Thermal Decomposition of 3,3-Dimethylcyclobutanone

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The thermal decomposition of 3,3-dimethylcyclobutanone in the gas phase in the temperature range 261—313 °C has been found to be homogeneous and to obey first-order kinetics; the rate constants fit the Arrhenius equation (i).

$$\log k/\mathrm{s}^{-1} = 14.573 \pm 0.078 - (192\,750 \pm 840)\ \mathrm{J\ mol}^{-1}/RT\ \ln 10 \qquad \text{(i)}$$

The results have been interpreted as showing strong support for a quasi-zwitterionic puckered ring activated complex.

THE present work represents a continuing effort to understand in detail the nature of the factors involved in the thermal decomposition of cyclobutanones. While cyclobutanones apparently undergo such reactions by unimolecular pathways they have received less attention than cyclobutanes. Even the work reported has been on bicyclic cyclobutanones[1] and highly substituted cyclobutanones[2,3] rather than on the simple alkyl derivatives. Again, the major pathway for decomposition leading to olefins and ketens has been discussed almost to the exclusion of the channel leading to cyclopropanes and carbon monoxide, yet this latter reaction almost certainly has a very different transition state. Finally, extensive work on the photochemistry of simple cyclobutanones has often required information which could in principle be obtained from thermal studies.

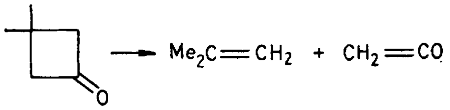
EXPERIMENTAL

3,3-Dimethylcyclobutanone was prepared[4] by the reaction of ethereal diazomethane with dimethylketen in ethyl acetate[5] at −78 °C. The bulk of the ether and ethyl acetate were removed by fractional distillation and the 3,3-dimethylcyclobutanone was obtained by preparative g.l.c. (5 m by 6.3 mm column containing 20% bis-2-methoxyethyl adipate on Chromosorb P). After drying over molecular sieves (4 Å) it was found to be better than 99.9% pure.

The kinetic apparatus has been described previously.[6] For most runs the progress of the reaction was monitored by pressure measurements (Texas Instruments 145 precision pressure gauge). For some runs the extent of reaction was determined analytically by g.l.c. (Perkin-Elmer F11 instrument equipped with a flame ionization detector and a gas sampling valve; signals from the detector were displayed on a recorder fitted with a ball and disc integrator).

RESULTS

Preliminary experiments were carried out at 287.8 °C. Samples of 3,3-dimethylcyclobutanone decomposed at this temperature and pressure measurements (without any corrections for dead-space, *etc.*) showed that after long periods the final pressure was 1.98 times the initial pressure. The gaseous products were analysed by using columns containing the following packings; 20% w/w Carbowax 20 M on Chromosorb P, 20% w/w squalane on Chromosorb W, 20% w/w bis-2-methoxyethyl adipate on Chromosorb P and Paropak Q. In addition, some analyses were also performed with a 50 m capillary column, with Carbowax 1 540 as the liquid phase. In all cases, other than the peak of the reactant itself, only one major peak was observed, whose retention time corresponded, on all columns, to isobutene. There were always some minor peaks. When reaction mixtures were treated with methanol prior to g.l.c. analysis, the minor peaks disappeared and a new major peak due to methyl acetate was observed. We interpret these observations in terms of an essentially quantitative decomposition of the cyclobutanone into isobutene and keten (the latter either reacting on the columns or in the metal chromatographic inlet system and the products of such reactions giving rise to the minor peaks). The observation of methyl acetate as a product after the methanol treatment confirms the production of keten. Careful search failed to show the presence of any 1,1-dimethylcyclopropane, and tests indicated that as little as 0.1% would have been easily detectable.



A series of kinetic runs was carried out at 291.8 °C. Plots of log $(2P_0 - P_t)$ against time, where P_0 was the initial pressure and P_t the pressure at time t, were linear up to 50% decomposition. When correction was made for dead-space by the method of Robinson,[7] the pressure plots were linear up to 85% decomposition. Rate constants were determined from these plots. With initial reactant pressures in the range 0.5—8.0 Torr, rate constants were independent of the intial pressure, and a mean value of (5.70 ±

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[1] A. T. Cocks and K. W. Egger, *J.C.S. Perkin II*, 1972, 211, 2014; 1973, 835.

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[4] J. M. Conia and J. Salaun, *Bull. Soc. chim. France*, 1964, 1961.

[5] *Org. Synth.*, 1953, **33**, 29.

[6] H. M. Frey, R. G. Hopkins, and N. S. Isaacs, *J.C.S. Perkin II*, 1972, 2082.

[7] P. J. Robinson, *Trans. Faraday Soc.*, 1965, **61**, 1655.

0.03) × 10^{-4} s^{-1} was obtained. To check that pressure changes were an accurate monitor of the extent of reaction a number of runs were performed by using g.l.c. analysis. In these, cyclohexane was added as an internal standard; previous runs having demonstrated that it was stable at 300 °C. The rate constant obtained in these experiments, by least-squares analysis of the analytical data and assuming first-order behaviour, was 5.74 × 10^{-4} s^{-1}. Finally, another group of experiments was carried out in a vessel packed with Pyrex tubes (surface to volume ratio *ca.* 12 times that of the unpacked vessel). The extent of reaction was followed by the internal standard technique, and a rate constant of 5.71 × 10^{-4} s^{-1} obtained.

The studies at 291.8 °C indicate that the decomposition is homogeneous, and kinetically first-order, and that pressure changes may be used to measure the rate of reaction. In the remainder of the work rate constants were obtained at 10 temperatures from 261 to 313 °C by measuring pressure changes and treating the results by the Robinson method. The values of the rate constants are shown in Table 1.

TABLE 1

Rate constants for thermal decomposition of 3,3-dimethylcyclobutanone

t/°C:	261.0	267.3	274.0
$10^4k/s^{-1}$:	0.537 ± 0.008	0.886 ± 0.017	1.46 ± 0.059
t/°C:	280.9	287.8	291.8
$10^4k/s^{-1}$:	2.51 ± 0.079	4.15 ± 0.064	5.70 ± 0.032
t/°C:	297.0	301.4	306.3
$10^4k/s^{-1}$:	8.02 ± 0.12	11.2 ± 0.39	16.2 ± 0.19
t/°C:	312.65		
$10^4k/s^{-1}$:	24.3 ± 0.11		

An Arrhenius plot of the rate constants gave a good straight line from which the Arrhenius parameters were calculated by the method of least squares, whence:

$$\log k/s^{-1} = 14.573 \pm 0.078 - (192\,750 \pm 840)\ \mathrm{J\ mol^{-1}}/RT\ln 10$$

or

$$\log k/s^{-1} = 14.573 \pm 0.078 - (46\,070 \pm 200)\ \mathrm{cal\ mol^{-1}}/RT\ln 10$$

(The errors quoted are standard deviations).

DISCUSSION

There are important similarities between the decompositions of cyclobutanes and cyclobutanones; however, a carful evaluation of much experimental information led to the conclusion that although both groups of compounds probably decomposed *via* a highly twisted activated complex, the former decomposition involved a diradical structure and the latter did not.[2] Kinetic studies on the thermal decomposition of 3-ethoxy-2,2-dimethylcyclobutanone led Egger[3] to suggest that this twisted complex had considerable zwitterionic character with appreciable charge separation. The zwitterionic nature of the activated complex would lead to a similarity in the effects of substitution in the cyclobutanone and cyclobutane systems, since for example alkyl groups will stabilise developing charge centres as well as radical centres, but the effect is likely to be greater in the former case. For 2,2,4,4-tetramethylcyclobutanone the methyl substituents are not located on the site where the charge generation occurs (C-3) and so there is no appreciable stabilisation. Further, the twisted nature of the complex leads to increased steric repulsion between these groups as compared with the reactant molecule; the net effect is a large reduction in rate as compared with cyclobutanone[8] itself. This applies only to the reaction pathway leading to an olefin and a keten; the pathway yielding carbon monoxide and a cyclopropane is much less affected by steric effects. The overall result is that *ca.* 7% of the decomposition occurs *via* the cyclopropane route whereas in the case of cyclobutanone[8] itself this pathway constitutes less than 1% of the decomposition leading to an olefin.

For 3,3-dimethylcyclobutanone the expectation was that the substitution would produce an appreciable reduction in the energy of activation, owing to stabilisation by the *gem*-methyl groups of the developing charge centre, coupled with the absence of increased steric crowding. The data obtained fully support this expectation (see Table 2). We have constructed a model relating the reduction in the energy of activation of various 3-substituted cyclobutanones, as compared with cyclobutanone itself, to the carbocation stabilisation of these groups. The details will be presented in a later paper; we merely note here that a value of 196 kJ mol^{-1} was predicted for the present study.

TABLE 2

Energies of activation and relative rates of some cyclobutanones

Cyclobutanone	E_a/kJ mol^{-1}	Relative rate at 600 K
Unsubst.	218	1.0
2,2,4,4-Me_4	235	0.072
3,3-Me_2	193	148

In addition, since the rate of reaction leading to dimethylcyclopropane is unlikely to differ appreciably from the corresponding rate of formation of cyclopropane from cyclobutanone, the inability to detect any 1,1-dimethylcyclopropane in the present work is understandable. We estimate that it would be unlikely to constitute more than 0.01% of the yield of isobutene.

The present work provides additional strong evidence for a zwitterionic twisted activated complex. More work is being undertaken on other simple cyclobutanones to test this assignment further. In particular for 2,2-dimethylcyclobutanone one expects no stabilisation by alkyl groups and, unlike the 2,2,4,4-tetramethyl compound, only a small steric crowding effect. This should lead to an overall rate of decomposition only a little less than for cyclobutanone itself.

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