

**804.** *The Thermal Unimolecular Decomposition of Bicyclo[3,2,0]-heptane.*

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The thermal decomposition of bicyclo[3,2,0]hexane has been investigated in the temperature range 426—464°. The decomposition was homogeneous and of first order, and the rate constant was independent of pressure from 2 to 20 mm. The primary decomposition proceeded by two paths, one to yield ethylene and cyclopentene, the other to yield hepta-1,6-diene. The latter compound itself decomposed to give butadiene and propene in equal amounts, together with small quantities of some C<sub>7</sub> hydrocarbons and some lower molecular weight cracking products.

The Arrhenius equations for the two primary reactions were found to be:

$$k_{\text{cyclopentene}} = 10^{14.84} \exp(-60,740/RT) \text{ sec.}^{-1}$$

$$k_{\text{hepta-1,6-diene}} = 10^{15.40} \exp(-63,970/RT) \text{ sec.}^{-1}$$

Both reactions are probably unimolecular.

CYCLOBUTANE and alkylcyclobutanes are known to undergo unimolecular decompositions to yield olefins.<sup>1</sup> In addition, a slower *cis-trans*-isomerization can occur.<sup>2</sup> This latter reaction is slower than the ring cleavage one. Similar reactions occur with cyclopropanes. In all cases it is possible to account for the results by assuming the intermediate formation of a biradical, though this mechanism has not been conclusively proved. To throw further light on this problem we have studied the decomposition of a bicyclic system containing a cyclobutane ring.

## EXPERIMENTAL

The various C<sub>7</sub> hydrocarbons used in this work were prepared by Mr. W. B. L. Evans of this Department. Before use, they were purified by preparative gas chromatography. The final products were at least 99.5%. The apparatus and experimental procedures were similar to those already described.<sup>3</sup> The only modification of importance was the replacement of the Toepler pump on the gas chromatograph inlet system by an Aerograph 2-position 6-way linear greaseless valve.

Most runs were analysed on a 30 ft. × 0.16 in. column packed with 40—60 mesh Chromosorb P containing 20% w/w of di(2-cyanoethyl) ether. In runs where it was necessary to separate ethylene, propene, and butadiene for ratio determinations, an additional column containing silver nitrate in ethylene glycol was used. Calibration mixtures of ethylene, propene, butadiene, cyclopentene, hepta-1,6-diene and bicyclo[3,2,0]heptane were prepared in a specially designed vacuum system which employed no greased stopcocks. All mixtures were stirred (magnetic stirrer) for 24 hr. before analysis. Identification of chromatographic peaks was by comparison of retention times with those of authentic samples.

## RESULTS AND DISCUSSION

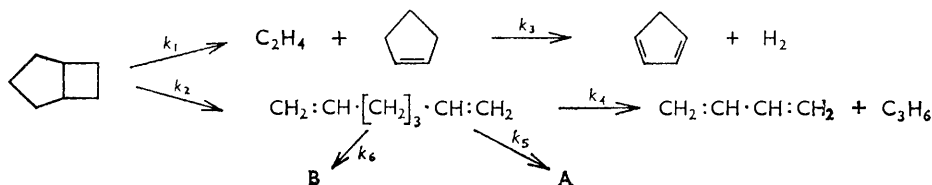
In the temperature range 426—464° in an aged vessel, the decomposition of bicyclo[3,2,0]heptane was found to be strictly of first order. A plot of the logarithm of undecomposed bicycloheptane against time was linear for decomposition carried to greater

<sup>1</sup> Genaux, Kern, and Walters, *J. Amer. Chem. Soc.*, 1953, **75**, 6196; Wellman and Walters, *ibid.*, 1957, **79**, 1542; Das and Walters, *Z. phys. Chem. (Frankfurt)*, 1958, **22**, 1958.

<sup>2</sup> Gerberich and Walters, *J. Amer. Chem. Soc.*, 1961, **83**, 4884.

<sup>3</sup> Frey and Smith, *Trans. Faraday Soc.*, 1962, **58**, 697.

than 50%. On the basis of the analytical data to be presented the following mechanism for the decomposition is suggested:



In the temperature range employed, the secondary decomposition of the initially formed cyclopentene and hepta-1,6-diene was important. The homogeneous decomposition of cyclopentene to cyclopentadiene has been studied previously by Vanas and Walters.<sup>4</sup> Using these authors' values for  $k_3$  it was found that at all temperatures, within experimental error, the cyclopentadiene arose entirely by this secondary decomposition. Further confirmation was obtained by plotting the yield of cyclopentadiene as a function of the percentage decomposition of the bicycloheptane. This yielded a plot showing positive curvature with zero initial slope. The yield of cyclopentene when corrected for decomposition to cyclopentadiene was equal to the yield of ethylene.

The homogeneous pyrolysis of hepta-1,7-diene does not appear to have been investigated previously. Accordingly, some preliminary experiments were carried out using the compound in the vessel subsequently used for the decomposition of the bicycloheptane. The diene was found to undergo a first-order decomposition to give as major products equimolar quantities of buta-1,3-diene and propene. In addition, small quantities of two other compounds, A and B, were formed together with some cracking products of much lower molecular weight (*e.g.*, methane, ethylene, and possibly some ethane). Products A and B were formed in approximately equal quantities and were not positively identified. From its retention time A is either a C<sub>7</sub> hydrocarbon or a C<sub>5</sub> acetylene, while B has the same retention time as methylenecyclohexane and 1-methylcyclohexene. Evidence with a packed vessel indicated that the decomposition of the diene to butadiene and propene was homogeneous.

The rate of decomposition of the hepta-1,6-diene ( $k_4 + k_5 + k_6$ ) was greater than its rate of formation from the bicycloheptane ( $k_2$ ), and hence in the decomposition of the bicyclo-compound the yield of the diene was found to go through a maximum. A plot of the yield of butadiene against percentage of bicycloheptane decomposed gave a graph of positive curvature and zero initial slope indicating that all the butadiene arose by decomposition of the hepta-1,6-diene and none from the bicycloheptane directly. In a similar manner, products A and B arose only from the diene.

The results obtained in a typical series of runs at 459.1° are shown in Table I. Since one molecule of bicycloheptane decomposing by path I ( $k_1$ ) gives rise to one molecule of cyclopentene and one molecule of ethylene, the yield of ethylene has been neglected in the calculation. For the same reason, since the decomposition of the hepta-1,6-diene gives equimolar quantities of butadiene and propene, the yield of the latter compound has not been used in calculating the percentages shown in the Table.

The composition of the products did not show a marked variation with temperature. There was a slight increase in the yields of butadiene (and propene) and of compounds A and B, and a corresponding decrease in hepta-1,6-diene, at the lowest temperature. This may be due to a small contribution from a surface-catalysed decomposition of the hepta-diene.

The decomposition was carried out with initial pressures of bicycloheptane in the range 2–20 mm. The rate of decomposition was found to be independent of pressure in this

<sup>4</sup> Vanas and Walters, *J. Amer. Chem. Soc.*, 1948, **70**, 4053.

range. In addition, a series of runs in a packed vessel of surface : volume ratio 10 times that of the unpacked vessel used in the other series of runs, gave the same rate constant as runs in the unpacked vessel at the same temperature. The absence of curvature in the first-order rate plots even at high percentage decomposition argues against the possibility of a radical chain mechanism. The results in the packed vessel indicate that there can be no

TABLE 1.

Composition of reaction mixtures for runs at 459.1°.

% Decompn.	C <sub>4</sub> H <sub>8</sub>	C <sub>5</sub> H <sub>8</sub> *	C <sub>5</sub> H <sub>6</sub> *	C <sub>7</sub> H <sub>12</sub> *	A	B
20.4	0.9	14.2	0.3	4.4	0.3	0.3
26.9	1.6	18.5	0.4	5.1	0.7	0.6
36.5	2.9	25.3	0.8	6.1	0.6	0.8
42.6	4.1	29.5	1.0	6.3	0.7	1.0
48.1	5.3	33.4	1.0	6.3	1.1	1.0
54.1	6.4	37.1	1.4	6.2	1.5	1.5
60.4	8.0	41.4	1.9	5.8	1.7	1.6
64.6	9.0	44.5	2.4	5.6	1.3	1.8
66.5	9.9	45.2	2.5	5.3	1.8	1.8
70.8	10.9	47.8	3.2	4.8	2.0	2.1

\* C<sub>5</sub>H<sub>8</sub> = cyclopentane; C<sub>5</sub>H<sub>6</sub> = cyclopenta-1,3-diene; C<sub>7</sub>H<sub>12</sub> = hepta-1,6-diene.

appreciable heterogeneous component of the reaction. We, therefore, believe the reaction to be a true unimolecular decomposition. It was, however, noted that the secondary decomposition of the hepta-1,6-diene was somewhat faster in the packed vessel, hence it is probable that this reaction has a heterogeneous component.

While the first-order plots for the overall decomposition gave straight lines at all temperatures, the experimentally determined ratios of products from the two reaction paths showed considerable scatter. This is entirely due to the analytical errors which become magnified when the products of the secondary decomposition of the hepta-1,6-diene are summed. Accordingly, the following procedure was adopted to determine the values of  $k_1$  and  $k_2$ . At each temperature  $k_1 + k_2$  was determined from the overall rate of decomposition. The corrected % yield of cyclopentene (cyclopentene + cyclopentadiene) was then plotted against  $1 - \exp [-(k_1 + k_2)t]$ , and a least squares evaluation of the slope of such plots was obtained. Since the slope of the line equals  $100k_1/k_1 + k_2$  the value of  $k_1$  could be evaluated;  $k_2$  could then be determined by the difference between  $k_1$  and the overall rate. The results obtained at a series of temperatures are shown in Table 2.

TABLE 2.

Rates of decomposition at various temperatures.

Temperature (°C) ...	464.6	461.6	459.1	453.2	447.7	441.4	435.7	431.5	426.2
10 <sup>4</sup> $k$ overall (sec. <sup>-1</sup> )	8.873	7.715	6.768	4.650	3.451	2.543	1.626	1.260	0.91
10 <sup>4</sup> $k_1$ (sec. <sup>-1</sup> )	6.49	5.43	4.80	3.24	2.44	1.78	1.17	0.89	0.67
10 <sup>4</sup> $k_2$ (sec. <sup>-1</sup> )	2.38	2.29	1.95	1.41	1.01	0.75	0.45	0.37	0.25

A plot of  $\log k_1$  against the reciprocal of the absolute temperature gave a straight line and the Arrhenius parameters were determined by the method of least squares whence:

$$k_1 = 10^{14.84} \exp (-60,740/RT) \text{ sec.}^{-1}$$

In a similar fashion, the Arrhenius equation for the decomposition to hepta-1,6-diene was found to be

$$k_2 = 10^{15.40} \exp (-63,970/RT) \text{ sec.}^{-1}$$

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The overall decomposition of the bicyclo[3,2,0]heptane also yielded an excellent Arrhenius plot. Again the Arrhenius parameters were calculated by least squares whence:

$$k = 10^{15.02} \exp(-61,000/RT) \text{ sec.}^{-1}$$

Too much significance cannot be attached to these values since they represent an average value for the two simultaneous processes. However, it is interesting to note that the energy of activation for the overall process differs by only 200 cal./mole from that for the overall decomposition of *cis*-1,2-dimethylcyclobutane.<sup>5</sup> It is, therefore, reasonably certain that there is no increase in the strain in the cyclobutane due to the fused five-membered ring.

The decomposition of cyclobutanes has been discussed in terms of a transition state involving the tetramethylene biradical.<sup>6,7</sup> The results obtained in the work presented in this paper are consistent with such a mechanism. The transition state leading to cyclopentene and ethylene can be pictured as biradical 1 and that leading to hepta-1,6-diene as biradical 2:



The relatively lower energy of activation of the route leading to cyclopentene would arise from two factors, the stabilisation of the free electron by the secondary carbon atom in the biradical 1, and because less energy is required to compress the appropriate carbon-carbon bond in the cyclopentane ring to yield the cyclopentene than to rupture the ring to give the diene. Comparison of these results with those obtained with the two paths for the decomposition of *cis*-1,2-dimethylcyclobutane suggests that these two factors are about equally important. Biradical 2 also represents a looser transition complex than biradical 1, which leads to the former reaction path having a higher *A* factor.

The secondary decomposition of the hepta-1,6-diene is predominantly homogeneous. The major reaction path leading to butadiene and propylene probably occurs by an intramolecular hydrogen atom shift involving a six-membered ring transition state.

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<sup>5</sup> Gerberich and Walters, *J. Amer. Chem. Soc.*, 1961, **83**, 3935.

<sup>6</sup> Benson and Nangia, *J. Chem. Phys.*, 1963, **38**, 18.

<sup>7</sup> Ellis and Frey, *Trans. Faraday Soc.*, 1963, **59**, 2076.