The Thermal Unimolecular Decomposition of 2,2,4,4-Tetramethylcyclobutanone

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The thermal decomposition of 2,2,4,4-tetramethylcyclobutanone has been studied in the gas phase between 364 and 427 °C. In this temperature range the reaction is kinetically first order and the major reaction pathway yields dimethylketen and isobutene. A minor pathway which represents *ca.* 6% of the overall reaction yields 1,1,2,2-tetramethylcyclopropane and carbon monoxide. Both decompositions are probably unimolecular and concerted. Arrhenius parameters for the reactions are reported and the results compared with those for other cyclobutanone decompositions.

UNTIL quite recently the paucity of work reported on the thermal decomposition of cyclobutanones contrasted vividly with that on cyclobutanes. This is all the more surprising in view of the possible difference in the detailed mechanism for the reactions and their relationship to problems of thermochemical kinetics and orbital symmetry control. However, much of the leeway has been made up in the past two years by the work of Egger and Cocks on a number of bicyclic cyclobutanones [1-3] and a careful reinvestigation of the pyrolysis of cyclobutanone itself by Blades and McGee and Schleifer [4] following the early work by Walters *et al.*[5] It now remains to obtain results for some methyl substituted cyclobutanones in the hope that it may be possible to relate these to the photochemistry of these compounds [6,7] and to the pyrolytic behaviour of corresponding cyclobutanes. In the present paper we present results on the pyrolysis of 2,2,4,4-tetramethylcyclobutanone.

EXPERIMENTAL

Materials.—2,2,4,4-Tetramethylcyclobutanone was prepared from commercially available 2,2,4,4-tetramethylcyclobutane-1,3-dione by a partial Wolff–Kishner reduction.[8] Its i.r. and n.m.r. spectra were in accordance with published data,[9] as was its refractive index and m.p. It was purified by preparative g.l.c. using a 2 m × 6 mm column containing fluorosilicone oil on Chromosorb P and operated at 65 °C. After drying over a molecular sieve it was stored in a sample vessel closed by a Teflon–glass (Rotoflo) high vacuum stopcock. G.l.c. analysis on three columns (Poropak Q, Carbowax 20M, and ββ′-oxydipropionitrile) showed the compound to be >99·8% pure with a small peak (<0·2%) tentatively ascribed to 1,1,3,3-tetramethylcyclobutane.

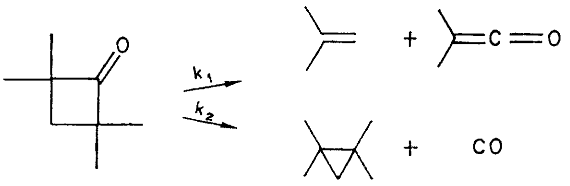
Isobutene, propene, and 1,1,2,2-tetramethylcyclopropane were commercial samples.

Apparatus.—A conventional high vacuum 'static' apparatus was used. Those parts of the line through which the reactant ketone passed were equipped with greaseless Teflon–glass (Rotoflo) stopcocks. Other parts of the line were equipped with greaseless stopcocks with Viton A diaphragms. (Preliminary experiments showed that the tetramethylcyclobutanone was 'soluble' in the Viton A diaphragms and diffused through them very rapidly.) The line was maintained at *ca.* 90 °C with Electrothermal tape. Pyrolyses were carried out in Pyrex reaction vessels mounted in a fused salt thermostat, whose temperature could be maintained constant, to within 0·05 °C at 400 °C. Pressures in the reaction vessel were monitored using a Bell and Howell model 4–327–003 transducer whose output was displayed on a potentiometric recorder.

RESULTS

Preliminary experiments were carried out at 375 °C and the reaction mixtures were analysed by g.l.c. using a column containing Poropak Q at 210 °C. The major reaction products detected were isobutene and 1,1,2,2-tetramethylcyclopropane (isobutene : cyclopropane ratio of *ca.* 15 : 1). There were also trace quantities of propene and an unidentified compound X. The yield of X represented a little less than 1% of the total products when about half the cyclobutanone had decomposed. However, its relative yield increased with increasing percentage decomposition and it appears clear that X is a secondary product.

A broad tailing peak (of rather irreproducible area) was tentatively ascribed to dimethylketen. This was confirmed by trapping reaction mixtures in methanol followed by g.l.c. analysis. The broad peak disappeared and a new one, with the same retention time as an authentic sample of the methyl ester of isobutyric acid, appeared.



SCHEME

Provided decomposition was restricted to about one half life the only products of importance were isobutene plus dimethylketen and 1,1,2,2-tetramethylcyclopropane plus carbon monoxide (Scheme). Analytical evidence showed that with initial reactant pressures below 20 Torr,† there was no dimerization of the dimethylketen and that the pressure changes in the system mirrored the chemical reaction. Plots of log $(2P_0 - P_t)$ against time where P_0

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† 1 Torr = 133 N m^{-2}.

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was the initial reactant pressure and P_t the total pressure at time t were linear up to more than one half life and from such plots (using a least squares procedure) values for $(k_1 + k_2)$ could be obtained.

The values for $(k_1 + k_2)$ were shown to be independent of initial reactant pressure in the range 2·4—19·6 Torr. For the majority of runs an initial reactant pressure between 6 and 8 Torr was used.

To confirm further that the pressure changes could be used to determine the rate constants, a series of runs was carried out at 379·7 °C using cyclopentanone as an internal standard and the percentage of the tetramethylcyclobutanone that had decomposed was determined by g.l.c. These analytical data confirmed that the decomposition was first order and yielded a value for $(k_1 + k_2)$ of $1{\cdot}32 \times 10^{-4}$ s^{-1}. The corresponding value from pressure data alone was $1{\cdot}36 \times 10^{-4}$ s^{-1}.

In a clean Pyrex reaction vessel the first few runs yielded irreproducible rates. This was probably due to a heterogeneous reaction. However, after relatively few runs reproducible rates were obtained. Some runs were carried out in a packed reaction vessel with a surface : volume ratio *ca.* 15 times that of the unpacked vessel. It proved to be more difficult to ' age ' the packed vessel, and this may have resulted in rate constants being determined before this process was complete. Six runs carried out at 364·2 °C using g.l.c. analysis, yielded an overall rate constant for decomposition of $5{\cdot}0 \times 10^{-5}$ s^{-1}. The calculated rate constant, using the Arrhenius equation (see later) obtained from pressure results in the unpacked vessel, was $4{\cdot}74 \times 10^{-5}$ s^{-1}. This difference of *ca.* 5% may be due to a small remaining heterogeneous component of the reaction in the packed vessel, but even this would imply a quite insignificant contribution in the unpacked vessel.

TABLE 1

Overall rate constants for decomposition of 2,2,4,4-tetramethylcyclobutanone

Temp./°C	$10^4(k_1 + k_2)$/s^{-1}	Temp./°C	$10^4(k_1 + k_2)$/s^{-1}
364·07	0·491	399·61	5·26
363·92	0·488	399·56	5·11
364·07	0·499	399·61	5·20
363·97	0·482	399·52	5·15
370·20	0·757	404·81	7·26
370·20	0·773	404·81	7·32
370·30	0·758	404·81	7·26
370·30	0·739	404·81	7·29
374·51	0·997	410·48	10·06
374·51	1·026	410·48	9·96
374·51	1·005	410·53	10·01
		410·48	10·04
379·75	1·466	410·48	10·18
379·80	1·431	410·48	10·18
379·75	1·439	410·48	10·08
384·08	1·908	415·87	13·40
384·08	1·920	415·96	13·58
384·08	1·957	415·92	13·72
384·08	1·871	415·87	14·05
384·08	1·934	415·96	13·77
384·08	1·926		
384·08	1·923	421·33	18·70
		421·33	19·15
389·86	2·753	421·24	18·90
389·95	2·741	421·24	19·47
		421·19	18·98
393·98	3·689	421·24	18·90
393·98	3·685		
393·98	3·669	426·95	26·65
393·98	3·600	426·95	26·35
393·98	3·734	427·05	27·21
		427·05	27·03
399·61	5·11	427·05	26·86

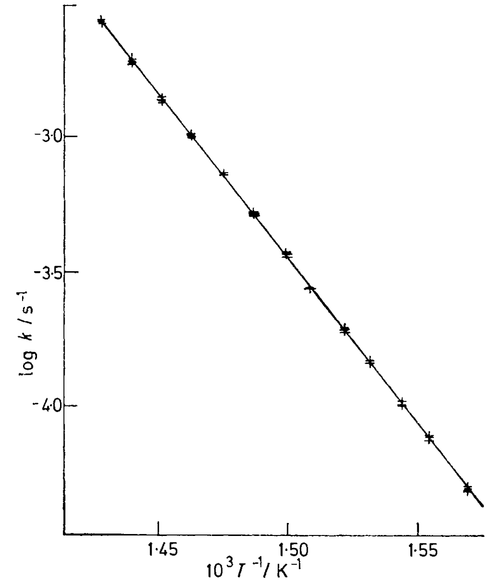
Values for $(k_1 + k_2)$ determined from pressure data were obtained at various temperatures from 364 to 427 °C. These data are shown in Table 1.

An Arrhenius plot of the data in Table 1 is shown in the Figure. The Arrhenius equation is given by (1) where the

$$\log [(k_1 + k_2)/\text{s}^{-1}] = 14{\cdot}96 \pm 0{\cdot}03 - (56{,}170 \pm 94 \text{ cal mol}^{-1})/2{\cdot}303RT \quad \text{(1a)}$$

$$\log [(k_1 + k_2)/\text{s}^{-1}] = 14{\cdot}96 \pm 0{\cdot}03 - (235{,}014 \pm 392 \text{ J mol}^{-1})/2{\cdot}303RT \quad \text{(1b)}$$

quoted errors are one standard deviation. (Note although many rate constants are quoted to four places this does not imply all the figures are significant. However, these were the numbers produced by the least squares analysis of the pressure data and were used without rounding off to compute the Arrhenius parameters.)



Arrhenius plot for overall decomposition

To determine the separate values of k_1 and k_2 the ratio of isobutene to 1,1,2,2-tetramethylcyclopropane was determined at 12 temperatures between 364 and 427 °C. Reaction mixtures were analysed using a 5·5 m × 2·2 mm column packed with 15% ββ'-oxydipropionitrile on 60—80 mesh Chromosorb W operated at 50 °C. Calibration factors for isobutene and tetramethylcyclopropane were obtained by analysing standard mixtures of known composition. At each temperature between five and eight determination were carried out. As an example we quote a typical set, the values obtained for the ratio at 370·25 °C, *viz.*, 16·73, 16·71, 16·82, 16·87, 16·87, 16·89, 16·84, and 16·89. Table 2 shows the average values for these ratios at various temperatures.

A plot of log k_1/k_2 against the reciprocal of the absolute temperature gave a good straight line and a least squares analysis yielded equation (2). The values of k_1 and k_2 at every temperature given in Table 1 were determined using

$$\log k_1/k_2 = (3642 \pm 36\ \text{cal mol}^{-1})/2{\cdot}303RT - 0{\cdot}0084 \pm 0{\cdot}012 \quad \text{(2a)}$$

$$\log k_1/k_2 = (15{,}237 \pm 150\ \text{J mol}^{-1})/2{\cdot}303RT - 0{\cdot}0084 \pm 0{\cdot}012 \quad \text{(2b)}$$

the data in Table 1, together with the value of k_1/k_2 determined using equation (2). These values were then used to obtain the Arrhenius equations (3) and (4). The errors

$$\log k_1/\text{s}^{-1} = 14{\cdot}859 \pm 0{\cdot}031 - (55{,}945 \pm 94\ \text{cal mol}^{-1})/2{\cdot}303RT \quad \text{(3a)}$$

$$\log k_1/\text{s}^{-1} = 14{\cdot}859 \pm 0{\cdot}031 - (234{,}070 \pm 390\ \text{J mol}^{-1})z2{\cdot}303RT \quad \text{(3b)}$$

$$\log k_2/\text{s}^{-1} = 14{\cdot}867 \pm 0{\cdot}031 - (59{,}587 \pm 94\ \text{cal mol}^{-1})/2{\cdot}303RT \quad \text{(4a)}$$

$$\log k_2/\text{s}^{-1} = 14{\cdot}867 \pm 0{\cdot}031 - (249{,}310 \pm 390\ \text{J mol}^{-1})/2{\cdot}303RT \quad \text{(4b)}$$

quoted are standard deviations computed by the normal statistical procedures. Such deviations can usually give a measure of the precision of the data but not of their accuracy, though the present situation is less favourable. The method employed to extract k_1 and k_2 from $(k_1 + k_2)$ ensures that equal deviations are obtained for the Arrhenius prameters for both rate constants, because k_1/k_2 is taken as an absolute datum. In addition, because the ratio is forced to fit an equation of the same algebraic form as the Arrhenius equation, errors associated with the determination of this ratio do not appear in the separate Arrhenius equations. This can be corrected by combining the errors in the Arrhenius equations and those from the van't Hoff plot, but the effect is very small indeed, the errors in the energies of activation only being increased from 94 to 100 cal K^{-1} mol^{-1}.

TABLE 2

Ratio of isobutene to 1,1,2,2-tetramethylcyclopropane at various temperatures

Temp./°C	k_1/k_2	Temp./°C	k_1/k_2
363·97	17·35	399·76	14·92
370·25	16·83	404·23	14·68
374·51	16·64	410·58	14·35
379·80	16·22	416·25	13·96
389·90	15·46	421·19	13·63
394·35	15·33	427·05	13·38

DISCUSSION

When the early results for cyclobutanone decomposition became available it was very tempting to rationalise them on the basis of a biradical mechanism, since this had been so successful in interpreting the data for cyclobutane decompositions.[10] Indeed, there are some striking parallels between the two systems, which leads us to suggest that while there are quite appreciable and energetically important differences between the two transition states, their geometries are similar.

The observation by Carless and Lee [11] of the retention of stereochemistry of the but-2-ene formed from *cis*- and *trans*-2,3-dimethylcyclobutanone ruled out the intermediacy of a biradical of appreciable lifetime and such observations were consistent with the experimental findings of Huisgen and his co-workers on the reverse reactions (addition of ketens to olefins, *etc.*) even though the latter results relate to liquid-phase studies, and in general deal with substituted reactants. Perhaps even more important was the determination of the heat of combustion of cyclobutanone [12] which leads to a strain energy in this compound appreciably less than for cyclobutane and essentially rules out a biradical intermediate for cyclobutanone decomposition itself on energetic grounds. Nonetheless, the parallels between cyclobutanes and cyclobutanones mentioned earlier exist. The rate constants for decomposition of cyclobutanes at 700 K are similar to those for cyclobutanones at 600 K and for convenience we compare the relative effects of substituents on these compounds at these two temperatures. The greatest effect on the rate constant for cyclobutane decomposition occurs with vinyl substituents. Since the appropriate results are not yet available for the simplest compounds we compare the effects for bicyclic molecules. At 700 K the rate of decomposition of bicyclo[3.2.0]hept-2-ene is nearly 1500 greater than bicyclo[3.2.0]heptane; for the corresponding cyclobutanones at 600 K (bicyclo[3.2.0]heptan-6-one and bicyclo[3.2.0]hept-2-en-6-one) the rate acceleration is a factor of 2100. The highly twisted transition state suggested for cyclobutane decomposition [13] was an attempt to go some way towards incorporating the ideas of orbital symmetry conservation [14] and also to account for the effects of alkyl substituents on the rate constants for decomposition of cyclobutanes, in particular for the finding that 1,1,3,3-tetramethylcyclobutane decomposed more slowly than cyclobutane itself whereas, for example, 1,1,2-trimethylcyclobutane decomposes more than 7 times faster (at 700 K). If one accepts the same activated geometry for cyclobutanone, similar effects are to be expected and, indeed, are observed. The activated complex suggested by Egger [15] for the decomposition of 2,2-dimethyl-3-ethoxycyclobutanone is of this structure but with large charge separation giving a ' quasi-zwitterion ' transition state. The work reported here supports this suggestion. Certainly the geometric requirements of the activated complex would lead to a prediction that 2,2,4,4-tetramethylcyclobutanone will decompose appreciably more slowly than cyclobutanone itself. Since cyclobutanones decompose with lower *A* factors than cyclobutanes, indicating a more constrained complex one does expect geometric factors to be more

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important than for cyclobutanes. Finally, accepting the charge distribution suggested by Egger for the zwitterion, results in the expectation that alkyl substituents in the 2- and 4-positions will have a much smaller accelerating effect than in the 3-position. These factors taken together, provide an explanation for the rate reduction of a factor of over 14 observed in the present work, compared with cyclobutanone itself, whereas for the corresponding cyclobutanes the rate reduction is only a factor of 1·3.

The observation of 1,1,2,2-tetramethylcyclopropane as a minor product in the present study whereas cyclopropane is present in only trace quantities in the decomposition of cyclobutanone is worthy of comment. The Arrhenius equation for the formation of cyclopropanes in the two systems are appreciably different, but owing to the large experimental errors attendant of their being trace or minor products one cannot be certain to what extent they are significant. It is, therefore, more appropriate to compare directly the rate constants for formation at a particular temperature (600 K). When this is done, perhaps surprisingly, it is found that these rates are very similar, with cyclopropane being formed from cyclobutanone *ca.* 30% *faster* than the tetramethylcyclopropane from the tetramethylcyclobutanone. Thus the large increase in relative yield of the tetramethylcyclopropane arises not because this reaction pathway has become more facile by substitution, but rather because the effect of substitution has had a vastly greater effect on the (competing) decomposition to olefins. More information will be required (using other substituents) before we are in a position to make suggestions about the nature of the transition state for the pathway leading to cyclopropanes. However, even at this stage it appears reasonably certain that the relatively higher yields of cyclopropanes observed in the photochemical decomposition of cyclobutanones arise from purely energetic effects, and there appears to be no necessity to involve other spin states to account for these observations.

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