The Pyrolysis of Cyclopentanone

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Abstract: The vapor-phase thermal decomposition of cyclopentanone has been studied over the temperature range 532–581° at pressures of 11–30 mm. During the initial stages of the reaction the major products were ethylene, carbon monoxide, butene-1, hydrogen, 2-cyclopentenone, and 4-pentenal. The study has shown that the decomposition is not kinetically simple and the addition of 5% nitric oxide greatly reduced the rate of the reaction.

Studies on the thermal decomposition of cyclopentanone have been reported by Ibuki[2] and by Johnson and Walters.[3] The temperature range employed in these studies was 488–550° with the major products reported being carbon monoxide, ethylene, 1-butene, hydrogen, and a small amount of acetylene. The photochemical decomposition of cyclopentanone has been studied in several laboratories[4–6] and involved a ring cleavage with the major products being carbon monoxide, ethylene, cyclobutane, and 4-pentenal. The radiolysis studies[7,8] have shown that the products found are similar to those found in the photolysis studies. Because of the complexity of the reaction and the similarity of the products found in the reported pyrolysis, photolysis, and radiolysis studies (with the exception of 4-pentenal), it seemed of interest to further study the thermal decomposition of cyclopentanone.

Experimental Section

The experiments were conducted in a 290-ml cylindrical Pyrex reaction vessel contained in an electrically heated furnace. The furnace, temperature control, and vacuum system were similar in design to those described by Walters[9] with minor improvements. A second bulb packed with thin-walled Pyrex tubing which increased the surface-to-volume ratio 22-fold was used to study the surface effects. The temperature at the center of the reaction bulb was measured by means of a platinum—platinum–13% rhodium thermocouple connected to a Leeds and Northrup Type K-3 potentiometer. Pressures were measured with a heated 17-mm bore mercury manometer which was read with a Gaertner cathetometer (M940-303). The stopcocks adjacent to the reaction vessel were heated electrically to prevent any condensation of liquids and were lubricated with Dow Corning high-vacuum silicone lubricant.

The infrared absorption measurements were made on a Perkin-Elmer Model 137 sodium chloride spectrophotometer and a Beckman IR-8. Some quantitative and qualitative analyses were made on a Consolidated Electrodynamics Corp. 21-104 mass spectrometer. The gas chromatography work was carried out using both a Beckman GC-2a and a Perkin-Elmer Model 800. The cyclopentanone used in these experiments was purchased from Eastman Kodak Co. and purified by fractionation in a Widmer column at a reflux ratio of about 10:1, the middle fraction of each distillation being used for the subsequent work. Periodically, the purity of the cyclopentanone was tested using a Beckman GC-2a gas chromatograph with a Carbowax column.

Products of the Reactions. The reaction mixture was separated into three fractions: (1) gases volatile at −196°, (2) gases volatile at −78° but condensable at −196°, (3) substances nonvolatile at −78°. By use of a Perkin-Elmer infrared spectrophotometer, Model 137, and a 1-m gas cell, infrared absorption curves were made of the products in fraction 1. The absorption peaks were similar to those reported in the literature for carbon monoxide[10] and methane. These products were further verified by mass spectrometer measurements. The mass spectrometer measurements also yielded a significant peak at *m/e* 2 showing also the presence of hydrogen in this fraction.

The products of fraction 2 were placed in the 1-m gas cell, and the absorption peaks were similar to those reported in the literature[11] for ethylene and corresponded also to the peaks of pure ethylene determined on the same instrument.

Fraction 3 would be expected to contain various liquid products and undecomposed cyclopentanone. The products from a series of experiments carried to 20–30% decomposition were analyzed by infrared spectroscopy and showed peaks at 6, 7, and 9.8 μ. The peaks compared to those in the literature[12] for butene-1.

A gas chromatographic spectrum of the reaction mixture (using the Perkin-Elmer Model 800 with a V900 column—2% by weight Versamid 900 on HMDS-treated Chromosorb W, 80–100 mesh—and CH_2Cl_2 as a solvent) gave a series of peaks which corresponded to the unreacted cyclopentanone (at 2.3 min) and several low molecular weight fragments (at peaks at 0.5, 0.6, and 0.8 min). The same chromatographic curve also showed a peak emerging just after the cyclopentanone itself. A series of butyraldehyde, valeraldehyde, and crotonaldehyde was run on the same column. Neither 2-pentenal nor 4-pentenal was available at the time. The retention times of these compounds were: crotonaldehyde, 1.7 min; butyraldehyde, 1.0 min; pentenal, 2.5 min (hypothesized); valeraldehyde, 1.7 min; and the unknown compound, 2.5 min.

A close examination of the infrared absorption spectra of the products of fraction 3 from a series of experiments carried out to $t = \infty$ showed absorption peaks at 3.4, 7.1, a doublet at 10.5, and a peak at 14 μ, all indicating the presence of a vinyl grouping. This analysis when considered in conjunction with previous radiolysis[7,8] and photolysis[4–6] data indicates the presence of 4-pentenal.

Stoichiometry

The qualitative analysis indicates that the decomposition follows the paths reported by Johnson and Walters with the addition of the formation of the pentenal products.

In an attempt to clarify the products, analysis was made using a mass spectrometer. Typical results are shown in Table I. These results agree with those of Johnson and Walters in that the concentrations of some of the various products change with the length of time

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[1] Abstracted from the M.S. theses of F. M. Delles and L. F. Lowden and the B. S. theses of L. T. Dodd and F. J. Romano.

[2] E. Ibuki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 71, 96 (1950).

[3] E. R. Johnson and W. D. Walters, *J. Am. Chem. Soc.*, **76**, 6266 (1954).

[4] S. W. Benson and G. B. Kistiakowsky, *ibid.*, **64**, 80 (1942).

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[7] D. L. Dugle and G. R. Freeman, *Trans. Faraday Soc.*, **61**, 1174 (1965).

[8] M. Katayama, J. C. Whitmer, and C. N. Trumbore, *J. Am. Chem. Soc.*, **84**, 4025 (1962).

[9] D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948).

[10] The Sadtler Standard Spectra, No. 1142, Sadtler Research Laboratories, Philadelphia, Pa.

[11] Infrared Spectral Data Curve 18, American Petroleum Institute, Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.

[12] Infrared Spectral Data Curve 20, ref 11.

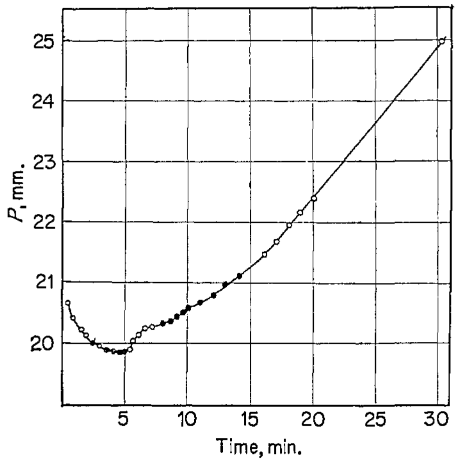
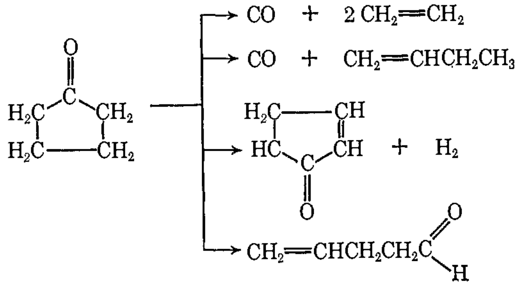


Figure 1. Pressure–time curve for cyclopentanone decomposition at 517°.



the reaction was allowed to proceed. To date, we have no exact analysis on the amount of 4-pentenal produced; however, it is a major component of fraction 3 and also a major component of the total products formed.

Table I. Analysis of the Products of the Decomposition of Cyclopentanone

Temp, °C	$\Delta P/P_0$	Time, min	% C_2H_4	% H_2	% CH_4	% CO
569	1.38	15.0	28.0	13.6	12.6	44.5
569	1.36	7.0	41.0	10.6	3.5	45.0
580	1.55	4.5	49.5	21.7	7.5	23.0
575	1.34	5.0	31.0	4.8	5.5	59.7
578	1.70	8.5	38.2	5.5	7.9	48.5

Results

Homogeneity. Experiments were performed with both packed and unpacked reaction vessels with initial pressures of 23–37 mm and 520°. The rates in the packed vessel did not average more than a 19% difference from those in the unpacked vessels. Since the packed vessel gave a 22-fold increase in surface-to-volume ratios, it would appear that the amount of reaction occurring on the surface of the packed vessel amounted to only 2–3% of the total reaction.

Pressure–Time Curves. From this study there appeared to be two types of pressure–time curves dependent on the condition of the experiment. For the temperature range 510–580° and a short reaction time, the curve exhibited three distinct regions. The first region is apparently the induction period; however, it exhibits a pressure decrease rather than being a horizontal line. Induction periods have been observed by others.[3,9] In the second region the curve has a constant slope. This region starts at the end of the induction period and continues until approximately 15% of the decomposition has occurred. At this point there is an inflection point leading to the third region. This region also has a constant slope and only begins to approximate the expected logarithmic curve; see Figure 1.

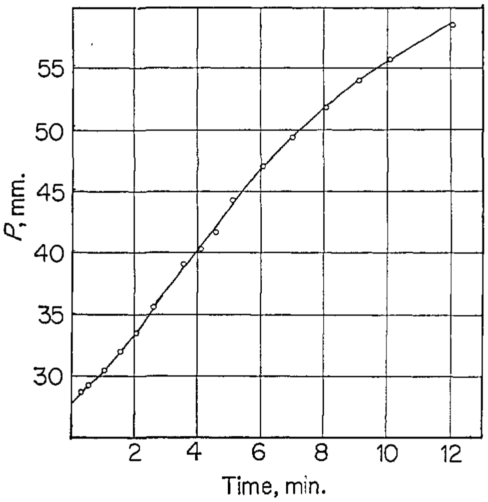


Figure 2. Pressure–time curve for cyclopentanone decomposition at 573°.

At high temperatures and longer reaction time (50% decomposition or greater), the typical logarithmic type curve is approximated; see Figure 2.

Order of the Reaction. To establish the over-all order of the reaction several experiments were made using a fairly high temperature, 540°, and a pressure range of 11–27 mm. Some of these results are shown in Table II. By assuming the over-all reaction to be approximately first order, and using the resulting relation to find the reaction rate constant ($k = \ln(4/3)/t_{1/4}$), it was observed that the calculated values for k remained approximately constant over the range of initial pressures employed. The first-order approximation was therefore considered to be valid.

Table II. Thermal Decomposition of Cyclopentanone[a]

P_0, mm	$t_{1/4}$, min	$k \times 10^4$ sec^{-1}
11.53	17.37	2.8
19.26	19.26	2.5
21.19	18.14	2.7
26.65	18.16	2.7

[a] Rate values found using $k = \ln(4/3)/t_{1/4}$ at 540.0 ± 0.4°.

Activation Energy. Experiments were carried out over the temperature range 533–581° and a pressure range of 12.7–32.7 mm. The data are summarized in Figure 3 in which the logarithm of the first-order rate constant in second^{-1} is plotted against the reciprocal of the absolute temperature. The activation energy was then evaluated from the slope of the best fit line and least-squares analysis. From these calculations the apparent activation energy lies within the range of 58.9 ± 2.3 kcal/mole.

From these experiments, the following rate expression was calculated.

$$k = 1.5 \times 10^{12} \exp(-58,900/RT) \text{ sec}^{-1}$$

Influence of Added Substances. Since nitric oxide has the ability to inhibit certain free-radical chain reactions, a series of experiments was carried out over the temperature range 532–580° with approximately 5% of the reaction mixture being the added oxide. It was observed that at this concentration the rate of the reaction was greatly reduced. Assuming a continuation of first-order kinetics, in order to obtain a measure of the effect of the nitric oxide, a new rate expression was calculated as

$$k = 1 \times 10^4 \exp(-27{,}000/RT) \text{ sec}^{-1}$$

This indicates a major reduction in the rate of the reaction along with a probable change in mechanism.

Discussion

These experimental results indicate that the decomposition of cyclopentanone under the conditions studied is more complex than reported earlier. Our study was made over the temperature range of 532–581° and pressure range of 12–30 mm, whereas the earlier work was carried out over the temperature range of 488–543° and pressures from 99 to 314 mm. In addition to the products observed by Johnson and Walters, we found what appears to be 4-pentenal. The precedence for this product in the decomposition was set with the earlier photolysis and radiolysis studies with the free-radical mechanism for the formation of 4-penental from cyclopentanone shown by Srinivasan.[13]

Our studies also observed the fact that the rate is increased by the addition of the reaction products, especially ethylene and 1-butene. It is still not clear whether the acceleration is a molecular or free-radical process; however, our studies with nitric oxide indicate a portion of the decomposition appears to proceed by a free-radical mechanism of some sort.

The frequency factor for the decomposition lies within the region expected for unimolecular reactions. Based on the absolute reaction rate theory, the experimental frequency factor A can be expressed as

$$A = \kappa e \frac{kT}{h} \exp(\Delta S^{\ddagger}/R) \text{ sec}^{-1}$$

where κ is the transmission coefficient and $\Delta S^{\ddagger}$ is the entropy of activation.[14] With the assumption that the transmission coefficient is unity and using the frequency factor of the experiments, a value of −7.7 cal/(deg mole) was obtained for the entropy of activation at 578°. The negative entropy change indicates a tightening of bonds or a more ordered configuration in the intermediate complex that is formed. This also appears to be indicative of a reaction that yields an induction period. Using the data of Vanas and Walters[9] in the pyrolysis of cyclopentane, which also exhibits an induction period, we calculated a value for the entropy of activation of −2.7 cal/(deg mole) at 450°. One might expect the entropy of activation of cyclopentane to be less negative but of the same sign as the cyclopentanone entropy of activation if both reactions proceeded by similar mechanisms and if the cyclopentane ring were more constricted before the start of the reaction than the cyclopentanone ring.

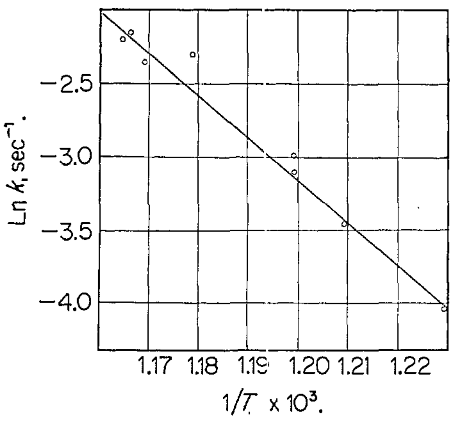


Figure 3. Rate of decomposition of cyclopentanone at different temperatures.

As a result of this study, the mechanism for the pyrolysis of cyclopentanone has been shown to be more complex than originally thought, especially with the introduction of the pentenal product.

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