The Thermal Unimolecular Decomposition of t-Butylcyclobutane

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The thermal decomposition of t-butylcyclobutane has been studied in the gas phase from 401 to 478 °C. In an 'aged' reaction vessel the decomposition is homogeneous, kinetically of the first order, and yields an equimolar mixture of ethylene and 3,3-dimethylbut-1-ene as primary products. Rate constants were independent of pressure in the range 6—40 Torr and fit the Arrhenius equation (1). Some decomposition of the 3,3-dimethylbut-1-ene

$$k = 10^{15 \cdot 94} \exp(-63,860 \text{ cal. mole}^{-1}/RT) \sec^{-1}$$
 (1)

occurs at the reaction temperatures but is appreciably slower than the primary decomposition.

The decomposition of cyclobutane and alkyl-substituted cyclobutanes are good examples of unimolecular reactions. There has been considerable discussion about their mechanism. Most available evidence strongly supports a biradical intermediate mechanism. Recently we have suggested ¹ that the reaction pathway to the biradical involves some 1,3-interaction and hence it is possible to account for an apparent anomaly in the slow rate of decomposition of 1,1,3,3-tetramethylcyclobutane. This suggestion leads to the expectation that t-butylcyclobutane unlike methyl- and ethyl-cyclobutanes will decompose at a slower rate than cyclobutane itself. The present work reports a study to test this prediction.

EXPERIMENTAL

A mixture of 2-t-butylcyclobutanone and 3-t-butylcyclobutanone was prepared by the reaction of diazomethane on t-butylketene by the method of Salaün and Conia.² The cyclobutanones were converted into their semicarbazones, which were treated with sodium in diethylene glycol³ to give t-butylcyclobutane. This was separated by steam distillation followed by washing with sulphuric acid and water. Reduced-pressure distillation yielded the hydrocarbon of 98% purity. A sample better than 99.8% was obtained by preparative g.l.c. on a 5 m. \times 6 mm. column containing 20% (w/w) of squalane on Chromosorb P operated at 80 °C followed by drying on a molecular sieve. The structure of the t-butylcyclobutane was confirmed by n.m.r. spectroscopy.

Apparatus and Analysis.—The kinetic apparatus and pressure measuring system were virtually the same as described previously.¹ To reduce absorption problems the gas handling line and gas pipettes were maintained at 80 °C. The coldest part of the entire system (part of the pressure transducer) was at about 70 °C. Analysis was by g.l.c. with a gas sampling valve, electronic integrator, and a 50 m. capillary column coated with squalane and operated at 40 °C. Products were identified by comparison of retention

³ H. L. Herzog and E. R. Buchman, J. Org. Chem., 1951, **16**, 99.

¹ A. T. Cocks and H. M. Frey, *J. Chem. Soc.* (A), 1969, 1671. ² J. Salaün and J. M. Conia, *Bull. Soc. chim. France*, 1968, **9**, 3730.

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times with those of authentic samples on four different chromatographic columns.

RESULTS

In the temperature range 401 to 478 °C the pyrolysis (1) of t-butylcyclobutane gave ethylene and 3,3-dimethylbut-1ene as the primary products. Before any kinetic study was



made, large samples of the cyclobutane and also 3,3-dimethylbut-1-ene were pyrolysed in the reaction vessel for 24 hr. at 500 °C. After this treatment reproducible results were obtained for the cyclobutane pyrolyses. Plots of $\log(2P_0 - P)$ against time were linear up to 20% decomposition. The effective dead space in the system was less than 0.4% and no correction was made for this. In an initial series of experiments the reactant pressure was varied in the range 6-40 Torr. All these runs gave the same rate constant within experimental error. In all subsequent work an initial reactant pressure in the range 12-15 Torr was used. Two complete runs were carried out at each of 10 temperatures, and the pressure at various intervals was obtained from a potentiometric recorder trace of the transducer output. Rate constants were obtained from the slopes of plots of $\log(2P_0 - P)$ against time by the method of least squares using data from the linear region. Duplicate runs gave rate constants which agreed within 2%. The average values of the rate constants obtained in this way are shown in Table 1.

TABLE 1

Rate of	decompositio	on of t-buty	lcyclobutane

Temp. (°C) 10 ⁴ k (sec. ⁻¹)	$400.9 \\ 0.175$	$406.4 \\ 0.256$	$412 \cdot 3 \\ 0 \cdot 381$	$423 \cdot 4 \\ 0 \cdot 814$	$434 \cdot 9 \\ 1 \cdot 72$
Temp. (°C) 10 ⁴ (sec. ⁻¹)	$447.6 \\ 3.87$	$459 \cdot 9 \\ 8 \cdot 14$	$465 \cdot 6 \\ 11 \cdot 1$	$471.8 \\ 16.4$	$478.2 \\ 23.3$

An Arrhenius plot of these data gave a good straight line from which the Arrhenius parameters were obtained by the method of least squares, whence equation (2) (the quoted error limits are standard deviations).

$$k = 10^{15.94} \pm 0.04 \exp(-63,860 \pm 120 \text{ cal. mole}^{-1}/\mathbf{R}T) \text{ sec.}^{-1}$$
 (2)

Runs carried out at 447.0 °C in a cylindrical reaction vessel packed with glass tubes to give it a surface : volume ratio 8 times that of the unpacked vessel, gave a rate constant within 2% of that calculated from the Arrhenius equation. There can thus be no appreciable heterogeneous component of the reaction. A series of pyrolyses carried out at 437.8 °C were followed analytically by g.l.c. A plot of the logarithm of percentage of undecomposed reactant against time was linear to 20% decomposition and gave a rate constant identical with that calculated from the Arrhenius equation obtained from pressure measurements.

Thus the pressure change accurately reflects the extent of decomposition. Such exact agreement is fortuitous since the analytical data are in general less precise than the pressure measurements owing to errors in determining exact calibration factors for the reactant and products. Above 20% decomposition, several new peaks were observed on the chromatograms. One of these was methane, others which were not identified had retention times which indicated they were hydrocarbons containing 3-6 carbon atoms. Up to 20% decomposition, the ratio of ethylene to 3,3-dimethylbut-1-ene was always unity within experimental error, but the ratio becomes progressively larger with further decomposition. Pyrolysis of pure samples of 3,3-dimethylbut-1-ene at several temperatures for the time required for 20% decomposition of the cyclobutane gave no detectable pressure change although a small amount of decomposition occurred. Prolonged pyrolysis produced a pressure increase and gave the same product pattern as that obtained by the pyrolysis of t-butylcyclobutane taken to greater than 20% decomposition. It appears that all these products arise from the secondary decomposition of the 3,3-dimethylbut-1-ene (probably by a free-radical process initiated by the fission of one of the β -C-C bonds in the olefin). The secondary reactions should have no appreciable effect on the rate constants calculated for the primary decomposition based on pressure measurements of up to

DISCUSSION

20% reaction.

Kinetic studies of 1,1,3,3-tetramethylcyclobutane¹ have been interpreted in terms of a transition complex which is formed by twisting the molecule such that 1,3-interactions are increased relative to the reactant. Recent work on 6,7-dimethylbicyclo[3,2,0]heptane 4 indicates that this twisting leads to a biradical intermediate and not to concerted product formation (with inversion at one centre). However, the pyrolysis ⁵ of 7,8-cis-exodideuteriobicyclo[4,2,0]octane yields data which can be interpreted as showing that a small fraction of the reaction does go by the concerted pathway, which would indicate that the overall rate parameters for both processes make the processes nearly competitive at around 450 °C. The activation energy for the decomposition of t-butylcyclobutane is larger than that for any of the other monoalkylcyclobutanes studied to date. For comparison purposes we prefer to consider the free energies of activation, ΔG^{\ddagger} at 450 °C, which is near the mean temperature for most of the cyclobutane studies. The errors in ΔG^{\ddagger} at any temperature in or near the range of temperatures investigated are much smaller than those for the derived quantities E_a and A. The Arrhenius parameters and $\Delta G^{\ddagger}_{450}$ values of relevant substituted cyclobutanes are in Table 2.6-11

The rate of decomposition of t-butylcyclobutane at

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⁶ R. W. Carr and W. D. Walters, J. Phys. Chem., 1963, 67, 1370.

⁷ M. N. Das and W. D. Walters, Z. phys. Chem. (Frankfurt),

^{1958, 15, 22.} ⁸ R. E. Wellman and W. D. Walters, J. Amer. Chem. Soc., 1957, 79, 1542.

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450 °C is slower than that of other monosubstituted cyclobutanes and fits the scheme $Me > Et > Pr^i > Bu^t$. As noted previously,¹ the results for the n-propyl compound appear to be anomalous. This order of reactivities can be explained qualitatively if it is assumed that 1,3-interactions in the transition complex are more important than inductive stabilization and steric destabilization of the ground state. We have attempted a more quantitative approach by considering the possible bond-breaking steps and their related 1,3-interactions in the cyclobutane series.

For cyclobutane itself, there are 4 bonds which can be broken via a twisting to give a biradical intermediate

Table	2
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Rate data for alkylcyclobutanes

Compound	$\log A$	E (kcal. mole ⁻¹)	$\Delta G^{\ddagger_{450}}$ (kcal. mole ⁻¹)	Ref.
Cyclobutane	15.62	62.5	54.453	6
Methylcyclobutane	15.38	61.2	53.914	7
Ethylcyclobutane	15.56	$62 \cdot 0$	54.119	8
n-Propylcyclobutane	15.53	61.6	$53 \cdot 818$	9
i-Propylcyclobutane	15.63	$62 \cdot 6$	54.487	10
t-Butylcyclobutane	15.94	63.9	54.698	
1,1-Dimethylcyclobutane	15.68	61 ·0	52.721	11
1,1,3,3-Tetramethyl-				
cyclobutane	16.31	$65 \cdot 2$	54.803	1
(Errors in $\Delta G^{\ddagger}_{450}$ are of the order of \pm 0.03 kcal. mole ⁻¹)				

and in breaking each bond, the hydrogen atoms at each end can move into or out of the ring. For the breaking of each bond, we regard the passage to the transition complex as consisting of a rotation of the methylene group at one end of the bond into the ring, and a rotation of the methylene group at the other end of the bond away from the ring. The result of this twisting is that two H-H 1,3-interactions are important, one above and one below the plane of the ring, and these interactions are assumed to be equal. In cyclobutane, therefore,



Axes are parallel to diagonals of the ring.

there are 8 modes of decomposition (all equivalent) and each mode has two H–H 1,3-interactions. The $\Delta G^{\ddagger}_{450}$ value for each mode is 57.44 kcal. mole⁻¹. For monosubstituted cyclobutanes, four of these modes have the H-H interactions replaced by R-H and H-H interactions, and of these, two produce a biradical stabilized

by the R group. The 4 modes with only H-H interactions also divide into two sets one of which produces the stabilized biradical. By taking methylcyclobutane and t-butylcyclobutane as limiting cases in which the R-H interaction energies are zero and infinity respectively, and assuming that the stabilization by both alkyl groups is the same, we find that this stabilization must fall between 940 and 1240 cal. mole⁻¹. If we arbitrarily assume that all alkyl groups stabilize the transition complex in which a free electron is being placed on a substituted carbon atom by 1 kcal. mole⁻¹, the 1,3-interactions for various groups can be evaluated with respect to the H-H interaction taken as zero. These values are in Table 3.

TABLE 3						
Substituent	н	Me	Et	Pri	But	
(cal. mole ⁻¹)	0	95	560	1 73 0	3020	

If it is assumed that the bond twisting is symmetric, these calculations can be extended to 1,1-dimethylcyclobutane, which leads to a stabilization due to the dimethyl substitution of 2600 cal. mole⁻¹. Using this figure and the data from 1,1,3,3-tetramethylcyclobutane, we find the free energy of the Me-Me interaction to be 2950 cal. mole⁻¹. These results enable us to predict the values of $\Delta G^{\ddagger}_{450}$ for *cis*- and *trans*-1,3-dimethylcyclobutane. For the *cis*-compound we find $\Delta G_{450}^{\ddagger} =$ 54,275 cal. mole⁻¹ and for the trans-compound 53,547 cal. mole⁻¹. Preliminary results¹² indicate that the ciscompound decomposes at about the same rate as cyclobutane itself so the calculated and experimental free energies of activation are in good agreement. However our estimates suggest that the trans-compound should decompose at 1.66 times the rate of the *cis*-compound whereas experimentally the preliminary data yield a value of 1.25. Thus our model appears to be only semiquantitative. There are close similarities between our model and that suggested for the thermal rearrangements of 1,2-dimethylenecyclobutane.¹³ However until precise data on other 1,3-substituted cyclobutanes are available it is not profitable to attempt to refine the calculations further.

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¹³ J. J. Gajewski and C. N. Shih, J. Amer. Chem. Soc., 1969, **91**, 5900.

¹² A Venkitaraman, personal communication.