The Gas-phase Thermal Unimolecular Elimination of Keten from Bicyclo-[3.2.0]heptan-6-one

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The gas-phase thermal decomposition of bicyclo[3.2.0]heptan-6-one to yield cyclopentene and keten as primary products was studied in the temperature range 564—652 K. First-order rate constants for the depletion of bicycloheptanone, obtained by an internal standard technique, were independent of initial starting pressure in the range 3·8—40 Torr † and fit the Arrhenius relationship (i). The activation parameters, when compared with those

$$\log k/\mathrm{s}^{-1} = 14{\cdot}21 \pm 0{\cdot}10 - (48{\cdot}55 \pm 0{\cdot}29\ \mathrm{kcal\ mol}^{-1})/(2{\cdot}303RT) \qquad \text{(i)}$$

for cyclobutanone itself, indicate that alkyl groups have a relatively small stabilizing influence on the transition state, in contrast to the large effect found previously for the vinyl group.

STUDIES of the liquid phase [2 + 2] additions of ketens to olefins have demonstrated that, in general, this reaction occurs with retention of olefin stereochemistry [1-3] and, in the case of conjugated dienes, to the exclusion of the 'allowed' 4*s* + 2*s* Diels–Alder reaction.[4-7] These facts have been rationalized on orbital symmetry grounds by invoking an orthogonal [2*s* + 2*a*] transition state

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† Throughout this paper, 1 Torr = (101·325/760) kN m^{-2} and 1 cal = 4·184 J.

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with charge separation along the reaction co-ordinate initiated by the pseudo-vinylium-ion character of the keten [8] in the ground state. The effect of olefin substituents on the rate [9,10] and orientation [3,5,7,10-12] of addition substantiate the concept of a polar transition state but the relatively small solvent effects observed [5,9,10] indicate that the differences between the extent of charge separation in the reactants and transition state is not large. Evidence for the orthogonal nature of the transition state has been obtained from studies of the *exo* : *endo* product ratios from reactions of asymmetrically substituted ketens with cyclopentadiene.[7]

Retention of stereochemistry in the product olefin has been established in gas-phase keten eliminations from cyclobutanone derivatives,[13] and relative rates of decomposition of *exo*- and *endo*-7-alkyl substituted bicyclo[3.2.0]hept-2-en-6-ones have been rationalized on the basis of an orthogonal transition state.[14]

Gas-phase kinetic data for the decompositions of cyclobutanones would be expected to yield useful information with respect to the detailed nature of the transition state of the cyclobutanone–keten + olefin system, but little work has been reported in this area. Earlier studies of the keten elimination from bicyclo[3.2.0]hept-2-en-6-one in the gas phase [15] revealed a surprisingly large effect of the vinylic substituent on the reaction rate, and the present study was undertaken to examine further the effect of substituents on keten elimination–addition reactions.

EXPERIMENTAL

Materials.—Two samples of bicyclo[3.2.0]heptan-6-one of 96 and 99% purity, prepared by hydrogenation of bicyclo-[3.2.0]hept-2-en-6-one, were supplied by Mr. M. Rey of the University of Zürich. The structure of this material was confirmed by n.m.r. spectroscopy. *o*-Xylene and 2-methylcyclohexanone, used as internal standards, were 99·9 and 97% pure respectively. The major impurity in the methylcyclohexanone was the 4-isomer. Several mixtures of bicycloheptanone and internal standard with mole ratios of *ca.* 1 : 1 were used as starting materials in the kinetic work. The composition of these standard mixtures varied by less than 1% during periods of up to 14 days.

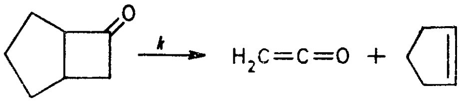
Apparatus and Procedure.—The conventional static reaction system used for the kinetic studies was essentially as described previously.[16] Cylindrical Pyrex reaction vessels of 1 l and 2 l volume were normally employed. For testing for heterogeneity, a 2 l cylindrical Pyrex vessel packed with thin-walled Pyrex tubes giving a surface-to-volume ratio 14 times that of the unpacked vessel was used.

Pressures in the reaction system, were measured with a Pace pressure transducer.

The starting material, consisting of a 1 : 1 mixture of bicyclo[3.2.0]heptan-6-one and internal standard (*o*-xylene or 2-methylcyclohexanone) was injected into the reaction vessel *via* a silicone rubber septum. The reaction vessel was isolated from the injection volume by means of a Teflon valve and all material remaining in the dead-space was removed. A reaction was quenched by condensing the contents of the reaction vessel into a trap cooled in liquid nitrogen. Amounts of material non-condensable at liquid-nitrogen temperature were negligible. The trap was warmed to −120 °C and the evolved gases were transferred to a gas burette by means of an automated Toepler pump. This fraction gave no g.l.c. signal and was identified as keten by reaction with ethanol which yielded ethyl acetate. After removal of the keten, the trap was warmed to −40 °C and the non-condensable gases transferred to the burette. This fraction gave only one g.l.c. peak and was identified as cyclopentene by n.m.r. spectroscopy. The remaining contents of the trap, consisting of bicyclo[3.2.0]heptan-6-one and internal standard, were transferred to a small-volume sampling vial and stored under nitrogen at 0 °C. This material was analysed by g.l.c. with liquid injections. An F + M model 810 gas chromatograph fitted with T.C. detectors was employed. A 7 ft × 0·25 in column packed with 33% Carbowax 20 M on Chromosorb W operated at 130 °C with a helium flow rate of 100 ml min^{-1} gave a good separation between reactant and internal standards. Peak areas were measured with a ‘ Disc ’ integrator and duplicate analyses agreed within 0·5%.

RESULTS

In the temperature range 564—652 K, bicyclo[3.2.0]-heptan-6-one decomposes to yield keten and cyclopentene as principal observable products [reaction (1)]. Below 80% conversion, no other product was detected by g.l.c. or n.m.r. spectroscopy. Above 80% conversion, a small quantity (less than 1% of the initial amount of bicycloheptanone) of a product with a slightly longer retention time than bicyclo[3.2.0]heptan-6-one was observed but was not identified.



(1)

Using the concept of direct additivity of thermodynamic increments,[17] we calculate the van't Hoff relationship for the equilibrium in system (1) to be (2). Under the most

$$\log(K/\text{atm}) = 8{\cdot}7 - (16{\cdot}3\ \text{kcal mol}^{-1})/(2{\cdot}303RT) \quad (2)$$

favourable conditions for the back reaction in the present study, the equilibrium concentration of bicyclo[3.2.0]-heptan-6-one is calculated to be less than 0·01% of the initial concentration and the reaction is, therefore, essentially irreversible, as depicted in equation (1).

First-order rate constants for the depletion of bicyclo-[3.2.0]heptan-6-one obtained by the internal standard

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[16] K. W. Egger, *J. Amer. Chem. Soc.*, 1969, **91**, 2867.

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method, together with relevant experimental details, are in Table 1. An Arrhenius plot of these data is shown in Figure 1. No systematic variation in rate constant with initial bicycloheptanone pressure (3·8—40 Torr) or conversion (10·7—87·5%) is apparent.

TABLE 1

Kinetic data for the unimolecular elimination of keten from bicyclo[3.2.0]heptan-6-one

T/K	Time/ min		$[BCH]_0$ [a] / Torr	Conversion (% of $[BCH]_0$)	10^4k/s^{-1}
546·1	120	*b*	10·0	15·80	0·239
564·4	240	*b*	7·4	31·47	0·262
564·4	360	*b*	4·7	41·78	0·251
567·2	960	*b*	4·9	84·04	0·319
580·7	180	*c*	33·6	57·47	0·792
581·1	60	*c*	22·3	26·51	0·856
581·7	40	*c*	26·9	20·15	0·938
581·7	240	*c*	18·8	74·01	0·936
582·5	120	*c*	17·8	50·43	0·975
597·6	60	*b*	3·8	65·01	2·92
597·7	20	*b*	4·1	27·87	2·72
598·0	8·7	*b*	10·0	14·74	3·07
598·2	6	*b*	5·0	10·73	3·15
599·5	30	*b*	4·3	43·63	3·19
600·6	5	*b*	5·0	10·71	3·78
601·3	10	*c*	4·6	20·28	3·78
612·1 [d]	10	*b*	20·2	35·31	7·26
612·7 [d]	5	*b*	10·2	22·37	8·43
618·5	3	*b*	8·2	18·33	11·3
618·8	7	*b*	40·0	35·65	10·5
619·2	5	*b*	8·0	30·12	12·0
619·4	10	*b*	6·4	51·29	12·0
636·9	4	*c*	10·0	58·34	36·5
637·1	8	*c*	10·0	79·95	33·5
637·7	2	*c*	16·0	41·27	44·4
637·7	10	*c*	16·0	87·48	34·6
638·0	3	*c*	16·1	52·00	40·8
649·4	5	*b*	9·8	86·13	65·9
649·5	4	*b*	5·8	82·16	71·8
650·2	2	*b*	9·8	59·46	75·3
651·6	3	*b*	10·0	75·75	78·7
651·9	1·5	*b*	4·9	56·64	88·0

[a] Initial pressure of bicyclo[3.2.0]heptan-6-one. [b] 2-methylcyclohexanone as internal standard. [c] *o*-Xylene as internal standard. [d] Packed reaction vessel, not included in least-squares analysis.

Conversions based on pressure changes were normally within 85—99% of those based on the internal standard, whilst those based on the amount of cyclopentene ranged from 80 to 100%.

In the large vessel at pressures less than 30 Torr, the amounts of cyclopentene and keten produced normally agreed within 5%. With higher pressures and particularly in the packed vessel, this agreement was poorer, probably owing to the oligomerization of keten.

Additional experiments performed with pure bicyclo-[3.2.0]heptan-6-one with initial pressures up to 100 Torr gave conversions based on pressure changes of 92—95% of those obtained in analogous runs based on internal standard measurements. The corresponding conversions based on cyclopentene were 92—100% of those from the internal standard runs. The discrepancies observed between the conversions based on the internal standard and those based on pressure changes and the amount of cyclopentene produced are due to errors in the pressure measurements and losses incurred in separating and measuring the small amounts of material involved, and other pathways contributing measurably to the depletion of bicyclo[3.2.0]-heptan-6-one can be ruled out.

Least-squares analysis of the rate constants in Table 1 yields the Arrhenius relationship (3). The quoted errors are

$$\log (k/\text{s}^{-1}) = 14{\cdot}21 \pm 0{\cdot}10 - (48{\cdot}55 \pm 0{\cdot}29 \text{ kcal mol}^{-1})/(2{\cdot}303RT) \quad (3)$$

standard deviations. Standard deviations of the rate constants within a temperature block ranged from ±2·7% to ±9% and, based on these, the *maximum* likely error in the activation energy [18] is calculated to be *ca.* ±0 9 kcal mol^{-1}.

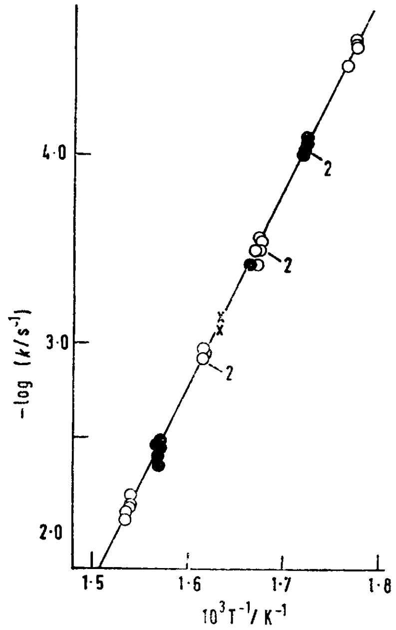

FIGURE 1 Arrhenius plot for the thermal decomposition of bicyclo[3.2.0]heptan-6-one. ○, Runs with 2-methylcyclohexanone as internal standard; ●, runs with *o*-xylene as internal standard; ×, packed vessel runs. Numerals indicate overlapping points

Rate constants obtained in the packed reaction vessel were within 4—8% of those calculated from the Arrhenius equation obtained with unpacked vessels. Any heterogeneous component of the primary reaction is, therefore, negligible.

DISCUSSION

The effect of a 2,3-fused cyclopentane ring on the rate of the cyclobutanone decomposition is approximately the same as that of two alkyl substituents.[19] In contrast to the large effect of a cyclopentene ring, observed in the decomposition of bicyclo[3.2.0]hept-2-en-6-one,[15] alkyl substitution enhances the rate only slightly. In the temperature range of this study, the title compound decomposes at about eight times the rate observed for

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[18] S. W. Benson, 'The Foundations of Chemical Kinetics,' Wiley, New York, 1960, p. 91.

[19] E. K. C. Lee, personal communication.

cyclobutanone itself,[20] but only 0·001 of the rate for bicyclo[3.2.0]hept-2-en-6-one.[15] In order to evaluate the activation parameters observed for the thermal decomposition of cyclobutanone derivatives in terms of the detailed reaction mechanism involved, it is of interest to compare these data with those for similar reactions involving hydrocarbons, for which many reliable kinetic and mechanistic data are available.

TABLE 2

Arrhenius parameters for the thermal decompositions of cyclobutanones and related hydrocarbons

Reaction	log (A/s^{-1})	E_a/kcal mol^{-1}	Ref.
Cyclobutane $\longrightarrow$ $2C_2H_4$	15·6	62·5	21
Methylenecyclobutane $\longrightarrow$ $C_3H_4 + C_2H_4$	15·7	63·3	22
Cyclobutanone $\longrightarrow$ $C_2H_2O + C_2H_4$	14·6	52·0	20
Bicyclo[3.2.0]heptane $\longrightarrow$ cyclopentene + C_2H_4	14·8	60·7	23
Bicyclo[3.2.0]hept-2-ene $\longrightarrow$ cyclopentadiene + C_2H_4	14·3	49·0	24
Bicyclo[3.2.0]heptan-6-one $\longrightarrow$ cyclopentene + C_2H_2O	14·2	48·6	This work
Bicyclo[3.2.0]hept-2-en-6-one $\longrightarrow$ cyclopentadiene + C_2H_2O	13·2	37·5	15

The Arrhenius parameters [21-24] for the decomposition of cyclobutanone derivatives published so far, together with those for relevant hydrocarbons, are shown in Table 2. Comparison of the cyclobutane and cyclobutanone series reveals a similar trend in A factors and activation-energy increments. In the case of cyclobutanes, decomposition appears to occur mainly *via* a non-concerted pathway involving a biradical intermediate [25,26] and it has been suggested that the biradical formation proceeds through a twisted transition state.[27] The self-consistency of the biradical model for cyclobutane decompositions has been amply illustrated.[17] A biradical analysis of the decomposition of cyclobutanone,[17] however, implies, that a resonance stabilization energy of 7·9 kcal mol^{-1} is generated in the substituted acetonyl radical end in the biradical transition state. This analysis is, however, incompatible with the similar analysis for methylenecyclobutane [17] in which the resonance energy released in ring-opening is lost again in the decomposition of the biradical. Further, recent studies indicate that the resonance energy in the substituted acetonyl radical is appreciably less than 7·9 kcal mol^{-1}.[28] It appears, therefore, that the thermal decomposition of cyclobutanones, *i.e.*, the retro-keten additions, are normally concerted processes, although the two C–C bonds are not necessarily broken in a completely synchronous manner. There is some evidence, that in keten–olefin systems in which steric interactions disfavour the concerted process, a biradical pathway may become competitive.[29] One of the most important aspects of the detailed mechanism involved in the keten + olefin $\rightleftharpoons$ cyclobutanone systems is the nature and amount of charge separation in the ground and transition state. For the liquid-phase keten addition to olefins a zwitterion transition state with the negative charge on the oxygen and the positive charge on the bridgehead carbon atom has been postulated.[9] However, the existence of such an extreme form of polar transition state at low temperatures in the gas phase has no precedent and is extremely unlikely.

By analogy with the ' classic ' polar gas-phase eliminations of hydrogen halides from alkyl halides, the kinetic results for bicyclo[3.2.0]hept-2-en-6-one were rationalized on the basis of a quadrupolar four-centre concerted mechanism with some extra stabilizing contribution from an interaction of the carbonyl bond with the C=C bond in the twisted transition state.[15] The magnitude of this interaction was estimated to be *ca.* 4·5 kcal mol^{-1}.

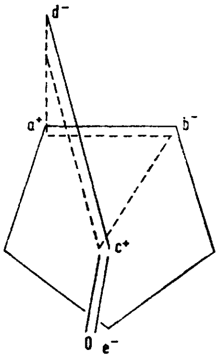

FIGURE 2 Orthogonal transition state for keten elimination from bicyclo[3.2.0]heptan-6-one; a, b, c, d, and e represent fractional charges and a + c = b + d + e

A recent critical review of the kinetic parameters for thermal elimination reactions of alkyl halides [30] indicated the following substituent stabilizing effects (in kcal mol^{-1}) on the partially charged centres in the transition state: alkyl-positive 5·5 ± 0·9, alkyl-negative 1·5 ± 0·4, vinyl-positive 8·2 ± 0·3, vinyl-negative 1·5 ± 0·1. From the present study, the total stabilization energy of alkyl substituents on both positive [C(1)] and negative [C(5)] centres in the suggested orthogonal quadrupolar transition state shown in Figure 2, is 3·4 kcal mol^{-1} or only about half the effect observed for alkyl halides. It appears, therefore, that the differences in polarities between ground state and transition state for keten eliminations are appreciably less than for hydrogen halide

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eliminations although the actual charge separation may be larger. On this basis, the stabilizing effect of a vinyl substituent would be expected to be less than that in the alkyl halide series, and the simple quadrupolar concept does not, therefore, provide a ready rationale for the large transition-state stabilization (>11 kcal mol^{-1}) observed for the vinyl group. Although the low *A*-factor for bicyclo[3.2.0]hept-2-en-6-one supports the postulate of an additional carbonyl C–C double-bond interaction, the resulting stabilization effect would have to be appreciably greater than the 4·5 kcal mol^{-1} originally suggested,[15] which appears to be unreasonable for a simple ‘ loose ’ interaction.

It is conceivable that for alkylcyclobutanones, the biradical path is only marginally disfavoured energetically with respect to the concerted path. The presence of a double bond, which provides 12·5 kcal mol^{-1} of radical stabilization energy, could then possibly bring about a change in mechanism from concerted to biradical. Further work on the effects of substituents on cyclobutanone decompositions is in progress.

We thank Mr. M. Rey of the University of Zürich for the samples of bicyclo[3.2.0]heptan-6-one and for help in the identification of keten, and Mr. B. Weber for experimental assistance.

[2/1098 *Received, 15th May,* 1972]