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The Thermal Decomposition of *cis*- and *trans*-2-Methoxy-4-methyl-3,4-dihydro-2*H*-pyran

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The thermal decomposition of both *cis*- and *trans*-2-methoxy-4-methyl-3,4-dihydro-2*H*-pyran has been investigated in the gas phase from 287 to 345°. In this temperature range both isomers decomposed to give crotonaldehyde and methyl vinyl ether by a homogeneous process that obeyed first-order kinetics. The data for the *trans*-isomer yielded the Arrhenius equation (i). Similarly the *cis*-isomer gave equation (ii). These results

$$\log k_1/\mathrm{s}^{-1} = 14{\cdot}246 \pm 0{\cdot}106 - (201{\cdot}46 + 1{\cdot}20\ \mathrm{kJ\ mol^{-1}})/RT\ln 10 \qquad \text{(i)}$$

$$\log k_2/\mathrm{s}^{-1} = 13{\cdot}958 \pm 0{\cdot}062 - (196{\cdot}00 \pm 0{\cdot}70\ \mathrm{kJ\ mol^{-1}})/RT\ln 10 \qquad \text{(ii)}$$

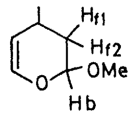
are discussed in terms of a unimolecular decomposition occurring by a concerted mechanism.

THE thermal decomposition of 3,4-dihydro-2*H*-pyran is a homogeneous first-order process in the gas phase.[1] The available evidence suggests that the reaction is unimolecular and concerted. Further support for this mechanism has been obtained from studies on the pyrolysis of some substituted dihydropyrans, especially the kinetic measurements on the 2-methoxy [2] and 6-methyl derivatives.[3] This work has allowed more detailed suggestions to be made about the structure of the activated complex and leads to the conclusion that the complex is far from symmetrical in the sense that C–O bond rupture is appreciably more developed than C–C bond rupture (and, conversely, C=O bond formation 'leads' C=C bond formation). To determine the effects of stereochemistry on reaction rate and see whether further insight could be gained into the nature of the activated complex, by determining rate parameters for geometrical isomers, we undertook the work reported in this paper.

EXPERIMENTAL

Materials.—A mixture of *cis*- and *trans*-2-methoxy-4-methyl-3,4-dihydro-2*H*-pyran (MMDP) was prepared by heating equimolar quantities of methyl vinyl ether and crotonaldehyde in a bomb at 160° overnight. The required MMDP was obtained from the reaction mixture as a pale yellow liquid by distillation under reduced pressure (15 mmHg; 56°). Analysis by g.l.c. on four different columns showed the presence of two major components with peak areas in the ratio of 2 : 3 with the smaller peak emerging first. We designated these isomers A and B, respectively. The two isomers were separated by preparative g.l.c. using a Perkin-Elmer 452 instrument with a fluorosilicone oil column and operated at 65°. Liquid samples (*ca.* 60 μl) were the largest that could be injected if reasonable resolution was to be obtained. The samples of the two isomers were essentially free from impurity save for the presence of the other isomer. Thus 'pure' A contained 6% B and 'pure' B *ca.* 4% A.

In the n.m.r. spectra of the two isomers, double resonance experiments showed that H_b was coupled to H_{f1} and H_{f2} and no others. In isomer A the two *J* values were almost identical at *ca.* 2·6 Hz whereas in isomer B they were 7·4 and 2·4 Hz. Identical couplings would arise with H_b equatorial and H_{f1} and H_{f2} axial and equatorial. Non-identical couplings would result from H_b in the axial conformation. The methyl group is expected to be ψ-equatorial and the preferred conformation for the methoxy-group axial. Thus A was identified as the *trans*- and B as the *cis*-isomer.



Both isomers were dried over a sodium mirror and degassed before each run. All other compounds used were commercially available samples.

Apparatus.—A conventional 'static' high vacuum

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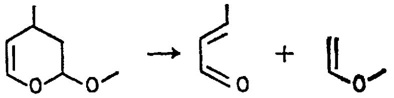
[1] C. A. Wellington, *J. Chem. Soc.* (*A*), 1966, 2584.
[2] H. M. Frey, R. G. Hopkins, and N. S. Isaacs, *J.C.S. Perkin II*, 1972, 2082.
[3] C. S. Caton, *J. Amer. Chem. Soc.*, 1969, **91**, 7569.

kinetic apparatus equipped with greaseless stopcocks was used which was identical in all important details with those described earlier.[2] Pyrolyses were carried out in Pyrex reaction vessels immersed in a high temperature fused salt thermostat.[4] Pressure changes were monitored using a Bell and Howell model 4-327-0003 transducer whose output was fed to a potentiometric recorder. Analysis of reaction mixtures was by g.l.c. using a Perkin-Elmer F11 instrument fitted with a heated gas sampling valve and a flame ionisation detector. Signals from the detector were fed to a recorder fitted with a ball and disc integrator.

RESULTS

In preliminary studies both *cis*- and *trans*-MMDP were pyrolysed and the reaction mixtures analysed by g.l.c. Both isomers gave the same two products which were identified as methyl vinyl ether and crotonaldehyde with only trace amounts of any other compounds. These trace components which were eluted before the ether on the chromatogram totalled well under 0·1% of the products and no further attempt was made to identify them. Several pyrolyses were required before reproducible results were obtained and this was attributed to the necessity of ' ageing ' the reaction vessel surface.



trans-*MMDP*.—In a series of runs, *trans*-MMDP was admitted to the heated reaction vessel and the pressure changes monitored by displaying the output of the transducer using a variable speed potentiometric recorder. Hence the total pressure at any time could be obtained from chart measurements. For each run a number of pressure, time pairs of datum points were obtained and from these the corresponding rate constant obtained by a least squares treatment of the log $(2P_0 - P_t)$ against time plot (where P_0 is the initial pressure and P_t the total pressure at time t). These plots were accurately linear (correlation coefficients $>0{\cdot}9998$) and the rate constants were independent of the initial reactant pressure from 4 to 12 Torr. At each of 10 temperatures in the range 291—345° several runs were carried out and rate constants evaluated from the pressure changes. The mean values obtained at each temperature are shown in Table 1.

TABLE 1

Rate constants for the decomposition of *trans*-MMDP

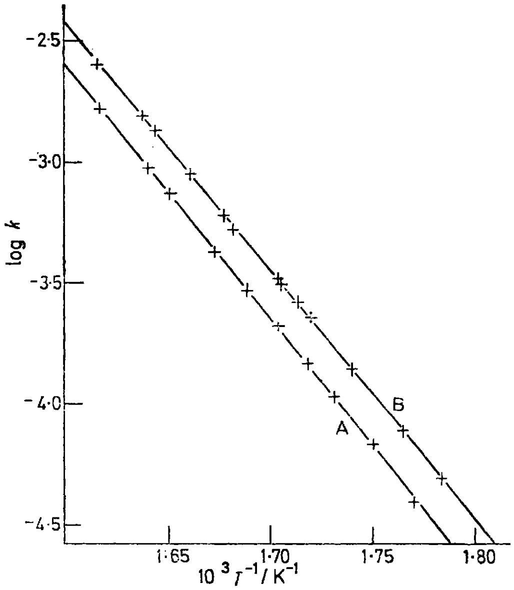
T/°C	291·65	298·2	304·4	308·7	313·6
10^4k_1/s^{-1}	0·395	0·681	1·069	1·47	2·10
T/°C	318·9	324·4	332·3	336·0	345·1
10^4k_1/s^{-1}	2·96	4·245	7·41	9·37	16·43

The results in Table 1 are shown as an Arrhenius plot in the Figure. From this plot the Arrhenius parameters were determined by least squares [equation (1)]. The error limits are 1 standard deviation.

$$\log k_1/\text{s}^{-1} = 14{\cdot}246 \pm 0{\cdot}106 - (201{\cdot}46 \pm 1{\cdot}20\ \text{kJ mol}^{-1}/RT\ln 10) \quad (1)$$

To confirm that pressure changes were an appropriate method to monitor composition, a series of runs was carried out at 312·2° in which the extent of reaction was determined analytically by g.l.c. Since it proved difficult to determine all the components of the reaction mixture with the same precision, 1-methylcyclohexene was used as an internal standard and the percentage of *trans*-MMDP decomposed determined by reference to this standard. In this way a rate constant of $1{\cdot}90 \times 10^{-4}$ s^{-1} was obtained. The value calculated from the Arrhenius equation (based only on pressure data) is $1{\cdot}86 \times 10^{-4}$ s^{-1} which indicated the validity of using pressure change to determine rate constants in this system.

cis-*MMDP*.—Rate constants for the thermal decomposition of the *cis*-isomer were determined in the same manner as for the *trans*-compound. The mean rate constants obtained at 13 temperatures in the range 287·4—345·4° are given in Table 2. As with the *trans*-isomer the appropriate first-order plots were linear and the rate constants independent of pressure from 4 to 12 Torr.



Arrhenius plots for A, *trans*- and B, *cis*-MMDP

TABLE 2

Rate constants for the decomposition of *cis*-MMDP

T/°C	287·4	293·4	301·55	308·25	310·5
10^4k_2/s^{-1}	0·489	0·772	1·40	2·269	2·656
T/°C	313·35	313·80	321·2	322·9	328·7
10^4k_2/s^{-1}	3·15	3·276	5·284	5·974	8·94
T/°C	334·9	337·15	345·4		
10^4k_2/s^{-1}	13·37	15·49	25·03		

While 4 figures are often shown for the rate constants, this is not intended to indicate such a high precision. However, these were the values used without rounding in the subsequent least squares analysis to obtain the Arrhenius parameters.

The results in Table 2 are shown in the Figure and the Arrhenius equation (2) was obtained from these results.

$$\log k_2/\text{s}^{-1} = 13{\cdot}958 \pm 0{\cdot}062 - (196{\cdot}00 \pm 0{\cdot}70\ \text{kJ mol}^{-1}/RT\ln 10) \quad (2)$$

A series of runs was carried out at 313·5° where the extent of reaction was determined by g.l.c. analysis using 1-methylcyclohexene as an internal standard. These runs

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[4] A. T. Cocks and H. M. Frey, *J. Chem. Soc.* (*A*), 1969, 1671.

yielded a rate constant of $3{\cdot}40 \times 10^{-4}$ s^{-1} which compares reasonably with the value of $3{\cdot}21 \times 10^{-4}$ s^{-1} obtained from the Arrhenius equation.

To determine whether there was an appreciable heterogeneous component of the reaction some pyrolyses of mixtures of 1-methylcyclohexene and *cis*-MMDP were carried out in a reaction vessel packed with Pyrex tubes. The packed reaction vessel had a surface : volume ratio 14 times that of the unpacked vessel. Several pyrolyses were necessary before anything approaching reproducible results could be obtained. Thus initially large and variable amounts of two ' new ' products appeared in the chromatogram and there was considerable conversion of *cis*- into *trans*-MMDP. Even after many pyrolyses some of the ' new ' products were still formed and there remained some *cis–trans*-isomerisation of the reactant. Nevertheless the overall rate of decomposition of the *cis*-MMDP (corrected for the formation of the *trans*-isomer) was close to that obtained in the unpacked vessel. Since the two new products were not observed in the unpacked vessel we attribute these entirely to a heterogeneous reaction process, and their absence as indicative that such processes were not significant in the unpacked vessel. While it did not prove possible to identify the heterogeneous products, the one formed in larger yield (*ca.* 5% of the total product yield) was eluted before the methyl vinyl ether and is therefore a low molecular weight (fragmentation) product.

DISCUSSION

Evidence that the decomposition of 3,4-dihydro-2*H*-pyran (DHP) as well as some of its derivatives occurs by a concerted process has already been discussed.[2] Further, it has been suggested that the activated complex is asymmetric with respect to the extent of C–O and C–C breakage but only slightly polar. The data obtained in the present work together with relevant previous studies are given in Table 3. Inspection of Table 3 makes it immediately clear that the free energies of activation for the two compounds reported here are very close to that for 2-methoxy-DHP. Thus the overall effect of the methyl group in the 4-position is small. *trans*-MMDP can exist in the most favourable conformation with the methyl group in the equatorial and methoxy-group in the axial position, whereas for *cis*-MMDP this is not possible. This isomer is presumed to have both the methyl and methoxy-groups in equatorial positions. For a large number of cases in six-membered rings the value for ΔG(equatorial ⟶ axial) for the methyl group is *ca.* 7·5 kJ mol^{-1}. In the sugars, pyranosides are more stable with the methoxy-group axial when next to oxygen and ΔG for this is *ca.* 6 kJ mol^{-1}. Thus for *trans*-MMDP one expects virtually all molecules to be in the single conformation since here $\Delta G = 13{\cdot}5$ kJ mol^{-1}. This is in complete agreement with the observed n.m.r. spectrum of this isomer. For *cis*-MMDP the difference between the two conformations would only be between 1 and 2 kJ mol^{-1} on the basis of the values quoted above. This would yield a ratio of conformers of *ca.* 2 : 1 and with the normal fast chair–chair conversion should have led to a less well defined n.m.r. spectrum than that observed. This suggests that the value for ΔG corresponding to axial ⟶ equatorial conformations of the methoxy-group is rather less in MMDP than the 6 kJ mol^{-1} found for the sugars. A conformer ratio of 5—10 : 1 for *cis*-MMDP would certainly be consistent with the observed spectrum and this would correspond to a value for ΔG of between 2 and 4·5 kJ mol^{-1} rather than 6 kJ mol^{-1}. This would imply that ΔG for *trans*-MMDP ⟶ *cis*-MMDP is also small and of this magnitude (*i.e.* $3{\cdot}3 \pm 1{\cdot}8$ kJ mol^{-1}).

TABLE 3

Kinetic parameters for dihydropyran decompositions

	$\log(A/\mathrm{s}^{-1})$	E/kJ mol^{-1}	$\Delta G^{\ddagger}_{600}$/ kJ mol^{-1}
DHP	14·63	219·4	201·8
6-Methyl-DHP	14·45	214·2	198·7
2-Methoxy-DHP	14·42	203·1	187·9
trans-MMDP	14·25	201·5	188·2
cis-MMDP	13·96	196·0	186·1

At 160° the ratio of *cis*- to *trans*-MMDP formed from crotonaldehyde and methyl vinyl ether was 3 : 2. This corresponds to an activated complex for *cis*-formation with a free energy of activation *ca.* 1·5 kJ mol^{-1} *less* than that for the *trans*-isomer. This preference for *cis*-formation is exactly analogous to the frequent occurrence of preferential formation of *endo*-isomers in Diels–Alder reactions. In the present case stabilisation of the activated complex by interaction between the highest occupied molecular orbital of the vinyl ether π system with that of the lowest unoccupied molecular orbital of the crotonaldehyde leads to the slight *cis*-isomer preference. (There may also be a small effect due to coulombic terms.)

If the energetic data on the *cis*- and *trans*-isomer stabilities which refer to room temperature remained the same at 600 K then we would expect the difference in the values of $\Delta G^{\ddagger}_{600}$ for the two isomers to be $3{\cdot}3 + 1{\cdot}5 = 4{\cdot}8$ kJ mol^{-1}. In fact, the observed value is only 2·1 kJ mol^{-1}. It would appear likely that both the difference in the free energies of the isomers at room temperature and the stabilisation of the complex decrease with increasing temperature.

Finally, we note that since *trans*-MMDP has a value for $\Delta G^{\ddagger}_{600}$ greater than for 2-methoxy-DHP any effect on the activated complex due to the methyl group stabilising an incipient radical centre is more than offset by steric effects.

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