The Isomerization and Pyrolysis of Cyclopropane in a Single-Pulse Shock Tube*

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The isomerization of cyclopropane has been studied by several researchers.[1,2] However, no data at high temperatures (above 900°K) have been reported so far. Therefore, we have studied the isomerization and pyrolysis of cyclopropane over the temperature range from 1020 to 1660°K by using a single-pulse shock tube developed at Cornell University.[3]

The shock tube was fabricated from stainless steel tubing of 2.5 cm. i. d. The length of the driver section could be varied from 50 to 200 cm. by a piston mounted on a screw. A quick valve, placed at a distance of 22 cm. from the end-plate, was used to prevent the mixing and diffusion

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

[2] B. R. Davis and D. S. Scott, *Ind. Eng. Chem., Fundamentals*, **3**, 20 (1964).

[3] A. Lifshitz and S. H. Bauer, *J. Chem. Phys.*, **38**, 2056 (1963).

TABLE I. THE EXPERIMENTAL CONDITIONS AND RESULTS
The composition of gas mixture is 88% Ar, 10% cyclo-C_3H_6, and 2% Ne[a)]

T °K	P mmHg	t μsec.	Conversion of product, %[b)]						k 10^3 sec^{-1}
			Cyclo-C_3H_6	C_3H_6	CH_4	C_2H_6	C_2H_4	C_2H_2	
1047	3060	425	77.2	1.7	0.0	0.0	0.0	0.0	0.608
1097	3390	435	58.3	23.8	0.0	0.0	0.0	0.0	1.240
1173	3950	520	45.9	34.9	0.5	0.0	1.0	0.0	1.498
1226	2140	540	46.4	44.1	1.5	Trace	2.2	0.0	1.422
1271	4630	440	41.9	35.4	2.6	Trace	3.6	1.1	1.978
1279	2340	465	35.6	29.1	2.8	Trace	4.3	Trace	2.222
1294	4800	430	42.1	32.3	3.8	0.0	5.0	2.1	2.012
1493	3180	355	31.4	30.7	7.6	Trace	8.9	6.4	3.263
1657	3920	200	31.6	23.5	8.5	0.0	9.6	8.3	5.762

a) Used as an internal standard.
b) Conversions of C_1, C_2 and C_3 hydrocarbons are obtained by multiplying the molar percentages of those products to the initial concentration of cyclo-C_3H_6 by 1/3, 2/3 and 1, respectively.

TABLE II. THE EXPERIMENTAL CONDITIONS AND RESULTS
The composition of gas mixture is 93% Ar, 5% cyclo-C_3H_6, and 2% Ne[a)]

T °K	P mmHg	t μsec.	Conversion of product, %[b)]						k 10^3 sec^{-1}
			Cyclo-C_3H_6	C_3H_6	CH_4	C_2H_6	C_2H_4	C_2H_2	
1021	2090	615	84.4	0.0	0.0	0.0	0.0	0.0	0.276
1046	2226	650	83.9	13.5	0.0	0.0	0.0	0.0	0.270
1053	4480	695	61.8	8.9	0.0	0.0	0.0	0.0	0.693
1106	2476	580	46.6	33.8	0.0	0.0	0.0	0.0	1.317
1140	2640	670	47.4	43.7	Trace	0.0	Trace	0.0	1.115
1156	2725	500	34.0	47.7	0.6	0.0	1.0	0.0	2.158
1187	4680	640	50.4	19.5	0.0	0.0	0.0	0.0	1.070
1245	6220	735	35.6	34.5	1.8	0.0	2.8	Trace	1.406
1364	3730	580	25.0	26.6	5.3	0.3	6.0	3.5	2.391
1432	4080	480	28.8	20.4	7.0	Trace	7.5	6.4	2.593
1540	4605	405	26.7	20.5	8.1	Trace	9.1	11.5	3.513
1598	4966	325	22.7	22.8	7.7	Trace	8.2	13.1	3.659
1602	4930	490	27.6	17.2	9.1	Trace	7.9	11.6	2.628

of gases in the cold and hot regions. Five piezogauges were placed in a line over 90 cm. upstream of the endplate in order to measure incident shock velocities, and an additional piezogauge on the endplate, to record the reaction times. Matheson cyclopropane (99.5% pure), Takachiho propylene (99.90% pure) Nippon Sanso argon (99.999% pure), and Takachiho neon (99.9% pure) were used without further purification.

After each run, a 5 cc. sample was taken from the end section and analyzed by a gas chromatograph (Yanagimoto GCG-2) at 55°C by using columns of silica gel (1 m.) and β, β'-oxydipropionitrile (2 m.) for the analysis of C_2 and C_3 hydrocarbons and a column of molecular sieve 5A (1 m.) for the analysis of methane, with helium as the carrier. The other details of the experiment and calculation were almost the same as those described in Ref. 3, except that the incident shock velocities were used for the calculation of shock parameters.

The experimental conditions and results are shown in Tables I and II, where T, P, t and k

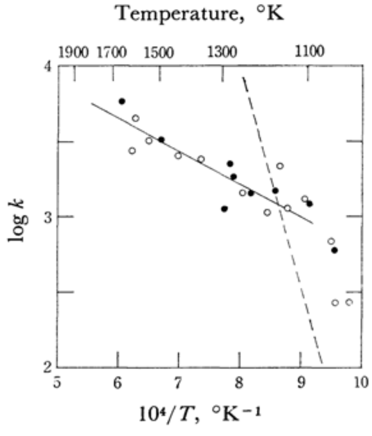

Fig. 1. Arrhenius plot of first-order rate constant. Open and solid circles are, respectively, obtained from mixtures, 93% Ar, 2% Ne, and 5% cyclo-C_3H_6 and 88% Ar, 2% Ne, and 10% cyclo-C_3H_6. Solid line is the least-squares fit to the points above 1200°K.
Dashed line represents the following relation[2)] obtained at lower temperatures.
$2.303 \log k = 35.431 - 65570/\boldsymbol{RT}$

TABLE III. THE EXPERIMENTAL CONDITIONS AND RESULTS
The composition of gas mixture is 88% Ar, 10% C_3H_6, and 2% Ne

T, °K	P, mmHg	t, μsec.	Conversion of product, %				
			C_3H_6	CH_4	C_2H_6	C_2H_4	C_2H_2
1268	4600	385	88.7	0.2	0.0	0.5	0.0
1283	2360	550	80.8	0.5	0.0	0.7	0.0
1291	2430	440	80.1	0.7	0.0	0.9	0.0
1346	5130	410	85.3	1.0	0.0	2.0	Trace
1374	2710	560	78.6	1.6	Trace	2.5	Trace
1420	2880	380	69.3	2.3	Trace	4.0	1.8
1582	3560	510	53.8	5.6	0.3	6.8	4.5
1615	3680	210	59.4	5.4	0.4	7.2	5.6
1638	3800	370	52.0	6.6	0.4	7.9	6.8
1649	3920	220	60.5	5.3	0.3	7.2	5.8

TABLE IV. THE EXPERIMENTAL CONDITIONS AND RESULTS
The composition of gas mixture is 93% Ar, 5% C_3H_6, and 2% Ne

T, °K	P, mmHg	t, μsec.	Conversion of product, %				
			C_3H_6	CH_4	C_2H_6	C_2H_4	C_2H_2
1161	2720	610	95.6	0.0	0.0	0.0	0.0
1219	5980	590	83.7	0.4	0.0	0.6	0.0
1384	3830	580	72.5	3.3	0.0	5.5	2.5
1422	4020	575	72.9	3.7	0.3	6.7	3.2
1436	4080	645	68.0	3.7	0.0	0.0	2.8
1577	4790	575	52.6	7.0	Trace	8.4	8.4
1582	4860	500	52.9	6.1	Trace	8.7	8.8
1616	5030	535	46.9	6.6	Trace	7.0	11.2
1683	5380	540	44.9	7.0	Trace	7.2	9.6

are the reaction temperature, the pressure, the time, and the first-order rate constant respectively.

The first-order rate constant was calculated by the following equation:

$$k=\ln (C_0/C_f)/t$$

Here C_0 and C_f are the initial and final concentrations of cyclopropane. An Arrhenius plot of the rate constants is shown in Fig. 1; it may be compared with the dashed-line extrapolated from the results obtained at lower temperatures.[2] There is apparently a bend at about 1200°K. The points of the low-temperature region fall somewhat above the extrapolated line; this seems due to the experimental difference between the shock-tube and conventional techniques.[4] Those of the high-temperature region fall below it and present a straight line with an apparent activation energy of 9.2 kcal./mol.

A comparison of Tables I and II with Fig. 1 would suggest that the production of methane and C_2 hydrocarbons affects the bend of k values at 1200°K, although the materials recovered after each run are deficient; this deficiency can not be explained by the present study, because not all species in the reaction products could be analyzed in terms of the columns described above. A pyrolysis experiment with propylene under the same conditions as in the present study gave almost the same dependence of the composition of the reaction products upon the temperature, as is shown in Tables III and IV.

Therefore, it may be concluded that, at higher temperatures, the isomerization of cyclopropane occurs first, followed by pyrolysis, and that some of reaction products inhibit the isomerization. However, further experimentation will be necessary in order to establish a more detailed mechanism.

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[4] A. Lifshitz, H. F. Carroll and S. H. Bauer, ibid., **39**, 1661 (1963).