Thermal Decomposition of 3-Vinylcyclobutanone

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The thermal decomposition of 3-vinylcyclobutanone has been studied in the gas phase in the temperature range 239—290 °C. The reaction is kinetically first order and probably unimolecular and yields butadiene and keten quantitatively. The rate constants fit the Arrhenius equation (i). A comparison of these results with those for

$$\log k/\text{s}^{-1} = 13.71 \pm 0.07 - (176\,300 \pm 700 \text{ J mol}^{-1})/RT\ln 10 \qquad \text{(i)}$$

other cyclobutanone decompositions gives further support for a twisted activated complex with a partial zwitterionic charge distribution.

We report in the present work a further study on the pyrolysis of simple cyclobutanones.[1,2] Previous work has shown that cyclobutanones probably decompose by unimolecular processes. Further a detailed examination of the influence of substituents on the rate parameters together with thermochemical kinetic calculations lead to the conclusion that the activated complexes have a quasi-zwitterionic charge distribution with a highly twisted non-planar ring structure.[3,4] It is hoped that when the quantitative effects of various substituents are considered together it will be possible to be rather more specific about the charge distribution in the activated complex and be in a position to make semi-quantitative predictions about energies of activation.

EXPERIMENTAL

Materials.—Two samples of 3-vinylcyclobutanone were supplied by Ghosez.[5] A small sample of vinylcyclopropane was prepared by the mercury photosensitised decomposition of cyclopentene.[6] All other compounds were obtained from commercial sources.

Apparatus.—The kinetic apparatus has been described previously.[7] Earlier work had shown that some cyclobutanones were ' soluble ' in Viton A diaphragms so those parts of the vacuum system where the 3-vinylcyclobutanone was stored, sampled, and reacted were fitted with Teflon–glass (Rotoflo) stopcocks. The progress of a reaction was usually monitored by following pressure changes using a Texas Instrument precision pressure gauge (model 145). Confirmation that pressure changes were an accurate measure of the extent of reaction was obtained by gas chromatographic analysis using a Perkin-Elmer F11 instrument equipped with a gas sampling system.

RESULTS

Analysis of the two samples of the vinylcyclobutanone on four different chromatographic columns, 2 m × 2.2 mm 20% w/w squalane on Chromosorb W, 3 m × 2.2 mm Poropak Q, 3.5 m × 2.2 mm 15% PPG on Chromosorb W, and 4 m × 2.2 mm 20% w/w Silicone oil on Chromosorb P, showed that both samples contained the same single impurity (though in slightly different amounts).

Preliminary pyrolyses were carried out at 264.5 °C and gaseous reaction products were analysed on the four columns. The ' impurity peak ' was found to be unchanged and only one major product was found and identified as buta-1,3-diene. Several minor peaks were also observed.

After several pyrolyses the combined reaction mixtures were frozen into a small tube containing a little methanol. The methanol solution was then analysed, again on all four

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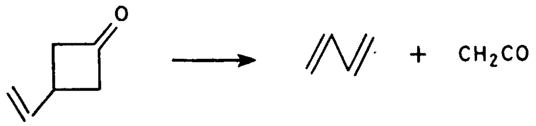
columns. The impurity and buta-1,3-diene peaks (and undecomposed vinylcyclobutanone) were still present but all the minor peaks were absent and were replaced by one peak with the same retention time as methyl acetate. We interpret these findings in terms of the decomposition of the 3-vinylcyclobutanone yielding only butadiene and keten.



Keten reacts on our chromatographic columns and is responsible for the minor peaks. The methanol trapping experiments confirm the presence of the keten. A careful search for cyclohexenone indicated that it was not formed even in trace quantities. This compound would have been an expected product if the decomposition had involved a biradical intermediate. Kinetic runs were carried out at 264.5 °C. Rate constants were determined from plots of log $(P_\infty - P_t)$ against time. Such plots were found to be linear to at least 75% conversion. Rate constants were found to be independent of initial pressure in the range 0.5—7 Torr. In all subsequent runs at other temperatures initial pressures in the range 0.7—2 Torr were used.

The pressure data yielded a value for the rate constant of 3.90×10^{-4} s^{-1} (at 264.5 °C). G.l.c. analysis using 1,4-dioxan (which was found to be stable at the reaction temperature) as an internal standard gave a value of 4.10×10^{-4} s^{-1}. A similar set of experiments at 274.3 °C gave 7.64×10^{-4} and 7.76×10^{-4} s^{-1} by the two methods, respectively. In addition some pyrolyses were carried out in a reaction vessel packed with Pyrex tubes to give it a surface : volume ratio *ca.* 14 times that of the unpacked reaction vessel. Analysis was by chromatography and a rate constant of 7.59×10^{-4} s^{-1} was obtained. Finally runs were carried out at 251.3 °C using both samples of vinylcyclobutanone and following the reactions by pressure change and analytically. All the rate constants were within 3% of 1.44×10^{-4} s^{-1}. In the analysis of the packed vessel runs, two small new product peaks appeared which totalled *ca.* 0.25% of the butadiene peak. They were identified as cyclopentene and vinylcyclopropane.

Rate constants for the thermal decomposition of 3-vinylcyclobutanone

T/°C	239.8	245.5	251.3
10^4k/s^{-1}	0.583 ± 0.005	0.922 ± 0.002	1.44 ± 0.019
T/°C	258.0	264.5	270.2
10^4k/s^{-1}	2.42 ± 0.024	3.90 ± 0.034	5.74 ± 0.036
T/°C	274.3	280.3	285.5
10^4k/s^{-1}	7.64 ± 0.051	12.2 ± 0.050	17.2 ± 0.06
T/°C	289.5		
10^4k/s^{-1}	22.6 ± 0.24		

From the results we conclude that the decomposition of 3-vinylcyclobutanone to butadiene and keten is a homogeneous first-order process whose progress may be monitored by following pressure changes in the system. Sets of runs were carried out at 10 temperatures in the range 239—290 °C and the rate constants obtained at the various temperatures are shown in the Table. An Arrhenius plot of the data in the Table gave a good straight line from which the Arrhenius parameters were obtained by the method of least squares, whence, equation (1) is obtained where the error limits are one standard deviation.

$$\log k/\mathrm{s}^{-1} = 13.714 \pm 0.066 - (176\,270 \pm 680 \text{ J mol}^{-1})/RT\ln 10 \quad (1)$$

DISCUSSION

As has been pointed out previously, there are important similarities between the decompositions of cyclobutanes and cyclobutanones.[2] Both groups of compounds probably undergo ring fission *via* a highly twisted activated complex which leads to strong steric 1,3 (or 2,4) interactions. Thus both 1,1,3,3-tetramethylcyclobutane and 2,2,4,4-tetramethylcyclobutanone decompose more slowly than the corresponding unsubstituted molecules. The rate reduction in the case of the cyclobutanone is of considerably greater magnitude than for the cyclobutane and suggests a more crowded or tighter activated complex. This in turn is consistent with the observation that cyclobutanones decompose with smaller A factors than the corresponding cyclobutanes.

The observation that an ethoxy-group in the 3-position in cyclobutanone led to a large reduction in the energy of activation for reaction was rationalised in terms of a partial zwitterionic charge distribution in the complex with the positive centre developing on the carbon atom in the 3-position of the ring.[4] Recent work on the effect of *gem*-dimethyl groups supports this assignment.[2]

In the present work we have obtained further evidence on this point. Comparison of the energy of activation obtained in the present study with that for cyclobutanone shows that the vinyl substituent in the 3-position leads to a reduction of 42 kJ mol^{-1}. This is certainly consistent with the stabilisation of the positive charge centre by the vinyl group, and the magnitude of the effect is quite reasonable in comparison with the effect of methyl groups.

It is perhaps worthy of note that the reduction in energy of activation produced by the vinyl substitution is almost exactly equal to the allyl resonance energy. It is therefore what would have been expected if the reaction mechanism had involved a biradical intermediate as has been suggested for cyclobutanes. This illustrates a possible pitfall in the use of thermochemical kinetic calculations which might well have been used to support such an assignment.

The reduction of the A factor for 3-vinylcyclobutanone compared with cyclobutanone by a factor of *ca.* 8 is again in reasonable accord with the suggested activated complexes (though a similar effect would also have been anticipated for a biradical). Stabilisation of the charge centre in the complex by the vinyl group will inevitably result in a large increase in the barrier to rotation of the vinyl group when compared with the reactant itself. This will result in relative decrease in the entropy of activation for the substituted compared with the unsubstituted reactant.

Finally we note that the structures suggested for the activated complexes involved in cyclobutanone decompositions are virtually the same as those suggested for the reverse reaction, *i.e.* the addition of ketens to olefins. It could perhaps be argued that this must be so on the basis of microscopic reversibility. This would surely be naïve since the decomposition has been studied as a high temperature gas-phase reaction whereas the addition has normally been investigated at much lower temperatures in the liquid phase. Nevertheless the near identity of the complexes must indicate the insensitivity of the transition state region to ' external ' factors.

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