Kinetics of the Thermal Isomerization of Bicyclo[1.1.1]pentane and 1,3-Dimethylbicyclo[1.1.1]pentane

R. Srinivasan

Contribution from IBM Watson Research Center, Yorktown Heights, New York.
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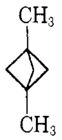
Abstract: The thermal decomposition of bicyclo[1.1.1]pentane (I) in the vapor phase in the temperature range from 553.0 to 582.0°K led to 1,4-pentadiene as the only detectable product. The kinetics of the decomposition obeyed the first-order rate equation up to 93% conversion. The rate of the reaction was unaffected by a 17-fold increase in the surface-to-volume ratio of the reaction vessel. The rate constant at 576.1°K was studied as a function of pressure. At 0.25 torr, the rate constant had fallen off to almost one-half of its value at 35 torr, the highest pressure that was used. The value at infinite pressure was estimated to be about 8% higher. From the temperature dependence of the reaction, the first-order rate constant, at about 5 torr, was observed to fit the equation: $k = 10^{15.24}e^{-49,000\pm500/RT}$ sec^{-1}. The thermal decomposition of 1,3-dimethylbicyclo[1.1.1]pentane (II) was studied at a pressure of about 3 torr in the temperature range from 568.2 to 594.3°K. The kinetics of the process fitted a first-order rate equation, the rate constant being given by $10^{16.20}e^{-53,000\pm2000/RT}$ sec^{-1}.

The kinetics of the thermal decomposition of a number of small-ring bicyclic hydrocarbons, including bicyclo[1.1.0]butane,[1,2] bicyclo[2.1.0]pentane,[3,4] bicyclo[2.1.1]hexane,[5] bicyclo[2.2.0]hexane,[4] and bicyclo[3.1.0]hexane,[6] have been reported. The only missing member of this group is bicyclo[1.1.1]pentane (I). We report here the kinetics of the thermal decomposition of two members of this ring system, including the parent hydrocarbon and its 1,3-dimethyl derivative (II).


I



II

The thermal cleavage of both cyclopropane and cyclobutane, as well as many other molecules which incorporate either of these ring systems, has been explained in terms of a diradical intermediate.[7] The recent interpretation of the reverse reaction, *viz.* the photochemical closure of dienes to give bicyclic compounds in terms of the same diradical as an intermediate,[8] lends added interest to the measurement of the kinetics of the thermal reactions in these systems.

Experimental Section

Bicyclo[1.1.1]pentane (I) was prepared both by the Hg($^3P_1$)-sensitized isomerization of 1,4-pentadiene[8] and by the photolysis of bicyclo[2.1.1]hexan-2-one.[9] The latter method gave a product that was easier to purify by vapor phase chromatography. It was hence used in all except some preliminary experiments. The sample was dried over Drierite and degassed at −150° from time to time. The final sample showed no detectable impurities in its chromatogram.

1,3-Dimethylbicyclo[1.1.1]pentane (II) was prepared by the Hg($^3P_1$)-sensitized isomerization of 2,4-dimethyl-1,4-pentadiene.[8] It was purified by repeated passage through a gas chromatograph, drying over Drierite, and degassing at −78°. The product that was used was shown to be free from impurities by gas chromatography.

The apparatus that was used has been described.[5] The cell of 120-ml volume was always conditioned before use by the introduction of propadiene at 400° for 40 hr or more.

The system was checked out by studying the pyrolysis of bicyclo[2.1.1]hexane. Both the rates and the activation energy reported in the literature could be satisfactorily reproduced.[5]

Analyses were performed on an F & M Model 5750 gas chromatograph with a 12-ft column of UCON 550-X at room temperature for bicyclo[1.1.1]pentane, and a 6-ft column of the same material in series with a 6-ft column of *n*-decyl phthalate at room temperature for the studies on 1,3-dimethylbicyclo[1.1.1]pentane.

Results

Kinetic data on the pyrolysis of bicyclo[1.1.1]pentane are given in Table I.

Over the whole range of temperature, there was no measurable change in the total pressure in the system after various fractions of the material had been decomposed. The pyrolyzed sample could be condensed completely at −195°. Analysis by vapor-phase chromatography indicated the presence of only one product. This was identified as 1,4-pentadiene from its retention time and from its infrared spectrum.

The rate of disappearance of bicyclo[1.1.1]pentane fitted a first-order equation. The value of the rate constant was unchanged within experimental error at conversions which ranged from 12.4 to 92.9%.

The rate of the reaction was unaffected when a sample of bicyclo[1.1.1]pentane which had been prepyrolyzed was used. This showed that an impurity which may have been present in trace amount was not influencing the kinetics.

On packing the reaction vessel with glass tubes, which increased its surface-to-volume ratio by a factor of 17, the rate was not effected beyond the experimental uncertainty. The temperature coefficient of the rate in the packed cell was essentially the same as in the unpacked cell. Evidently the surface reaction in the packed cell was insignificant, the reaction being truly homogeneous.

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(1) H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965).

(2) R. Srinivasan, A. A. Levi, and I. Haller, *J. Phys. Chem.*, **69**, 1775 (1965).

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

(4) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *ibid.*, **86**, 679 (1964).

(5) R. Srinivasan and A. A. Levi, *ibid.*, **85**, 3363 (1963).

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(8) R. Srinivasan and K. H. Carlough, *J. Am. Chem. Soc.*, **89**, 4932 (1967).

(9) J. Meinwald, W. Szerybalo, and D. R. Dimmel, *Tetrahedron Letters*, 731 (1967).

Table I. Thermal Decomposition of Bicyclo[1.1.1]pentane

Temp, °K	Reactant pressure, torr	Time, sec	% conversion	$k \times 10^4$, sec^{-1}
553.0	5.45	7200	41.0	0.733
553.0	5.30	5400	33.0	0.741
555.7	2.45	5400	39.3	0.924[a]
559.2	5.25	3600	33.9	1.15
559.2	4.95	2700	27.6	1.20
566.7	5.35	1800	32.4	2.17
266.7	5.05	3600	54.1	2.16
569.6	3.85	1900	39.4	2.63[a]
576.1	34.90	360	16.0	4.59
	15.90	900	34.6	4.79
	5.50	900	31.6	4.22
	5.50	1800	54.4	4.38
	5.30	5400	92.9	4.78
	5.20	2700	69.6	4.41
	5.20	3600	78.9	4.32
	5.51	310	12.4	4.28
	5.15	600	23.3	4.41
	3.75	900	32.1	4.31
	3.50	900	31.5	4.24
	3.40	900	31.1	4.17
	2.70	900	31.0	4.25
	2.70	900	30.6	4.09
	2.25	900	30.0	3.97
	1.40	900	28.2	2.62
	1.00	900	28.5	3.73
	0.90	900	26.9	3.48
	0.78	900	27.1	3.56
	0.63	900	26.6	3.49
	0.60	900	26.4	3.40
	0.35	900	22.7	2.86
	0.25	900	23.9	3.03
	0.25	900	22.0	2.84
581.6	5.00	480	28.3	6.92[a]
582.0	9.35	600	34.6	7.07
	3.50	300	18.0	6.62
	5.55	480	28.2	6.89

[a] Packed cell.

Table II. Thermal Decomposition of 1,3-Dimethylbicyclo[1.1.1]pentane

Temp, °K	Reactant pressure, torr	Time, sec	% conversion	$k \times 10^4$, sec^{-1}
594.3	3.30	900	27.0	3.50
594.0	4.50	900	27.7	3.60[a]
588.2	2.70	1,800	31.3	2.09
583.7	4.45	1,800	23.6	1.50
579.9	4.50	4,050	40.4	1.28[a]
578.7	3.40	4,050	35.1	1.07
576.0	3.50	11,300	55.0	0.71
572.8	4.10	10,800	51.8	0.68
568.3	3.22	15,100	47.8	0.43
568.1	3.75	15,300	51.1	0.47[a]
556.0	4.20	14,900	21.9	0.17[a]

[a] Packed cell.

A series of experiments were carried out at 576.1 °K at pressures of bicyclo[1.1.1]pentane which ranged from 0.25 to 34.9 torr. The first-order rate constants were observed to decrease with decreasing pressure as predicted by unimolecular reaction rate theories. A plot of $1/k$ *vs.* $1/\sqrt{P}$ in the range of pressure from 35 to 1 torr was satisfactorily linear. The extrapolation to $P = \infty$ gave a value of $5.17 \times 10^{-4}\ \text{sec}^{-1}$ for the limiting high-pressure rate constant. At 35 torr, the rate constant had already reached 92% of its value at infinite pressure. A plot of log k/k_∞ *vs.* log P is shown in Figure 1. The region of significant fall-off seems to begin between 5 and 10 torr.

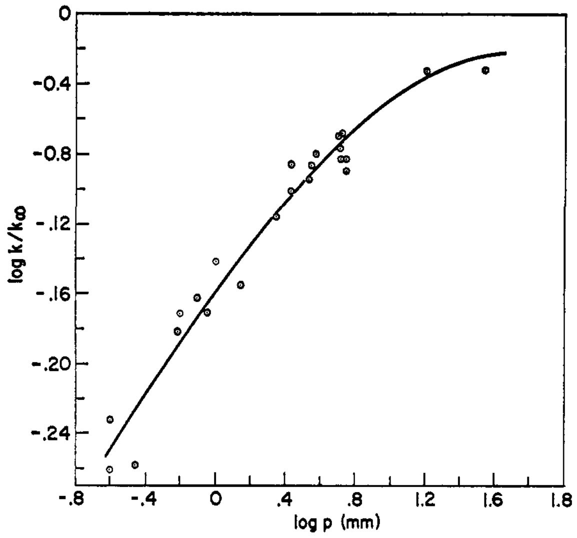


Figure 1. Pressure dependence of the first-order rate constant for bicyclo[1.1.1]pentane at 576.1 °K. Solid line is calculated from the Kassel integral with $s = 20$.

A plot of the logarithm of the first-order rate constant *vs.* $1/T$ for runs at an average pressure of 5 torr is given in Figure 2. The best straight line through the points, as determined by the least-squares method, gave an activation energy of 49.0 ± 0.5 kcal/mole and an A factor of $10^{15.24}\ \text{sec}^{-1}$.

Kinetic data on the pyrolysis of 1,3-dimethylbicyclo[1.1.1]pentane are given in Table II.

The only product that was observed in the thermal decomposition of this molecule was 2,4-dimethyl-1,4-pentadiene. There was no net increase in pressure after various fractions of the material had been decomposed. On packing the reaction vessel with glass tubes, no significant change in the first-order rate constant was observed.

The logarithms of the first-order rate constants are plotted against the reciprocal of the absolute temperature in Figure 3. The best straight line through all of the points, as determined by the least-squares method, corresponded to a value of 53.0 ± 2.0 kcal/mole for the activation energy and a value of $10^{16.20}\ \text{sec}^{-1}$ for the A factor.

Discussion

The thermal decomposition of bicyclo[1.1.1]pentane is observed to be a homogeneous, unimolecular process which can be represented by

(1)

In comparing the results of the present study with the earlier ones[3,4] on bicyclo[2.1.0]pentane, it should be borne in mind that the latter decomposes principally with the migration of a hydrogen atom, the reaction being

(2)

The process analogous to (1), *i.e.*, (3), is so slow in comparison to (2) that it was barely detectable. The A

(3)

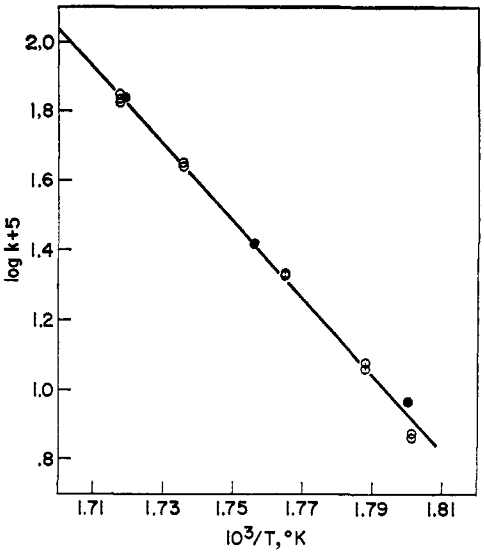


Figure 2. Logarithm of the first-order rate constant for bicyclo-[1.1.1]pentane *vs.* reciprocal of the absolute temperature: open circles, unpacked cell; filled circles, packed cell.

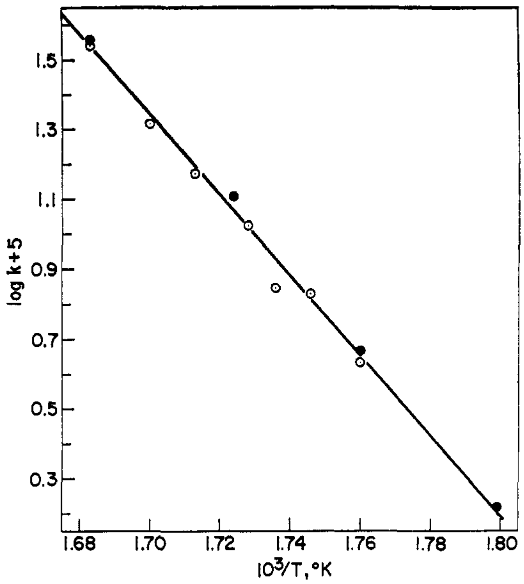
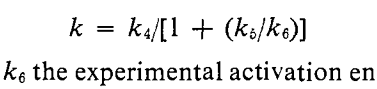


Figure 3. Logarithm of the first-order rate constant for 1,3-dimethylbicyclo[1.1.1]pentane *vs.* reciprocal of the absolute temperature: open circles, unpacked cell; filled circles, packed cell.

factor and the activation energy for (3) were $10^{14.4}$ and 52.3 kcal/mole, respectively.[4]

The pressure dependence of the rate constant for bicyclo[2.1.0]pentane was analyzed by Halberstadt and Chesick[3] using the Kassel integral based on classical vibrations. The value of *s*, the effective number of oscillators contributing to dissociation (in the Kassel theory), was found to be 18 ± 2. The pressure dependence of the rate constants for bicyclo[1.1.1]pentane was analyzed by using exactly the same interpolative procedure. The solid line in Figure 1 corresponds to $s = 20$.[10] The limited pressure range over which experimental points are available, as well as the scatter in their magnitude, impose an uncertainty of ±2 on this value. The *s* values for both bicyclopentanes seem to agree, but this may be without significance as the chemistry of the principal decomposition processes is different, as was pointed out already.

Benson[7] has interpreted the kinetics of the decomposition of cyclobutane in terms of a two-step mechanism which involves a tetramethylene diradical as an intermediate. This treatment has recently been extended by Benson and O'Neal to a number of bicyclic compounds which contain cyclobutane rings. The general mechanism proposed by them is probably applicable to bicyclo[1.1.1]pentane as well, since the experimental *A* factor seems "high" as in all of these cases. The mechanism is as follows



from which it can be derived that

$$k = k_4/[1 + (k_5/k_6)] \qquad (7)$$

When $k_5 \sim k_6$ the experimental activation energy will be the same as E_4 (as is true in cyclobutane), while in the case in which $k_6 >> k_5$, the experimental activation energy will be $E_4 - E_5 + E_6$ (as is true in bicyclo[2.1.1]hexane). $H_{4,5}$ (*i.e.*, $E_4 - E_5$), the enthalpy change in the opening of the first ring, can be estimated to be $E_{\text{C-C}}$, the energy of a "normal" C–C bond minus E_s, the strain energy in bicyclo[1.1.1]pentane, plus E_D, the strain energy in the diradical intermediate. Setting $E_{\text{C-C}} = 80$ and $E_D = 25$ as in cyclobutane itself[11]

$$H_{4,5} = 105 - E_s \qquad (8)$$

The minimum value for E_s that is reasonable is 50 kcal/mole, which is twice the strain energy in a single cyclobutane. Then $H_{4,5}$ would be 55 kcal/mole. This value is 6 kcal/mole greater than the experimental activation energy, which indicates that any agreement with the experimental value will be possible only if (i) the value for E_s is several kilocalories/mole larger than 50 kcal/mole,[12] and (ii) $E_5 \sim E_6 < 5$ kcal/mole. These conditions do not seem reasonable.

In simple alkylcyclobutanes, the first-order rate constants for decomposition are only slightly affected by the presence of substituents.[13] In bicyclo[1.1.1]pentane, the substitution of two methyl groups in the 1 and 3 positions is found to affect the *A* factor by a factor of 7 and the activation energy to the extent of 4 kcal/mole. These changes are greater in magnitude than those seen in going from cyclobutane to *cis*-1,2-dimethylcyclobutane. However (in bicyclo[1.1.1]pentane), since the changes balance each other to a large measure, the rate of decomposition of the 1,3-dimethyl derivative is only four- to sevenfold slower than bicyclo[1.1.1]pentane itself.

Acknowledgment. The author acknowledges with pleasure the skillful technical assistance provided by Mr. A. R. Taranko. He is deeply grateful to Dr. Edward M. O'Neal of The San Diego State College for helpful correspondence and advice.

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(10) The diameter of the bicyclo[1.1.1]pentane molecule was assumed to be 5 Å.

(11) R. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, p 45.

(12) It is difficult to believe that bicyclo[1.1.1]pentane would have a larger strain energy than bicyclo[2.1.0]pentane. The latter is known to be 51 kcal/mole.[11]

(13) H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 3935 (1961).