Thermal Decomposition of Cyclopent-3-enone

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The thermal decomposition of cyclopent-3-enone has been studied in the gas phase in the temperature range 325—380°. The reaction is homogeneous, first order, and probably unimolecular and yields butadiene and carbon monoxide quantitatively. The rate constants fit the Arrhenius equation (i). The decomposition is probably concerted.

$$\log(k/\text{s}^{-1}) = 14{\cdot}519 \pm 0{\cdot}069 - 214{,}440 \pm 830\ \text{J mol}^{-1}/2{\cdot}303RT \qquad \text{(i)}$$

THERE is little information in the literature regarding the elimination of carbon monoxide from simple cyclopent-3-enones. Several strained polycyclic molecules containing this system do indeed eliminate carbon monoxide readily but little quantitative information is apparently known about the kinetics of the processes.[1] In principle the decompositions may proceed *via* a two step (biradical) process or may be concerted. In fact, orbital symmetry arguments lead to the conclusion that the concerted elimination is an allowed process. In some systems it is possible to distinguish between these two extreme mechanistic types by accurate rate studies coupled with simple calculations on the thermochemical kinetics of the system. A kinetic study[2] of the elimination of carbon monoxide from ' dicyclopentadiene-1,8-dione ' (tricyclo-[5.2.1.0^{2,6}]deca-4,8-diene-3,10-dione) showed this to be a ready process and rate constants obtained in solution (dioxan) yielded the Arrhenius parameters of 15·47 and 35·2 kcal mol^{-1} for log (A/s^{-1}) and the energy of activation respectively. Unfortunately the A factor is consistent with either a biradical mechanism or a concerted process involving a ' loose ' activated complex. Further, because of unknown strain energies it is not possible to eliminate a biradical mechanism on energetic grounds in that system. The present work was undertaken to see if these problems could be resolved by studying much simpler cyclopent-3-enones and we report here the results obtained with the unsubstituted molecule.

EXPERIMENTAL

Materials.—Cyclopent-3-enone was prepared by the procedure described by Hess and Brown.[3] Following a simple distillation it was purified by fractional distillation using a spinning band column. Attempts to determine the purity of the final product by g.l.c. initially proved to be troublesome since on all the columns tried appreciable isomerization to the conjugated cyclopent-2-enone occurred. The use of Teflon tubing to contain the column packing did not reduce the extent of isomerization. The problem was overcome by using a stainless steel column containing silicone oil (MS 550) on Chromosorb P at 100° and injecting *ca.* 50 µl of concentrated aqueous ammonia onto the column every night. It appears that the isomerization was catalysed by acid sites on the column packing and the ammonia treatment removed these (though not permanently). It is possible that the incorporation of a little sodium hydroxide onto the Chromosorb would be even more efficacious. Analysis using the base treated column showed cyclopent-3-enone to be at least 99·8% pure.

All other hydrocarbon samples used were obtained commercially.

Apparatus.—Pyrolyses were carried out in Pyrex reaction vessels immersed in a high temperature (fused salt) thermostat which could be maintained to $< \pm 0{\cdot}1°$ indefinitely. A high vacuum system was used which employed greaseless stopcocks throughout and in particular those parts of the system used for storage and transfer of the reactant used only Teflon–glass high vacuum valves. The pressure in one reaction vessel was monitored using a sensitive transducer (Bell and Howell model 4-327-0003) connected to a potentiometric recorder such that a change in pressure of 1 mmHg produced a recorder chart change of 30 mm. Analysis was by g.l.c. using a Perkin-Elmer F11 instrument equipped with gas sampling valve, heated sample loop, and a flame ionization detector. Signals from the detector were integrated electronically (Hewlett–Packard model 3371 B).

RESULTS

Preliminary experiments were carried out using initial pressures of cyclopent-3-enone in the range 3—15 Torr.† Plots of log ($2P_0 - P_t$) against time were found to be linear up to at least a pressure increase of 50% (P_0 is the initial reactant pressure and P_t the total pressure at time t). Runs left for at least eight half-lives gave values of P_∞ close to $2P_0$ (within 5%). These results suggested that the decomposition was first order and that one reactant molecule gave two product molecules.

G.l.c. analysis of reaction mixtures showed the major product to be butadiene with small irreproducible amounts

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† Throughout this paper 1 Torr = 133 N m^{-2}.

[1] C. F. H. Allen, *Chem. Rev.*, 1962, **62**, 653.

[2] J. E. Baldwin, *Canad. J. Chem.*, 1966, **44**, 2051.

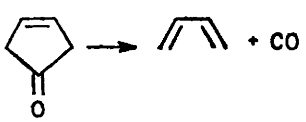
[3] H. M. Hess and H. C. Brown, *J. Org. Chem.*, 1967, **32**, 4138.

of cyclopent-2-enone. (Note that with our chromatograph carbon monoxide, the other assumed major product, could not be detected.) Subsequently we were able to show that almost all the cyclopent-2-enone observed resulted from isomerization occurring on the metal gas sample inlet system to the chromatograph or on the chromatographic column. When this difficulty was circumvented it was found that only *ca.* 0·1% of the conjugated isomer was actually produced in the reaction vessel.

At very high percentage decomposition (>90%) there were some minor fragmentation products (C_1, C_2, and C_3 hydrocarbons) probably resulting from reaction of butadiene, but even under these conditions they totalled <0·1% of butadiene.

After >50% reaction, in one case, the reaction vessel was opened to a small evacuated tube containing a small piece of silica gel cooled in liquid nitrogen. After a few minutes the transducer showed all the contents of the reaction vessel had been adsorbed (hence there could have been no appreciable hydrogen production). Finally, a run was analysed on a Perkin-Elmer 452 chromatograph using a katharometer detector and carbon monoxide was shown to be a major product.

The evidence presented strongly suggests that the thermal decomposition of cyclopent-3-enone is first order and yields butadiene and carbon monoxide quantitatively.



A series of runs was carried out at 348·2° where the pressure change was recorded using the pressure transducer and followed by analysis of the cyclopent-3-enone and butadiene by g.l.c. These results showed the pressure change to be an excellent measure of the percentage decomposition up to 50% reaction.* For subsequent experiments in the unpacked Pyrex vessel rate constants were determined from pressure change by a least squares analysis of plots of log ($2P_0 - P_t$) against time. At each temperature studied several runs were carried out and an average value for the rate constant obtained. These rate constants were found to be independent of initial reactant pressure in the range studied (3—20 Torr). The values for the rate constants at 10 temperatures from 325 to 380° are given in the Table.

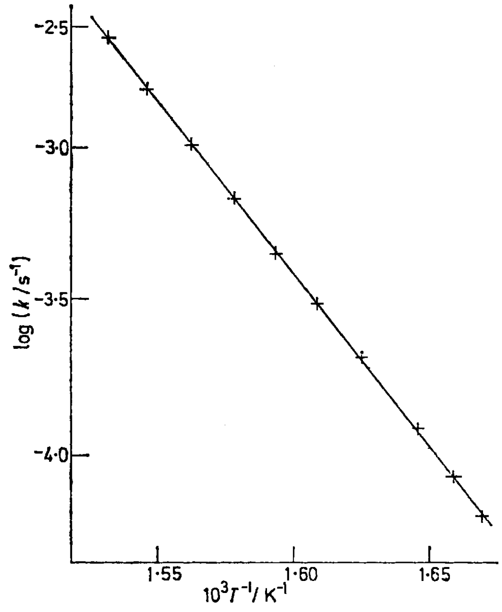
Rate constants for the thermal decomposition of cyclopent-3-enone

T/°C	325·75	329·5	334·45	342·1	348·2
$10^4k/s^{-1}$	0·643	0·862	1·233	2·10	3·12
T/°C	354·2	360·3	366·6	373·1	379·3
$10^4k/s^{-1}$	4·53	6·84	10·25	15·3	22·7

An Arrhenius plot of the results given in the Table yielded a good straight line (Figure) whose equation (1) was obtained by the usual least-squares procedure. The errors in equation (1) are standard deviations.

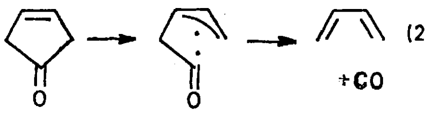
$$\log (k/\mathrm{s}^{-1}) = 14{\cdot}519 \pm 0{\cdot}069 - 214{,}440 \pm 830\ \mathrm{J\ mol^{-1}}/2{\cdot}303RT \quad (1)$$

Some pyrolyses were carried out at 345·0° in a vessel packed with Pyrex tubes which had a surface : volume ratio *ca.* 10 times that of the normal vessel. Several runs were required before reproducible results were obtained and the calculated rate constants decreased during this period and then became constant and reproducible. It is almost certain that some surface 'conditioning' takes place. The extent of reaction was determined by g.l.c. analysis and rate constants were calculated assuming first-order behaviour. The mean value for the rate constant obtained in this fashion was 2·56 × 10^{-4} s^{-1}. The calculated rate constant for this temperature using the Arrhenius equation (obtained from results only for the unpacked vessel) is 2·50 × 10^{-4} s^{-1} which indicates there can be no appreciable surface component of the reaction.



Arrhenius plot for decomposition of cyclopent-3-enone

DISCUSSION



The kinetic information makes it reasonably certain that the thermal decomposition of cyclopent-3-enone is a unimolecular process. In the present study it is possible to calculate approximately the minimum energy of activation that such a decomposition would have if it occurred by a two-step biradical mechanism (2). For the first step we calculate the energy of activation by assuming the strain energy of the ring to be the same as that for cyclopentene (21 kJ mol^{-1}) and the carbon–carbon bond strength [C(1)–C(2)] as the same as that of the corresponding bond in methyl ethyl ketone less the allylic stabilization energy (274 kJ mol^{-1}). Thus the *minimum* activation energy for the first step would be 253 kJ mol^{-1}. (This is equivalent to assuming that the reverse of the first step, the recyclization of the biradical, has a zero energy of activation.) The overall energy of activation will be 253 kJ mol^{-1} plus the energy of activation of the second step. This is likely to be small,

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* The analytical results yielded a rate constant of 3·19 ± 0·05 × 10^{-4} s^{-1} compared with the value of 3·12 × 10^{-4} s^{-1} obtained from the pressure data.

perhaps 10—20 kJ mol^{-1} but even on the unlikely assumption that it were zero the overall energy of activation could not be less than 253 kJ mol^{-1} which is still 38·5 kJ mol^{-1} *more* than the experimental value obtained in this study. We conclude therefore that the decomposition cannot occur in this fashion and must be concerted. Some additional support for this conclusion comes from a consideration of the A factor for the decomposition which implies an entropy of activation of 18·6 J mol^{-1} K^{-1}. The biradical pathway with the biradical itself being 'close to' the activated complex would be expected to have a high entropy of activation which would be unlikely to be less than 30 J mol^{-1} K^{-1} or more probably 35 J mol^{-1} K^{-1} or more. Thus the observed entropy of activation also supports a concerted process.

As mentioned in the introduction, there have been few quantitative kinetic studies of the thermal elimination of carbon monoxide from cyclopentenones. The only comparable work on dicyclopentadiene-1,8-dione was carried out in solution, but assuming these reactions are true unimolecular transformations, the change in phase should have little effect on the Arrhenius parameters. For the thermal elimination of carbon monoxide from this compound Baldwin [2] obtained an energy of activation of *ca.* 147·5 ± 3·3 kJ mol^{-1} and an entropy of activation of 41 ± 10 J mol^{-1} K^{-1}. The energy of activation obtained in the present study is thus *ca.* 67 kJ mol^{-1} greater than for the more complex compound and it is tempting to ascribe much of this difference to the differences in strain energy between cyclopentenone and bicyclo[2.2.1]hept-2-en-7-one (the appropriate system in dicyclopentadiene-1,8-dione) and the strain energies of the respective activated complexes.

The difference in strain energy between norbornene and cyclopentene is probably close to the difference between cyclopentenone and bicyclo[2.2.1]hept-2-en-7-one and taking the strain energy in the activated complex for the decompositions to be close to zero we find the required value to be $X - 21$ kJ mol^{-1} where X is the strain energy for norbornene. If our analysis is correct this would be 88 kJ mol^{-1}. Unfortunately there is some uncertainty about the exact value for the strain energy of norbornene. Turner *et al.*[4] obtained a value for the enthalpy of formation of norbornene of 86·6 kJ mol^{-1} which leads to a strain energy of 97 kJ mol^{-1}; however more recently Hall *et al.*[5] have reported a value for the enthalpy of formation of 63·3 kJ mol^{-1} which would lead to a value of only 73·6 kJ mol^{-1} for the strain energy. These differences are remarkably large and would appear well outside the expected errors in the determinations. Further work is clearly desirable. We note that our own figure falls almost half-way between the two quoted values.

Implicit in the estimation just discussed is the assumption that the activated complex is product-like in character. Thus the incipient carbon monoxide molecule will be weakly bonded in the complex with associated very low torsional modes. Hence an appreciable positive entropy of activation is to be expected. The values of $\Delta S^{\ddagger}$ obtained in the two studies are obviously consistent with this interpretation.

[4/611 *Received, 26th March,* 1974]

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[4] R. B. Turner, P. Goebel, B. J. Mallon, W. E. Doering, J. F. Coburn, jun., and M. Pomerantz, *J. Amer. Chem. Soc.*, 1968, **90**, 4314.

[5] H. K. Hall, jun., C. D. Smith, and J. H. Baldt, *J. Amer. Chem. Soc.*, 1973, **95**, 3197.