The Thermal Decomposition of *cis*-2,6-Dimethyl-3,6-dihydro-2*H*-pyran

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The pyrolysis of the title compound has been studied in the gas phase, in the temperature range 300—351 °C. The decomposition yields acetaldehyde and *trans*-penta-1,3-diene by a homogeneous process which is kinetically first order and probably unimolecular. The rate constants fit the Arrhenius equation (i). Consideration of the energetics of the process as well as the stereospecific nature of the products lead to the conclusion that the decomposition is a concerted process.

$$\log k/\mathrm{s}^{-1} = 13.91 \pm 0.10 - (196\,300 \pm 1\,200\ \mathrm{J\ mol^{-1}})/RT\ln 10 \qquad \text{(i)}$$

THE kinetics of the thermal decompositions of a large number of cyclic molecules have been studied in the past decade. The motivations have been very diverse, but where accurate results were pursued in the gas phase the studies have often been related to the determination of Arrhenius parameters. These in turn were used for attempts to determine detailed structures of activated complexes, to see to what extent thermochemical kinetics could be used to predict Arrhenius parameters, and in some cases to test various aspects of unimolecular reaction rate theories. In many cases the molecules were also of interest in relation to suggestions based on orbital symmetry control of chemical reactions.

Several studies have been reported on the pyrolysis of 3,4-dihydropyran[1] and various derivatives[2] but no detailed data have appeared on the 5,6-dihydropyrans. While the reason for the present work was partly related to our general interest in the unimolecular decomposition of cyclic molecules, it was also related to some studies being carried out on an oxetan pyrolysis where a 5,6-dihydropyran could have been a major or minor product depending on its thermal stability.

EXPERIMENTAL

2,6-Dimethyl-3,6-dihydro-2*H*-pyran (DMDHP) was prepared by hydrogenation (3 atm.; 2 h) of 2,6-dimethyl-γ-pyrone (Aldrich; 0.069 mol) in ethanol (100 ml) in the presence of platinum dioxide (0.002 mol) until the uptake of hydrogen (3.1 equiv.) ceased. The mixture of stereoisomers of 2,6-dimethyltetrahydropyran-4-ol (0.046 mol) was refluxed (2 h) with thionyl chloride (0.05 mol) and pyridine (0.05 mol) to yield, after work-up and distillation (50° and 15 mmHg), a mixture of isomers of 4-chloro-2,6-dimethyltetrahydropyran (0.024 mol). Dehydrochlorination of the mixture by heating with potassium hydroxide (0.1 mol) and ethane-1,2-diol (20 ml) allowed the separation by distillation of the crude dihydropyran (0.015 mol), b.p. 110—120° at 760 mmHg.[3] Preparative g.l.c. (20 ft × $\frac{1}{4}$ in 10% Carbowax 20M column at 100°) gave the major component as pure *cis*-2,6-dimethyl-3,6-dihydro-2*H*-pyran, $\nu_{\max.}$ (film) 3 030, 2 970, 1 370, 1 360, 1 310, 1 185, 1 110, 1 095, 1 065, 1 050, and 765 cm^{-1}; δ_H (100 MHz; CCl_4) 1.18 (3 H, d, *J* 7.3 Hz, CH_3), 1.20 (3 H, d, *J* 6.8 Hz, CH_3), 1.94 (2 H, m, 2 × H-5), 3.70 (1 H, sextet, *J* 6.6 Hz, H-6), 4.26 (1 H, m, H-2), and 5.6—6.0 (2 H, m, H-3 and -4); δ_C ($CDCl_3$) 21.5, 21.8, 32.7, 70.1, 71.0, 124.2, and 131.4 p.p.m.

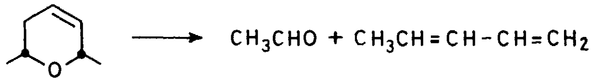
Acetaldehyde and *cis*- and *trans*-penta-1,3-diene were commercial samples.

Apparatus.—A conventional high vacuum system was used as described previously.[4] Pressure changes were monitored using a pressure transducer (Bell and Howell model 4–327–0003) whose output was displayed on a chart recorder.

Analysis was by g.l.c. using a Perkin-Elmer F33 fitted with a gas sampling valve and a flame ionization detector. Signals from the detector were fed to a Hewlett–Packard model 3380A integrator. Several columns were found to be satisfactory but in runs where an accurate ratio of *cis*- and *trans*-pentadiene isomers was required a 4 m × 2 mm column containing bis-2-ethylhexyl sebacate was used.

RESULTS

A preliminary experiment carried out at 320 °C showed that the only products of the reaction were acetaldehyde and *cis*- and *trans*-penta-1,3-diene. Careful analysis of runs at 353 °C showed that the pentadienes consisted of 97% *trans*- and 3% *cis*-isomer. However, at these temperatures there is a slow isomerisation to the equilibrium mixture[5] (30% *cis*) and separate pyrolyses of pure *trans*-penta-1,3-diene under the same experimental conditions as the pyran pyrolyses suggest that much of the *cis*-diene probably arises by the secondary decomposition of the initially formed *trans*-isomer.



It proved possible to monitor the extent of reaction by pressure measurements. Pressure changes were shown by g.l.c. analysis to be a good measure of percentage decomposition and plots of $\log(2P_0 - P_t)$ against time were linear (where P_0 was the initial reactant pressure and P_t the total pressure at time t) indicating that first-order kinetics were obeyed. Runs carried out at 328.8 °C with initial reactant pressures from 0.3 to 9 mmHg and in one case with the addition of 40 mmHg of nitrogen were analysed by g.l.c. and all yielded the same rate constant, confirming the first-order nature of the kinetics.

Runs were carried out with initial reactant pressures in the range 3—7 mmHg and within the temperature range 300—351 °C. At each temperature, rate constants were determined from a least squares analysis of the appropriate pressure plots. These results are shown in the Table.

Rate constants for the decomposition of DMDHP

t/°C	10^4k/s^{-1}	t/°C	10^4k/s^{-1}
300.8	1.161	328.3	7.539
300.8	1.127	328.3	7.007
300.9	1.219	336.4	12.09
300.8	1.046	336.4	12.22
311.1	2.203	336.4	11.71
311.1	2.164	336.4	12.42
311.2	2.353	336.4	12.03
311.2	2.372	343.4	19.49
311.1	2.218	343.4	19.64
320.9	4.279	343.35	18.88
320.8	4.294	343.35	19.84
320.8	4.607	343.35	18.62
320.9	4.474	350.5	29.62
328.1	7.267	350.5	30.08
328.1	7.325	351.0	29.65
328.1	7.144		

Note the rate constants are quoted as obtained from the least squares analysis and are not further ' rounded.' This does not imply an accuracy of better than 1%.

An Arrhenius plot of the results in the Table yielded equation (1) where the quoted errors are one standard deviation.

$$\log k/\mathrm{s}^{-1} = 13.91 \pm 0.10 - (196\,300 \pm 1\,200\ \mathrm{J\ mol^{-1}})/RT\ln 10 \quad (1)$$

A series of experiments was carried out at 328.9 °C using the normal unpacked reaction vessel and one filled by glass tubes to increase its surface : volume ratio by a factor of 14. For runs in both reaction vessels the extent of reaction was determined by g.l.c. analysis. The rate constants obtained for the runs in the packed vessel were between 5 and 6% greater than in the unpacked vessel and suggests that any heterogeneous component of the reaction in the unpacked vessel must be negligible.

DISCUSSION

The experimental results show the thermal decomposition to be a homogeneous, kinetically first-order process. By comparison with decompositions of other cyclic molecules and taking into account the experimental findings, it seems probable that the reaction is unimolecular.

Two mechanistic extremes have been used to discuss the decomposition of small ring compounds. In one, the so-called biradical mechanism, the initial process involves the breaking of a single ring bond leading to a biradical capable, for example, of free or relatively free internal rotation. In the other extreme, bond breaking and making takes place in a concerted manner which in the limit is completely synchronous. Of course, while most decompositions will be somewhere between these extremes they may be appreciably closer to one than the other. It is sometimes possible to say quite a lot about the decomposition pathway and hence the structure of the activated complex based on such considerations as thermochemical kinetics, orbital symmetry control, and experimental observations on the stereochemistry of reactants and products.

In the present case, the Arrhenius parameters that have been obtained rule out a biradical mechanism. Thus the low A factor for a ring fragmentation reaction make it clear that the activated complex must be a ' tight ' one since its entropy is little different to that of the reactant itself. The low energy of activation also rules out a simple bond cleavage process. If we consider first the unsubstituted 3,6-dihydro-2*H*-pyran molecule then the two weakest bonds in the molecule are those between the oxygen and C(2) and between C(5) and C(6). Breaking of either of these bonds leads to the biradicals (I) and (II), respectively.


(I)


(II)

We estimate the energy required to break the bond to form (I) as *ca.* 276 and to form (II) as *ca.* 290 kJ mol^{-1}. The effect of the presence of the two methyl substituents are likely to be small. We would expect the structure corresponding to (I) to be little stabilised by the methyl groups, certainly by not more than 4 kJ mol^{-1}. For structure (II) the stabilisation effect might be a little greater, though even here most unlikely to exceed 8 kJ mol^{-1}. Thus the overall effect, though small, makes the energy required to break the two weakest bonds fairly close to one another. The next stage of the reaction requires the breaking of another bond in the biradical and even if this were to proceed with zero energy of activation, the overall energy of activation could not be much less than 276 kJ mol^{-1}, *i.e.* some 80 kJ mol^{-1} more than experimentally observed.

It therefore appears certain that the decomposition occurs *via* a concerted process and in this respect is similar to the decompositions of the 3,4-dihydro-2*H*-pyrans.[2] It is probable that a similar activated complex is involved.

As for the 3,4-dihydro-2*H*-pyrans, it is probable that the rupture of the O–C(2) bond is more developed in the complex than that of the C(5)–C(6) bond and further that the complex is likely to have appreciable polar character [with a positive charge developing on C(2) and a negative charge on the oxygen atom].

The preferred conformation of the methyl groups in the reactant is with them both pseudo-equatorial since there is strong steric interaction if they are axial. In the concerted decomposition the methyl group on C(2) must rotate through a relatively small angle, away from the pyran ring, to yield the *trans*-penta-1,3-diene. The *cis*-diene can only be obtained by a large angle rotation of the methyl group into the plane of the ring. Since the A factor indicates a tight complex, this latter process would involve strong steric repulsion and hence would be an appreciably higher energy pathway than the *trans*-diene forming pathway. Hence the essentially stereospecific decomposition to the *trans*-diene is easily explicable.

We may make a crude estimate of the energy difference between the pathways leading to the *trans*- and *cis*-dienes as follows. Direct pyrolyses of the *trans*-diene under our reaction conditions show that not more than 50% of the observed *cis*-diene can have been formed from the dihydropyran directly. If we assume that both pathways have the same *A* factor this would imply an energy difference of 21 kJ mol^{-1}. This represents a minimum value since it is possible that the direct pathway to the *cis*-diene has been over-estimated and it is almost certain that the higher energy process also has a higher *A* factor.

A more detailed discussion of the energetics of the decomposition and the effect of substituents must await data on unsubstituted 3,6-dihydro-2*H*-pyran.

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