Thermal Unimolecular Decomposition of 2-Ethoxy-3,4-dihydro-2*H*-pyran

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The thermal decomposition of 2-ethoxy-3,4-dihydro-2*H*-pyran in the gas phase in the temperature range 288—355 °C has been studied. Ethyl vinyl ether and acrylaldehyde are formed quantitatively by a process which is homogeneous, kinetically first order and almost certainly unimolecular. The rate constants fit the Arrhenius equation (i). Comparison of these results with those obtained for some other dihydropyran decompositions suggests that they are all concerted.

$$\log k/\mathrm{s}^{-1} = 14.465 \pm 0.055 - (202\,090 \pm 620)\ \mathrm{J\ mol^{-1}}/RT\ln 10 \qquad \text{(i)}$$

THE thermal decompositions of a 3,4-dihydro-2*H*-pyran and a number of its derivatives in the gas phase have been studied and Arrhenius parameters have been reported for the reactions.[1-5] Evidence has been presented that the reactions are unimolecular and occur by a concerted process with a rather unsymmetrical activated complex in which carbonyl double bond formation leads olefinic double bond formation. Thus substituents in the 2-position on the ring are likely to influence the energetics of the decompositions to a considerably greater extent than substituents in the 3- or 4-position. The work reported here represents a further study to obtain quantitative information about these reactions.

EXPERIMENTAL

Materials.—2-Ethoxy-3,4-dihydro-2*H*-pyran was prepared by heating a mixture of ethyl vinyl ether and acrylaldehyde (molar ratio 1.1 : 1.0) with a little hydroquinone (as a radical inhibitor) for 1 h at 190 °C in a Carius tube.[6]

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[1] C. A. Wellington, *J. Chem. Soc.* (*A*), 1966, 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, 1671.

[5] J. F. Collins, H. M. Frey, and N. S. Isaacs, *J.C.S. Perkin II*, 1975, 1.

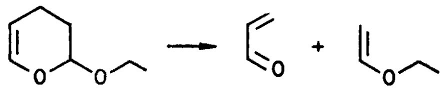
[6] C. W. Smith, D. G. Norton, and S. A. Ballard, *J. Amer. Chem. Soc.*, 1951, **73**, 5267.

The ethoxydihydropyran was separated by distillation under reduced pressure and purified by preparative g.l.c. (column packed with silicone oil on Chromosorb P followed by a column with di-isodecyl phthalate as the liquid phase). Subsequent analysis on various columns yielded chromatograms in which the major peak due to the ethoxydihydropyran was preceded by a very broad peak of rather irreproducible size. This was ultimately shown to be due to glutaraldehyde formed by acid-catalysed hydrolysis on the column or in the inlet system. (Acid-catalysed hydrolysis is known to be rapid in solution.[7]) The hydrolysis was very much reduced, though not completely eliminated, by injecting 10 μl of concentrated aqueous ammonia onto the column, and this treatment had to be repeated at intervals (whenever the broad peak reappeared). The final purity of the dihydropyran was greater than 99.9%. Before use it was dried over molecular sieves.

Apparatus.—A conventional high-vacuum static system was used. Pyrolyses were carried out in Pyrex vessels immersed in a fused salt thermostat. To minimise absorption and adsorption problems, Teflon glass valves were employed and the vacuum system was wrapped with heating tape to maintain a temperature of not less than 65 °C. The gas pipettes used to transfer mixtures from the reaction vessel to the analytical system and the inlet gas sample system of the gas chromatograph (Perkin-Elmer F11) were maintained at 85 °C. Pressures in the reaction vessel were measured by using a pressure transducer (Bell and Howell model 4.327–0003), the output from which was fed to a recorder.

RESULTS

Preliminary experiments were carried out at 329.7 °C. Analysis of reaction mixtures showed that the only products were ethyl vinyl ether and acrylaldehyde. Reproducible kinetic results were obtained after the Pyrex reaction vessel had been 'aged' by several pyrolyses of the reactant to high percentage decomposition.



Plots of ln $(2P_0 - P_t)$ against time, where P_0 is the initial reactant pressure and P_t the pressure at time t, were linear, and the rate constant was obtained by the method of least squares, assuming first-order behaviour. Correlation coefficients were better than 0.999. A series of experiments was carried out with initial pressures in the range 1—13 Torr, and, within experimental error, the rate constants were found to be independent of initial pressure. In another set of experiments the extent of decomposition was determined by g.l.c. analysis with dioxan as an internal standard. These data gave a first-order rate constant within 3% of the value obtained from the runs in which pressure changes alone were used to monitor the extent of decomposition. Finally a set of runs were carried out in a packed reaction vessel and followed by g.l.c. analysis. The surface-to-volume ratio of the packed vessel was *ca.* 28 times that of the unpacked vessel. The rate constant obtained was within 1% of the value obtained (from pressure data) in the unpacked vessel.

These preliminary experiments strongly support the view that the decomposition is homogeneous and kinetically first-order, and yields ethyl vinyl ether and acrylaldehyde quantitatively. Further, it is apparent that pressure changes may be used to monitor the extent of decomposition and hence measure rate constants.

Sets of experiments were then carried out at 14 temperatures in the range 288—350 °C. At each temperature four separate runs were followed and rate constants were determined by analysis of the pressure data as described earlier. The results are shown in Table 1. An Arrhenius plot of the data gave a good straight line from which the equation $\log k/\mathrm{s}^{-1} = 14.465 \pm 0.055 - (202\,090 \pm 620)\ \mathrm{J\ mol^{-1}}/RT\ln 10$ was obtained by the method of least squares. (The errors shown are standard deviations.)

TABLE 1

Rate constants for decomposition of 2-ethoxy-3,4-dihydropyran

Temp. (°C)	288.2	292.8	297.7	301.85
$10^4k/\mathrm{s}^{-1}$	0.451	0.613	0.936	1.29
	0.478	0.619	0.945	1.29
	0.456	0.617	0.948	1.32
	0.483	0.618	0.933	1.30
Temp. (°C)	306.5	311.2	315.8	320.6
$10^4k/\mathrm{s}^{-1}$	1.81	2.41	3.50	4.75
	1.83	2.39	3.61	4.77
	1.84	2.45	3.58	4.78
	1.86	2.48	3.61	4.74
Temp. (°C)	325.05	329.7	334.6	339.6
$10^4k/\mathrm{s}^{-1}$	6.65	9.19	12.8	17.5
	6.81	9.17	12.6	16.9
	6.91	9.40	12.8	17.2
	6.91	9.35	12.9	17.4
Temp. (°C)	344.6	349.5		
$10^4k/\mathrm{s}^{-1}$	23.1	31.4		
	23.2	31.8		
	23.1	32.6		
	23.4	31.7		

DISCUSSION

The present results are in accord with other studies on dihydropyran pyrolyses and indicate that the decompositions are all unimolecular. Table 2 presents the Arrhenius parameters and free energies of activation for a number of dihydropyrans. Because the *A* factors

TABLE 2

Arrhenius parameters and free energies of activation for some dihydropyrans

3,4-Dihydropyran	$\log A/\mathrm{s}^{-1}$	$E_a/\mathrm{kJ\ mol^{-1}}$	$\Delta G^{\ddagger}$ 600/ kJ mol^{-1}
Unsubst.	14.63	219.4	201.8
6-Me	14.45	214.2	198.7
2-MeO	14.42	203.1	187.9
2-EtO	14.47	202.1	186.4
trans-2-MeO-4-Me	14.25	201.5	188.2
cis-2-MeO-4-Me	13.96	196	186.1

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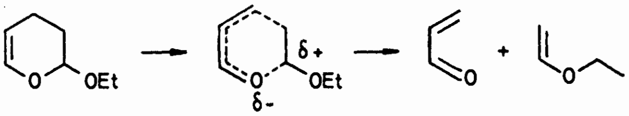
[7] R. I. Longby, jun., and W. S. Emerson, *J. Amer. Chem. Soc.*, 1950, **72**, 3079.

for the decomposition of dihydropyran and the monosubstituted derivatives are all closely similar, the reactions probably have essentially the same transition states. By comparison of the results for dihydropyran with those for cyclobutanecarbaldehyde,[2] it has been argued that dihydropyran and its derivatives decompose by a concerted (orbital-symmetry-allowed) process. Although concerted, however, the process is not completely symmetric in the sense that the carbon–oxygen bond rupture is further developed in the activated complex than the carbon–carbon bond break, with some increased polar character developing in the complex. Groups which stabilise the charge developing on C-2 will lower the energy of the complex and hence $\Delta G^{\ddagger}$. This is shown in Table 2. The stabilisation by the ethoxy-group, not unexpectedly, is little different from that by the methoxy-group; hence for the two compounds 2-methoxy- and 2-ethoxy-3,4-dihydropyran the rates of decomposition only differ by a factor of 2.



Stabilisation by the methyl group is appreciably less than that by the methoxy-group, and the methoxy-derivative decomposes nearly 200 times faster than the methyl-substituted compound. The asymmetry of the activated complex also accounts for the negligible effect of methyl substituents in the 4-position, as illustrated by the disubstituted derivatives.

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