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The Kinetics of Thermal Isomerization of Methylcyclopropane

BY JOHN P. CHESICK

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Methylcyclopropane undergoes a homogeneous thermal isomerization to the four isomeric butenes. This reaction has been studied in the gas phase by static methods from 440 to 490° over a pressure range of 6×10^{-3} to 20 cm. At high pressures the reaction is first order with a rate constant $k = 2.8 \times 10^{15} \exp(-65.0 \text{ kcal.}/RT)\text{sec.}^{-1}$. At low pressures the rate decreases as predicted for unimolecular reactions in pressure regions where collisional activation becomes a rate controlling step. This decrease in rate occurs at about $^1/_{30}$ of the pressure at which the same effect has been observed in the cyclopropane rearrangement. The shift in the pressure dependence is interpreted as proof of the importance of intramolecular energy transfer in the lifetime of the activated molecule. This is contrary to the fundamental assumption of the Slater theory of unimolecular reactions, and therefore this theory in its present form appears to be inapplicable to molecules of the complexity of the cyclopropanes. The effects of added inert gases in increasing the low pressure rate were found to be similar to data published for the cyclobutane decomposition reaction. The temperature and pressure dependencies in the butene isomer product distributions are reported.

Introduction

Theories of unimolecular reactions must in general cope with the questions of intra- and intermolecular energy transfer and the factors which determine the probability of rearrangement of a molecule once it becomes activated. The criteria for "activation" vary according to the theory being considered. Experimental work to date has been confined chiefly to measurements of rate constants of suitable reactions over ranges of pressure and temperature. To be useful in experimental tests of the theories, the reactant molecule must undergo a unimolecular reaction which is free of complicating side or chain reactions over a pressure range varying by a factor of at least 10^4. The molecule should also be fairly simple, in order to place the transition between the limiting high pressure first order behavior and the second order region in an experimentally observable pressure region. It is in the low pressure region that collisional activation becomes rate controlling.

To date studies have been carried out on the unimolecular reactions of cyclopropane,[1] cyclobutane,[2,3] nitrous oxide[4] and a few other molecules.[5] No systematic studies have been performed, however, on the effects of added internal degrees of freedom on the lifetime of an activated molecule. In the similar theories of Rice, Ramsperger and Kassel,[6] energy is free to flow throughout a number of internal degrees of freedom which in general has been found to be less than $3N - 6$, where N is the number of atoms in the molecule. Reaction occurs when sufficient energy accumulates in the key oscillator or degree of freedom. Slater[7] treats the problem by forbidding energy transfer between normal modes and then calculating the probability that the combined effects of the different modes of vibration will cause a particular bond or "critical coördinate" to exceed some minimum value. See Gill and Laidler[5] for a more complete comparison of the Kassel and Slater treatments.

It was decided to carry out investigations of the isomerization of substituted cyclopropanes to olefins in order to determine the exact effect of the substituents on the lifetime of the molecule in the rearrangement. Current work on the production and isomerization of highly excited methyl cyclopropanes by addition of CH_2 from photolysis of ketene or diazomethane to propylene or cyclopropane[8] has also made studies of the thermal reaction desirable for purposes of comparison of activated molecule lifetimes and product yields. The results of the thermal isomerization of methylcyclopropane to the four isomeric butenes are reported here.

Experimental

Methylcyclopropane was prepared by the reaction of zinc with 1,3-dibromobutane following the procedure of Weston.[9] The product gas was frozen in a liquid nitrogen trap as it emerged from the reflux condenser. This gas was then bubbled successively through saturated solutions of iodine, bromine and potassium hydroxide. The product of this treatment then was distilled into storage flasks on the vacuum manifold after passage through Ascarite and anhydrous $CaSO_4$ to remove carbon dioxide and water. The methylcyclopropane was analyzed by gas chromatography using a silicone oil column, a dimethylformamide column and a silver nitrate saturated 1,3-propanediol column. The methyl cyclopropane was found to contain 1.2% butane as impurity. No other peaks were detected; therefore, other impurities are certainly less than 0.1%. No products of side reactions attributable to the butane impurity could be observed in the kinetic runs. A second batch of methylcyclopropane was freed of butane by trapping the methylcyclopropane fraction as it emerged from a four meter silicone oil column in a preparative gas chromatography apparatus. Results of runs made with this specially purified methylcyclopropane were identical with those from runs made with the first batch of starting material. Other gases used were: helium, Matheson high purity; methane, Phillips research grade; ethane, Matheson 99% purity further purified by gas chromatographic separation using a 4 meter silicone oil column; nitrogen, Matheson Prepurified; toluene, Merck C.P. grade; hydrogen, Matheson Prepurified; butenes, Matheson C.P. grade; argon, Matheson C.P. grade.

A standard high vacuum system was employed. Mercury cutoffs and float valves were used in the portion of the vacuum system containing the reaction vessel, a mixing flask with magnetic stirrer for preparation of inert gas mixtures, manometer, McLeod gauge and product trap. The mercury valves were intended to prevent selective absorption of components from the hydrocarbon mixtures by stopcock grease. Stopcocks through which the product mixtures were swept

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(1) H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (*London*), **A217**, 563 (1953).

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

(3) H. Pritchard, R. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (*London*), **A218**, 416 (1953).

(4) H. S. Johnston, *J. Chem. Phys.*, **19**, 663 (1951).

(5) E. K. Gill and K. J. Laidler, *Proc. Roy. Soc.* (*London*), **A250**, 121 (1959).

(6) L. Kassel, "Kinetics of Homogeneous Gas Reactions," Reinhold Publishing Co., New York, N. Y., 1932.

(7) N. B. Slater, "Theory of Unimolecular Reactions," Cornell Univ. Press, Ithaca, N. Y., 1959.

(8) J. N. Butler and G. B. Kistiakowsky, private communication.

(9) R. Weston, *J. Chem. Phys.*, **26**, 975 (1957).

such as the gas chromatography sample valve were greased with perfluorinated hydrocarbon greases, either "Kel-F" or I.C.I. "Fluorlube," which have low solvent power for hydrocarbons.

Pressure measurements were made using either a 15-mm. bore mercury differential manometer with mirror scale or a calibrated McLeod gauge.

The reaction vessel consisted of a 10-cm. o.d. cylinder of 1800 ml. capacity. Two thermometer wells parallel to the main axis reached to the center of the vessel. The vessel was connected to the vacuum line outside the thermostat by means of 16-mm. i.d. tubing which made possible fast sample addition and removal and minimized thermal transpiration errors in the pressure measurements at low pressures. A suitable dead volume correction was applied to the product gas analysis.

The thermostat was similar to the type used by Pritchard, *et al.*[1] The reaction vessel was surrounded by a cylinder of aluminum sheet of $^3/_{16}''$ thickness. This fitted into a 2-l. wide-mouth Dewar vessel which had been modified to serve as a gas thermometer by connection to a capillary tubing. The capillary was connected to a mercury manometer which possessed contacts controlling a thyratron relay circuit. The gas thermometer was filled with 126 cm. of pure nitrogen, and the thermal expansion or contraction of this gas turned off or on (by means of the mercury manometer switch) a 24 watt heater wound on the gas thermometer. Changes in the volume and therefore the level of the mercury in the control manometer caused by drifts in room temperature were compensated by expansion of a calculated amount of gas added to the low pressure side of the control manometer. The reaction vessel and gas thermometer were placed inside a cylindrical aluminum casting with walls and ends of 2″ thickness. The bulk of the heat load was supplied by separately adjustable heating coils wound on this block and placed at the ends. All heaters were fed by Sola constant voltage transformers.

The aluminum block was then supported inside a 55-gal. steel drum and insulated with vermiculite. During the kinetic runs the maximum temperature fluctuation remained within ±0.05°.

Temperature homogeneity throughout the length of the reaction vessel was measured by differential thermocouples of varying lengths. The temperature was found to be uniform to better than 0.2 degree.

Working temperature measurements were made with four-junction Chromel-Alumel thermocouples inserted into the thermometer wells in the reaction vessel. The potentials relative to the cold junctions in a distilled water-ice bath were measured with a Leeds & Northrup Type K potentiometer. These thermocouples were calibrated against the melting points of N.B.S. certified samples of lead and zinc. Comparisons were also made between a four-junction couple in one thermometer well and temperatures measured by a L & N certified No. 8163-C platinum resistance thermometer. Resistance readings were taken with a L & N Mueller bridge. Absolute temperatures obtained are probably accurate to ±0.5 degree. Relative temperatures measured in this work should be precise to 0.2 degree.

Quantitative analyses of methylcyclopropane–product mixtures were performed by measurement of peak areas obtained in gas chromatographic separations. A 3-meter column, 4-mm. i.d., packed with silver nitrate saturated 1,3-propanediol supported on 60–80 mesh firebrick was used to separate the olefins from the methylcyclopropane. This column was preceded by a 16-cm. column with silicone oil as substrate in order to improve the separation of methylcyclopropane from butane and any lower paraffins. Butane, ethane, methylcyclopropane, ethylene, propylene, butene-2-*trans*, isobutylene and the pair butene-2-*cis* and butene-1 were completely resolved. The butene-2 *cis* and butene-1 peaks were well enough resolved that division of the peaks at the minimum gave the butene-2 *cis*/butene-1 ratio to ±5% as determined by calibration mixtures. The relative peak sizes were obtained by weighing cut out peaks with a microbalance. The accuracy of the whole procedure was checked by use of calibration mixtures. Analyses were performed in triplicate for runs yielding more than 40 μmoles of gas sample; below reactant pressures of about 0.7 mm., only a single analysis was performed using all gas trapped from the reaction vessel.

Before use, the methylcyclopropane was frozen twice in a liquid nitrogen cooled trap and degassed to remove any traces of oxygen which might be present. A run was commenced by expanding the methylcyclopropane (or methylcyclopropane–inert gas mixture) from the mixing flask into the reaction vessel, which had been evacuated to better than 10^{-5} mm. The float valve to the reaction vessel was then closed and the gas pressure was measured by means of the precision manometer or McLeod gauge. At the end of the desired time interval, the gas in the vessel was allowed to expand into an evacuated cold trap at liquid nitrogen temperature.

For the runs with mixtures of methylcyclopropane and inert gas, the mixing flask was used both as a mixing and as a storage vessel. The desired amount of methylcyclopropane was added to the flask, the float valve was closed, and the manifold was evacuated. The chosen inert gas was admitted to the manifold and then to the mixture flask until the total pressure reached the desired value. A magnetic stirrer sealed inside the flask was run from 3 to 18 hr. to ensure complete mixture of the gases. The final mixture was then expanded into the reaction vessel for a series of runs at successively reduced pressures. Product mixtures from the inert gas runs were pumped through a trap consisting of a three-turn loop of 6-mm. i.d. tubing; one end of the trap was immersed in liquid nitrogen.

The reaction was followed to conversions of the methylcyclopropane ranging between 15 and 50%; 25% was the usual extent of reaction. The reaction was found to be first order in methylcyclopropane throughout this range of reaction at any given pressure of gas.

Preseasoning of the reaction vessel with reactant had been cited as necessary in the earlier work with cyclopropane[1]; this practice was followed in the reaction of methylcyclopropane. The vessel was exposed to the starting material for approximately three or four half lives of the reactant after admission of any air and before runs were made for record.

The pressure in the reaction vessel was remeasured after the reaction had gone to the desired degree of completion for a few runs at each temperature. No change in the gas pressure could be observed, *i.e.*, less than 0.2% change at the highest pressures.

The gas chromatographic analysis affords a sensitive probe for the presence of products, other than butenes, which might be formed in side reactions. The total of C_2, C_3 and C_5 hydrocarbons formed in side reactions amounts to as much as 2% of the total reaction products at the highest temperatures employed; in the runs at the lower temperatures these products were less abundant. To ascertain the source of these trace products at the high temperatures, separate samples of the butene isomers were held in the reaction vessel for times longer than used in the runs with the methylcyclopropane. Extremes of temperature and pressure were employed for each butene. Aside from the *cis-trans* isomerization of butene-2, only a slight decomposition of butene-1 at 490° was observed. The products were ethylene, propylene and pentenes. Traces of methane or hydrogen would not have been trapped. These products formed the trace products observed in the methylcyclopropane pyrolysis; hence these were ascribed to side reactions of butene-1 in the isomerization experiments. This decomposition of butene-1 has been reported elsewhere in detail.[10] The butene-2 *cis-trans* isomerization has been studied by Rabinovitch and Michel[11]; it was found to take place at a rate slower than the methylcyclopropane reaction by at least a factor of ten. The side reactions observed by them at high pressures probably were much less important in this work because of the shorter residence times involved.

In summary, the isomerization reaction of methylcyclopropane as observed is concluded to be a truly homogeneous unimolecular reaction for the following reasons. The reaction appears to be kinetically first order in reactant. Side reactions giving products of lower molecular weight than the starting material would form products which have not been observed in significant amounts. If such cracking reactions are absent, then polymerization reactions such as might occur on the walls would cause a fall of pressure with time; this has not been observed. Previous studies with cyclopropane have yielded negative results in the search for het-

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(10) W. A. Bryce and P. Kebarle, *Trans. Faraday Soc.*, **54**, 1660 (1958).

(11) B. S. Rabinovitch and K. W. Michel, THIS JOURNAL, **81**, 5065 (1959).

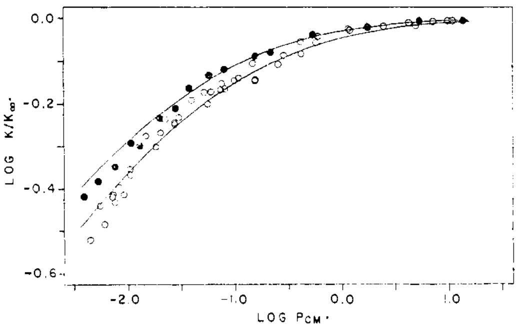


Fig. 1.—Experimental and theoretical pressure dependence of first order rate constant at two temperatures: ○, 490.4° and ●, 446.9°. Solid lines were computed from Kassel equation for nineteen oscillators at the corresponding temperatures.

erogeneous or radical components in the ring isomerization. The products of the reaction were found to be generally stable under the conditions of this work.

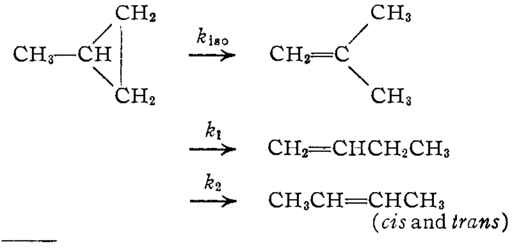
Results

Numerical data for individual runs are given in the appendix.

Figure 1 shows the pressure dependence of the first order rate constant for the isomerization of methylcyclopropane at two temperatures: 490.4 and 446.9°. In this plot k_∞ is the limiting high pressure rate constant for the particular temperature obtained by a $1/k$ *vs.* $P^{-1/2}$ extrapolation.[12] The rate constant has reached to 98% of its high pressure value at 10 cm. The shift of the log k *vs.* log P curve to the left with decreasing temperature is predicted both by the Slater and Kassel theories, since at low pressures molecules with decreased amounts of energy are responsible for the bulk of the reaction; this has the effect of reducing activation energy. Pressure data taken at two other temperatures intermediate between 490.4 and 446.9° lie on curves intermediate between the data of Fig. 1 and are not shown.

The over-all activation energy for isomerization, 65.0 ± 0.7 kcal./mole, was determined from an Arrhenius plot of fifteen runs at 10 cm. which spanned the temperature range from 441.2 to 490.8°. The scatter of the points from a straight line is too small to be visible in any plot which could be shown here.

For a reactant such as methylcyclopropane forming different products in parallel first order reactions, the relative amounts of the different products at any time give values of the relative rate constants for the different modes of reaction of the starting material. The system of parallel first order reactions being considered in this work is



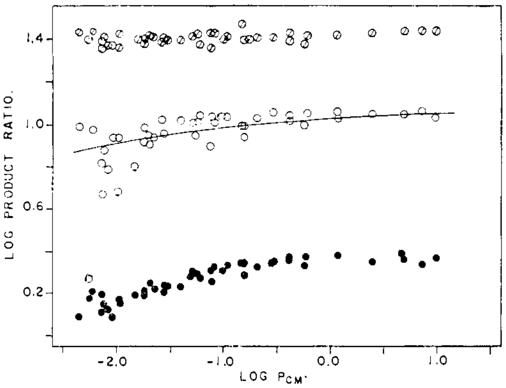


Fig. 2.—Pressure dependence of butene isomer distributions at 490.4°: ●, butene-2 *cis*/butene-2 *trans*; ○, isobutene/(butene-2 + butene-1); ⊖, butene-2/butene-1. An arbitrary constant was added to each set of points for purposes of display.

Here k_{iso}, k_1 and k_2 are the specific first order rate constants for the formation of the different products.

The pressure dependence of the isomer distributions is illustrated by the plots of log $[k_{iso}/(k_1 + k_2)]$, log (k_2/k_1) and log [(butene-2-*cis*/butene-2 *trans*)] *vs.* log P which are given in Fig. 2. These runs were all at 490.4°. The vertical scales have been shifted by an arbitrary amount for purposes of display. At low pressures the isobutene analyses become more uncertain because the isobutene peak, the smallest of all butene peaks, is approaching the lower limit of measurement with the gas chromatography equipment employed. The scatter in ratios involving butene-2 *cis* and butene-1 separately arises from the incomplete separation of the two peaks in analysis. The relative decrease in k_{iso} with a decrease in pressure is not an artifact resulting from a reduced sample size, since added inert gas increased the relative isobutene yield as well as the over-all rate constant at low partial pressures of reactant.

The difference in activation energy for isobutene production and butene-2 and butene-1 production is shown by a plot of log $[k_{iso}/(k_1 + k_2)]$ *vs.* $1/T$ in Fig. 3. These data were taken from the same series of runs at 10 cm. that was used in obtaining the over-all activation energy for the methylcyclopropane isomerization. A plot of log (k_2/k_1) *vs.* $1/T$ for the same runs had too much scatter to give useful information. This scatter resulted from the incomplete separation of butene-1 and butene-2 *cis* in analysis. However, Fig. 2 indicates that k_2/k_1 probably changes by 10% or less over the total pressure range at a given temperature, so average values were calculated for k_2/k_1 from each of four series of runs at different temperatures. Data from sixteen to twenty-six runs at varying pressures for each temperature were averaged, and the four average values are shown in Fig. 3. From this plot one can say that the activation energies for production of butene-2 and butene-1 are the same to ±0.6 kcal./mole. From the same Fig. 3 it is found that the activation energy for production of isobutene is greater than for production of butene-1 or butene-2 by 2.3 ± 0.7 kcal./mole.

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[12] E. W. Schlag, Ph.D. Thesis, Univ. of Washington (1958).

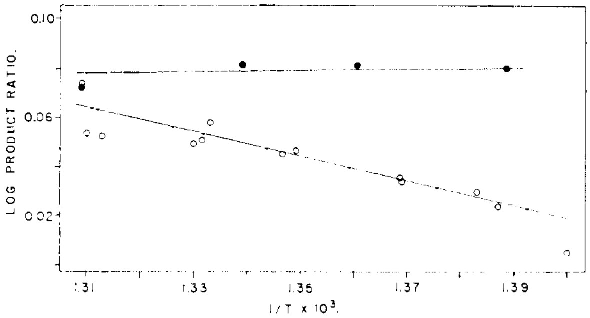

Fig. 3.—Temperature dependence of butene isomer yields: O, isobutene/(butene-2 + butene-1); ●, butene-2/butene-1, average of sixteen to twenty-six runs for each of the four temperatures. An arbitrary constant was added to each set of points for purposes of display.

In the analyses of the results of the runs with the inert gas mixtures, the procedure employed was to observe the effects of the inert gas on the log (k/k_∞) *vs.* log P curve, where P is the reactant pressure. If f is defined as the efficiency of the added gas relative to the reactant molecule in the activation-deactivation process and if R is the pressure ratio of the foreign gas to the reactant gas, then the log (k/k_∞) curve will be shifted to the left on the log P axis by an amount log $(1 + fR)$. In Table I are found values for f, in terms of pressure ratios, which were obtained in this work. Included for comparison are the results from the previous studies of cyclopropane and cyclobutane. Values of collision cross-sections taken from kinetic theory are assumed in order to get the efficiency of an inert gas on a collision for collision basis with the reactant molecule. Collisional efficiencies were calculated using the same cross-sections as in the cyclobutane work and the results are shown in Table I. Ethane was used with methylcyclopropane instead of ethylene because of greater ease of separation and analysis of the large amount of inert gas from small amounts of product with the gas chromatography columns employed. The efficiencies quoted, both from this and the earlier work, have probable errors ranging from 10 to 25%. The toluene efficiency obtained in this work seems low relative to the results obtained for cyclobutane, although the data with the toluene mixtures were relatively free from scatter. Each pressure efficiency obtained in this work is the result of at least four runs with each mixture.

TABLE I

RELATIVE EFFICIENCIES OF ADDED GASES BASED ON PRESSURES AND COLLISION FOR COLLISION

Reactant	Methylcyclopropane	Cyclopropane[1]	Cyclobutane[3]
Added gas			
Reactant	1/1	1/1	1/1
He	0.07/0.05	0.06/0.05	0.10/0.07
A	.14/ .17	.05/ .07	.17/ .21
H_2	.20/ .07	.24/ .12	.28/ .10
N_2	.20/ .23	.06/ .07	.18/ .21
CH_4	.34/ .26	.27/ .24	.50/ .38
C_2H_4	.....	.....	.50/ .49
C_2H_6	0.45/0.44	.....	.....
Butenes	1/1	.....	.....
Toluene	0.89/0.75	1.59/1.1	1.5/1.1

The solid lines in Fig. 1 are curves calculated from the Kassel[6] equation for the two values of the temperature considered in the graph.

$$k/k_\infty = \frac{1}{(s-1)!}\int_0^\infty \frac{x^{s-1}\,e^{-x}\,dx}{1+\frac{A}{k_{-1}(M)}\left(\frac{x}{b+x}\right)^{s-1}} \quad (1)$$

In this equation, s is the number of vibrational degrees of freedom assumed to participate as sources and sinks of energy for the isomerization. It is assumed that intramolecular energy transfer is rapid compared to the lifetime of the energized molecule. These values were used in computing the curves shown in Fig. 1.

$A = 10^{15.45}$ sec.$^{-1}$
$b = 65.0$ kcal./RT
$k_{-1} = (2.16 \times 10^{-11}T^{1/2})$ cc./molecule sec.
$s = 19$

The value for k_{-1} assumes a collision diameter of 5 Å. for methylcyclopropane and also assumes that deactivation occurs on every collision. This last assumption certainly is in error; however, this standard assumption is made so that the results of the Kassel calculation may be compared with previous work. A decrease in k_{-1} would necessitate a corresponding increase in s to give a solution to equation 1 which would fit the data. Since computer facilities and time were available, the integration of equation 1 was performed numerically by means of a digital computer.

Table II lists the relative rates and preëxponential factors for formation of the different butenes from methylcyclopropane at 468.0°, which is in the middle of the temperature range covered. The rate of butene-1 production was arbitrarily set as 1.00.

TABLE II

RELATIVE RATES FOR BUTENE ISOMER PRODUCTION, T = 468.0°

Product	Relative rate	Relative pre-exponential factor, A
Butene-1	1.00	1.00
Butene-2, *cis*	0.63	0.91
Butene-2, *trans*	.28	
Isobutene	.16	0.76

If pressure dependencies for the decomposition of individual isomers are to be computed on the basis of the simple Kassel model, then equation 1 must be modified to include the effects of all reactions in depleting the supply of activated molecules. The equations for calculation of the pressure effect on branched and straight chain olefin production take the forms (2) and (3) for $b_1 = b_2 \equiv b_{1,2}$ and $b_{\text{iso}} > b_{1,2}$.

The A_{iso} term in the denominator of (3) is zero for $x + b_{1,2} \leq b_{\text{iso}}$. Calculations were made by the referee for $k_{\text{iso}}/k_{\text{iso}\,\infty}$ and $(k_1 + k_2)/(k_{1\,\infty} + k_{2\,\infty})$ using the modifications of (1); the results are presented as the solid line in Fig. 2.

For purposes of comparison, the limiting high pressure rate constants which have been obtained for isomerizations to olefins are methylcyclopropane, $k = 10^{15.45}\exp(65.0\text{ kcal.}/RT)$ sec.$^{-1}$; cyclo-

$$k_{\text{iso}}/k_{\text{iso}\,\infty} = \frac{1}{(s-1)!}\int_0^\infty \frac{x^{s-1}\,e^{-x}\,\mathrm{d}x}{1 + \frac{1}{k_{-1}(M)}\left[A_{\text{iso}}\left(\frac{x}{x+b_{\text{iso}}}\right)^{s-1} + A_{1,2}\left(\frac{x+b_{\text{iso}}-b_{1,2}}{x+b_{\text{iso}}}\right)^{s-1}\right]} \tag{2}$$

$$(k_1+k_2)/(k_{1\,\infty}+k_{2\,\infty}) = \frac{1}{(s-1)!}\int_0^\infty \frac{x^{s-1}\,e^{-x}\,\mathrm{d}x}{1 + \frac{1}{k_{-1}(M)}\left[A_{\text{iso}}\left(\frac{x+b_{1,2}-b_{\text{iso}}}{x+b_{1,2}}\right)^{s-1} + (A_1+A_2)\left(\frac{x}{x+b_{1,2}}\right)^{s-1}\right]} \tag{3}$$

propane,[1] $k = 10^{15.17} \exp(65.0 \text{ kcal.}/RT)$ sec.$^{-1}$; cyclobutane,[2] $k = 10^{15.6} \exp(62.5 \text{ kcal.}/RT)$ sec.$^{-1}$.

Discussion

General Pressure Effects.—In order to compare the effects of additional degrees of freedom on the lifetime of an activated molecule, the activation energy for all cases should remain constant through the series of reactions. This condition seems to be satisfied in the comparison of methylcyclopropane with cyclopropane; the activation energies for isomerization to the olefins are identical within experimental error. Thus the presence of the methyl group in the ring has not greatly perturbed the energetics of the reaction. The replacement of the methyl group for a hydrogen atom increased the lifetime of the reactant molecule roughly by a factor of thirty. In terms of the Kassel model, the number of effective degrees of freedom of energy storage was increased from twelve or thirteen for cyclopropane to nineteen for methyl cyclopropane. The fit of the Kassel curves to the data is reasonably good except for the greater curvature of the experimental points. In Fig. 4 are illustrated curves which were drawn through the data for methylcyclopropane, cyclopropane and cyclobutane for purposes of comparison.

A partial explanation of the shift of the log k vs. log P curve to the left for methylcyclopropane compared to cyclopropane might lie in the splitting of the seven doubly degenerate modes of cyclopropane on methyl substitution. On the basis of the Slater treatment this effect alone could increase the number of normal modes participating in the reaction coördinate by as much as seven. However Weston[9] has measured the pressure dependence of the rate of isomerization of tritiated cyclopropane relative to normal cyclopropane. Tritium substitution certainly breaks the symmetry of the cyclopropane molecule, and one would expect to see a large pressure effect on the ratio of rate constants for isomerization of the unsymmetrical and symmetrical molecules if the preceding point is important. Weston observed that $k'/k = 0.98$ at $P = 1$ mm. and $k'/k = 0.90$ at $P = 1$ atm., where k' and k are the rate constants for the isomerization of unsymmetrical and symmetrical cyclopropane. The 9% increase in k'/k in going from the high pressure limit to a pressure where k/k_∞ is about 0.5 was attributed by Weston to the loss of isotope effect as the pressure approaches the second order region. At $k/k_\infty = 0.5$, the addition of even one more effective mode should cause $k'k_\infty/kk'_\infty$ to increase by about 10%.[7] Thus loss of symmetry in the Slater theory would appear not to explain a significant amount of the shift of the log k/k_∞ vs. log P curve for methylcyclopropane.

The modes of vibration added to the cyclopropane molecule by methyl substitution may be expected to be confined chiefly to the methyl group. These nine methyl modes may be described as symmetric C–H stretching and bending modes, pairs of antisymmetric C–H stretching and bending modes, a hindered rotation of the whole methyl group and two group wagging modes. Of these nine modes, only the last two are expected to involve the rest of the molecule to any appreciable extent. Characteristic frequencies of the other modes change little with changes in the substituents of the carbon atom to which the methyl group is attached.[13]

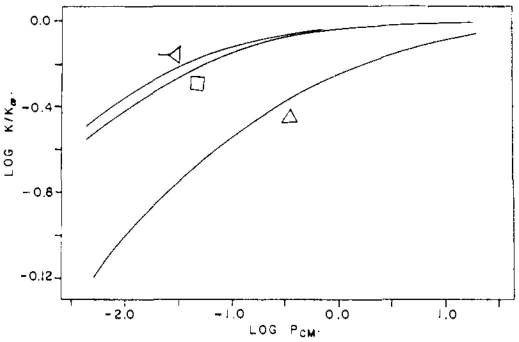

Fig. 4.—Experimental pressure dependence of first order rate constant for methylcyclopropane, cyclobutane[2] and cyclopropane.[1]

Thus Kilpatrick and Pitzer[14] were able to perform vibrational analyses of ethylene, butene-2, *cis* and *trans* and isobutene, getting results consistent with experimentally determined frequencies. Their calculation treated the CH_3 group as a point mass in computations of frequencies for modes involving the rest of the molecule. Only the two wagging modes of the methyl group had to be considered.

From Slater's representative calculations for a reasonable spread of amplitude factors among the normal modes,[7] increasing the number of effective modes by two from 13 to 15 should shift the point for $k/k_\infty = 0.5$ to the left on the log P axis by 0.61 log P unit. This is less than half the observed shift illustrated in Fig. 1.

It is concluded that Slater's theories as currently applied do not explain these experimental results, but that a model allowing for energy transfer is successful.

It might be noted that this work and the work of Butler and Kistiakowsky provide complementary information (at different parts of the energy scale) concerning the question of intramolecular energy transfer. The photochemical work produces molecules with an average energy in excess of the activation energy, 65 kcal., by about 30 kcal. For such molecules the higher vibrational states exhibiting more anharmonic character would be populated. For these states one would expect the

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[13] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., Methuen & Co., Ltd., London, 1958.

[14] J. E. Kilpatrick and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **38**, 191 (1947).

normal modes to be strongly coupled and hence intramolecular energy transfer would be a relatively probable process. It has seemed obvious to this author and to other workers[5] who have published studies of gas phase unimolecular reactions that intramolecular energy transfer must be important in unimolecular reactions activated thermally. This present work indicates that such energy transfer certainly takes place. Hence the Slater theory in its present form is based on an unrealistic model for molecules of the complexity of cyclopropane.

Butler and Kistiakowsky[8] calculated lifetimes for the photochemically produced hot methylcyclopropane ranging from 2×10^{-10} to 2×10^{-9} sec. The corresponding lifetime of the thermally activated molecules is calculated to be 8.3×10^{-7} sec. by equating collisional frequency to the reciprocal of the lifetime at the pressure for which k/k_∞ equals 0.5. A calculation based on the treatment of Johnston and White[15] gives an average lifetime before isomerization of 1.5×10^{-7} sec. for activated molecules with the equilibrium high pressure energy distribution. The decrease in lifetime, or increase in reaction probability, with an increase in energy of the activated molecule is as expected.

It is interesting to note that the reaction of cyclobutane splitting into two molecules of ethylene has values for the activation energy, frequency factor and pressure dependence of rate constant which are quite similar to those for the methylcyclopropane reaction. It would seem unlikely on the basis of the Slater theory that the pressure dependencies would be this much alike, for the two reactions. On the other hand, if energy can be transferred among the vibrational modes in a time less than the lifetime of the activated molecule, then the two hydrocarbons of identical numbers of atoms might be expected to behave in a similar manner as reactant pressure is varied if activation energies and pre-exponential factors are similar for the high pressure rate constants.

The temperature dependence of the pressure effect is of the amount predicted by the Kassel theory, as may be seen from the shift in both the theoretical and experimental curves in Fig. 1 with a change in temperature. The Slater theory also predicts the same shift.

Inert Gas Effects.—Within experimental error, the efficiencies of the inert gases in activating methylcyclopropane are the same as for cyclobutane. It should be noted that the same region of the log (k/k_∞) *vs.* log P curve was involved in both studies. There seem to be differences beyond experimental error for nitrogen and argon with cyclobutane and methylcyclopropane as compared to cyclopropane. Volpe and Johnston[16] have pointed out that, if the relative probability of activation of deactivation of different energy states of reactant molecules does not depend strongly on the nature of the second body in the collision process, then efficiencies of inert gases can be obtained by the method used in this work. They formulated this in terms of f_{Mi}, the efficiency for deactivation from state i of the reactant molecule by collision with a molecule of type M. If $f_{Mi} = f_M\phi_i$, then the shift of the log k *vs.* log P curve on the addition of inert gas can be used to obtain the value for f_M. If this factoring of f_{Mi} is in considerable error, then the efficiencies measured by the methods of this and similar work will depend strongly on the reference pressure and the pressure interval covered. Unfortunately, it is not possible by the technique used in this study to work in pressure regions low enough to observe the truly second order kinetics of the activation process. It is concluded that in the same general pressure region the three hydrocarbon ring isomerizations are quite similar with respect to gross aspects of energy transfer from foreign gases.

Isomer Yields.—The pressure dependence of the rate of production of isobutene relative to the production of straight chain products is explained by the Kassel model. As the supply of the more energetic molecules is depleted at low pressures by reaction, the reaction with the greatest energy requirement, namely, isobutene production, becomes relatively less important.

The decrease in the ratio butene-2 *cis*/butene-2 *trans* with decreasing pressure is explained by the consecutive *cis-trans* isomerization which can occur after the initial isomerization of methylcyclopropane to butene-2 *cis*. The butene-2 *cis* molecules produced from the ring isomerization still have the activation energy required to go to the *trans* form immediately after the ring opening. At high pressures this energy is removed by collisions before the reaction can take place, and the *cis*/*trans* ratio is typical of the products formed in the primary reaction. At low pressure the average time between collisions becomes long enough that the *cis-trans* isomerization can take place.

One of the main supports of the Slater theory of unimolecular reactions has been its successful prediction of the pressure dependence of the rate constant of isomerization of a relatively complicated molecule, cyclopropane, starting with the fundamental vibration frequencies and the experimental activation energy. To achieve this success it was necessary to assume that a carbon–hydrogen stretch was the critical coördinate for reaction. Recent work by Rabinovitch, *et al.*,[17] has shown that 1,2-dideuteriocyclopropane undergoes a *cis-trans* geometrical isomerization which is faster than the structural isomerization to propene. Work with 1,2-dimethylcyclopropane has shown the same geometrical isomerization,[18] so the reaction appears to be a general one with cyclopropanes. From the experiments, Rabinovitch considered that a carbon–carbon bond scission with resulting rotation of the ring groups was the mechanism involved. Ring closure would then regenerate the ring; hydrogen shift before closure would give propene. It appeared most likely that this carbon–carbon bond rupture was the starting point for the structural rearrangement to propene. Smith[19] pointed out that the data were also consistent with a mechanism whereby one carbon with its substituents became

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

[16] M. Volpe and H. S. Johnston, THIS JOURNAL, **78**, 3903 (1956).

[17] B. S. Rabinovitch, E. W. Schlag, K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

[18] J. Chesick, unpublished work; H. M. Frey, private communication.

[19] F. T. Smith, *J. Chem. Phys.*, **29**, 235 (1958).

planar with the cyclopropane ring. From the configuration the geometrical isomerization would occur. If a hydrogen started to migrate before the group left the planar configuration, then the ring might open. If the carbon–carbon bond rupture as proposed by Rabinovitch is the correct path for reaction, then any agreement of the Slater calculations for cyclopropane with the experimental evidence would appear fortuitous when the fundamental assumptions involved concerning the critical coordinate are considered.

Examination of the isomer distributions obtained in this work is therefore worth while to see whether some limitations can be placed on the mechanisms for the cyclopropane reactions.

Bond energy data, chiefly from measurements of activation energies involved in the bond rupture steps, suggest that a carbon–carbon bond is weakened by substitution of other groups for hydrogen atoms on either carbon. If a carbon–carbon bond stretch is the key step in the methylcyclopropane reaction, then the rate constant for production of isobutene, k_{iso}, should have a higher activation energy than the rate constants for production of butene-1 and butene-2, k_1 and k_2, since a bond between less substituted carbon atoms is being broken in the mode of reaction giving isobutene. The observed energy difference of 2.3 kcal./mole is in accord with this reasoning. However, by this argument the over-all activation energy for the methylcyclopropane reaction should be lower than the activation energy for the cyclopropane reaction by about 2 kcal./mole since two of the three possible carbon–carbon bond ruptures involve a more substituted carbon. This difference, well outside of experimental error in this work, was not observed. It is concluded that either the 2.3 kcal./mole energy is involved in a subsequent step such as the hydrogen migration or that the carbon–carbon stretch is not the characteristic feature of the transition state.

From Table II it should be noted that the butene-2 *cis/trans* ratio is approximately 2. This is in the opposite direction from the ratio of thermodynamic stability.[20] The predominance of the *cis* isomer might argue against a loose transition state in which the ring is opened wide and long enough to allow extensive rotation around all bonds of the ring. Subtle energy or steric effects, however, could be enough to cause the predominance of the *cis* isomer formation in the rate controlling part of the reaction.

The isomer distributions found in this work can be correlated with those found by Butler and Kistiakowsky[8] from the isomerization of hot methylcyclopropane formed in addition reactions of photochemically produced CH_2 to propene or cyclopropane. In these reactions the methylcyclopropane has enough excess energy that the products formed should be in the ratio of the pre-exponential factors in the rate constants since differences in the activation energies are small compared to the total energy of the reactant molecule.

Butler concluded that within experimental error the relative rates of production for the different butene isomers from the hot methylcyclopropane were the same regardless of the source of methylene and whether propylene or cyclopropane was used. The ratio of k_2 to k_1 of 0.91 found in this work may be compared with the corresponding ratio of 1.0 found by Butler. The agreement tends to corroborate the data which indicate no difference in temperature dependence for the modes of reaction giving butene-1 and butene-2.

The rate for isobutene production relative to butene-1 is given by Butler as 0.30, which may be compared to the ratio of isobutene–butene-1 pre-exponential factors of 0.76 calculated in this work taking the activation energy difference to be 2.3 kcal./mole. The discrepancy between 0.76 and 0.30 may be caused by an error of 1.4 kcal./mole in this energy difference; such an error seems to be beyond the scatter of data in Fig. 3.

Butler and Kistiakowsky observed equal amounts of butene-2 *cis* and butene-2 *trans* from isomerization of hot methylcyclopropane. Here again the excess energy from the photochemically initiated reaction would effectively wipe out any energy barriers favoring *cis* formation in the rate determining steps.

If the different products of the methylcyclopropane isomerization are formed on the basis of statistical migration of hydrogen atoms, and energy factors are absent, then the relative amounts of isobutene, butene-1, and butene-2 should be as 0.5:1.0:1.0. These numbers are obtained from either the transition state involving a carbon–carbon stretch or from the planar transition state as suggested by Smith. These numbers would correspond to the relative pre-exponential A factors tabulated in Table II. The difference between the observed factor of 0.76 for isobutene and the predicted factor of 0.50 is probably within experimental error for the determinations of the energy factors.

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Appendix

A. DATA FOR RUNS WITHOUT ADDED GASES

				Products, parts/100 parts of butenes				
T, °C.	React. P, cm.	Convers., %	$k \times 10^4$, sec.$^{-1}$	Butene-1	Butene-2c	Butene-2t	Isobutene	Propylene
446.9	13.58	30.2	0.535	47.7	30.8	14.5	7.10	0.33
	4.93	29.6	.531	48.4	30.8	13.8	6.98	.50
	1.79	29.0	.518	47.6	30.9	14.4	7.17	.47
	0.60	28.4	.500	49.0	30.3	13.8	6.98	.51
	.217	27.3	.456	49.2	30.3	14.2	6.31	.90
	.157	28.7	.443	49.0	30.9	14.0	6.11	1.0
	.079	26.6	.415	49.0	30.0	15.0	6.00	0.90
	.057	28.3	.403	49.1	29.3	15.2	6.41	.91
	.037	26.8	.376	49.0	29.6	15.3	6.04	.98
	.028	21.6	.337	49.3	29.2	15.7	5.8	.76
	.021	23.3	.321	47.2	28.0	17.0	7.73	1.2
	.013	19.7	.275	50.1	28.8	17.1	3.99	..[a,b]
	.0108	20.5	.279	46.8	29.1	19.2	4.99	..
	.0076	21.8	.245	49.0	30.7	16.2	4.15	..
	.0052	24.5	.227	50.9	28.5	16.7	3.89	..
	.0038	20.5	.208	51.1	28.2	20.7	2.0	..
459.2	17.42	31.9	1.153	49.0	30.6	14.6	7.84	0.60
	16.32	28.2	1.105	47.8	30.1	14.4	7.66	.33

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[20] H. H. Voge and N. C. May, THIS JOURNAL, **68**, 550 (1946).

	5.95	28.8	1.109	47.6	30.0	14.2	8.0	.40
	4.81	31.7	1.17	46.6	31.0	14.8	7.70	.50
	2.06	30.0	1.098	48.2	31.0	13.2	7.58	.48
	0.71	28.5	1.06	46.7	31.8	13.9	7.65	.52
	.68	27.9	1.052	47.6	31.7	13.2	7.55	.76
	.38	25.4	0.956	47.5	31.4	13.9	7.06	.40
	.27	31.3	1.076	48.1	31.0	14.4	6.55	1.0
	.179	28.0	0.975	48.6	29.8	14.1	7.52	0.71
	.0975	26.4	.761	49.1	29.0	15.0	6.86	..
	.0745	23.5	.862	47.9	30.3	15.0	6.71	0.46
	.0643	25.5	.820	48.2	29.4	15.0	7.36	0.64
	.043	35.3	.843	49.2	28.6	15.85	6.37	1.1
	.037	24.6	.761	49.1	27.8	16.6	6.50	0.44
	.036	26.8	.745	48.3	29.7	16.3	5.64	.72
	.023	22.1	.644	49.1	27.6	16.8	6.54	.31
	.0155	30.5	.641	49.4	27.5	18.02	5.02	1.3
	.013	28.3	.555	47.5	28.6	17.9	6.02	..
	.012	20.8	.529	50.0	27.8	18.2	3.87	..
	.0089	28.7	.523	50.7	27.5	18.5	3.22	..
	.0080	25.0	.510	48.3	26.9	18.1	6.67	0.68
	.0057	23.7	.445	47.6	29.7	19.9	2.83	..
	.0051	21.4	.443	47.7	29.1	16.8	6.43	....
473.7	24.68	32.5	2.66	46.7	28.9	16.4	8.02	0.68
	20.16	27.7	2.80	46.9	29.5	15.6	7.96	.33
	16.14	32.7	2.72	46.6	29.9	15.2	8.36	.80
	8.36	25.6	2.72	47.5	30.8	13.8	8.0	.64
	2.51	28.1	2.66	46.8	30.7	14.4	8.19	.75
	1.17	56.4	2.65	47.1	29.6	15.3	8.02	1.9
	0.94	26.0	2.50	46.8	31.4	13.9	7.80	1.00
	.87	23.2	2.53	48.3	29.7	14.5	7.65	..
	.35	34.2	2.42	49.2	28.6	14.3	7.83	1.1
	.25	30.4	2.36	51.2	26.8	14.2	7.75	1.1
	.244	35.4	2.41	49.95	27.8	14.4	7.89	0.51
	.120	22.1	2.11	49.2	29.4	14.6	6.80	0.90
	.078	22.2	1.98	43.6	33.6	16.7	6.08	..
	.051	25.8	1.78	46.5	30.6	17.3	5.53	0.60
	.043	26.0	1.75	46.7	30.9	16.3	6.99	0.80
	.028	19.3	1.59	51.0	27.2	16.1	5.71	..
	.0195	22.7	1.38	46.9	27.8	18.8	6.37	..
	.015	24.2	1.30	50.2	26.3	17.8	5.73	..
	.0070	22.1	1.08	49.0	26.9	19.4	4.70	..
	.0061	21.3	1.04	45.7	29.4	20.2	4.8	..
490.6	9.67	29.1	6.79	47.4	30.7	15.0	7.05	0.53
	7.24	39.7	6.77	47.0	29.9	15.6	7.48	.89
	4.90	31.9	6.62	47.3	30.4	15.0	7.33	.76
	2.45	34.5	6.63	47.7	29.9	15.1	7.31	.93
	1.16	35.9	6.47	48.5	30.4	14.1	6.95	.91
	1.15	33.4	6.52	48.0	30.4	14.2	7.44	1.1
	0.607	33.5	6.29	48.0	30.2	14.4	7.36	0.90
	.58	29.7	6.11	50.7	27.9	14.8	6.55	.80
	.414	27.4	6.10	49.6	29.2	14.0	7.27	.45
	.414	35.9	5.72	47.7	30.5	15.0	6.84	1.08
	.289	33.9	5.70	48.6	29.1	14.8	7.45	1.10
	.205	29.3	5.45	48.5	29.0	15.4	7.09	1.7
	.156	28.4	4.92	50.1	27.8	16.3	5.78	2.01
	.153	25.9	4.99	49.5	29.1	14.9	6.48	0.86
	.147	29.7	5.50	45.8	31.4	16.1	6.55	.85
	.106	18.8	5.01	48.6	29.0	15.2	7.28	.53
	.099	20.1	4.99	49.2	28.0	15.7	7.18	.55
	.080	25.3	4.75	48.1	29.3	15.8	6.75	.65
	.077	32.7	4.90	47.7	29.0	16.1	7.20	1.00
	.075	29.6	4.71	52.3	26.1	16.3	5.25	0.95
	.060	25.8	4.68	50.4	26.4	15.9	7.29	.74
	.057	23.1	4.36	48.1	28.7	16.5	6.76	.66
	.055	27.9	4.62	49.6	28.2	16.2	5.88	1.14
	.053	27.3	4.67	48.9	28.5	15.8	6.68	0.67
	.0400	45.0	4.46	49.8	26.0	17.4	6.81	1.04
	.0300	26.0	4.06	50.1	26.5	17.4	6.01	0.90
	.0285	30.9	3.96	49.9	26.6	17.5	6.03	.53
	.0272	23.9	3.95	50.2	25.2	17.7	6.86	.56
	.0222	24.0	3.61	49.3	26.7	18.1	5.82	.38
	.0204	30.4	3.74	49.4	27.5	17.7	5.39	.68
	.0200	19.3	4.06	42.4	25.8	25.9	5.86	..
	.0183	37.4	3.48	50.3	25.5	18.8	5.50	0.75
	.0180	25.6	3.43	50.5	25.4	17.7	6.37	.15
	.0146	24.3	3.68	51.1	25.9	18.8	4.28	.64
	.0106	34.2	3.09	53.5	24.5	18.6	3.34	..
	.0100	25.3	2.98	48.7	25.6	20.0	0.98	..
	.0092	40.4	2.68	51.8	22.1	20.3	5.79	0.65
	.0084	40.1	2.78	52.4	23.5	19.9	4.15	0.35
	.0075	33.8	2.56	49.9	25.0	20.1	5.03	..
	.0072	31.5	2.66	52.9	22.8	19.9	4.41	..
	.0072	24.1	2.68	51.9	26.0	18.9	3.19	..
	.0061	28.2	2.28	47.5	27.2	19.1	6.24	..
	.0055	31.6	2.52	53.2	25.5	20.0	1.28	..
	.0044	26.1	2.09	47.9	23.8	21.9	6.44	..
490.8	10.34	41.7	6.88	49.0	28.1	14.5	8.41	0.70
490.5	9.67	29.9	6.79	47.4	30.7	15.0	7.05	.58
490.3	9.62	28.0	6.71	50.3	28.2	13.7	8.05	.38
488.6	10.68	34.5	6.21	51.1	27.1	13.8	8.03	.44
478.7	10.09	22.8	3.58	48.7	30.7	12.6	7.98	.27
476.8	9.64	32.2	3.32	50.3	27.5	14.0	8.13	.47
469.5	9.77	25.1	2.06	49.2	30.0	12.6	7.9	.34
468.0	9.91	22.0	1.92	50.3	28.7	13.1	7.93	.19
457.6	9.52	23.2	1.04	48.6	31.0	12.5	7.75	.22
457.4	9.22	21.9	1.01	50.9	29.0	12.4	7.72	.19
449.9	10.24	21.9	0.632	50.7	28.8	12.6	7.85	.17
447.7	9.89	20.8	0.561	50.0	29.6	12.5	7.64	.19
441.2	10.04	17.6	0.359	50.7	29.7	12.3	7.25	.12

[a] None detected. [b] Ethylene was found only in runs with hydrogen and ethane as added gases.

B. DATA FOR RUNS WITH ADDED GASES
ALL RUNS AT 490.6°

R = Pressure of added gas/pressure of methylcyclopropane

			Products, parts/100 parts of butenes					
React. P, cm.	Convers., %	$k \times 10^4$, sec.$^{-1}$	Butene-1	Butene-2c	Butene-2t	Isobutene	Propylene	Ethylene
H_2, R = 9.67								
0.094	46.0	6.07	47.8	29.7	14.0	8.49	9.7	1.44
.0300	28.4	5.11	49.2	28.6	14.8	7.42	6.0	1.27
.0221	27.4	5.36	50.8	27.6	14.2	7.47	4.86	0.93
.0157	23.4	4.23	49.8	28.5	16.7	5.49	4.97	..
R = 16.8								
0.074	40.9	5.73	46.6	30.0	14.1	9.25	12.3	1.44
.0261	38.8	5.10	47.3	29.6	14.4	8.71	11.1	0.62
.0093	34.1	4.27	45.5	30.7	16.0	7.87	12.9	1.64
He, R = 32.5								
0.0286	30.5	5.40	49.9	28.4	14.4	7.34	0.99	
.0220	25.9	4.59	49.9	29.3	14.7	6.08	.62	
.0190	28.3	4.71	50.7	27.5	15.2	6.56	.43	
.0159	27.3	4.51	49.5	29.5	15.0	6.01	..	
.0141	26.7	4.73	49.7	30.8	13.4	6.06	..	
.0128	24.6	4.19	50.5	27.9	16.1	5.51	0.47	
.0127	30.0	4.47	51.4	27.9	15.2	5.63	.41	
.0111	36.2	4.26	49.8	28.5	16.2	5.52	.77	
.0103	26.1	3.68	41.9	34.1	18.4	5.53	..	
.00636	35.2	3.97	50.8	27.9	17.0	4.37	0.66	
R = 29.5								
0.0404	29.1	5.13	50.1	28.2	14.0	7.67	0.73	
.01408	33.9	4.51	49.5	27.6	16.0	6.91	0.51	
.00508	37.6	3.61	47.7	26.6	19.4	6.28	..	
Ar, R = 50.4								
0.0221	33.8	5.70	49.9	30.1	14.0	6.02	0.27	
.0177	34.9	5.71	51.5	27.5	14.5	6.54	0.25	
.165	46.0	5.47	48.7	29.9	15.2	6.27	2.3	
.141	23.0	5.59	51.6	28.4	14.5	5.51	1.45	
.0134	35.3	5.14	50.8	29.1	14.3	5.82	2.35	
.0134	44.1	5.53	50.0	28.3	15.2	6.55	2.5	
.00985	49.8	5.09	49.8	28.6	15.3	6.63	2.58	
.00965	47.0	4.84	49.1	28.5	16.9	5.50	2.10	
.00843	38.9	4.87	50.7	28.8	15.1	5.38	2.00	
.00734	47.4	4.70	48.0	29.6	15.5	6.98	2.20	
.00702	49.3	4.62	50.5	28.3	15.2	5.89	2.19	
.0050	43.4	4.29	49.9	27.9	15.9	6.22	0.53	
N_2, R = 24.2								
0.0263	35.9	5.26	49.7	28.1	25.0	7.29	0.40	
.0190	29.8	5.03	50.2	28.5	15.0	6.24	.26	
.0188	35.8	5.10	48.9	29.3	15.4	6.39	.47	
.0155	28.9	4.87	48.3	30.8	15.3	5.61	..	
.0117	38.1	4.74	49.5	28.5	15.2	6.83	0.51	
.0113	25.5	4.69	53.4	25.7	14.7	6.21	..	
.00853	33.6	4.28	50.6	27.5	15.0	6.91	..	
.0059	31.7	3.75	48.9	28.9	17.8	4.37	..	
.0055	40.5	3.70	47.8	29.2	16.7	6.32	..	
CH_4, R = 2.80								
0.0512	30.4	5.38	50.0	20.0	14.9	7.09	0.85	
.0286	25.2	4.61	49.6	28.1	15.5	6.85	.59	
.0234	25.4	4.34	49.6	27.2	16.4	6.85	.75	
.0176	38.0	4.13	47.9	28.2	17.2	6.69	1.11	
.01275	32.5	3.88	48.8	26.9	18.4	5.83	1.03	

.01173	42.1	3.85	51.5	26.0	16.8	5.66	1.03	
.00945	33.3	3.40	48.9	26.9	19.1	5.09	0.87	
.00917	43.9	3.61	50.3	26.2	17.9	5.62	1.21	
.00868	37.1	3.62	48.2	28.6	17.4	5.87	..	
.00786	41.2	3.54	51.2	25.6	18.7	4.50	..	
.0059	40.7	3.34	49.9	27.4	18.3	4.35	..	
C_2H_6, $R = 2.43$								
0.05998	26.7	4.44	51.5	27.4	14.9	6.13	1.30	
.0161	24.1	4.22	48.1	30.1	15.5	6.26	1.27	3.0
.0534	20.7	4.22	48.3	29.8	15.2	6.75	0.97	..
.0131	26.6	3.95	47.2	29.3	16.4	7.12	0.38	3.3
.0116	28.0	3.94	48.6	27.9	17.7	5.81	1.19	..
.0105	47.7	3.94	49.5	27.6	16.8	6.16	1.06	..
.00891	42.7	3.60	48.6	26.7	18.4	6.21	0.79	..
.0076	44.7	3.72	50.7	26.0	17.2	6.11	1.03	..
.00702	44.2	3.66	48.7	27.1	17.4	6.90	0.81	1.31
.00613	34.5	3.24	48.8	28.2	16.8	6.29	0.85	..
Toluene, $R = 1.90$								
0.0152	30.6	4.41	49.4	27.0	16.3	7.18	0.60	
.0433	40.2	4.50	49.7	27.4	16.0	6.89	.23	
.0127	42.6	4.20	50.4	25.1	17.6	6.87	.52	
.0101	38.3	4.06	48.7	27.7	16.7	6.86	.22	
.0101	45.1	4.02	51.4	25.2	17.4	6.11	.67	
.0082	37.6	3.77	50.5	25.3	17.9	6.24	.45	
.00721	44.2	3.59	48.5	27.0	18.4	6.04	..	

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY AT HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Dimethyltin Salts of Carboxylic Acids

BY ROKURO OKAWARA[1] AND EUGENE G. ROCHOW

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Reactions of dimethyltin oxide and dichloride with formic and acetic acids and their salts have been studied. Formic acid did not react with the dichloride, but $(CH_3)_2SnCl(OOCH)$ and $(CH_3)_2Sn(OOCH)_2$ were obtained by the action of sodium formate. Acetic acid and the dichloride gave $(CH_3)_2SnCl(OOCCH_3)$ in poor yield; this compound was obtained in better yield by using acetic anhydride. Dimethyltin diacetate could not be obtained, but the dimeric compound, tetramethyl-1,3-diacetoxydistannoxane, was obtained from the oxide and acetic anhydride. Dimethylchloroformoxytin and dimethylchloroacetoxytin gave tetramethyl-1,3-dichlorodistannoxane by hydrolysis. The reverse reaction could be carried out by cleaving the dichlorodistannoxane with formic or acetic acid. Infrared spectra showed the presence of carboxylate ions in the solid state.

Various methods have been applied to the preparation of organotin esters.[2a] Van der Kerk and Luitjen[3] described trimethyltin acetate, obtained from acetic acid and trimethyltin hydroxide. Halogenoacetates of dimethyltin were prepared by the acid cleavage of dimethyldivinyltin,[2b] and some esters were obtained by the reaction of dimethyltin dichloride with alkali metal salts in aqueous solution.[4] Of the esters of the monomethyltin group, linear and cyclic tristannoxanes were obtained from the reaction of methylstannoic acid and carboxylic acids.[5]

Dimethyltin dichloride is readily available,[6] and it was thought to be interesting to attempt the preparation of esters directly from the dichloride.[7] To this end, dimethyltin dichloride was allowed to react with formic and acetic acids or their anhydrides or sodium salts. The reaction of an excess of acetic anhydride gave dimethylchloroacetoxystannane. By the reaction of glacial acetic acid, a small amount of dimethylchloroacetoxystannane was also obtained. Experiments to obtain dimethyldiacetoxystannane from chlorides or from dimethyltin oxide were carried out, but it was impossible to isolate this compound because of decomposition in the course of sublimation or because of polymerization during recrystallization. The only well-characterized product was the dimeric one, tetramethyl-1,3-diacetoxydistannoxane, $(CH_3COO)(CH_3)_2Sn–O–Sn(CH_3)_2(OOCCH_3)$, which was obtained by recrystallization. A compound having the similar distannoxane structure has been reported recently.[8] These results suggest why Lambourne[5] has obtained compounds having cyclic and linear tristannoxane structures.

While formic acid and dimethyltin dichloride showed no reaction, addition of an insufficient amount of sodium formate to the dichloride gave the chloroformoxystannane; addition of an excess amount of sodium formate gave dimethyldiformoxystannane. These compounds were also derived from polymeric dimethyltin oxide as demonstrated in the reaction scheme shown below.
This reaction scheme is also applicable in principle to the case of acetoxy compounds with slight changes; dimethylchloroacetoxystannane can be obtained by the action of acetic anhydride on the dichloride, and the position of dimethyldiacetoxystannane in this reaction scheme should be substituted by tetramethyl-1,3-diacetoxydistannoxane.

For the compounds investigated here, differences between the behavior of the Sn–Cl bond from that of the Si–Cl bond during hydrolysis are clearly shown in this scheme. In an alkaline medium, the Sn–Cl bond hydrolyzes completely to form an Sn–O–Sn linkage, but it does not react in a neutral or acidic medium.[4,9] Another difference is shown in the infrared spectra[10] of carboxylates of these two ele-

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[1] Research Fellow in Chemistry at Harvard University, 1958–1959.

[2] (a) See references 4–8 of (2b). (b) A. Saitow, E. G. Rochow and D. Seyferth, *J. Org. Chem.*, **23**, 116 (1958).

[3] G. J. M. van der Kerk and J. G. A. Luitjen, *J. Appl. Chem.*, **6**, 49 (1956).

[4] E. G. Rochow, D. Seyferth and A. C. Smith, Jr., THIS JOURNAL, **75**, 3099 (1953).

[5] H. Lambourne, *J. Chem. Soc.*, **121**, 2533 (1922); **125**, 2013 (1924).

[6] A. C. Smith, Jr., and E. G. Rochow, THIS JOURNAL, **75**, 4103, 4105 (1953).

[7] The experiment to obtain triorganotin acetate directly from the reaction of triorganotin bromide and sodium acetate has not been successful. See ref. 8.

[8] S. D. Rosenberg, E. Debreczeni and E. T. Weinberg, THIS JOURNAL, **81**, 972 (1959).

[9] E. G. Rochow and D. Seyferth, *ibid.*, **75**, 2877 (1953).

[10] See also R. Okawara, D. E. Webster and E. G. Rochow, *ibid.*, **82**, 3287 (1960).