Kinetics of the Four-centre Elimination of Keten from Bicyclo[3,2,0]hept-2-en-6-one in the Gas Phase

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The gas-phase pyrolysis of bicyclo[3,2,0]hept-2-en-6-one (BCH) to yield cyclopentadiene and keten as main products was studied in the range 471—534 K, using a static reaction system. The rate of depletion of BCH with time was followed gas chromatographically using cyclohexanone as an internal standard. The reaction is essentially homogeneous and consistent first-order rate constants were obtained for conversions ranging from 8 to 97% and a variation in total initial pressures from 15 to 485 Torr [= 2·0—64·66 kN m^{-2}] (using propene as a diluent). The observed rate constants yield the following Arrhenius relationship (with standard errors): log k (s^{-1}) = (13·16 ± 0·11) − (37·53 ± 0·25)/θ where θ equals 2·303 RT (K) in kcal mol^{-1}.

The results are consistent with a concerted polar four-centre elimination mechanism and are in general agreement with the well documented observations for the back reaction, the 2 + 2-addition of ketens to conjugated dienes. The surprisingly low activation parameters observed in this study when compared with those for the similar cyclobutanone reaction ($10^{14\cdot56-52\cdot0/\theta}$) are attributed partly to large stabilizing effects of the substituents onto the induced positive (*ca.* 8·5 kcal mol^{-1}) and negative (*ca.* 1·5 kcal mol^{-1}) charges on the bridgehead carbon atoms and partly to an additional stabilizing effect resulting from the interaction of the carbonyl group with the extra double bond in the proposed twisted transition state.

THE reactions of ketens with olefins to form cyclobutanone derivatives have long been known and are well documented.[1-7] Of these reactions, the addition of ketens to conjugated olefins to form exclusively cyclobutanone derivatives in a [2 + 2]-reaction rather than cyclohexanone [2 + 4]-derivatives [3b,4b,5,7] has attracted particular interest in view of the implications with respect to the principle of conservation of orbital symmetry in this concerted process.[5-8] The concerted nature, the supra- and antara-facial role of olefins and keten respectively, as well as the polarity controlled mechanistics have been established.[3-5,7,8]

Woodward and Hoffmann [8] rationalized the fact, that the [$_{\pi}2_s$ + $_{\pi}2_a$] process in the keten + diolefin reaction occurs to the exclusion of the 'allowed' [9] [2_s + 4_s] mode by invoking an ionic-type charge separation in the

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

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[2] J. D. Roberts and C. M. Sharts, *Org. Reactions*, 1962, **12**, 26.

[3] (*a*) W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, 1967, **32**, 612; (*b*) 1967, **32**, 2704.

[4] (*a*) R. Huisgen, L. A. Feiler, and P. Otto, *Tetrahedron Letters*, 1968, 4485; (*b*) *Chem. Ber.*, 1969, **102**, 3444.

[5] R. Huisgen and P. Otto, *Tetrahedron Letters*, 1968, 4491.

[6] G. Binsch, L. A. Feiler, and R. Huisgen, *Tetrahedron Letters*, 1968, 4497.

[7] M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, 1970, **53**, 417.

[8] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, 1970, p. 163.

[9] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 1965, **87**, 2046.

approach of the two reactants, initiated by the pseudovinylium ion-character of the keten in the ground state. It is evident that the experimental data indicate a substantial polar character in the transition state.[3,6-8] There is some question however about the exact structure and the amount of charge separation in the transition state and in the ground state of the keten.

It has also been shown, that the *endo*-isomers of the substituted keten adducts are, in general, thermodynamically more stable [7] and kinetically favoured. In the case of very bulky substituents (*e.g.* t-butyl) this behaviour is reversed.

The addition reactions are not readily susceptible to quantitative kinetic studies owing to the instability of the keten and the fact that the equilibrium position of the system is practically completely on the side of the dissociation products. In an attempt to obtain more information about the detailed mechanistics involved in these reactions it then appears to be a more promising approach, to look at the reverse reaction, the unimolecular concerted four-centre elimination of keten from the corresponding adducts. In a recent publication [10] based on decomposition on a g.c. injection block, relative rates of pyrolysis for a series of *endo*- and *exo*-isomers of 7-alkyl substituted bicyclo[3,2,0]hept-2-en-6-ones (BCH) have been reported. The large substituent effects observed (*endo* $\gg$ [BCH] $\gg$ *exo*), are consistent with a twisted transition state.

The only comprehensive gas-phase kinetic study on the pyrolysis of cyclobutanone derivatives is that observed for cyclobutanone itself,[11] which yields ethylene and keten in a first-order elimination process. The Arrhenius relationship observed was $\log k\ (\mathrm{s}^{-1}) = 14{\cdot}5 - 52/\theta$.

It now appears to be generally accepted, that this reaction indeed involves a concerted mechanism, rather than a biradical path, which has been demonstrated by the findings, that *trans*- and *cis*-2,3-dimethylcyclobutanone eliminate *trans*- or *cis*-butene with better than 98% retention of stereochemical configuration.[12] Furthermore, contrary to earlier interpretations,[13] the biradical concept for this reaction has been shown to be unfeasible in view of the observed absence of any stabilization energy in the $\mathrm{O{\dot{:}}CR{\cdot}\dot{C}H_2}$ radical.[14,15]

EXPERIMENTAL

Apparatus and Procedures.—The principal features of the static reaction system and the procedures used have been described earlier.[16] A Teflon-coated reactor [16] of 1·745 l volume was used in most experiments. Two experiments were carried out in a glass vessel of 1·34 l packed with glass tubing (surface to volume ratio 11·5).

An experiment was started by injecting between 0·02 and 0·4 ml of a mixture of BCH and cyclohexanone into the reaction volume. In half the experiments propene was added as a diluent. An experiment was stopped, by quenching the total reaction mixture into a trap cooled with liquid nitrogen, followed by fractionated distillation and volumetric measurement of keten (170 K) and cyclopentadiene (230 K). The gas chromatographic analysis of the cyclopentadiene fraction did not reveal any additional products. The BCH-fraction, retained at 230 K was analysed gas chromatographically. Pressures were measured with a PACE pressure transducer.

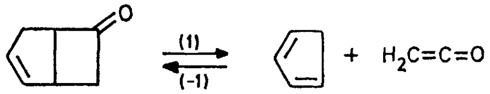
Materials.—A sample of bicyclo[3,2,0]hept-2-en-6-one was supplied by Mr. M. Rey.[7]*

Cyclohexanone and n-decane used as internal standards were >99% and propene *ca.* 99% pure (g.l.p.c.). The following mixtures of BCH with cyclohexanone (CH) or n-decane (D) as internal gas chromatographic standards were used in this study (molar ratios): (*a*) (BCH)/(D) = 2·322, (*b*) (BCH)/(CH) = 1·578, (*c*) (BCH)/(CH) = 2·049, (*d*) (BCH)/(CH) = 1·913. The composition of these mixtures was periodically checked and found to vary by only 2% over a period of 14 days.

Gas Chromatographic Analysis (GCA).—These analyses were carried out using a model 810 F + M research gas chromatograph equipped with thermal conductivity detectors. A 6 ft × 0·25 in column of 20% Carbowax 20M on Chromosorb W operated at 150 °C with a helium flow-rate of *ca.* 100 ml min^{-1} was used to analyse the BCH-fractions.

RESULTS

The pyrolysis of bicyclo[3,2,0]hept-2-en-6-one has been studied in the gas phase in the range 471—534 K. In half of the experiments propene, amounting to 16-fold the pressure of the BCH-mixture was added as diluent to the reaction system. The total pressures varied from 15 to 485 Torr. The principal reaction products are keten and cyclopentadiene. Cyclopentadiene was unambiguously identified as a reaction product. Considering the straightforward chemistry and kinetics involved in this study, it appeared superfluous to identify keten independently.



In most experiments gas chromatographic analysis was carried out only on the fraction which was quantitatively retained at 230 K; this consisted of BCH, the internal standard (cyclohexanone or n-decane), and small amounts of higher-boiling side-products (*e.g.* dicyclopentadiene). The combined light-boiling fraction consisting of keten and cyclopentadiene were usually not investigated further. In 10 experiments however, carried out in the absence of propene, both a cyclopentadiene and keten fraction were collected and volumetrically analysed. The cyclopentadiene fraction was shown by gas chromatography to consist of more than 99% cyclopentadiene. The cyclopentadiene collected amounted to between 60 and 110% and the keten-fraction only between 29 and 63% of the quantity expected

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* University of Zürich.

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[15] K. D. King, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 1970, **92**, 5541.

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on the basis of the gas-chromatographic analysis of the BCH-fraction.

In principle, our measurements would allow for a threefold kinetic analysis of the system *via* (*a*) the depletion of the starting material measured with respect to an internal standard, (*b*) the observed pressure change with time, and (*c*) the formation of cyclopentadiene measured volumetrically. Only method (*a*), using an internal standard gave reliable results due to partial oligomerization of the products. Pressure changes resulted in conversions that were consistently low. The rate constants based on pressure measurements were between 67 and 95% of those obtained from g.c. analysis.

Kinetic data for the unimolecular elimination of keten from bicyclo[3,2,0]hept-2-en-6-one

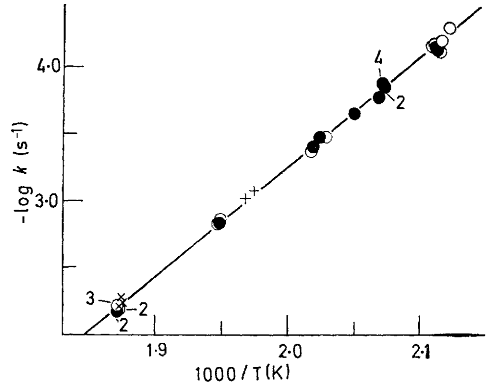
Temp. (K)	Time (min)	Starting materials BCH [a] (Torr)	Starting materials Propene (Torr)	Conversion in % of $[BCH]_0$	$k \times 10^5$ (s^{-1})
471·0	30	c 19·8	197·5	8·45	4·913
472·3	100	c 20·1	131·9	30·94	6·171
472·6	20	c 19·8	159	8·52	7·427
473·1	40	c 20·2		15·90	7·216
473·5	80	c 19·7		28·02	6·851
473·6	181	c 20·4	134·3	50·60	6·496
474·1	120	c 19·8	168	38·65	6·784
481·9	25	d 17·8		18·47	13·60
482·3	20	c 16·9		15·22	13·76
482·7	40	c 17·2		26·98	13·11
	80	d 16·3		48·62	13·88
482·8	50	d 16·9		34·26	13·98
482·9	60	c 14·8		38·00	13·28
483·5	12	c 18·0		10·94	16·09
487·8	30	c 16·4		32·61	21·94
493·0	30	b 22·5	186·2	44·35	32·56
494·1	10	b 16·0		17·94	32·97
495·3	40	c 19·8		60·67	38·89
495·7	20	c 20·0	182·8	39·73	42·20
513·1	30	c 82·3	199·2	91·78	138·8
513·3	20	c 39·4		82·76	146·5
513·6	10·58	c 223·0	184	59·18	148·0
533·1	10	a	459·2	96·83	575·7
533·4	5	a	355·2	79·91	535·1
533·9	3	a	*ca.* 500	68·15	618·6
	2	b	*ca.* 200	54·54	657·1
	3	b	*ca.* 500	68·91	649·2
	7	b 46·8	435·5	92·37	612·8
534·4	4·17	b 66·1		81·26	669·9
	4·5	b 20·0		83·60	669·6
	5	b 39·4	387·3	84·60	623·7
	10	b 32·5	297·9	97·33	603·8
506·5 [b]	10	d 25·2		39·57	83·97 [b]
508·2 [b]	20	d 25·5		68·43	96·09 [b]

[a] a, b, c, and d denote different mixtures of BCH with the internal standard (cyclohexanone or n-decane.). For details compare Experimental section. [b] Data obtained using a packed glass vessel.

First-order rate constants k_1 were calculated based on cyclohexanone or n-decane as internal standard. The back-reaction k_{-1} can be neglected, as the equilibrium position lies almost completely on the side of the dissociation products.

The kinetic data are summarized in the Table and an Arrhenius plot of the rate constants is shown in the Figure. As can be seen from these data, consistent first-order rate constants were obtained despite a more than 30-fold variation in initial pressures and conversions ranging from 8·5 to 97·3% overall and from 8·5 to 50·6% at a given temperature (471 K). Experiments carried out in a glass vessel packed with glass tubing gave rate constants in agreement with those calculated on the basis of the results obtained using the Teflon-coated reactor.

The reliability of the g.c.-internal standard method in calculating rate constants has been demonstrated by using four different starting mixtures and two totally different internal standards. Duplicate g.c. analysis of the BCH-fraction always agreed within 2·2% of the BCH present and in 24 out of the 34 experiments agreement was observed within 1·0%. The computed least-squares analysis gave (with standard errors) the Arrhenius relationship:



Arrhenius plot of the rate constants for elimination of keten from BCH, based on cyclohexanone as internal standard. Numbers indicate overlapping points; ○, propylene added; +, packed reaction vessel; ×, n-decane used as internal standard

$$\log k_1\,(s^{-1}) = (13\cdot16 \pm 0\cdot11) - (37\cdot53 \pm 0\cdot25)/\theta$$

where θ equals $2\cdot303\ RT$ in kcal mol^{-1} or $\log k_1\,(s^{-1}) = (13\cdot16 \pm 0\cdot11) - (157\cdot0 \pm 1\cdot0)/2\cdot303RT$ in kJ mol^{-1}.

DISCUSSION

Compared with the activation parameters reported for the reaction of cyclobutanone [11] the results of the present study appear to be unreasonably low. The activation energies differ by 14·5 kcal and the pre-exponential factors by $10^{1\cdot4}$. As was discussed in the introduction section, the experimental data suggest for both reactions a concerted four-centre-type reaction path, and there is no apparent reason why two basically different transition states should be involved. On the other hand it has always been assumed, that orbital symmetry-allowed concerted processes having the same type of transition states, are relatively insensitive to substituent effects. This has been shown for *e.g.* retro-Diels–Alder reactions,[17] intramolecular H-transfer reactions,[18] and others. Large differences in activation parameters and particularly in activation energies (10 kcal mol^{-1} and more) have generally been associated with biradical transition states and 'extra' stabilization energies in allyl-type radical ends.[13,19] Indeed such large differences have widely been used as a criterion to discriminate between biradical and concerted mechanisms, *e.g.* in the thermal cyclopropane, cyclobutane, and cyclobutene reactions.[19,20]

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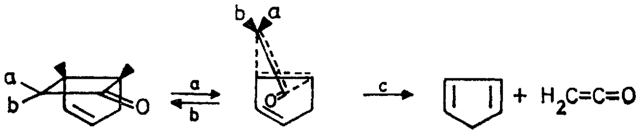
Relatively large substituent effects in a concerted reaction have been observed however for the four-centre addition–elimination reactions of the type olefin + HX $\rightleftharpoons$ alkyl halides,[21,22] involving a quadrupolar semi-ion pair-type transition state.[23,24] Based on the kinetic data observed for the elimination of HCl from chloroethane,[13] 1-chloro- and 2-chloro-butane,[13,25] 4-chlorobut-1-ene [26] and 3-chlorobut-1-ene [22] the following stabilization energies resulting from the interaction of the adjacent alkyl and vinyl groups with the positive and negative charges in these quadrupolar loose transition states are calculated: alkyl-positive 5·3, vinyl-positive 8·0, alkyl-negative 1·4, vinyl-negative 1·5.

In this context it is interesting to note, that cyclopentadiene adds exclusively to form bicyclo[3,2,0]hept-2-en-6-ones and not bicyclo[3,2,0]hept-2-en-7-ones,[7] which is to be expected from the polar considerations outlined above. The proposed detailed reaction mechanism involving a twisted polar transition state is shown below:



The twisted structure of the transition state [7,8] has been substantiated earlier [10] with the observed substituent effects. If we assume a similar amount of charge separation in the transition state as was observed for the HX eliminations from alkyl halides, one would predict about 10 kcal mol^{-1} of extra charge-stabilization energy in the polar BCH-transition state compared to cyclobutanone. The remaining 14·5—10 = 4·5 kcal mol^{-1} would then have to originate from the π-interaction of the carbonyl bond with the C=C bond in the twisted transition state.

The relatively low *A*-factor observed, which suggests a small loss of entropy in forming the transition state, would be in agreement with such an additional interaction between the two π-systems. This conclusion is also corroborated by the observed relative rates of addition of diphenylketen to cyclopentene [4b] (1·0), cyclopentadiene [3b,4b] ($3·04 \times 10^4$) and butadiene [3b] ($1·27 \times 10^2$). While the difference between butadiene and cyclopentene can be largely rationalized on polar effects alone, with only about 1·5 kcal mol^{-1} stabilization due to the interaction between the double bond and the carbonyl group, cyclopentadiene involves 3·7 kcal mol^{-1} (assuming the same pre-exponential factor).

Thus it would appear that if the thermal unimolecular keten eliminations in both bicyclo[3,2,0]hept-2-en-6-one and cyclobutanone are similar concerted processes, then it must follow, that the observed differences in activation parameters originate to a large extent from the pronounced polar character of the transition-state structure involving keten as the antarafacial partner. It is hoped that further studies on bicyclo[3,2,0]heptan-6-one and vinylcyclobutanone will clarify the nature of the transition-state interaction. From the arguments presented above we would predict the activation energies for the two processes to be about 43 and 45 kcal mol^{-1} respectively, with *A*-factors closer to that observed for cyclobutanone itself.

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