# Thermal Unimolecular Decomposition of 2,3-Dihydro-*p*-dioxin

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The thermal decomposition of 2,3-dihydro-*p*-dioxin has been studied at temperatures from 335 to 401° and pressures from 2 to 20 Torr. Under these conditions the reaction is kinetically of the first order and probably unimolecular and yields ethylene and glyoxal quantitatively. The rate constants fit the Arrhenius equation (i). The decomposition is almost certainly concerted.

$$\log (k/\mathrm{s}^{-1}) = 14{\cdot}550 \pm 0{\cdot}071 - (221{,}420 \pm 870\ \mathrm{J\ mol}^{-1})/RT\ln 10 \qquad \text{(i)}$$

THE thermal decomposition of 3,4-dihydro-2*H*-pyran to ethylene and acraldehyde is a first-order process which is almost certainly unimolecular.[1] The reaction is an orbital-symmetry-allowed one and the observed Arrhenius parameters are consistent with a concerted decomposition. Further studies of the 2-methoxy[2] and the 6-methyl[3] derivatives showed that they followed analogous pyrolytic pathways and the substituent effects were interpreted in terms of a slightly polar activated complex.[2] On the basis of the latter discussion it was concluded that the decomposition of 2,3-dihydro-*p*-dioxin would also be concerted with energetics not greatly different from those for the unsubstituted dihydropyran. The work reported in this paper represents an attempt to check this hypothesis.

## EXPERIMENTAL

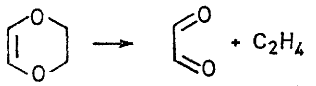
2,3-Dihydro-*p*-dioxin (Aldrich) was used as obtained except for drying over a sodium mirror; analysis by g.l.c. showed it to be >99·9% pure. Glyoxal was prepared from the commercially available aqueous solution. Removal of the water yielded a polymer which was heated with phosphorus pentaoxide and the glyoxal removed *in vacuo* and collected in a trap cooled in liquid nitrogen. All other compounds were commercially available samples.

*Apparatus*.—The kinetic apparatus used in this work has been described previously.[2,4] The progress of reactions was determined in most cases by monitoring pressure changes using a Texas Instruments precision pressure gauge model 145. In a few runs the extent of reaction was determined by g.l.c. analysis using a Perkin-Elmer F11 instrument equipped with a gas sampling system. The sample loop, transfer gas pipettes, and those parts of the vacuum system through which reaction mixtures passed were wrapped with heating tape and maintained at *ca.* 85°.

## RESULTS

Preliminary pyrolyses were carried out at 335·2° and with conversions (based on pressure measurements) up to 90%. Gaseous products were analysed using the following stainless steel columns: 3 m × 2·2 mm containing 20% w/w PPG on 60—80 mesh Chromosorb W, 3 m × 2·2 mm containing 10% w/w di-isodecyl phthalate on Chromosorb P, 2 m × 2·2 mm containing 20% w/w squalane on Chromosorb W, and 3 m × 2·2 mm containing 20% w/w fluorosilicone oil on Chromosorb W. On all these columns only one major product was found, ethylene; minor products totalled <0·5%. Some reaction mixtures after pyrolysis were transferred to a quartz cell and their near u.v. and visible spectra determined. The absorption was found to be identical with that of an authentic sample of glyoxal run under the same conditions. Finally, samples of glyoxal were analysed on the four columns described above. In no case was a major peak found, though several small peaks, initially felt to be impurity peaks in reaction mixtures, were detected. It therefore would appear that glyoxal polymerises on the columns with perhaps a small amount of chemical reaction with the various liquid phases. The apparent presence of only ethylene in reaction mixtures subjected to g.l.c. analysis is thus explained.

The information obtained from these preliminary experiments, taken together with results which showed final reaction pressures to be close to twice the initial values, is consistent with the hypothesis that 2,3-dihydro-*p*-dioxin yields ethylene and glyoxal quantitatively [reaction (1)].



(1)

Runs were carried out in the temperature range 335—401°. At each temperature plots of log $(2P_0 - P_t)$ against time were linear to at least 50% conversion (where $P_0$ is the initial reactant pressure and $P_t$ the total pressure at time $t$). When corrections were made for dead space by the method of Robinson,[5] linear behaviour was found to >85% conversion. From the appropriate plots first-order rate constants were obtained. These rate constants were found to be independent of initial reactant pressure in the range 2—20 Torr.† Thus the decomposition obeys strict first-order kinetics up to high percentage decomposition as measured by pressure changes. At conversion >90% there was evidence of some secondary decomposition of the glyoxal, which is consistent with some earlier work on this compound.[6] In a series of experiments carried out at 391·7°, the progress of reaction mixtures was monitored by both pressure change and g.l.c. analysis. As well as the normal Pyrex reaction vessel, one packed with Pyrex tubes to give it a surface : volume ratio *ca.* 14 times that of the unpacked vessel was used. For the runs which were followed by analysis *p*-dioxan was used as an internal standard (preliminary experiments showed it to be stable under the reaction conditions), and the di-isodecyl phthalate column was found to give good resolution between ethylene,

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† 1 Torr = 133 N m$^{-2}$.

[1] C. A. Wellington, *J. Chem. Soc.* (*A*), 1969, 2584.

[2] H. M. Frey, R. G. Hopkins, and N. S. Isaacs, *J.C.S. Perkin II*, 1972, 2082.

[3] C. S. Caton, *J. Amer. Chem. Soc.*, 1969, **91**, 7569.

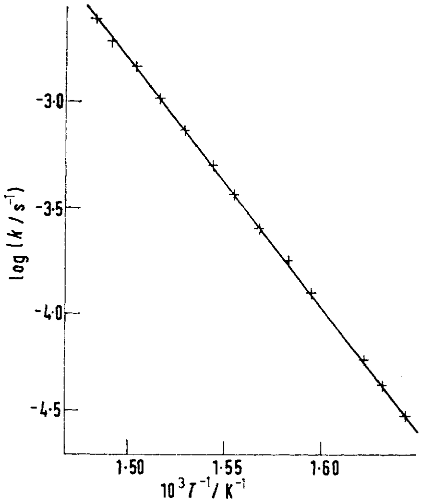
[4] A. T. Cocks and H. M. Frey, *J. Chem. Soc.* (*A*), 1969, 1971.

[5] P. J. Robinson, *Trans. Faraday Soc.*, 1965, **61**, 1655.

[6] E. W. R. Steacie, W. H. Hatcher, and J. F. Horwood, *J. Chem. Phys.*, 1935, **3**, 291.

*p*-dioxan, and 2,3-dihydro-*p*-dioxin. The rate constant obtained from pressure data alone was $1{\cdot}54 \times 10^{-3}\ \mathrm{s}^{-1}$ and that by analysis $1{\cdot}50 \pm 0{\cdot}06 \times 10^{-3}\ \mathrm{s}^{-1}$, both obtained for the normal reaction vessel. The results from the packed vessel yielded a rate constant of $1{\cdot}58 \pm 0{\cdot}07 \times 10^{-3}\ \mathrm{s}^{-1}$. The differences between these values are less than their standard deviations and show that pressure measurements provide an excellent means of determining the extent of reaction in this system. If there is any heterogeneous component of the reaction it is small in the packed vessel and almost certainly completely negligible in the unpacked reaction vessel.

The rate constants and their standard deviations obtained at 13 temperatures in the range studied are given below in Table 1, they were all obtained using the Robinson method for dead space correction. At each temperature at least four complete kinetic runs were carried out. An Arrhenius plot of the data in Table 1 gave an excellent straight line (Figure) from which the Arrhenius parameters were obtained by the method of least squares [equation (2) where the quoted errors are standard deviations].



Arrhenius plot for decomposition of 2,3-dihydro-*p*-dioxin

TABLE 1

Rate constants for thermal decomposition of 2,3-dihydro-*p*-dioxin

| | | | | |
|---|---|---|---|---|
| $t$/°C | 335·2 | 339·6 | 343·2 | 353·7 |
| $10^4k/\mathrm{s}^{-1}$ | 0·337 ± 0·003 | 0·470 ± 0·005 | 0·613 ± 0·003 | 1·28 ± 0·01 |
| $t$/°C | 358·5 | 364·6 | 370·0 | 374·5 |
| $10^4k/\mathrm{s}^{-1}$ | 1·80 ± 0·04 | 2·56 ± 0·01 | 3·68 ± 0·02 | 4·97 ± 0·05 |
| $t$/°C | 380·7 | 386·1 | 391·7 | 397·2 |
| $10^4k/\mathrm{s}^{-1}$ | 7·32 ± 0·07 | 10·3 ± 0·1 | 15·4 ± 0·1 | 19·2 ± 0·1 |
| $t$/°C | 400·9 | | | |
| $10^4k/\mathrm{s}^{-1}$ | 24·4 ± 1·0 | | | |

$$\log (k/\mathrm{s}^{-1}) = 14{\cdot}550 \pm 0{\cdot}071 - (52{,}920 \pm 210\ \mathrm{cal\ mol}^{-1})/2{\cdot}3026RT \quad (2a)$$

$$\log (k/\mathrm{s}^{-1}) = 14{\cdot}550 \pm 0{\cdot}071 - (221{,}420 \pm 870\ \mathrm{J\ mol}^{-1})/2{\cdot}3026RT \quad (2b)$$

DISCUSSION

The results obtained in the present study support the ideas presented earlier [2] and are consistent only with a concerted (one step) decomposition. However, though concerted, this reaction and many reactions of this general type are almost certainly not synchronous and the activated complex is probably very asymmetric. It is informative to compare the results obtained in the present work with those [1,7] for some related reactions whose Arrhenius parameters are given in Table 2.

TABLE 2

Arrhenius parameters for some concerted decompositions

| Reactant | $\log (A/\mathrm{s}^{-1})$ | $E_a/\mathrm{kJ\ mol}^{-1}$ | Ref. |
|---|---|---|---|
| Cyclohexene | 15·18 | 277 | 7 |
| 3,4-Dihydro-2*H*-pyran | 14·63 | 219 | 1 |
| 2,3-Dihydro-*p*-dioxin | 14·55 | 221 | This work |

It is immediately apparent that there is no simple trend in the Arrhenius parameters and in no sense does 3,4-dihydro-2*H*-pyran fall between cyclohexene and 2,3-dihydro-*p*-dioxin. We prefer the parameters obtained by Wellington (quoted in ref. 1) to those reported by Retzloff *et al.*[8] for dihydropyran. We have recalculated the Arrhenius parameters obtained by the latter workers using their published rate constants and obtain essentially the same values though with very much greater probable errors than they report, *viz.*, for log *A*, 12·83 ± 0·55 rather than 12·81 ± 0·02. However, even with the new larger errors this *A* factor appears to us unreasonably low for a fission reaction and is inconsistent with the values obtained for substitured dihydropyrans. The large increase in the rate constant for decomposition for dihydropyran compared with cyclohexene, results entirely from the big reduction in energy of activation and this has been partly rationalised on the basis of a slightly polar activated complex with extensive carbonyl double bond formation and appreciably less carbon double bond formation in the case of the heterocyclic molecule. Thus, while concerted, the activated complex is fairly close to a biradical. If a similar situation exists for the decomposition of 2,3-dihydro-*p*-dioxin then the Arrhenius parameters for its decomposition would be expected to be close to those for dihydropyran and a further large reduction in energy of activation would not be expected. This is exactly in line with the findings of this study. Were all the reactions synchronous then a further large reduction in the energy of activation similar to that between cyclohexene and dihydropyran would seem reasonable. Not only is this not observed but 2,3-dihydro-*p*-dioxin actually decomposes a little slower than dihydropyran but the factor (1·7) is too small to allow sensible discussion of its probable cause.

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[4/696 *Received, 5th April*, 1974]

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[7] M. Uchiyama, T. Tomioka, and A. Amano, *J. Phys. Chem.*, 1964, **68**, 1878.

[8] D. G. Retzloff, B. M. Coull, and J. Coull, *J. Phys. Chem.*, 1970, **74**, 2455.