swelling agents by heating at elevated temperatures even though in the unswollen condition certain of these materials may tend to harden because the rate of cross-linking may be more rapid when the molecules are close together than the rate of scission.

The measurement of relaxation of stress at constant extension isolates and measures only the scission reaction since the cross linking which is occurring simultaneously takes place in such a way as not to affect the stress in samples maintained at constant elongation (to a first approximation).[16,17] On the other hand, intermittent measurements of modulus, with the sample kept in a relaxed state between modulus determinations measure the sum of cross-linking and scission reactions. Measurements of this kind on vulcanizates of natural rubber and various synthetic rubbers demonstrate that scission and cross-linking are occurring at comparable rates in all rubbers and confirm the very important role of oxygen in these processes.[16,17] Recent experiments proving the simultaneous existence of polymerization and degradation in toluene solutions of styrene and polystyrene also appear to fit into the general kinetic picture developed here.[18]

Summary

A general mechanism for various reactions of vinyl and diene polymers is presented which emphasizes the role of the hydrocarbon free radical as the activated state which can undergo various competing subsidiary reactions that profoundly affect the physical properties of these materials.

The mechanism further emphasizes the chain characteristics of depolymerization processes, occurring by reversal of the steps in the chain growth processes, at velocities which are significant even at moderate temperatures owing to the small activation energies involved.

PRINCETON, N. J.

RECEIVED JULY 21, 1945

---

[16] A. V. Tobolsky, I. B. Prettyman and J. H. Dillon, *J. Applied Phys. (U. S. S. R.)*, **15**, 380 (1944).

[17] A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.*, **13**, 3 (1945).

[18] R. B. Mesrobian and A. V. Tobolsky, THIS JOURNAL, **67**, 785 (1945).

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Kinetics and Mechanism of the Isomerization of Cyclopropane

BY E. S. CORNER[1] AND R. N. PEASE

During recent years there has been a divided opinion on the status of the quasi-unimolecular reaction. Formerly the Hinshelwood–Lindemann theory[2] was almost universally accepted as providing the explanation for the breakdown of first order constants at low pressures. However, many of these reactions on further examination proved to be far more complex than demanded by the simple theory. The existence of free radicals in the reaction mixture was established in many cases, thus indicating a chain rather than a unimolecular mechanism.

The radical-chain theory, developed by F. O. Rice,[3] allows for greater latitude in the kinetic expression, depending upon the type of chain mechanism adopted. The available data occasionally may be equally well fitted to either a quasi-unimolecular or a 1.5 order rate law, permitting no clear decision. In fact, it has been questioned whether any reaction offers confirmatory evidence of the quasi-unimolecular type, with the possible exception of certain isomerization reactions.[4] These appear to be free of complicating side reactions and a chain mechanism has seemed improbable.

Among such reactions, the isomerization of cyclopropane to propylene is of special interest. Preliminary measurements by Trautz and Winkler[5] indicated that the reaction is first-order and homogeneous. Subsequent investigation by Chambers and Kistiakowsky[6] revealed that first-order constants fell by about 45% between 700 and 10 mm. initial pressure (500°), although maintaining reasonable constancy with increased conversion at any one pressure. Formal classification as a quasi-unimolecular type was thus strongly indicated, and data were successfully treated on this basis.

Although this evidence appeared fairly conclusive, there remained the question of the effects of added gases. In addition, the method of analysis employed by Chambers and Kistiakowsky is open to question, since it involved determination of propylene by absorption in 3% potassium permanganate solution and calculation of cyclopropane by difference. Results would be vitiated if propylene polymerized or decomposed. For these and other reasons, we have re-investigated the reaction.

Experimental

Apparatus.—The reaction was studied in a static system of conventional design, consisting of a 200-cc. clean Pyrex reaction bulb, manometer and storage bulbs. The system was evacuated by means of a mercury diffusion pump.

---

[1] Present address: Esso Laboratories, Standard Oil Development Company, Elizabeth, New Jersey.

[2] Hinshelwood, "Kinetics of Chemical Change," Oxford Univ. Press, New York, N. Y., 1940, p. 78 *et seq.*

[3] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

[4] Pease, "Equilibrium and Kinetics of Gas Reactions," Princeton University Press, Princeton, N. J., 1942, p. 122 *et seq.*

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

[6] Chambers and Kistiakowsky, THIS JOURNAL, **56**, 399 (1934).

The temperature during a run was held well within ±0.02° by a thyratron, saturable-reactor control, patterned after a design described by Penther and Pompeo.[7] A 25-ohm platinum wire resistance replaced the 200-ohm nickel resistance thermometer. Resistances of appropriate values were placed in the other arms of the alternating current bridge. The platinum wire was wound non-inductively on a mica form and placed adjacent to the reaction bulb. The thyratron circuit, providing continuous control, overcame temperature oscillations inherent in the usual "on-off" types. The reaction temperature was measured by means of three chromel–alumel thermocouples placed symmetrically about the reaction bulb; cold junctions were immersed in a melting ice-bath. To minimize the temperature gradient, the reaction bulb was placed inside an aluminum sleeve in the center of a long furnace with asbestos fiber packing several inches above and below the bulb.

Materials.—Cyclopropane of 99.5% purity was purchased from the Ohio Chemical Company. As a precaution, it was condensed and distilled, only the middle portion being transferred to the storage bulbs, which were fitted with mercury-seal stopcocks. Propylene, ethylene and *n*-butane were also obtained from the same company, and were treated similarly. Tank hydrogen was purified by passing over heated platinized asbestos and then through a liquid air trap to remove the water produced.

Procedure.—Cyclopropane runs were made by rapidly admitting the gas to the reaction bulb from a bulb filled to a definite pressure. At the end of a run the reaction mixture was "flashed" into a 500-cc. evacuated bulb, from which it was transferred to the analytical system by displacement with mercury.

Studies of the effect of hydrogen, propylene and ethylene on the isomerization of cyclopropane were carried out by first admitting the diluent, followed rapidly by the cyclopropane. *n*-Butane–cyclopropane mixtures were studied by first introducing cyclopropane to the reaction bulb because of the rapid initial rate of the butane decomposition in the absence of cyclopropane.

Analysis.—In order to determine olefin (propylene) and unreacted cyclopropane, we resorted to selective catalytic hydrogenation, the method being described in detail elsewhere.[8] Essentially this method consists in passing the sample with hydrogen first over a mercury-poisoned nickel catalyst to hydrogenate olefins and subsequently over an unpoisoned nickel catalyst to hydrogenate cyclopropane. With suitable precautions, excellent checks (±0.5%) could be obtained on known mixtures even with quite small samples of gas, which were treated at low pressures.

Application of this method was straightforward except for runs with *n*-butane as the added gas. In order to obtain a measure of the amount of *n*-butane decomposed, it was necessary to resort to the pressure increase during reaction.[9] Allowing that this corresponded to an equivalent of olefin,[10] a satisfactory check on the propylene formed from cyclopropane could be obtained. Hydrogenation of the latter was of course unaffected. Moreover, the total of unreactive paraffins checked satisfactorily with *n*-butane originally taken.

Corrections were applied throughout for "dead space" in capillaries.

Results

Detailed studies were carried out at 500°. These included pressure and time dependence as well as the effects of added gases. Additional runs for the temperature dependence were made at 20° intervals from 440 to 520° at approximately 600 mm. pressure.

Table I summarizes the data for the isomerization of cyclopropane alone at 500.0°. Runs were made over a pressure range of 10 to 900 mm. and time intervals covering approximately 25 to 75% reaction. Pressure changes during the course of a run were small. At 600 mm. initial pressure, a decrease of 1 mm. was observed after twenty minutes while after forty minutes, representing approximately 75% conversion, the decrease was 3 mm. or 0.5%. These observations are in agreement with those of Chambers and Kistiakowsky. The almost complete absence of side reactions

TABLE I

CYCLOPROPANE ISOMERIZATION AT 500.0°

Initial pressure, mm.	Cyclo. reacted, mm.	Time, sec.	$k_{uni} \times 10^{4\,a}$	$k_1 \times 10^{4\,a}$
910	450	1200	5.68	2.87
905	451	1200	5.75	2.92
845	394	1200	5.70	2.87
649	143	420	5.92	2.99
608	131	420	5.75	2.90
602	131	420	5.81	2.92
613	300	1200	5.59	2.84
612	299	1200	5.59	2.84
605	297	1200	5.62	2.85
597	434	2400	5.42	2.79
596	440	2460	5.45	2.80
517	249	1200	5.46	2.77
510	248	1200	5.55	2.83
377	182	1200	5.50	2.83
290	140	1200	5.49	2.84
288	138	1200	5.45	2.83
255	53.8	420	5.62	2.89
247	52.9	420	5.65	2.86
240	114	1200	5.40	2.83
239	115	1200	5.47	2.85
243	119	1230	5.46	2.85
259	187	2400	5.35	2.83
251	180	2400	5.27	2.78
250	180	2400	5.30	2.81
200	95.4	1200	5.41	2.85
165	82.8	1320	5.31	2.84
161	78.1	1260	5.26	2.80
160	78.6	1260	5.35	2.84
154	71.9	1200	5.25	2.80
151	70.8	1200	5.28	2.82
150	71.4	1200	5.37	2.85
65	34.1	1500	4.95	2.90
52	26.5	1500	4.75	2.80
50	25.7	1500	4.80	2.85
28	15.4	1800	4.44	2.91
25	11.7	1500	4.22	2.80
25	12.5	1620	4.29	2.84
10.0	4.63	1800	3.45	2.77
10.0	4.72	1800	3.55	2.88

[a] The constants were calculated directly from pressure differences in the analytical data, not given here. Initial pressures are given only to the nearest mm. (except at 10 mm.). Mm. of cyclopropane reacted were calculated relative to the rounded initial pressures from the analytical data.

---

(7) Penther and Pompeo, "Electronics," April, 1941, p. 20.

(8) Corner and Pease, *Ind. Eng. Chem., Anal. Ed.*, **17**, 564 (1945).

(9) There is negligible pressure change in the cyclopropane isomerization.

(10) Echols and Pease, THIS JOURNAL, **61**, 208 (1939).

was also indicated by analysis. The amount of saturated hydrocarbons formed at 75% reaction, as measured by hydrogenation of the sample, was approximately 1%.

Unimolecular constants are tabulated in column 4 of Table I. Constants in the last column were calculated according to a new mechanism based upon the formation of a di-radical followed by a sequence of reactions

$$\begin{aligned} C &\longrightarrow R && (1)\\ R &\longrightarrow C && (2)\\ R &\longrightarrow P && (3)\\ R + C &\longrightarrow 2P && (4)\end{aligned}$$

where C refers to cyclopropane, R to the trimethylene di-radical, and P to propylene. This mechanism is discussed later. For the moment it is only necessary to point out that pressure dependence enters through reaction (4), which is second order.

TABLE II

APPLICATION OF DI-RADICAL THEORY TO DATA OF CHAMBERS AND KISTIAKOWSKY

Initial pressure, mm.	Cyclo.[a] reacted, mm.	Time, sec.	$k_{\text{uni}} \times 10^4$	$k_1 \times 10^4$
		Temperature 499.5°		
702.6	245.6	720	5.95	6.02
380.3	153.8	900	5.73	5.90
372.2	240.2	1800	5.76	6.05
195.4	65.2	720	5.60	5.94
193.2	62.7	720	5.42	5.75
108.6	33.7	720	5.12	5.67
55.3	15.8	720	4.70	5.81
37.5	10.2	720	4.42	5.80
36.4	10.3	720	4.75	6.44
25.9	13.4	1800	4.05	6.02
25.7	6.37	720	3.96	5.61
25.2	6.5	720	4.14	5.85
24.5	6.35	720	4.17	6.00
24.2	12.95	1800	4.26	6.50
14.1	3.47	720	3.93	6.55
12.7	2.74	720	3.36	5.55
		Temperature 469.6°		
762.7	219.3	3000	1.13	1.15
757.0	211.1	3000	1.09	1.12
389.1	109.3	3000	1.10	1.15
388.1	106.4	3000	1.07	1.12
213.7	57.2	3000	1.04	1.12
207.6	56.1	3000	1.05	1.12
110.2	27.5	3000	0.955	1.06
109.0	27.3	3000	.961	1.08
50.5	11.3	3000	.848	1.05
36.3	8.08	3000	.840	1.10
26.7	5.77	3000	.812	1.13
26.6	5.47	3000	.769	1.07
26.6	5.73	3000	.809	1.13
25.9	5.47	3000	.791	1.11

[a] Values of mm. cyclopropane reacted are not given by Chambers and Kistiakowsky. They had to be re-calculated from their values of k_{uni} in order to obtain data for calculation of our k_1.

It will be noted that there is a consistent fall in first order constant with initial pressure, as was found by Chambers and Kistiakowsky, whose data are given in Table II. Agreement with the latter is in fact remarkably good at 500°, except that we find a decrease in first order constant with time as well as with initial pressure. Our constant, k_1, on the other hand, shows no such trend.

Added Gases.—Possible effects due to added gases include increase in rate if the reaction is quasi-unimolecular, and either increase or decrease if a reaction chain is involved.

In respect to the latter, a few experiments were made several years ago in this Laboratory by L. S. Echols to determine whether nitric oxide acted as inhibitor. The results were negative. At 520°, no change in amount of propylene formed from 200 mm. cyclopropane could be detected in the presence of 30 mm. of nitric oxide.[11] Thus, there was no positive evidence of long chains in the reaction.

Runs in the presence of propylene, ethylene or hydrogen are summarized in Table III. For purposes of comparison, the amount of cyclopropane reacted in mm. is compared with that to be expected in absence of the added gas. Changes are seen to be remarkably small with a probable net decrease in the presence of propylene or ethylene as against a slight increase in the presence of hydrogen.[12] Thus, under conditions such that the first-order constant is 10–20% below the "high pressure" value calculated by Chambers and

TABLE III

EFFECT OF ADDED GASES ON CYCLOPROPANE ISOMERIZATION

Twenty minute runs; temp. 500.0°

Initial cyclopropane pressure, mm.	Pressure added gas, mm.	Cyclopropane reacted, mm. Found	Calcd.
	Propylene added		
129	128	59.6	60.4
135.5	125.5	62.9	63.6
169	126.5	80.3	80.2
267	299	128.4	128.3
268	302	126.2	128.8
	Ethylene added		
243	296	115.1	116.5
312	303	147.8	150.1
	Hydrogen added		
204	399	100.2	97.3
214	401.5	104.7	102.3
258	405	127.3	124.0
299.5	601	147.3	143.9

---

(11) The method of analysis involved measuring the vapor pressure of the condensed mixture after pumping out the system to remove nitric oxide.

(12) This includes something less than 1% actual hydrogenation as indicated by analysis. Pressure decrease during a run was less than 1% of cyclopropane present.

Kistiakowsky (6.25×10^{-4} sec.$^{-1}$ at 500°), these "inert gases" in the amounts taken cause only minor changes, which may be either positive or negative. Although this is not conclusive, it is certainly not positive evidence of a quasi-unimolecular mechanism nor of a free radical chain mechanism.

TABLE IV

n-BUTANE–CYCLOPROPANE MIXTURES

Twenty-minute runs; temp. 500.0°

Initial pressure, mm.		Cyclo. reacted, mm.			n-C_4H_{10} reacted, mm.		
Cyclo.	n-C_4H_{10}	Found	Calcd.	Excess	Found	Calcd.	Deficit
107.5	91	51.3	49.9	1.4	1.5	6.5	5.0
106	304	54.2	49.2	5.0	15.0	25	10
249	156	122.0	119.5	2.5	2.0	11.5	9.5
252	274	127.0	121.0	6.0	8.5	23	14.5
295	320	148.0	142.0	6.0	11.0	27	16
302.5	589.5	158.0	145.6	12.4	25	68	43
692	145	344.0	340.0	4.0	1.2	10.5	9.3
613	307	304.5	300.0	4.5	4.0	26	22

Experiments with added *n*-butane were more fruitful, although they have perhaps only an indirect bearing on the question of reaction mechanism with cyclopropane alone. Results (Table IV) reveal that both gases are affected. As shown in Fig. 1, the decomposition of *n*-butane is first suppressed but subsequently accelerates to nearly normal rate. Such behavior has already been observed with either nitric oxide or propylene as inhibitor, and has been attributed to a "feedback" of chain carriers due to reversibility of complex formation between the latter and the inhibitor.[13] In addition, it is found that the cyclopropane isomerization is accelerated to the extent of 1–10%, by the free radicals resulting from primary decomposition of *n*-butane. One may in fact assume that the free radical takes part in an exchange of hydrogen atoms which is an essential feature of the ultimate conversion of cyclopropane into propylene.

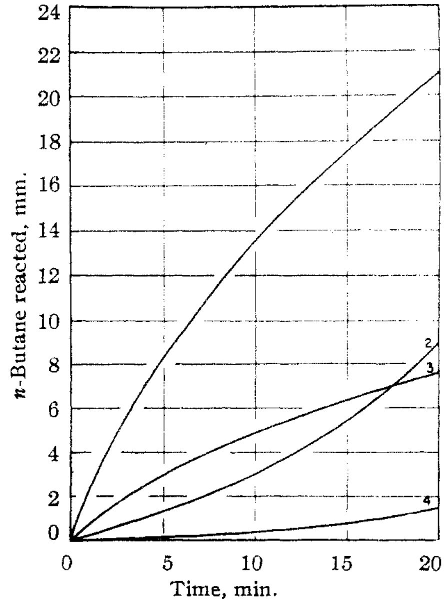

Fig. 1.—Effect of cyclopropane on the decomposition of *n*-butane: 1, 269 mm. *n*-butane; 2, 274 mm. *n*-butane, 252 mm. cyclopropane; 3, 110 mm. *n*-butane; 4, 91 mm. *n*-butane, 107.5 mm. cyclopropane.

Although too few runs are available for complete analysis, it is of interest to note the parallelism between the initial pressure ratio and the ratio of excess cyclopropane reacting to total butane reacting.

Reaction Mechanism

Our experiments with added gases did not give compelling evidence for either a quasi-unimolecular or a chain mechanism. Additional evidence against the latter are the negative effects of added nitric oxide observed by Echols and the failure of a packed reaction bulb to influence the rate (Chambers and Kistiakowsky).[6] Accordingly other possibilities were examined. In view of the predominantly first order character, it is apparent that the primary reaction should be unimolecular. For this, the opening of the cyclopropane ring to form the trimethylene di-radical, $—CH_2CH_2CH_2—$, with two unpaired electrons seems to be indicated. Although we recognize that at some sufficiently low pressure this primary reaction would of itself acquire some second order character, we prefer to ascribe the observed effects at ordinary pressures to a subsequent reaction. In any event, the activation energy of 65,200 calories (see next section) seems to be consistent with a process involving the scission of the C–C bond.

We then assume that the di-radical may undergo one of three alternative reactions. It may revert to cyclopropane by re-pairing of the odd electrons, or it may isomerize to propylene with the shift of a proton. As a third alternative, the di-radical may exchange hydrogen atoms with a colliding cyclopropane molecule in a second order process to give two molecules of propylene.

That the first two alternatives are possible seems to be clearly indicated by the observations of Bawn and Hunter[14] on the low-pressure flame reaction between sodium vapor and 1,3-dibromopropane. It was found that only propylene and cyclopropane were formed, the products being presumed to result from the primary formation of the di-radical.

As to the third alternative, which is the one assumed to provide the second order character to the experimental observations, it is required that a di-radical and a cyclopropane molecule enter into an activated complex containing two unpaired electrons. This complex then re-arranges to yield two normal propylene molecules. Such a mechanism bears some resemblance to what appears to occur in the isomerization of

---

(13) Echols and Pease, THIS JOURNAL, **61**, 1024 (1939).

(14) Bawn and Hunter, *Trans. Faraday Soc.*, **34**, 608 (1938).

cyclopropane under the influence of methyl radicals from decomposing butane (Table IV).

This mechanism may be formulated as follows in which C represents cyclopropane, R the trimethylene di-radical, and P propylene

$$\mathrm{C} \xrightarrow{k_1} \mathrm{R} \tag{1}$$

$$\mathrm{R} \xrightarrow{k_2} \mathrm{C} \tag{2}$$

$$\mathrm{R} \xrightarrow{k_3} \mathrm{P} \tag{3}$$

$$\mathrm{R} + \mathrm{C} \xrightarrow{k_4} 2\mathrm{P} \tag{4}$$

The steady-state approximation gives the over-all rate expression

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = k_1 C\left(\frac{k_3 + 2k_4 C}{k_2 + k_3 + k_4 C}\right)$$

which integrates to

$$k_1 = \frac{k_2 + k_3}{k_3 t}\left[\ln\frac{C_0}{C} + \left(1 - \frac{k_3}{2(k_2 + k_3)}\right)\ln\frac{k_3 + 2k_4 C}{k_3 + 2k_4 C_0}\right]$$

where $k_1 \cdots k_4$ are the rate constants of the corresponding reactions. Values of k_1 are satisfactorily constant (Table I) if we set $k_3/(k_2 + k_3) = 0.88$ and $k_3 = 12\,k_4$. The data of Chambers and Kistiakowsky are likewise well fitted (Table II), although the value of $k_3/(k_2 + k_3)$ has to be taken as 0.34. This smaller value gives greater weight to the second, "non-unimolecular" term in the integrated equation. Thus, their data show somewhat greater deviations at low pressures than ours, a result which may reflect the difference in method of analysis.

It may also be noted that the equation calls for a fall in unimolecular constant at high conversions. This is noticeable in our results (at 600 and 250 mm. initial pressures) but not in the data of Chambers and Kistiakowsky.

Temperature Coefficient and Absolute Rate

Further evidence for the proposed mechanism is afforded by the temperature coefficient measurements. Data for runs at five temperatures between 440 and 520° are given in Table V. These data are satisfactorily fitted by the equation

$$k_1 = 7.77 \times 10^{14} e^{-65200/RT}\ \mathrm{sec.}^{-1}$$

TABLE V

TEMPERATURE DEPENDENCE

Temp., °C.	Time, sec.	Init. pressure, mm.	Cyclo. reacted, mm.	k_{uni}	k_1
520.4	420	600	306.2	1.70×10^{-3}	0.86×10^{-3}
520.4	360	606	283.2	1.75×10^{-3}	$.89 \times 10^{-3}$
520.4	420	603	302.7	1.66×10^{-3}	$.84 \times 10^{-3}$
500.0	1200	612	299.0	5.59×10^{-4}	2.84×10^{-4}
480.2	3600	621	311.0	1.93×10^{-4}	0.98×10^{-4}
480.2	3000	602	267.6	1.96×10^{-4}	1.00×10^{-4}
459.8	12000	604	295.9	5.61×10^{-5}	2.85×10^{-5}
439.7	34200	600	240.3	1.50×10^{-5}	0.76×10^{-5}
439.7	46920	600	294.7	1.44×10^{-5}	$.73 \times 10^{-5}$

In calculating k_1, we have assumed that the ratios k_3/k_4 and $k_3/(k_2 + k_3)$ do not vary with temperature. These assumptions appear to be justified by the calculation of k_1 from the data of Chambers and Kistiakowsky at 469.6 and 499.5° (Table II).

By Eyring's activated complex theory,[15] the constant, k_1, should be given by

$$k_1 = \frac{kT}{h}\frac{f^{\ddagger}}{f^0}\,e^{-\Delta E^0/RT}$$

Since the value of kT/h at 500° is 1.61×10^{13}, there is a factor of 48 to be supplied by the ratio of partition functions $f^{\ddagger}/f^0$. Assuming the intermediate complex to be the di-radical, symmetry numbers (6 for cyclopropane and 2 for the di-radical) will supply a factor of 3, leaving 16 for the remainder of the partition function ratio. Without going into possible sources in detail, it may be pointed out that the product of the moments of inertia of the di-radical exceed that of cyclopropane slightly, and the vibrational frequencies are lower. Moreover, there is an increase in electron multiplicity. All of these effects increase the partition function ratio.

In view of the above considerations, we are suggesting that a "chemical" mechanism, as contrasted to the predominantly "physical" picture offered by the quasi-unimolecular reaction theory, is possible for cyclopropane isomerization.

Summary

1. New measurements of the rate of homogeneous isomerization of cyclopropane to propylene have been made. A method of selective catalytic hydrogenation has been employed to analyze for both propylene and unreacted cyclopropane.

2. Hydrogen, ethylene and propylene have little effect on the rate.

3. In the presence of decomposing *n*-butane the isomerization is accelerated. The butane decomposition is retarded.

4. A mechanism involving primary formation of the trimethylene di-radical, which may activate additional cyclopropane molecules, is found to fit the facts. This is proposed as an alternative to the quasi-unimolecular reaction mechanism.

PRINCETON, NEW JERSEY

RECEIVED[16] SEPTEMBER 27, 1945

---

(15) Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

(16) Original manuscript received January 4, 1945