

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## Kinetics of the Thermal Isomerization of Cyclopropane

BY THOMAS SEAL CHAMBERS AND G. B. KISTIAKOWSKY

### I. Introduction

The alicyclic hydrocarbon cyclopropane has been reported to be thermally converted into its open chain ethylenic isomer propylene both homogeneously and under the influence of heterogeneous catalysts. The catalytic reaction has been studied by a number of investigators.<sup>1</sup> Trautz and Winkler<sup>2</sup> have reported kinetic data on the homogeneous uncatalyzed reaction, but doubt as to the validity of their results has been expressed by at least two authors.<sup>3</sup> They worked chiefly between 550 and 650°, and interpreted their data to mean that the isomerization is unimolecular and predominantly homogeneous within this range. But the worth of these conclusions suffers first from the fact that they employed a flow system, the inadequacies of which, particularly at high pressures, are only too well-known; and second from the fact that their method of analyzing the reaction products (low temperature density determinations) may easily lead to erroneous results. Finally, their work was carried out before the advent of modern statistical theories of unimolecular reactions, and lacks data concerning the dependence of the rate constants on pressure. The present investigation was carried out in order to secure results accurate enough to be applied to a quantitative study by one of us (T. S. C.) of the reactions of three-carbon rings.

The reaction was studied in a static system over a temperature range of 49°, from 469.6 to 518.6°, and was found to be homogeneous and unimolecular, with the velocity dependent on the pressure of the reacting gas.

### II. Preparation of Cyclopropane

Cyclopropane (b. p. -34°) was prepared from zinc and trimethylene bromide in aqueous alcohol by the method of Lott and Christiansen.<sup>4</sup> It was freed of propylene by shaking for several hours in large flasks with 3% aqueous neutral permanganate, and then passed slowly through a

(1) Ipatieff, *Ber.*, **35**, 1063 (1902); Ipatieff and Huhn, *ibid.*, **36**, 2014 (1903); Tanatar, *Z. physik. Chem.*, **41**, 735 (1902); *et al.*

(2) Trautz and Winkler, *J. prakt. Chem.*, [2] **104**, 53 (1922).

(3) Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Clarendon Press, Oxford, 1929, p. 140; Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Company, New York, 1931, p. 235.

(4) Lott and Christiansen, *J. Am. Pharm. Assoc.*, **19**, 341 (1930).

train of potassium hydroxide and phosphorus pentoxide towers into a distillation tube cooled in liquid air, where it solidified to a white crystalline mass. It was alternately warmed above the melting point and frozen several times, evacuating each time after freezing in order to remove permanent gases. The liquid hydrocarbon was distilled several times, each time discarding the first and last fractions. In this way cyclopropane of undoubted purity was obtained. After the final distillation, the liquid cyclopropane was allowed to evaporate into a large storage flask.

### III. Experimental Details

This storage bulb was directly connected with the all-glass line leading to the reaction chamber, the pumping system, and the analytical apparatus. Adjacent to the storage bulb was a smaller flask provided with a small side arm, so that gas could be condensed therein and the pressure in this "pre-furnace bulb" adjusted to any desired value. Both flasks were connected to an open-arm mercury manometer. Gas was allowed to flow from this last bulb into the reaction vessel in the furnace, an electrically heated air-bath thermostat with hand temperature control. To the reaction vessel was attached a capillary manometer, from which the pressure of the reacting gas could be determined. Capillary tubing was necessary in order to minimize the amount of cold "dead" space outside the furnace, for which a suitable correction was applied in calculating the results. Upon completion of an experiment the gas in the reaction vessel was allowed to expand rapidly into a large flask, from which it was transferred to small thermostated storage bulbs by means of a Töpler pump. The entire system was capable of evacuation to  $10^{-4}$  mm. by a mercury vapor pump.

The pressure in the "pre-furnace" bulb necessary to produce some definite pressure in the reaction vessel was determined by trial. In making a run, then, this pressure was adjusted to the desired value, and the gas was allowed to expand as rapidly as possible into the reaction vessel; after remaining here for the desired interval, measured by a stop watch, it was allowed to expand into the large flask and collected and stored prior to analysis.

New spherical Pyrex bulbs of liter and half-liter volume were used as reaction vessels. The quantity of cold gas suddenly admitted to the hot vessel was in some cases sufficient to require as much as one minute to be heated completely to the furnace temperature; in no case, however, was as much as one degree fall in temperature noted. The fall was appreciable only in the case of experiments at half atmospheric pressure and over. In these cases the temperature was taken at such frequent intervals that no correction in the ultimate results was necessary.

The temperature was measured by a calibrated chromel-alumel thermocouple placed in a well extending to the center of the reaction vessel. Measurements were made at frequent intervals during the course of a run, and the

average of these was taken as the temperature of the experiment. The relative precision of the temperatures may be safely placed at  $\pm 0.25^\circ$ .

#### IV. Analysis of the Product Gases

The most serious experimental difficulty arises from the necessity of determining the amount of propylene produced during the course of an experiment. Manometric methods are obviously of no use, since the isomerization involves no pressure change, and there are no appreciable concurrent or consecutive reactions. Trautz and Winkler<sup>5</sup> found a linear density-composition relationship at  $-80^\circ$  for liquid mixtures of cyclopropane and propylene, but the determinations are not as accurate as desirable for the present work and require so much material that the use of a static system becomes impractical.

Cyclopropane was found to be unattacked, and propylene quantitatively absorbed by a 3% aqueous neutral solution of potassium permanganate. This observation is in harmony with certain statements in the literature,<sup>6</sup> and not in agreement with others.<sup>7</sup> It is probable that these latter authors have neglected the rather large solubility of the gas in the absorbing solutions. This can easily account for the misunderstanding, inasmuch as the determinations were for the most part made with apparatus having a large volume of aqueous solution, in comparison with the volume of gas to be examined. By minimizing the ratio of these two volumes, it was found practical to use permanganate absorption as a method of analyzing cyclopropane-propylene mixtures.

In order to establish definitely that the small absorption of cyclopropane by 3% neutral aqueous permanganate is simply a matter of physical solubility, blank analyses were run using both water and saturated salt solutions in place of the reagent solution. Average percentage solubilities<sup>8</sup> at  $23.5^\circ$  of 2.6 (water) and 0.65 (satd. salt soln.) were found, using 5.5 cc. of absorbent and varying gas pressures in a 45 cc. volume. This is to be compared with absorptions by permanganate varying from 2.4 to 3.0%, depending on the particular preparation of gas employed. It is obvious that practically all of the absorption is due

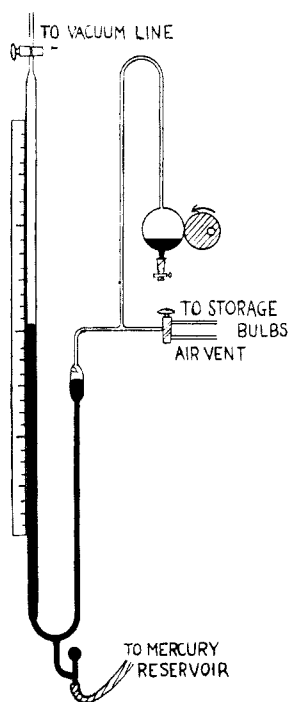


Fig. 1.—Apparatus for analysis of the product gases.

simply to solubility. There is a possibility that the sample showing 3% absorption reacted to a small extent, since traces of manganese dioxide were noted on the walls of the analysis chamber. It is more likely, however, that a minute fraction of propylene was present, and that this was responsible for the small excess noted. In any case, the amount of gas absorbed was found to be constant and small for a given sample, so that an empirical correction could easily be applied to the analysis of the product gases.

The analytical apparatus is illustrated in Fig. 1. A flask provided with a drainage tube was attached to a mercury manometer by means of capillary tubing long enough, and therefore flexible enough to withstand shaking by means of a small eccentric. This absorption apparatus was connected with the main all-glass train through a suitable stopcock. The reagent solution was introduced into the absorption flask through the tube in the bottom, and the system was evacuated as far as possible. After thermostating the flask, the manometer reading (at constant volume) was taken. By using this as the zero for pressure measurements, one obviates the necessity of measuring the vapor pressure of the solution. The gas to be analyzed was allowed to flow rapidly from a thermostated storage bulb into the absorption flask, and the manometer was read immediately. The thermostat was removed, and the flask shaken effectively by the eccentric. One hour was found to be sufficient for the quantitative absorption of the propylene, during which the mercury in the manometer was raised and lowered in order to allow the gas in the capillary to be in contact with the absorbent. The flask was shaken for two hours in order to provide an ample margin of safety. The vapor pressure of the reagent solution was found to be unchanged after absorption.

The average deviation from the mean for duplicate experiments was very close to 0.1 cc. for every 10 cc. of gas absorbed. Since the empirical corrections involve no great error, this method of analyzing cyclopropane-propylene mixtures is quite satisfactory for the purposes of this investigation.

#### V. Nature of the Reaction

The principal, and beyond a reasonable doubt the only, reaction measured is the transformation of cyclopropane to propylene. This requires that the proportion of reacting molecules to reaction products be strictly unity; the best evidence that this is realized is offered by the absence of any pressure change during the course of the reaction at various stages of completion, and at varying temperatures and pressures. Any variations noted are always less than 1% of the total pressure, and occur quite at random; this is within the accuracy of the capillary manometer employed. It does not rule out, however, the possibility of nicely balanced concurrent decomposition and polymerization reactions, which propylene might be expected to undergo. The complete lack of trend in the rate constants dur-

(5) Trautz and Winkler, *J. prakt. Chem.*, [2] **104**, 50 (1922).

(6) Wagner, *Ber.*, **21**, 1236 (1888); Gustavson, *J. prakt. Chem.*, [2] **62**, 285 (1900).

(7) Roginski and Rathmann, *THIS JOURNAL*, **55**, 2802 (1933).

(8)  $[(\text{Mm. gas absorbed}) / (\text{mm. gas present})] \times 100 = \text{percentage solubility}$ .

ing the course of a run indicates that even if such reactions do occur, the unsaturation of the products is not changed sufficiently to invalidate the results of the permanganate analysis. The data reported by Hurd and Meinert<sup>9</sup> on the pyrolysis of propylene in Pyrex at 600° are not well-suited for extrapolation to our temperatures; a rough calculation indicates, however, that not more than 1% of the propylene formed will escape detection. The only evidence of any thermal degradation observed was a brown film about 1 cm. in length which appeared in the capillary just outside the furnace after several experiments.

In view of the lack of experimental data on the subject, we must consider the possibility of the reverse reaction, *i. e.*, the conversion of propylene into cyclopropane. The exact position of the equilibrium at the temperatures which concern us cannot be calculated at present, since the measured heat of combustion of cyclopropane is acknowledged to be uncertain; and, further, since the specific heat and entropy of cyclopropane are not known. It is not likely that the specific heats of the two compounds will be much different; if we assume that the difference between the measured heats of combustion for cyclopropane<sup>10</sup> and propylene<sup>10</sup> represents a minimum, due to the possible presence of the latter in Thomsen's cyclopropane, and if we follow Parks and Huffman<sup>11</sup> in adopting 8 e. u. as the entropy change in the reaction cyclopropane → propylene, we find that the free energy change at the lowest temperature investigated is  $-6600 - 743 \times 8 = -12,600$  cal. Thus the maximum fraction of cyclopropane which might be present at equilibrium is less than 1 in 1000. This means that the detection of the reverse reaction is beyond the range of the analytical procedure. The lack of trend in the constants bears out this conclusion.

It should be pointed out that any possible errors arising from this source and from polymerization of propylene will be additive, and will not cancel each other. This is based on the probability that the latter process will result in the formation of a mono-olefin. We have no reason for suspecting that cyclopropane undergoes any change other than the measured one at the temperatures investigated, although Trautz and Winkler report

that it is slightly less stable to thermal degradation than propylene in porcelain tubes at 600°.

TABLE I

No.	Press., cm.	Time, sec.	$K_p$ , sec. <sup>-1</sup> × 10 <sup>4</sup>	Vessel, cc.
Temp., 499.5°				
12	70.26	720	5.95	500
13	71.04	720	5.94	500
14	37.43	720	5.79*	500
6	37.91	480	5.74	500
7	37.22	1800	5.76	500
9	38.03	900	5.73	500
11	19.54	720	5.60	500
15	19.32	720	5.42	500
16	10.86	720	5.12	500
17	9.94	720	5.12	500
29	10.70	720	5.08	1000
18	5.36	720	4.84	1000
21	5.53	720	4.70	1000
49	3.75	720	4.42	1000
50	3.64	720	4.74	1000
19	2.44	720	4.11	1000
20	2.52	720	4.14	1000
27	2.59	1800	4.05	1000
28	2.42	1800	4.26	1000
34	2.57	720	3.96	1000 packed
35-36	2.45	720	4.17	1000 packed
23-24	1.30	720	4.06	1000 empty
25-26	1.41	720	3.93	1000
31-32-33	1.27	720	3.36	1000
501°				
1	38.57	900	6.35*	500 empty
2	38.29	900	6.26	500 rinsed
4	38.99	900	6.55	500 packed
5	36.55	180	6.59	500 empty
469.6°				
53	76.27	3000	1.13	500
54	75.70	3000	1.09	500
51	38.81	3000	1.07	500
52	38.91	3000	1.10	500
55	20.76	3000	1.05	500
56	21.37	3000	1.04	500
45	11.02	3000	0.955	1000
46	10.90	3000	0.961	1000
42	5.05	3000	0.846	1000
48	3.63	3000	0.840	1000
43	2.66	3000	0.767	1000
44	2.67	3000	0.812	1000
37-38	2.59	3000	0.791	1000 packed
39-40	2.66	3000	0.809	1000 packed
518.6°				
61	76.49	300	16.7	500
62	76.35	300	17.3	500
59	37.45	300	16.4	500
60	37.14	300	16.1	500
57	20.16	300	14.6	500
58	20.34	300	16.3	500

(9) Hurd and Meinert, *THIS JOURNAL*, **52**, 4978 (1930).(10) Kharasch, *Bur. Stds. J. Res.*, **2**, 374, 376 (1929).

(11) Parks and Huffman, "Free Energies of Some Organic Compounds," Chemical Catalog Company, New York, 1932, pp. 81, 96.

There is every reason to believe that we are on safe ground in assuming that the reaction measured is the conversion of cyclopropane to propylene.

## VI. Evaluation and Interpretation of the Data

The experimental results are presented in Table I. The unimolecular constants have been calculated by inserting the fraction of propylene (corrected for dead space in the reaction system) into the ordinary integrated equation  $k = (1/t)\ln(a/a-x)$ , and then adjusting for small temperature differences (less than  $1^\circ$ ) between separate experiments. The separate groups represent experiments performed in the same pressure and temperature ranges. The only experiments omitted are those performed under unfavorable conditions, for which the manually controlled furnace temperature was chiefly responsible. The agreement between duplicate experiments is in the aggregate quite good. The experiments in the neighborhood of 1.3 cm. had to be run a number of times in order to collect enough gas for even one analysis; the results are uncertain, and have not been considered in any of the calculations. Experiments marked with an asterisk were made with a different preparation of gas from that used in other runs in the same group.

It is evident from a comparison of experiments made in packed and unpacked reaction vessels that there is no appreciable amount of heterogeneity present. The surface/volume ratio was increased 6.2 times and 4.6 times when packed liter and half-liter vessels, respectively, were substituted for the empty flasks, and in one experiment a flask rinsed with 10% aqueous potassium chloride solution was used. In no case was a change in rate greater than the experimental error observed. That this was found at the lowest temperature and pressure studied as well as in other regions is good evidence that the reaction is really homogeneous.

From an inspection of the data it is at once seen that the reaction is unimolecular as well as homogeneous. Remarkably good values are obtained for the unimolecular constant at  $499.5^\circ$  and 37.5 cm. pressure; here the reaction was followed from 25 to 65% completion, with no appreciable trend in the constants. Similar, though not as striking, results are obtained in the neighborhood of 2.5 cm. The lack of trend in these constants furnishes confirmatory evidence

for the assumption that polymerization and decomposition reactions are absent, or at least occur in such a manner that they do not vitiate the analytical results. Since all the measurements were made in regions where the calculated constants are dependent on the pressure of the reacting system, it is evident that propylene must be as effective as cyclopropane in maintaining the rate of activation. It should be pointed out that the unimolecular course of the reaction was investigated at one temperature only.

The dependence of the rate on pressure is evident at a glance. A thirty-fold decrease in pressure is accompanied by a drop in the unimolecular constant of slightly more than 30% at both  $499.5$  and  $469.6^\circ$ . Because of this dependence of the rate on pressure, it is necessary at each temperature to arrive at the high pressure rate constant, designated as  $K_\infty$ , by extrapolation to infinite pressure. This is conveniently performed by plotting  $1/p$  against  $1/k$ , and determining the point of intersection of the apparent asymptote with the  $1/k$  axis. Points at the four highest pressures investigated in each case apparently determine a straight line; the equation of this line was evaluated by the method of least squares, and its intersection with the  $1/k$  axis determined. This method has an advantage over choice of the asymptote by mere inspection in that it gives perfectly definite<sup>12</sup> results which serve as convenient minima for the high pressure constants. The straight line is a limiting line; any appreciable deviation from it should be in the direction of increasing  $K_\infty$ . This provides for the contingency that the experimental curve may still have appreciable curvature. Of course this assumes reasonable accuracy in the individual experimental constants. The extrapolation at  $499.5^\circ$  is presented graphically in Fig. 2.

The second row of the following table contains values for  $K_\infty$  at various temperatures obtained by this essentially objective method.

TABLE II

Temp., $^\circ\text{C}$ .	469.6	499.5	518.6
$K_\infty$ , sec. <sup>-1</sup> $\times 10^4$	1.14	6.08	17.8
$K_\infty$ , calcd.	1.14	6.25	17.35

When the logarithm of these constants is plotted against inverse absolute temperature, the points fall very near a straight line. If the slope and position of this line is weighted to favor

(12) Cf. Prentiss and Scatchard, *Chem. Rev.*, **13**, 1 (1933).

the more certain results at the two lower temperatures, we find that the high pressure constants are given very nearly within experimental error by the equation

$$\log K_{\infty} = 15.17 - 65,000/2.3RT$$

The third row in Table II contains these calculated values. The crossed circle in Fig. 2 repre-

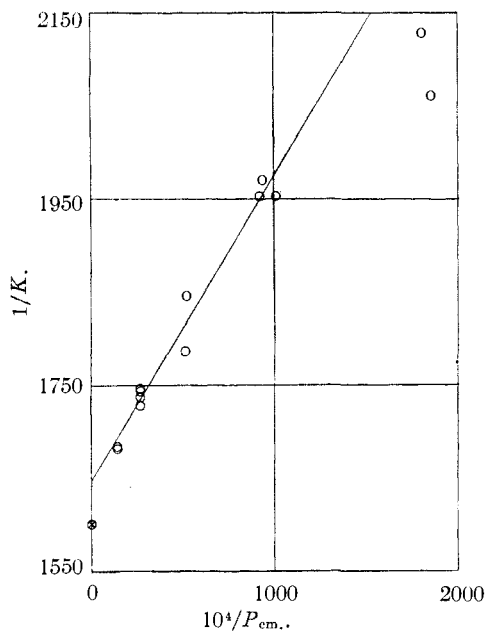


Fig. 2.—Extrapolation to the high pressure rate at 499.5°. The point in the crossed circle is calculated from the equation  $\log K_{\infty} = 15.17 - 65,000/4.578 T$ .

sents this calculated constant for 499.5°. Unless we are sure that the experimental points in this figure should fall on a straight line, we are not in a position to choose between this point and the asymptotic intercept. The discrepancy between the values at 518.6° attended by greater experimental uncertainty is probably due to errors in the extrapolation. The value for the activation energy is certainly correct within  $\pm 2000$  calories. Figure 3 is simply a plot of  $\log K_{\infty}$  against reciprocal absolute temperature.

The decrease in the rate constants with decreasing pressure is sufficiently large to justify the application of the detailed theories of unimolecular reactions in a comparison of theoretical with experimental results. By adopting suitable values for the parameters in the equation presented by Kassel,<sup>13</sup> and performing the necessary graphical integrations, it is possible to draw curves

(13) Kassel, *J. Phys. Chem.*, **32**, 235 (1928).

which fit the experimental data in a very satisfactory manner. In Fig. 4 a log-log plot of pressure versus  $K/K_{\infty}$  is presented; the curves are theoretical, and the points represent averages for experiments in a definite pressure region. When the high pressure rate constants found by extrapolation are employed in calculating the experimental points for this graph, the results for the two temperatures are found to be practically superimposed. The obvious uncertainties in the extrapolation justify the adoption of values for  $K_{\infty}$  which lead to more reasonable results; for this purpose the calculated constants in Table II have been used. These differ from the extrapolated values by 0 and 3% at 469.6 and 499.5°, respectively.

The curves presented in the plot have been obtained by setting the number of degrees of freedom in the molecule equal to thirteen, and choosing  $3.9 \times 10^{-8}$  cm. as the molecular diameter. Since this value has been obtained from gas viscosity measurements,<sup>14</sup> we have no assurance that it represents the diameter for collisional deactivation. The agreement between the calculated and experimental values is quite good.

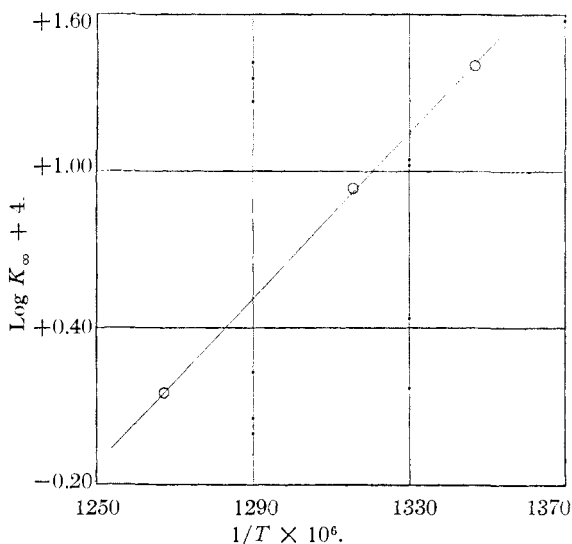


Fig. 3.— $\log K_{\infty}$  plotted against reciprocal absolute temperature.

Slightly better agreement can be obtained by using a diameter of  $5.6 \times 10^{-8}$  cm., and twelve degrees of freedom. The curves now fall away a bit more rapidly, but the diameter necessary is probably too large. Neither the experimental accuracy nor the drop in rate observed are suf-

(14) Titani, *Bull. Chem. Soc. Japan*, **5**, 98 (1930).

ficient to establish either of these values for the number of degrees of freedom. It is particularly desirable to have rate constants for a wider pressure range, since local variations in the trend of the points are sometimes observed. For the present the question can be satisfactorily settled by expressing the results as squared terms instead of degrees of freedom, whereupon the value 25 becomes the obvious choice. The maximum allowable variations in the activation energy shift this number by only about 2 in either direction.

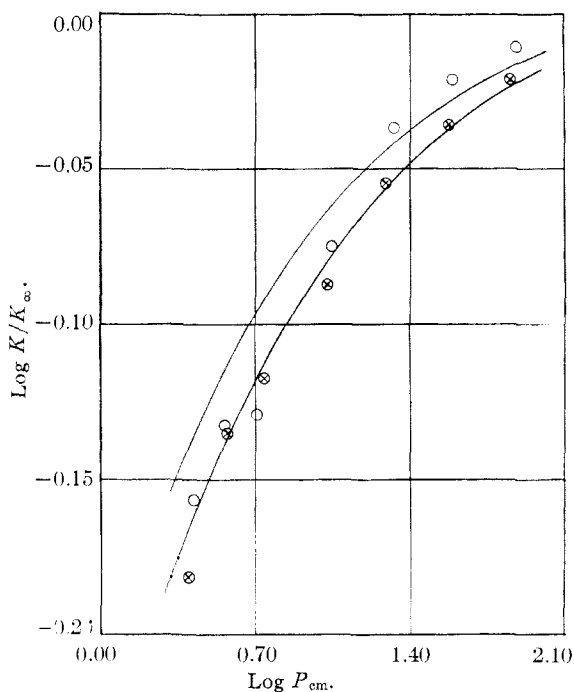
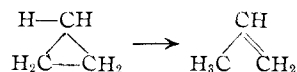


Fig. 4.—Dependence of the rate constants on pressure. The curves are theoretical; circles and crossed circles represent experiments at 469.6 and 499.5°, respectively. The values for  $K_\infty$  have been adjusted as described in the text.

## VII. Discussion

Just how the reaction occurs is not certain. If the structure the organic chemist assumes for cyclopropane is the correct one, then we can be sure that at some stage the reaction involves the breaking of a carbon-carbon bond. In this respect the reaction does not differ in kind from paraffin hydrocarbon cracking; furthermore, the bonding energies of carbon atoms in paraffins and in the lower polymethylenes probably do not differ by more than 6–8 kcal. The agreement between the activation energies for the cyclopropane reaction and for the cracking of the lower paraffins probably is significant, and makes it reasonable to seek similar mechanisms for the

two reactions. This is possible in two ways. If we assume that the first step involves the direct rupture of one of the carbon-carbon bonds, the remainder of the reaction can be represented as a rearrangement of the radical initially produced. A rearrangement of this type is not at all unexpected; it is quite analogous to the commonly observed disproportionation of free radicals, and can be *formally* applied to both cyclopropane and paraffin cracking. On the other hand, we must also consider the possibility that the initial step in the former reaction may be 1,2-unsaturation, as has been recently suggested in the case of the paraffins.<sup>15</sup> For the cyclopropane reaction this is written



The available evidence does not permit a choice between either of these reaction mechanisms. One must be careful not to push the analogy between cyclopropane and the paraffins too far, since the highly efficient internal energy exchange in the former (as discussed in the following paragraphs) is probably not realized in straight chain hydrocarbons.

From the number of degrees of freedom necessary to account for the observed decrease in rate with decreasing pressure, it is evident that a larger proportion of the potential oscillators are excited in the cyclopropane isomerization than in most other unimolecular reactions. The number of oscillators needed when the calculations are made on the basis of a classical localized energy theory is usually equal to or less than half the total number possible; or, what turns out to be nearly the same thing, the maximum number of oscillators excited may be given by three times the number of heavy atoms. Reference to the slowly accumulating literature on unimolecular reactions will show that this generality is in the main true, remembering, of course, that comparison can only be made between results arrived at on the basis of like theories. Now half the total number of oscillators in the cyclopropane molecule is 21/2, or 10–11, while three times the number of heavy atoms is of course nine. These figures are to be compared with the 12–13 oscillators necessary to fit the experimental data. The difference between these last two sets of figures is undoubtedly real, although it may be

(15) Kassel, *J. Chem. Phys.*, **1**, 749 (1933).

due in part to uncertainties in the measured heat of activation. When one considers the high degree of symmetry of the cyclopropane molecule, the unusually large number of oscillators becomes understandable; the intimate structural association of the three methylene groups and the consequent interdependence of vibrations which the atoms composing the molecule carry out make it probable that at least the carbon-carbon oscillators will be excited more or less as a unit. It will be of interest to note the effect of reducing the molecular symmetry on the number of oscillators in the various methylated cyclopropanes; kinetic studies on these compounds are now in progress.

One must regret that Heckert and Mack<sup>16</sup> did not obtain unequivocal results from their studies on the decomposition of ethylene oxide, making possible a kinetic comparison of the two-carbon-oxygen ring with the three-carbon ring.

Further discussion of a theoretical and speculative nature can be made more profitably after the accumulation of additional data on the kinetics of cracking in small organic rings.

There is one striking difference between the data brought to light in this investigation, and as reported by Trautz and Winkler: the temperature independent factors in the rate equation differ by more than a power of ten. Trautz and Winkler report  $1.00 \times 10^{14}$ , while we found  $1.48 \times 10^{15}$ . The activation energies, 63,900 and 65,000 calories, are in good agreement, although this is probably fortuitous, particularly since the former value is an average of six, varying from 54,800 to 70,440. The only approximate homogeneity in the earlier work may have been due to an unfortunate choice of the material for the reaction vessel. In order to bring the individual rate constants into harmony, however, one must assume that the temperatures reported by Trautz and Winkler are nearly 40° too high. There is a likely factor which contributed to this discrepancy, which is that the contact times of the experiments which the authors chose to derive the kinetic equation are in no case greater than

seventeen seconds. It is generally recognized that serious errors in temperature measurement arise from the use of these short contact times in flow studies, particularly when (as in this case) the gas entering the furnace is not preheated and is nearly 600° below the thermostat temperature. The fact that the thermocouples were placed outside the reaction tube, thereby measuring the temperature of the furnace, and not that of the reacting gas, makes this argument all the more sound. This source of error probably accounts for most of the discrepancy. Furthermore, in the upper part of the temperature range used by Trautz and Winkler polymerization and decomposition reactions were seriously complicating factors, and it is doubtful whether accurate allowance could have been made for them in the combination of gas analyses and low temperature density determinations which served to determine the reaction products. The situation can probably be best expressed in the statement that the conclusions of the earlier workers as to the homogeneity and unimolecularity of the reaction have been substantiated, but on the basis of widely different data.

### VIII. Summary

1. The thermal transformation of cyclopropane to propylene has been investigated in a static system and found to be homogeneous and unimolecular. The rate constants are dependent on the pressure of the reacting system. The high pressure constants may be calculated from the equation

$$\log K_{\infty} = 15.17 - 65,000/2.3RT$$

2. To account theoretically for the dependence of the rate on pressure on the basis of classical localized energy theories of unimolecular reaction it is necessary to assume 25 squared terms in the energy function of the molecule.

3. A detailed discussion of the reaction process is deferred until completion of similar studies on derivatives of cyclopropane now in progress in this Laboratory.

CAMBRIDGE, MASS.

RECEIVED DECEMBER 11, 1933

(16) THIS JOURNAL, 51, 2706 (1929).