

## The Thermal Unimolecular Decomposition of 2-Methoxy-3,4-dihydro-2H-pyran

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The thermal decomposition of 2-methoxy-3,4-dihydro-2H-pyran has been studied in the gas phase from 296 to 353 °C. Methyl vinyl ether and acraldehyde are formed quantitatively by a process which is homogeneous, of the first order, and almost certainly unimolecular. The rate constants fit the Arrhenius equation (i). Comparison of the

$$\log k/s^{-1} = 14.42 \pm 0.04 - 203,100 \pm 450 \text{ J mol}^{-1}/2.303RT \quad (i)$$

results obtained here with those for the thermal decomposition of 3,4-dihydro-2H-pyran and 6-methyl-3,4-dihydro-2H-pyran suggest that all these reactions are concerted.

THE thermal decompositions of 3,4-dihydro-2H-pyran and its 6-methyl derivative have recently been studied in the gas phase.<sup>1,2</sup> These decompositions are clean first-order reactions that are probably unimolecular. The authors discuss the nature of the transition states and especially their relationship to cyclobutanecarbaldehyde and methyl cyclobutyl ketone decompositions, but no firm conclusions are reached. We have examined the 2-methoxy-derivative in an attempt to define more closely the nature of the reaction pathway.

### EXPERIMENTAL

**Materials.**—2-Methoxy-3,4-dihydro-2H-pyran was prepared by heating equimolar quantities of acraldehyde and methyl vinyl ether at about 200 °C for 8 h in sealed Carius tubes.<sup>3</sup> The methoxydihdropyran was separated by fractional distillation and purified by preparative g.l.c. on a column packed with di-isodecyl phthalate on Chromosorb P. The final purity was better than 99.9%. Immediately before kinetic runs the material was dried with sodium.

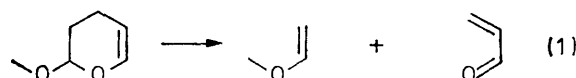
Acraldehyde and methyl vinyl ether were commercial samples.

**Apparatus.**—Pyrolyses were carried out in Pyrex reaction vessels maintained at the required temperature in a fused salt thermostat.<sup>4</sup> Greaseless stopcocks were used throughout the vacuum system to minimise problems associated with absorption of vapours in stopcock grease. To reduce adsorption of reactant on the glass tubing of the vacuum system this was wrapped with heating tape and maintained at ca. 90 °C. In a similar fashion gas pipettes and the gas sampling systems of the gas chromatograph were also maintained at 90 °C. The progress of the reaction was followed both by pressure change and analytically by g.l.c. For the former, pressures were measured with a Texas Instrument Quartz spiral manometer and for the latter a Perkin-Elmer F11 chromatograph equipped with a gas sampling valve.

### RESULTS

The thermal decomposition of 2-methoxy-3,4-dihydro-2H-pyran was investigated in the temperature range 296–353 °C. Pyrolyses in a Pyrex reaction vessel which had been 'aged' by preliminary experiments with the pyran gave reproducible kinetic results. Only two decom-

position products were observed under these conditions and they were identified as acraldehyde and methyl vinyl ether [reaction (1)]. For most of the work the progress of the



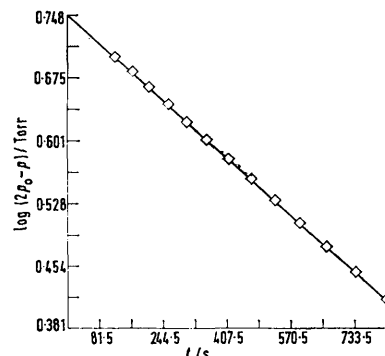
reaction was followed by monitoring the pressure of the system. That this procedure accurately mirrored the course of the decomposition was checked by analysis (see

TABLE 1

Rate constants for isomerisation at 335.7 °C

Initial reactant pressure/Torr	10 <sup>4</sup> k/s <sup>-1</sup> (ref. 6)	10 <sup>4</sup> k/s <sup>-1</sup> (ref. 5)
1.47	9.61	9.96
2.62	9.75	10.1
3.24	9.98	10.3
5.60	9.68	10.0
5.94	9.74	10.1
7.74	9.75	10.1
8.12	9.60	9.94
8.59	9.71	10.0

later). At 335.7 °C a series of runs were carried out with initial reactant pressures in the range 0.13–1.2 kN m<sup>-2</sup>



First-order rate plot (uncorrected) at 335.7 °C

(1–9 Torr). Within experimental error the rates were found to be kinetically strictly of the first order and the

\* R. I. Longley, jun., and W. S. Emerson, *J. Amer. Chem. Soc.*, 1950, **72**, 3079; C. W. Smith, D. G. Norton, and S. A. Ballard, *ibid.*, 1951, **73**, 5267.

<sup>4</sup> A. T. Cocks and H. M. Frey, *J. Chem. Soc. (A)*, 1969, 1671.

<sup>1</sup> C. A. Wellington, *J. Chem. Soc. (A)*, 1969, 2584.

<sup>2</sup> C. S. Caton, *J. Amer. Chem. Soc.*, 1969, **91**, 7569.

rate constants were independent of initial reactant concentration. Some of the values obtained are shown in Table 1. The Figure shows a typical rate plot (uncorrected) for a run at 335.7 °C. The effective dead space of the system was estimated to be *ca.* 2% and to correct for this, rate constants were determined by methods due to Allen<sup>5</sup> and Robinson.<sup>6</sup> These methods yielded rate constants which differed from one another by *ca.* 3%. The standard deviation of each rate plot was better than  $\pm 0.1\%$ .

At each of 11 temperatures in the quoted temperature range 4 complete kinetic runs were carried out, generally with an initial reactant pressure close to 0.6 kN m<sup>-2</sup>. The results are in Table 2.

Arrhenius plots of the results given in Table 2 yielded excellent straight lines from which equations (2) and (3) were obtained by the method of least squares (error limits quoted are standard deviations), where  $k_1$  refers to the rate

$$\log k_1/s^{-1} = 14.39 \pm 0.04 - 202,600 \pm 400 \text{ J mol}^{-1}/2.303RT \quad (2)$$

$$\log k_2/s^{-1} = 14.42 \pm 0.04 - 203,100 \pm 450 \text{ J mol}^{-1}/2.303RT \quad (3)$$

constant determined by the Allen method and  $k_2$  to that obtained by the Robinson procedure.

A series of runs were carried out at 340.5 °C in which the extent of reaction was determined by analytical g.l.c. By use of this procedure a rate constant of  $1.33 \times 10^{-3} \text{ s}^{-1}$  was

TABLE 2

Rate constants for the decomposition of 2-methoxy-3,4-dihydro-2H-pyran

		Allen method <sup>5</sup>					
<i>t</i> /°C		296.1	299.2	303.3	311.0	315.9	325.4
$10^4 k_1/s^{-1}$		0.634	0.782	1.08	1.88	2.65	5.16
		0.619	0.801	1.11	1.88	2.65	5.24
		0.621	0.811	1.09	1.89	2.69	5.20
		0.615	0.819	1.09	1.89	2.71	5.24
<i>t</i> /°C		335.7	340.5	345.5	350.7	353.4	
$10^4 k_1/s^{-1}$		10.2	14.2	19.5	26.6	32.2	
		10.1	13.9	19.2	26.5	32.4	
		10.3	14.0	19.0	27.1	30.7	
		10.0	14.1	19.3	26.9	31.7	
		Robinson method <sup>6</sup>					
<i>t</i> /°C		291.1	299.2	303.3	311.0	315.9	325.4
$10^4 k_2/s^{-1}$		0.610	0.759	1.05	1.80	2.55	4.98
		0.601	0.761	1.07	1.80	2.55	5.04
		0.598	0.770	1.05	1.82	2.60	5.01
		0.586	0.790	1.06	1.82	2.26	5.00
<i>t</i> /°C		335.7	340.5	345.5	350.7	353.4	
$10^4 k_2/s^{-1}$		9.78	13.7	18.8	25.7	31.0	
		9.75	13.2	18.5	25.7	31.3	
		9.98	13.6	18.7	26.3	29.7	
		9.68	13.6	18.6	25.9	30.6	

obtained. The values obtained by pressure measurements were  $1.40 \times 10^{-3} \text{ s}^{-1}$  and  $1.35 \times 10^{-3} \text{ s}^{-1}$  by the Allen and Robinson methods respectively. On this basis we prefer the Robinson procedure for this work, but recognise that this is largely a subjective choice. In any event, the Arrhenius parameters of the two equations differ by less than their standard deviations.

<sup>5</sup> A. O. Allen, *J. Amer. Chem. Soc.*, 1934, **56**, 2056.

<sup>6</sup> P. J. Robinson, *Trans. Faraday Soc.*, 1965, **61**, 1655.

A series of runs was carried out in a packed reaction vessel with a surface-to-volume ratio 10 times that of the unpacked vessel. Initially, as well as peaks corresponding to acraldehyde and methyl vinyl ether, another peak appeared on the gas chromatogram. After several runs this peak became smaller but still amounted to 2–3% of the products. Treatment of the vessel with a sample of hexamethyldisilazane resulted in a further diminution of this peak to *ca.* 1% of the observed products. This product was never observed in the unpacked vessel and is almost certainly the result of a heterogeneous reaction. After the treatment described the measured rate constant for the reaction in the packed reaction vessel at 340.5 °C was found to be  $1.42 \times 10^{-3} \text{ s}^{-1}$  which is in reasonable agreement with that obtained in the unpacked vessel.

## DISCUSSION

The thermal decompositions of 3,4-dihydro-2H-pyran and its 6-methyl and 2-methoxy-derivatives yield the data in Table 3. The close similarity of the *A* factors is

TABLE 3

Rate parameters for dihydropyran decompositions

	$\log A/s^{-1}$	<i>E</i> /kJ mol <sup>-1</sup>	$\Delta G^\ddagger_{600}/\text{kJ mol}^{-1}$
3,4-Dihydro-2H-pyran	14.63	219.4	201.8
6-Methyl-3,4-dihydro-2H-pyran	14.45	214.2	198.7
2-Methoxy-3,4-dihydro-2H-pyran	14.42	203.1	187.9

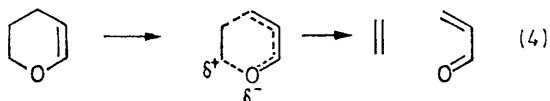
strong evidence that all three reactions have essentially the same transition states.

The decomposition of 3,4-dihydro-2H-pyran yields ethylene and acraldehyde, the same products as are obtained from the thermal decomposition of cyclobutanecarbaldehyde. Much evidence has been presented to show that the decomposition of the latter compound is *via* a biradical intermediate, and indeed a simple concerted process is orbital symmetry-forbidden. While the heat of formation of cyclobutanecarbaldehyde does not appear to have been determined we may estimate the difference between the heats of formation of the aldehyde and the dihydropyran as 43 kJ mol<sup>-1</sup> (at 298 K)<sup>7</sup> with a probable accuracy of *ca.*  $\pm 10\%$ . At 600 K the difference is unlikely to differ appreciably from 40 kJ mol<sup>-1</sup>. If the dihydropyran decomposed *via* the same biradical as suggested for the decomposition of cyclobutanecarbaldehyde then it would be expected to react more than 1000 times more slowly whereas it reacts approximately three times as rapidly as the aldehyde. An exactly similar argument applies to the decompositions of 6-methyl-3,4-dihydro-2H-pyran and methyl cyclobutyl ketone where again the dihydropyran derivative reacts more rapidly (by a factor of 10) rather than much more slowly than the ketone. The biradical involved in the cyclobutanecarbaldehyde decomposition

<sup>7</sup> For methods of estimating thermochemical properties see S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rogers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279. We estimate the heat of formation of cyclobutanecarbaldehyde at 298 K to be  $-82 \text{ kJ mol}^{-1}$ ; the value for 3,4-dihydro-2H-pyran is known ( $-125 \text{ kJ mol}^{-1}$ ).

is essentially that with the lowest energy, so even when allowances are made for possible differences in barriers to recyclisation of other isomeric biradicals, the conclusion appears inescapable, on energetic grounds alone, that the decomposition of the dihydropyran must be a concerted process. Unlike the decomposition of cyclobutanecarbaldehyde, the reaction of 3,4-dihydro-2*H*-pyran is an orbital symmetry-allowed concerted process.

Although it is clear that the decomposition of the dihydropyran and its 6-methyl derivative are concerted processes, it is not suggested that the breaking of both the C-O bond and the C-C bonds occurs symmetrically. In fact the evidence all points to a slightly polar transition state with the C-O bond rupture 'leading' that of the C-C bond. Again this is reasonable on energetic grounds since these two bonds are of intrinsically the same strength but the C-O bond rupture results in the formation (4) of a carbonyl group with much greater  $\pi$ -bond energy than the carbon double bond formed as a result of the C-C bond rupture.



In some ways the transition complex has close similarities with that for the aliphatic Claisen rearrangement, and indeed a comparison of the energetics of the Claisen with the Cope rearrangement (the former class have energies of activation more than 20 kJ mol<sup>-1</sup> less than the latter) suggests that the asymmetrical complex is of appreciably lower energy than a symmetrical one. These factors go some way towards explaining why the dihydropyran decomposes with a value for  $\Delta G^\ddagger$

nearly 50 kJ mol<sup>-1</sup> less than for the corresponding decomposition of cyclohexene, though it must be admitted that here the difference in reactivity is greater than could have been expected.<sup>8</sup>

Methyl substitution in the 6-position would be expected to lead to a small rate acceleration and this is observed with a reduction in  $\Delta G^\ddagger$  (see Table 3) of 3.1 kJ mol<sup>-1</sup>. In the analogous Claisen rearrangements (allyl vinyl ether and allyl propenyl ether) the corresponding change is a little larger, *viz.*, 5.4 kJ mol<sup>-1</sup>. Substitution in the 2-position should have a slightly bigger effect. Unfortunately data for the 2-methyl-3,4-dihydro-2*H*-pyran are not available. Certainly the 2-methoxy-compound reported here does show a large reduction in  $\Delta G^\ddagger$  of 13.9 kJ mol<sup>-1</sup>, but a greater effect is to be expected for a methoxy-group than a methyl group. In these compounds the effect of substituents appears relatively small and less than in the Claisen rearrangement (and very much less than for HX elimination from alkyl halides). We are led to conclude that while the complex is highly asymmetric with respect to the extent of C-O and C-C breakage it is not highly polar.

The foregoing considerations lead to the following expectations, (1) that 2-methyl-3,4-dihydro-2*H*-pyran should decompose with a value of  $\Delta G^\ddagger_{600}$  of *ca.* 197 kJ mol<sup>-1</sup>, and (2) dioxen should decompose to glyoxal and ethylene with rate constants not greatly different from those reported for the dihydropyran.

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<sup>8</sup> M. Uchiyama, T. Tomioka, and A. Amano, *J. Phys. Chem.*, 1964, **68**, 1878.