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Kinetics of the Thermal Isomerization of Bicyclo[2.1.1]hexane[1]

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Pyrolysis of bicyclo[2.1.1]hexane in the vapor phase in the temperature range from 327 to 366° led to 1,5-hexadiene as the only detectable product. The kinetics of this isomerization was studied over a pressure range from 0.2 to 20 mm. and found to obey a first-order rate equation under these conditions. The rate of the reaction was unaffected by a 15-fold increase in the surface-to-volume ratio of the reaction vessel or on the addition of nitric oxide or propylene. From the temperature dependence of the process, the first-order rate constant was observed to fit the equation $k = 1.49 \times 10^{15} \exp(-55{,}000 \pm 1000/RT)$ sec.$^{-1}$. The mechanism of the reaction is believed to be analogous to the thermal decomposition of cyclobutane to ethylene.

Introduction

The kinetics of the thermal decomposition of a great many hydrocarbons which incorporate a three- or four-membered ring system has been studied in recent years. It is logical to extend such studies to bicyclic compounds containing small rings. Halberstadt and Chesick[2] studied the kinetics of the thermal isomerization of bicyclo[2.1.0]pentane to cyclopentene. The reaction which was observed in the temperature range from 287 to 310° was homogeneous and unimolecular. The high pressure rate constant fitted the equation $k = 10^{14.58} \exp(-46{,}000/RT)$ sec.$^{-1}$. In a subsequent paper,[3a] Chesick has reported on the *cis* $\rightleftarrows$ *trans* isomerization of 2-methylbicyclo[2.1.0]pentane; Steel[3b] has investigated the thermal isomerization of bicyclo-[2.2.0]hexane to 1,5-hexadiene. This reaction was homogeneous and unimolecular and the rate constant fitted the equation $k = 10^{13.4} \exp(-36{,}000/RT)$ sec.$^{-1}$.

The present study is part of a systematic investigation of the pyrolysis of bicyclic compounds which incorporate a four-membered ring system. Apart from the intrinsic interest in the kinetics of the decomposition of such systems, it is expected that such studies would help to identify the reactions of thermal origin in the photochemical systems in which these compounds are generated.

Experimental

Bicyclo[2.2.1]hexane was prepared by the mercury-photosensitized decomposition of norcamphor.[4] From the photolysate, a mixture of C_6H_{10} isomers was collected by distillation at atmospheric pressure. Bicyclohexane[5] was separated from this fraction by gas chromatography on a 2-m. Ucon oil column. The sample was freed from impurities by repeated gas chromatographic separation using small portions (0.02 to 0.04 ml.) at a time, until its melting point was sharp and did not increase on further purification. The best sample that was used melted at 26.5° (uncor.). It was found to be at least 99.7% pure.

Nitric oxide (Matheson Co.) and propylene (Phillips Petroleum Co.) were used as obtained.

A conventional high vacuum line was used. Stopcocks were not excluded in order to keep the dead space to a minimum. Although bicyclohexane was found to dissolve in the Apiezon N grease that was used to lubricate the stopcocks, the problem was minimized by keeping the time of contact between the hydrocarbon and the stopcock grease to a minimum, and by handling the hydrocarbons at as low a pressure as possible in the various sections of the system. The results reported here would be in error only if either the reactant or the product was absorbed preferentially in the grease.

Pressures were measured in an 18-mm. bore manometer by means of a Gaertner cathetometer capable of reading to 0.05 mm.

The reaction cell was a cylindrical Pyrex vessel of 51 mm. o.d. tube and 260 ml. in volume. It had a thermocouple well along its axis which reached to the center of the reaction volume. The lead tube was of 2-mm. capillary tubing. The maximum volume of the dead space was 8 ml. A correction was applied to all the data for the vapor in this space.

The cell was placed in an aluminum cylinder of $^5/_8$ in. thickness and 16 in. length. The ends of the cylinder were closed with two machined aluminum blocks each 5 in. long. The temperature of the aluminum cylinder was sensed by a platinum resistance thermometer 50 ft. long (25 ohms at room temperature) interwound along with a Nichrome heating element around the aluminum core. The resistance of the platinum thermometer was measured with a Mueller bridge in which the null point was detected by a Keithley Model 150A d.c. millivoltmeter. The output of the millivoltmeter was used to control a thyratron-operated relay which energized the Nichrome heater. Surrounding the aluminum cylinder and the coils were the main heating elements which were in three sections. The power input to the end sections could be adjusted independently. The heating elements and the core were enclosed by a stainless steel drum 2 ft. long and 17 in. dia. which was packed with Fibrefrax ceramic fiber (The Carborundum Co.). The ends of the drum were closed with Transite plates.

The temperature gradient in the furnace was within 0.1°. The fluctuation in temperature during the course of a run was less than 0.1°.

The temperature in the cell was measured by a platinum: platinum–13% rhodium thermocouple inserted in the well at its center. The potential relative to a junction at melting ice temperature was measured with a Leeds & Northrup K-3 potentiometer. The thermocouple was calibrated against the melting points of National Bureau of Standards certified samples of lead, tin, and zinc. Relative temperatures that are reported here are probably accurate to within 0.1°.

The reliability of the whole system was checked by studying the decomposition of cyclobutane at three temperatures. The rate constants and activation energy reported in the literature[6] could be reproduced satisfactorily.

Preseasoning of the vessel was carried out routinely following the admission of air, before any runs were made. Pyrolysis of propylene for at least 40 hr. was the method that was used.

Quantitative analysis was performed by measurement of the areas under the peaks due to bicyclohexane and product in a gas chromatographic separation. A 2-m. column of Ucon oil (Perkin-Elmer R_x) at room temperature gave a clear separation of the reactant from the product.

Results

Pyrolysis of bicyclohexane (18 mm.) at about 340° caused no observable change in the total pressure of the system, even when the reaction was carried to many times the half-life of the reactant. At conversions from 5 to 50%, the pyrolyzate was completely condensible at −195°. Analysis of the pyrolyzate by gas chromatography showed only one peak other than the one due to bicyclohexane. The compound which gave rise to this peak was trapped from the gas stream and its infrared spectrum in solution was obtained. The spectrum was identical with that of 1,5-hexadiene.[7] The retention time of an authentic sample of 1,5-hexadiene was found to be identical with that of the product. When the pyrolysis of bicyclohexane

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[1] Taken, in part, from the M.S. Thesis of A. A. Levi to be submitted to Brooklyn Polytechnic Institute.

[2] M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 2688 (1962).

[3] (a) J. P. Chesick, *ibid.*, **84**, 3250 (1962); (b) C. Steel, paper presented at the Photochemical Symposium at Rochester, N. Y., March, 1963.

[4] R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4923 (1961).

[5] The name "bicyclohexane" used without any numerals will hereafter refer to bicyclo[2.1.1]hexane.

[6] C. T. Genaux, F. Kern, and W. D. Walters, *J. Am. Chem. Soc.*, **75**, 6196 (1953).

[7] American Petroleum Institute Research Project 44, Infrared Spectrum No. 1654.

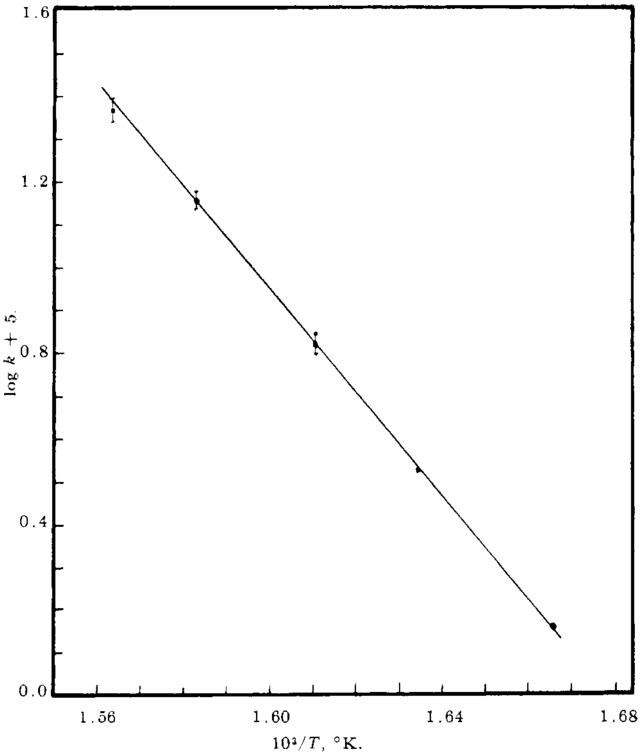
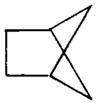


Fig. 1.—Plot of the logarithm of the first-order rate constants *vs.* the reciprocal of the temperature; average pressure 19 mm.

was carried out essentially to completion, small peaks due to other products were also observed in the gas chromatogram. These could have originated from a secondary decomposition of 1,5-hexadiene. Up to 70% conversion, the pyrolysis of bicyclohexane seems to proceed according to reaction 1



$\xrightarrow{\Delta}$ $CH_2{=}CHCH_2CH_2CH{=}CH_2$ (1)

Plots of the logarithm of the pressure of bicyclohexane *vs.* time at 366 and 347° were linear within experimental uncertainty up to about 70% conversion. In both cases, the initial pressures were about 19 mm. The half-lives for decomposition at 366° for a series of runs at pressures from 1 to 20 mm. were constant. At 347°, the half-lives remained constant over the smaller pressure range that was used. In six runs, which were carried out at three different temperatures, the reaction vessel was packed with glass tubes which increased the surface-to-volume ratio by a factor of 15. The rate of decomposition in the packed vessel was essentially the same as in the unpacked vessel, and the temperature coefficient in the two vessels was not significantly different.

In a few runs, the sample of bicyclohexane that was used had previously been decomposed to about 20% conversion and then purified by gas chromatography. No difference in the rate of decomposition was observed with this sample. Evidently a trace impurity was not present in the starting material and influencing the results.

TABLE I

Temp., °C.	Reactant press., mm.	Time, min.	Reactant remaining, %	$k \times 10^5$, sec.$^{-1}$	Remarks
327.2	18.4	120	90.0	1.46	
	18.3	60.0	94.9	1.43	
338.9	18.3	60.0	88.6	3.37	
	18.1	120.0	78.5	3.36	
	18.9	120.0	79.1	3.25	Packed cell
	18.6	60.0	89.0	3.44	Packed cell
347.4	22.5	60.0	78.7	6.64	
	19.9	30.0	87.7	6.64	
	19.5	15.0	93.8	7.00	
	19.5	60.0	78.2	6.84	
	19.2	45.1	82.7	7.02	
	19.2	90.0	69.6	6.72	
	18.7	150.0	58.2	6.02	
	18.4	60.0	79.5	6.38	
	18.3	60.0	80.0	6.20	
	10.5	60.0	79.0	6.55	
	3.3	30.0	88.3	6.91	
	3.0	90.0	71.2	6.29	
	2.8	150.0	57.6	6.13	
	0.9	90.4	71.5	6.19	
	.85	120.0	67.3	5.50	
	.75	60.0	81.3	5.99	
	.6	150.0	59.2	5.83	
	.5	60.0	81.6	5.65	
	.4	30.0	89.6	6.10	
	.4	90.0	74.1	5.55	
	.4	150.0	62.0	5.31	
	.35	60.0	81.3	5.75	
	.25	150.0	61.1	5.47	
	.20	90.0	74.2	5.53	
	26.0	60.0	80.2	6.13	Packed cell
	21.2	60.0	80.2	6.13	Packed cell
	18.5	60.0	80.4	6.07	p_{NO} 1.7 mm.
	19.2	60.0	79.4	6.40	p_{NO} 0.8 mm.
	17.9	60.0	80.4	6.07	$p_{propylene}$ 9.6 mm.
	18.5	60.0	79.9	6.24	$p_{propylene}$ 4.0 mm.
358.4	19.3	30.0	76.4	15.3	
	18.9	45.1	68.8	13.9	
	18.7	40.0	71.7	13.9	
	19.9	30.0	80.2	12.2	Packed cell
	19.9	45.0	69.5	13.5	Packed cell
366.3	24.3	15.0	80.8	23.6	
	20.2	30.0	65.5	23.5	
	19.4	90.0	30.9	21.8	
	18.7	25.0	68.9	24.8	
	18.4	60.1	43.7	23.0	
	3.4	60.0	42.5	23.8	
	2.9	30.0	63.8	25.0	
	1.1	30.0	65.9	23.2	
	0.9	60.0	44.9	22.3	
	.45	30.0	67.5	21.8	
	.45	60.0	46.8	21.1	
	.30	30.0	67.6	21.8	
	.25	60.0	49.7	19.4	

In four runs at 347°, the effect of the addition of nitric oxide or propylene on the rate was studied. Both these compounds are known to react with free-radical species very efficiently. It was observed that the addition of neither gas had any significant effect on the rate. It was inferred that the thermal isomerization of bicyclohexane is a homogeneous, unimolecular reaction. First-order rate constants at an initial pressure of 19 mm. were obtained at five temperatures in the range from 327 to 366°. The results of 21 runs were averaged and plotted against temperature in the usual way (Fig. 1). The best straight line through all the points as obtained by the least-square method fitted the equation

$$k = 1.49 \times 10^{15} \exp(-55{,}000 \pm 1000/RT) \text{ sec.}^{-1} \quad (2)$$

The fall-off in the first-order rate constant with pressure could be studied only within the narrow pressure range from 0.2 to 22 mm. The low vapor pressure of the hydrocarbon at room temperature determined the upper pressure limit, while the accuracy in the analysis and the pressure measurement determined the lower limit. The results which are plotted in Fig. 2 show a definite decrease in the first-order rate constants below 1 mm.

Discussion

Reaction 1 is analogous to the thermal decomposition of cyclobutane to two molecules of ethylene.[6] The mechanism of the two processes may also be entirely similar since they are both homogeneous, unimolecular reactions and are unaffected by the addition of molecules which serve to trap free-radical species. Whether this mechanism is a concerted process or proceeds through a short-lived diradical species[8] is not of primary concern here provided it is the same mechanism that is operative in both reactions.

Walters and his co-workers have observed that the thermal decompositions of a variety of mono- and dialkyl-substituted cyclobutanes are homogeneous, unimolecular reactions. In cyclobutane itself[6] and in the cases in which the substituents are methyl, ethyl, and *n*-propyl groups,[9] it was observed that the activation energy falls within ±0.7 kcal./mole of an average value of 61.8 kcal./mole and the pre-exponential factor within 1×10^{15} of the average value of 3.4×10^{15}. It would appear that alkyl substitution of the cyclobutane rings affects both the activation energy and the pre-exponential factor only slightly. The statement seems to be valid for the kinetics of the decomposition of dimethylcyclobutanes,[10] although in this instance the activation energies fall a little outside the limits stated previously.

In the case of bicyclohexane, the present study indicates that the pre-exponential factor is of the same order of magnitude as for the mono- and dialkyl-substituted cyclobutanes and only slightly smaller. But the activation energy is 6.8 kcal./mole lower when compared to an average value for the monocyclic compounds. It seems reasonable to interpret this lowering in the activation energy as being due to the contribution of the extra strain energy in the bicyclic compound (compared to cyclobutane) to the activation energy for the break-up of the four-membered ring. Unfortunately, the strain energy in bicyclohexane has not been calculated as thermochemical data for this molecule are not yet available. From the present data, it would appear that this energy is probably not more than 7 kcal./mole relative to cyclobutane, *if all of the strain energy is available for the rupture of the cyclobutane ring.*[11]

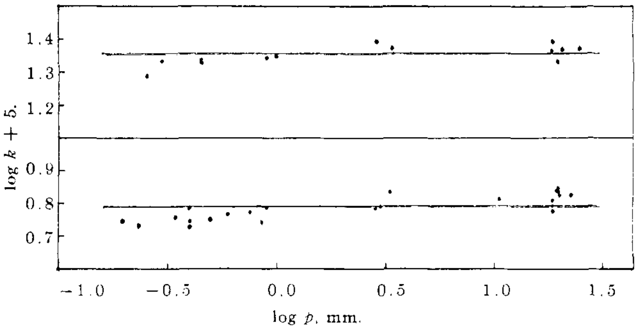


Fig. 2.—Plot of the first-order rate constants *vs.* initial pressure. The lines have been drawn parallel to the *x*-axis; top curve at 366.3°; lower curve at 347.4°.

Very little can be said about the dependence of the first-order rate constants on pressure, since the pressure range over which this was observed, and the magnitude of the effect, are quite small. The trend seems to fall in line with the commonly held view that the total number of atoms in a molecule is the chief factor which determines the initial observable part of the fall-off of rate constants in thermal unimolecular reactions of small hydrocarbons.

[8] S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, **38**, 18 (1963).

[9] M. N. Das and W. D. Walters, *Z. physik. Chem.*, **15**, 22 (1958); R. E. Wellman and W. D. Walters, *J. Am. Chem. Soc.*, **79**, 1542 (1957); S. M. E. Kellner and W. D. Walters, *J. Phys. Chem.*, **65**, 466 (1961).

[10] H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 3935, 4884 (1961).

[11] In a parallel case in which both hydrogenation and pyrolysis data are available, an interesting correlation can be found. In the thermal isomerization of bicyclo[2.1.0]pentane to cyclopentene,[1] the over-all reaction is analogous to the thermal isomerization of cyclopropane (T. S. Chambers and G. B. Kistiakowsky, *ibid.*, **56**, 399 (1934)). The preexponential factors for the two reactions are of the same order of magnitude. The activation energies for the two reactions differ by 18.4 kcal./mole. The difference between the heat of hydrogenation of bicyclo[2.1.0]pentane (R. B. Turner, "Kekulé Symposium on Theoretical Organic Chemistry," Butterworths, London, 1959, p. 67) and cyclopropane is 17.6 kcal./mole. The agreement between the two values may not be entirely fortuitous.

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Kinetic Evidence for the Migration of Reactive Intermediates in Surface Catalysis

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Rates of ethylene hydrogenation were measured on Pt/SiO_2 catalyst mixed with Al_2O_3 and with SiO_2. The rate of ethylene hydrogenation, at comparable conditions, was much greater when the Pt/SiO_2 catalyst was mixed with Al_2O_3. These results cannot be explained simply on the basis of additivity of separate catalytic contributions of the individual components of the mixtures. The data clearly show that a cooperative effect of the components of the mixtures is involved, at least in the case of the mixture of Pt/SiO_2 and Al_2O_3. It is concluded that this cooperative effect of the individual components involves migration of reactive intermediates from one component to the other. It is suggested that Pt centers on the Pt/SiO_2 catalyst activate hydrogen in some manner, and that the active hydrogen can migrate to other centers to react with chemisorbed ethylene. The fact that Al_2O_3 chemisorbs ethylene to a much greater degree than does SiO_2 then offers a reasonable explanation for the much higher activity of the mixture of Pt/SiO_2 and Al_2O_3.

Introduction

Supported metal catalysts are important industrially, and they have also received considerable attention from workers interested in the fundamental aspects of surface catalysis. For example, there have been several theories concerning the presence of two distinct types of sites *vs.* single or "complex sites" on supported metal catalysts.[1,2] The presence of two separate functions, one a hydrogenation–dehydrogenation function due to the metal, and the other an acidic function due to the

[1] G. A. Mills, H. Heinemann, T. H. Milliken, and A. G. Oblad, *Ind. Eng. Chem.*, **45**, 134 (1953).

[2] K. W. McHenry, R. J. Bertolacini, H. M. Brennan, J. L. Wilson, and H. S. Seelig, Proceedings of the Second International Congress on Catalysis, Section II, Paper 117, Paris, 1960.