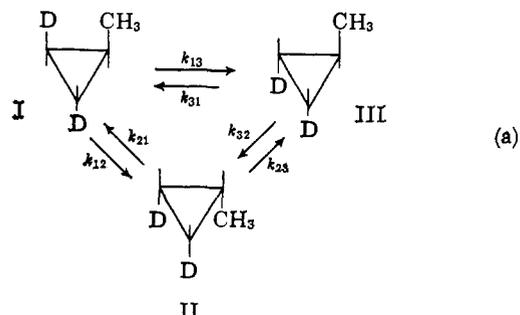
The structural isomerization provides a measure of the isotope effect as between methylcyclopropane and methylcyclopropane-*d*₂. In order to minimize error, and because an internal comparison technique was impossibly difficult, alternate runs were made using methylcyclopropane and methylcyclopropane-*d*₂ (mixture A, 97% -*d*₂) as reactant at each of the temperatures. For these runs the reaction vessel was modified so that small (0.02–0.04 cc.) samples could be withdrawn for g.l.p.c. analysis at various times without disturbing the run pressure significantly.

Results

Equilibrium Composition of Methylcyclopropane-*d*₂.

—The equilibrium ratio for the isomers I:II:III was found, within the experimental error, to be 2:1:1, the ratio of their statistical weights. A sample of mixture A was heated at 431.7° for a period corresponding to 7 half-lives. After removal of the butene products, the infrared absorption spectrum was virtually identical with that of a mixture prepared so as to have a methylcyclopropane-*d*₂ composition of 50% I, 25% II, and 25% III.

Geometric Isomerization Rate Constants.—For reasons of simplicity, the data were fitted to the following kinetic scheme. Somewhat more detailed alternate schemes can be written but are not necessary at the present time. It is shown later that butene formation from I, II, or III has the same rate and so does not perturb the measurement of geometric isomerization rate constants. It is evident that, very closely,



$$k_{21} = k_{31} = 2k_{12} = 2k_{13}; \quad k_{23} = k_{32}$$

From the measured equilibrium ratios, together with scheme (a) and the initial composition of mixture A, the following equations describing the variation of the concentration of II and III with time can be derived.

$$\text{II} = 25[1 + \exp(-(k_{23} + k_{32} + k_{12})t)] \quad (1)$$

$$\text{III} = 25[1 - \exp(-(k_{23} + k_{32} + k_{13})t)] \quad (2)$$

The 3% of (*-d*₁) impurity plays no role in the measured process; the first-order rate constants k_{II} and k_{III}

(15) (a) E. T-Roux, M.S. Thesis, University of Washington, 1958, and E. W. Schlag, Ph.D. Thesis, University of Washington, 1958, have detailed discussion and calculations of many points in ref. 6 and 7b which are related to these reactions; detailed rate and fall-off calculations based on these models are given in ref. 7c and 8b; (b) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(16) See T. D. Trotman-Dickenson, *Ann. Rev. Phys. Chem.*, **10**, 255 (1959).

(17) D. W. Setser and B. S. Rabinovitch, *J. Org. Chem.*, **26**, 2985 (1961).

TABLE I
SOME EXPERIMENTAL RATE PARAMETERS FOR METHYLCYCLOPROPANE ISOMERIZATIONS

Rate constant	k/k'	Methylcyclopropane		Methylcyclopropane- d_2	
		$\log A$	E_a , kcal./mole	$\log A$	E_a , kcal./mole
k_a	1.36 ± 0.03	14.61 ± 0.19 (15.45) ^a	62.4 ± 0.6 (65.0 \pm .7) ^a	14.43 ± 0.16	62.3 ± 0.5
k_t (b \rightarrow b)	1.30 ± 0.04	14.32 ± 0.19	$64.4 \pm .6$	14.26 ± 0.13	64.5 ± 0.6
k_o (b \rightarrow b)	$1.28 \pm .03$	$13.97 \pm .17$	$61.9 \pm .6$	$13.76 \pm .15$	$61.5 \pm .5$
k_i (a \rightarrow b)	$1.10 \pm .03$	$14.06 \pm .21$	$64.3 \pm .6$	$13.98 \pm .15$	$64.1 \pm .5$
k_b (b \rightarrow a)	$1.50 \pm .03$	$14.14 \pm .18$	$62.0 \pm .6$	$13.87 \pm .16$	$61.6 \pm .5$

^a Value of Chesick^{10a} at a pressure of 10 cm.; differences are given in this reference as $(E_i - E_b) = (E_i - E_{t+c}) = 2.3$ kcal. mole⁻¹. These compare favorably with the above values.

which were measured at constant concentration (2.0 cc. of gas at 25° in a 315.8-cc. vessel corresponding to an average pressure of 1.1 cm.) over the temperature range from 380 to 420° are shown in Fig. 2. Least-squares analysis gave $k_{II} = 10^{15.3} \pm 0.4 \exp(-60,400 \pm$

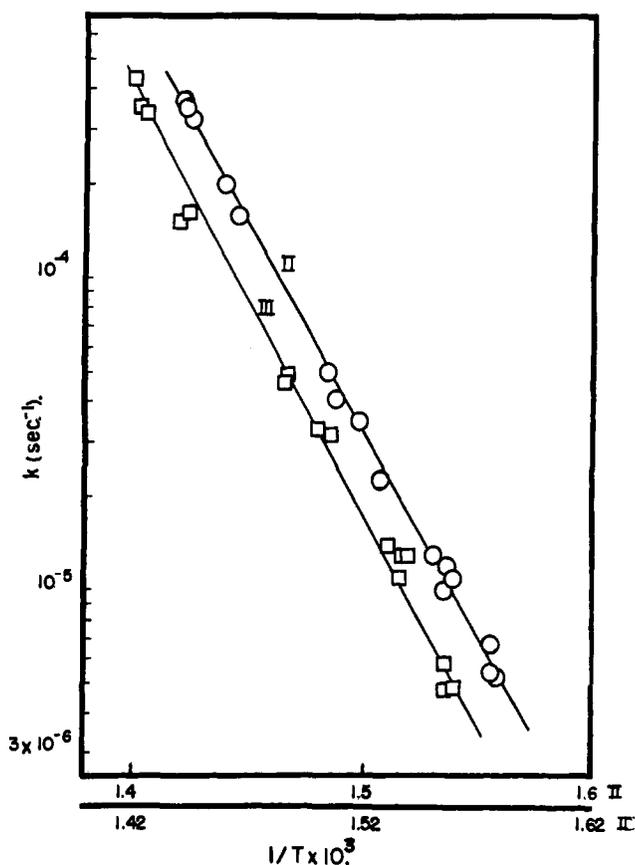
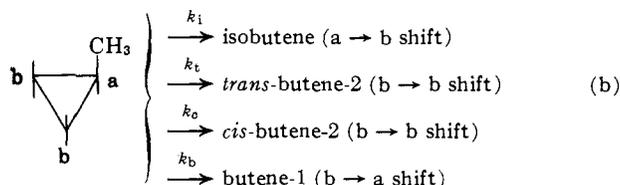


Fig. 2.—Arrhenius plot of k_{II} and k_{III} vs. $1/T$. For k_{III} , the abscissa was shifted for clarity.

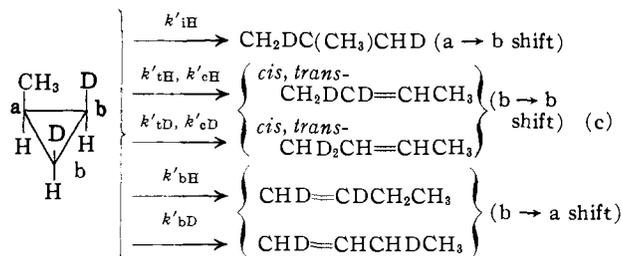
$900/RT$) and $k_{III} = 10^{15.4} \pm 0.5 \exp(-60,700 \pm 1700/RT)$, which are identical within experimental error.

Structural Isomerization Rate Constants.—The following kinetic scheme defines the system



The over-all rate constant, k_s , for methylcyclopropane isomerization is the sum of the individual butene formation rates, *i.e.*, is calculated from the total rate of disappearance of methylcyclopropane. The corresponding rate constants for methylcyclopropane- d_2 will be indicated by primes.

For the deuterio compounds the following type of scheme, illustrated for the *cis* isomer, applies



where the subscript H or D refers to the atom which migrates and the labeling of ring carbons follows reference 11: carbon a has an attached methyl group, while carbon b carries two hydrogen atoms.

Table I summarizes the relative product yields.

The following formulation,^{9b} illustrated for butene-1 formation, was used to obtain the relative isotope effect *per H or D atom* for a particular reaction

$$\frac{k_b}{k'_b} = \frac{\alpha_b k_{bH}}{\gamma_b k'_{bH} + \beta_b k'_{bD}}; \quad (\alpha_b = \gamma_b + \beta_b)$$

where α is the number of transferable H atoms in methylcyclopropane that lead to a particular product butene, and is 1 or 2; β and γ are the number of D and H atoms, respectively, that lead to the same butene- d_2 , where β is 0 or 1 and γ is 1; k_H is the rate constant per H atom for H transfer in methylcyclopropane; and k'_H and k'_D are the corresponding constants for H and D atom transfer, respectively, in methylcyclopropane- d_2 .

The ratio k_H/k'_H is simply an intermolecular secondary isotope effect since H migrates in both cases; only the isobutene ratio k_{iH}/k'_{iH} , which is 1.10 ± 0.03 , can be measured, owing to lack of knowledge of deuterium positions in the product deuteriobutenes. This is the first measurement of a secondary isotopic rate ratio in cyclopropane isomerization. It will be assumed that this is the correct order of magnitude of the corresponding ratio for formation of the other deuteriobutenes by H migration. Applying this correction to the data of Table I gives the intermolecular primary isotopic ratios: $k_{tH}/k'_{tD} = 1.59$, $k_{cH}/k'_{cD} = 1.41$, or an average of 1.50, and $k_{bH}/k'_{bD} = 2.36$. These values actually still contain a small residual secondary effect, since when a D atom migrates in the ($-d_2$) compound, the presence of the second D also contributes a small effect ($\sim 5\%$). These magnitudes compare favorably to $k_H/k_D = 2.18$ and 1.96 measured for cyclopropane- d_2 ⁶ and $-d_6$ ⁸ respectively, at or near the equilibrium high pressure region.¹⁸ The isotope effect for butene-1 and -2 formation is independent of the identity of the reactant isomer (II or III): some special short-time low per cent conversion runs were done with both mixtures A and B; measurement of the butene

(18) The pressure dependence of these mixed primary-secondary isotope effects should be remembered; under nonequilibrium thermal activation conditions, a large inverse secondary effect can predominate if there is sufficient deuteration of the molecule (see ref. 8b and F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **85**, 2365 (1963)).

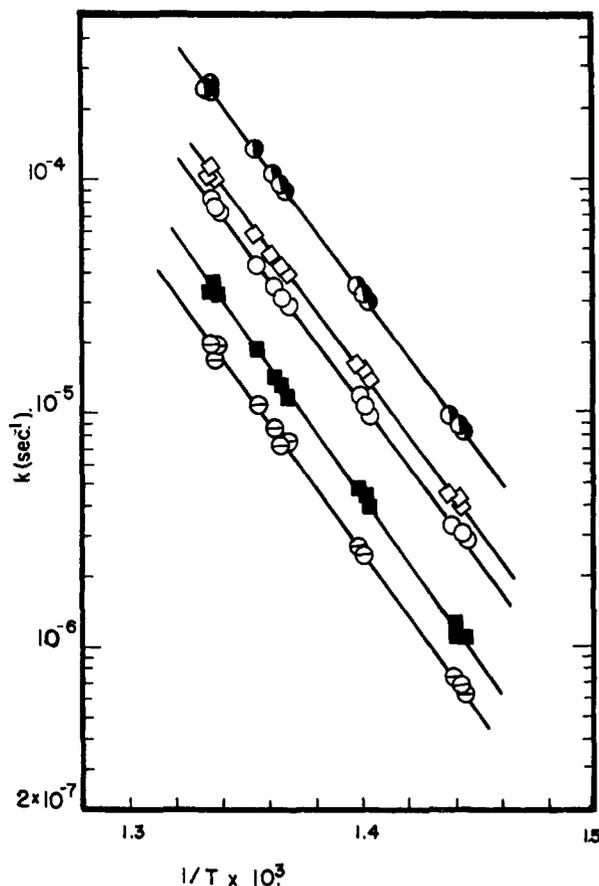


Fig. 3.—Arrhenius plot for light methylcyclopropane: \bullet , k_{a2} ; \square , k_t ; \circ , k_a ; \blacksquare , k_b ; \ominus , k_i .

ratios before more than 2% geometric isomerization had occurred revealed no detectable difference in structural isomerization rates between the two mixtures (the ratio butene-1:butene-2 was 0.871 for A and 0.873 for B).

The present study is in excellent agreement with that of Chesick^{10a} on the relative rates of butene product formation. At the center of the temperature range, these are $k_t:k_i:k_a:k_b = 0.138:0.082:0.33:0.46$ and $0.143:0.099:0.35:0.41$ for methylcyclopropane and methylcyclopropane- d_2 , respectively; Chesick gives for the former $0.135:0.077:0.30:0.48$.

In order to estimate the magnitude of fall-off at 1.1 cm. pressure, four runs at 465° were carried out using 65 cm. of methane as an inert gas, which was assumed to produce the high pressure rate. The measured $k_s/k_{s\infty}$ ratio varied between 0.88 and 0.94; an average of 0.9 was taken. This is of the expected magnitude, based on Chesick's fall-off curve.^{10a}

Activation Energy for Structural Isomerization.—The Arrhenius plots of the thermal structural isomerization rate constants for methylcyclopropane and methylcyclopropane- d_2 are shown in Fig. 3 and 4, respectively. The data were obtained under the same concentration conditions as the geometric isomerization data, Fig. 2; the temperature range was from 420 to 475°. Least-squares analysis of the structural isomerization data is summarized in Table I; the k/k' ratios are the average of the respective ratios over the entire temperature range. Since these data are not accurate enough to reveal a change in the activation energies for methylcyclopropane- d_2 , this is the best measure of the isotope effect that can be obtained.

Chesick reported $k_{s\infty} = A_{\infty} \exp(-E_{a\infty}/RT) = 2.8 \times 10^{15} \exp(-65,000 \text{ cal. mole}^{-1}/RT) \text{ sec.}^{-1}$. We find at 1.2 cm. pressure, *i.e.*, at $k/k_{\infty} \approx 0.9$, $k_s =$

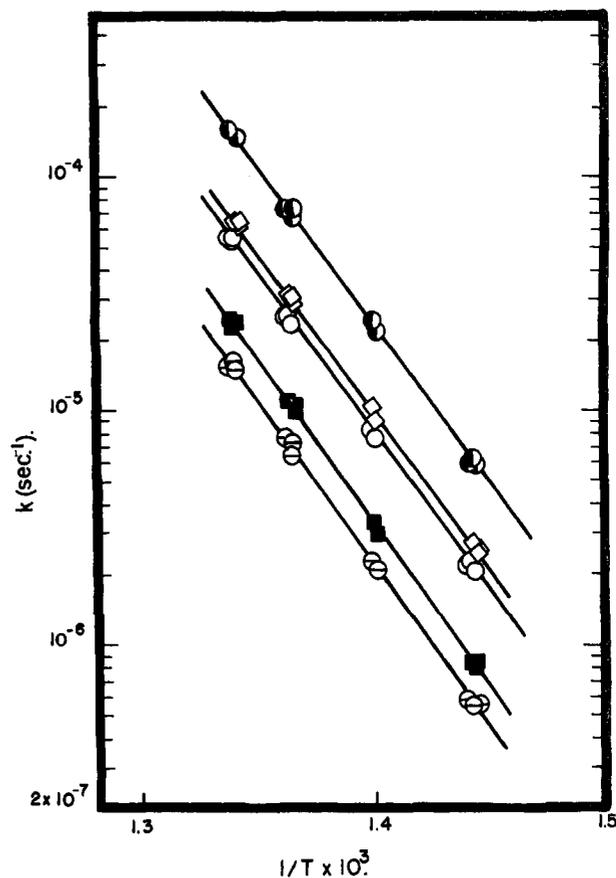


Fig. 4.—Arrhenius plot for methylcyclopropane- d_2 : \bullet , k'_s ; \square , k'_t ; \circ , k'_a ; \blacksquare , k'_b ; \ominus , k'_i .

$4.1 \times 10^{14} \exp(-62,400 \text{ cal. mole}^{-1}/RT) \text{ sec.}^{-1}$. The absolute magnitudes of the two rates are in good agreement, although there is a small disagreement in their temperature coefficients. An upper limit to $E_{a\infty}$ based on our data would be $63.2 \text{ kcal. mole}^{-1}$. On the basis of the general trend of lowered E_a values in structural isomerizations of dimethyl-substituted cyclopropanes (Table II), the activation energy for methylcyclopropane might be expected to be somewhat lower than $65.1 \text{ kcal. mole}^{-1}$, which is the well-established value for cyclopropane,⁴ and therefore we favor the lower value.

TABLE II
HIGH PRESSURE EXPERIMENTAL RATE PARAMETERS FOR
CYCLOPROPANE ISOMERIZATIONS

Compound	Geometric isomerization ^a		Structural isomerization ^b	
	E_g , kcal. mole ⁻¹	$\log A_g$, sec. ⁻¹	E_s , kcal. mole ⁻¹	$\log A_s$, sec. ⁻¹
Cyclopropane- d_3 ^b	65.1 ± 0.5	16.41	65.4 ± 1.1	15.12
Methylcyclopropane- d_2 ^c	60.5 ± 1	15.35	62.3 ± 0.5	14.43
<i>cis</i> -1,2-Dimethylcyclopropane ^d	59.4	15.25	61.7	14.60
1,1-Dimethylcyclopropane ^e	62.6	15.05
			63.6	15.37

^a It should be noted that different authors have defined this rate constant in different ways and the experimental rate constants must be related to the microscopic unimolecular rate constants. This affects only the A_g factor. ^b Reference 6. These authors stated that the observed difference of 0.3 kcal. for $E_s - E_g$ is too low and is quite likely at least 1 kcal. mole⁻¹ and that the A_g/A_s ratio is therefore slightly lower than the apparent value. ^c This work; the data were obtained at 1.1 cm. pressure; no corrections have been applied to give high pressure parameters, since the change would be very small; k_{11} and k_{111} have been averaged. ^d Reference 20; the structural isomerization parameters are our combination of the reported individual processes. ^e Reference 12.

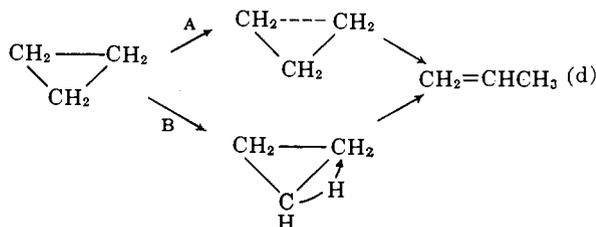
The activation energy trends, etc., are consistent for both methylcyclopropane and methylcyclopropane-

d_2 . The following points seem well established: the activation energy for isobutene formation is ~ 2.3 kcal. mole $^{-1}$ higher than butene-1; *cis*-butene-2 and butene-1 have nearly identical activation energies; and the activation energy for *trans*-butene-2 formation is higher (~ 2.5 kcal. mole $^{-1}$) than for *cis*-butene-2. Chesick did not separate his butene-2 data into individual *cis* and *trans* rate constants.

In a study of light and perdeuteriocyclopropane, Blades⁸ found $(k_H/k_D) = 0.82 \exp(1300/RT) = 1.96$ at 755°K. The failure to find (Table I) a small temperature coefficient for the isotope effect in the present less-accurate comparison is not surprising, and should not be considered as a conflict with Blades' work.

Discussion

Structural Isomerization Mechanism.—Rabinovitch and Schlag^{6,13} first suggested that a combination of the original cyclopropane mechanisms, A and B, of Kistiakowsky³ could explain structural isomerization



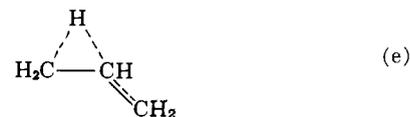
The present results bear on this general mechanism of isomerization of cyclopropanes.

The simultaneous labeling of the ring by methyl and D substituents allows clear distinction of primary and secondary isotope effects relative to the light compound. The larger ratios measured here, 1.50 and 2.36, are largely primary, reflecting the fact that in the activated complexes for structural isomerization to butene-1 and butene-2, the entropy and zero point energy factors associated with the breaking of the migrating C-D bond play an important role; thus mechanism B must be incorporated into the formulation. Such effects cannot be mainly secondary in nature, a possibility which has recently been alluded to,¹⁹ since the measured ratio for rupture of the carbon-carbon bond (which carries the two D atoms) with migration of H in both cases, to form isobutene, was given above as only 1.10 and is a secondary effect.

Evidence also exists in the present study which supports earlier work and the concept that the rupture of a particular C-C bond (*i.e.*, mechanism A) is also important in the formation of the transition state: The activation energy for isobutene formation is ~ 2.3 kcal. mole $^{-1}$ higher than for butene-2 or butene-1 (Table I). This indicates that the process in which the $a \rightarrow b$ hydrogen shift occurs involves higher activation energy than $b \rightarrow a$ or $b \rightarrow b$ shifts; this is difficult to explain on the basis of mechanism B alone, but it is well known that methyl substitution lowers C-C bond energies, and mechanism A should be responsive to these effects. (The b-b carbon bond is the stronger; there is a general trend (Table II) of decreasing E_a with methyl substitution on the cyclopropane ring.) The lower activation energy found by Flowers and Frey¹² for pentene-2 formation from *cis*-1,2-dimethylcyclopropane, as compared to *trans* isomer reactant ($\Delta E_a = 2$ kcal.),¹² is further evidence that supports an aspect of mechanism A, and indicates C-C bond extension and relief of methyl-methyl repulsion in the activated complex. That rotation of the $\text{C} \begin{array}{l} \text{CH}_3 \\ \diagdown \\ \text{H} \end{array}$ groups occurs before H transfer in 1,2-dimethylcyclo-

propane structural isomerization was further shown by their finding that the ratio of *cis*- and *trans*-pentene-2 ($b \rightarrow a$ shift) was the same for both *cis*- and *trans*-dimethylcyclopropane reactants and was near the equilibrium value. Vinylcyclopropane^{20a,b} and isopropenylcyclopropane^{20c} have been found to isomerize structurally with recyclization to cyclopentene and 1-methylcyclopentene, respectively.

Earlier from this Laboratory^{7c,8b,15a} has quantitatively defined the consequences of a transition state of type (e) for structural isomerization of cyclopropane and dimethylcyclopropane incorporating these features:



one C-C bond is completely or virtually broken and an H is bonded between two carbon atoms. This transition state is consistent with the above observations and was shown to reproduce both the fall-off behavior and k_∞ (*i.e.*, the entropy of activation or A factor) for cyclopropane and to fit, in addition, the magnitude of the hydrogen-deuterium isotope effects reported by Blades at high and lower pressures. More recently, Benson and Nangia¹⁹ have used a different frequency assignment in the complex for a calculation of the rate and isotope effect at the high pressure limit. Rabinovitch, Setser, and Schneider^{7c,8b} and Marcus and Wieder²¹ have shown that calculational results are insensitive to details of the activated complex assignment, as long as the high pressure A factor is fitted.

***cis-trans* Isomerization Reactions.**—Data on *cis-trans* isomerizations are summarized in Table II. The data for methylcyclopropane- d_2 fit with the other work: (a) The activation energy for geometric isomerization is lower than for structural isomerization. (b) The pre-exponential factor for geometric isomerization is larger than that for structural isomerization.

It was postulated by RSW that geometric isomerization proceeds *via* formation of a trimethylene singlet diradical intermediate, and that the activated complex is an expanded ring. The geometric transition state has a larger entropy than that for structural rearrangement, which was attributed largely to (hindered) internal rotations of the terminal CH₂ groups; these are absent in the structural complex. Seubold's^{22a} qualitative explanation as to why a short-lived diradical intermediate would not have been intercepted in various experimental attempts^{22b} was pertinent. Support for his conclusion was cited by RSW from their quantum statistical calculations of the internal energy level densities of cyclopropane and trimethylene (described in detail in ref. 15a and subsequently refined further) which provide a quantitative measure for the many-fold larger rate of intramolecular rate of recyclization of trimethylene relative to ring rupture of energized cyclopropane. These calculations, which were made for various levels of total energy and varying estimates of the depth of the potential well (barrier to cyclization) of trimethylene, were confirmed by some conventional thermodynamic equilibrium constant calculations subsequently reported.^{15b}

The cyclization barrier for trimethylene is not known; it is quite probably around 7–12 kcal. as most steric strain and thermochemical data suggest,^{22a,23}

(20) (a) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961); (b) C. A. Wellington, *J. Phys. Chem.*, **66**, 1671 (1962); (c) H. M. Frey and P. C. Marshall, *J. Chem. Soc.*, 3981 (1962).

(21) G. M. Wieder and R. A. Marcus, *J. Chem. Phys.*, **37**, 1835 (1962).

(22) (a) F. H. Seubold, Jr., *ibid.*, **22**, 945 (1954); (b) H. O. Pritchard, R. Sowden, and A. F. Trotman-Dickenson, *ibid.*, **22**, 945 (1954).

(19) S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, **38**, 32 (1963).

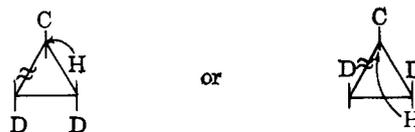
and only a fairly wide range of values for the recyclization rate constant can be given. In an absence of this knowledge, and in recognition of the mechanism of H "turn-over" of Smith¹⁴ (which was later modified by him⁶ to include some ring expansion, with consequent less real difference and increasing semantic difference between his and our viewpoints), we may simply characterize the mechanism by its activated complex, namely, as "expanded ring." On this basis, Simons²⁴ has calculated a complete fall-off curve for geometric isomerization of cyclopropane-*d*₂ in good agreement with experiment, both with respect to shape and absolute pressure.

The *cis-trans* isomerizations of cyclopropane-*d*₂ and dimethylcyclopropane involve, respectively, the rotations of $\text{>C}\langle\begin{smallmatrix} \text{H} \\ \text{D} \end{smallmatrix}\right\rangle$ or $\text{>C}\langle\begin{smallmatrix} \text{H} \\ \text{CH}_3 \end{smallmatrix}\right\rangle$ groups. Geometric isomerization of methylcyclopropane-*d*₂ may involve both motions and the total rate will reflect the magnitude of each. The rate constant obtained in this work is a measure of k_{12} (or k_{13}) and k_{32} (or k_{23}), but it is impossible so far to evaluate the individual contributions. We had hoped to determine the relative magnitude of k_{21} (or k_{31}) and k_{32} (or k_{23}), and whether only one group at a time can rotate, as proposed by Smith, or whether both groups of the expanded-ring complex can rotate simultaneously, as proposed by us. The starting reactant should be either isomer II or III, or, less desirably, data for I could be combined with present measurements; these preparative efforts continue.

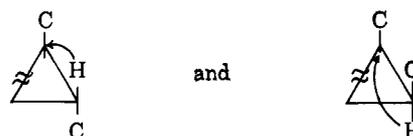
Some specific experimental evidence already can be cited, however, against the Smith mechanism. Consider the relative rates of formation of butene-1 by either

(23) H. J. Dauben, Jr., private communication, gives the value as 9.7 kcal. Reference 6 cites explicit experimental evidence from work of Flowers and Frey for a recyclization barrier. Owing to the relative rate^{15a} of internal rotation, absence of a barrier would support a Smith¹⁴ type mechanism.

(24) J. W. Simons and B. S. Rabinovitch, submitted to *J. Phys. Chem.*



Since H (or D) turn-down into the plane is involved in Smith's reaction coordinate, then a difference in rate would be expected when the more mobile H was *cis* or *trans* to the CH₃ substituent; as described in the results, none was found. Similarly, none was found earlier by Flowers and Frey¹² between the rates of formation of 2-methylbutene-1 from *cis*- and *trans*-dimethylcyclopropane



Benson^{15b} has given a qualitative argument that Smith's mechanism should involve an activation energy appreciably greater than 65 kcal.

Finally, it should be noted that calculation of the rate constant for cyclopropane structural isomerization in no way depends on formation of a trimethylene intermediate or its properties, since a separate activated complex for structural isomerization having higher free energy exists, as pointed out by Schlag and Rabinovitch^{6,25}; RSW noted that reasonable models for these complexes, considered as formed from a trimethylene intermediate (see also ref. 15a), gave back the proper relative magnitudes of *A* factors, *i.e.*, entropies of activation and relative observed rates of geometric (*cf.* ref. 22) and structural (*cf.* ref. 7c, 8b) isomerization of cyclopropane-*d*₂.

(25) The statement by Benson and Nangia⁹ that SR described the geometric and structural complexes to have the same *E*_a value is explicitly contradicted in ref. 6 (see also footnote b, Table II); various other statements in this and earlier references by these authors also reflect some misunderstandings concerning our interpretations.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

The Xenon-Radiosensitized Deuterium-Methane Exchange. Recombination Rate Constant for Deuterium Atoms and Methyl Radicals

By A. MASCHKE AND F. W. LAMPE

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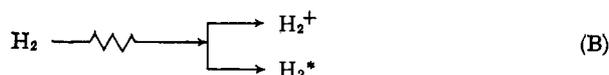
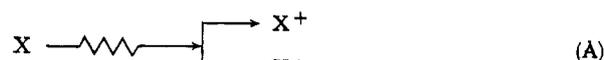
The radiation-induced deuterium-methane exchange, sensitized by xenon, is shown to proceed *via* deuterium atoms and methyl radicals. All deuteriomethanes (*d*₁-*d*₄) are formed simultaneously, and, at low partial pressures of deuterium, significant amounts of deuterioethanes, deuteriopropanes, and deuteriobutanes are formed. A kinetic treatment of the deuteriomethane formation results in an estimate of the recombination rate constant for deuterium atoms and methyl radicals that is in good agreement with the specific collision rate assuming a collision diameter of 2.6 Å.

Introduction

The use of rare gases to sensitize hydrogen atom reactions in gaseous systems subjected to ionizing radiation was reported some time ago.^{1,2} This technique potentially can provide rather high concentrations of hydrogen atoms and thus seems to afford a convenient way to study reactions of hydrogen atoms with molecules and free radicals. This paper reports the results of studies in which xenon was used to sensitize the deuterium atom-induced exchange between deuterium and methane.

Briefly, the technique is based upon the use of high concentrations of sensitizer and hydrogen (or deuterium) and relatively low concentrations of substrate.

In this way more than 90% of the energy absorbed by the system, in the passage of the ionizing radiation, can be absorbed by sensitizer and hydrogen (or deuterium); the result of such energy absorption is ionization and excitation. Letting X represent sensitizer, we may thus write for the primary act



Electronically and/or vibrationally excited hydrogen may dissociate, spontaneously or upon collision, to hydrogen atoms or may upon collision be deactivated.

(1) F. W. Lampe, *J. Am. Chem. Soc.*, **82**, 1551 (1960).

(2) C. F. Smith, B. G. Corman, and F. W. Lampe, *ibid.*, **83**, 3559 (1961).