Thermal Decomposition of 3,6-Dihydro-2*H*-pyran

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The thermal decomposition of the title compound has been studied in the gas phase in the temperature range 329—374 °C. The reaction yields formaldehyde and buta-1,3-diene quantitatively by a process that is homogeneous, kinetically strictly first order, and probably unimolecular. The measured rate constants yield the Arrhenius equation:

$$\log k/\mathrm{s}^{-1} = 14.31 \pm 0.14 - (208.1 \pm 1.7)\ kJ\ \mathrm{mol}^{-1}/RT\ln 10$$

The results of the present study are compared with those for some 3,4-dihydro-2*H*-pyrans and also *cis*-2,6-dimethyl-3,6-dihydro-2*H*-pyran. It is concluded that the decomposition is concerted and that the activated complexes, which are similar for these molecules, have some polar character.

In a study of the pyrolysis of some substituted vinyl oxetans the possible intermediacy of a substituted 3,6-dihydro-2*H*-pyran needed to be investigated. This led in turn to work on the thermal decomposition of *cis*-2,6-dimethyl-3,6-dihydro-2*H*-pyran. The reaction was found to be unimolecular and concerted, and largely stereospecific.[1] However, discussion of the details of the energetics of the decomposition and the effect of substituents required data on the reaction of the unsubstituted molecule. We report here a study to obtain the necessary information.

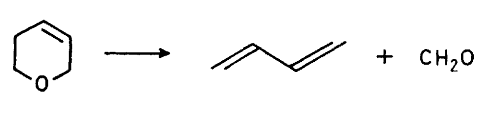
EXPERIMENTAL

3,6-*Dihydro*-2H-*pyran* (*DHP*).—A mixture of paraformaldehyde and but-3-en-1-ol was saturated with dry HBr, and the resulting 4-bromotetrahydropyran was obtained by pouring the mixture onto ice and water.[2] The bromo-compound was treated with KOH in ethylene glycol and the required DHP obtained by distillation.[3] The sample was purified by preparative g.l.c. (liquid phase bis-2-methoxyethyl adipate) and dried over molecular sieves; g.l.c. analysis indicated a purity of 99.9%.

Kinetics.—The apparatus was similar to one described previously.[4] To minimize adsorption problems, the gas handling system was maintained at between 70 and 80 °C. Pressure changes in the reaction vessel were monitored using a transducer (Bell and Howell model 4-327-0003) whose output was fed to a 1 mV potentiometric recorder. Reaction mixtures were analysed by gas chromatography using a Perkin-Elmer F11 instrument fitted with a flame ionization detector and a heated gas sampling valve. Signals from the detector went to a Hewlett-Packard 3380S electronic integrator.

RESULTS

In preliminary experiments the decomposition was found to produce buta-1,3-diene quantitatively, and the pressure changes were consistent with the stoicheiometric equation (1). With most chromatographic columns it was not possible to identify the formaldehyde because it polymerised on the column, but it was eluted from a column of Poropak N. However, even with this material quantitative analysis was not possible. Nevertheless, the absence of any other products and the measured pressure change strongly suggest that equation (1) is a good representation of the overall reaction.



(1)

Reproducible kinetic results could only be obtained after the reaction vessel had been treated extensively by pyrolyses of hexamethyldisilazane and penta-1,3-diene.

Kinetic runs were carried out at various temperatures in the range 329—376 °C. Runs were monitored by pressure change and plots of $\log(2P_0 - P_t)$ (where P_0 is the initial reactant pressure and P_t the total pressure at time t) against time were linear to greater than 50% decomposition. Rate constants were determined from these plots by the method of least squares. The results are presented in the Table. The rate constant at any particular temperature was independent of the initial reactant pressure in the range 2 to 10 Torr. The evidence presented indicates that the decomposition is strictly first order.

The data in the Table gave a good Arrhenius plot and the Arrhenius parameters were determined by the method of least squares:

$$\log k/\mathrm{s}^{-1} = 14.306 \pm 0.144 - (49\,750 \pm 410)\ \mathrm{cal\ mol}^{-1}/RT\ln 10$$

$$\log k/\mathrm{s}^{-1} = 14.306 \pm 0.144 - (208\,100 \pm 1\,700)\ \mathrm{J\ mol}^{-1}/RT\ln 10$$

The results were also treated by the weighted least squares procedure of Cvetanovic and Singleton [5] which yielded the equation:

$$\log k/\mathrm{s}^{-1} = 14.457 \pm 0.151 - (50\,180 \pm 440)\ \mathrm{cal\ mol}^{-1}/RT\ln 10$$

$$\log k/\mathrm{s}^{-1} = 14.457 \pm 0.151 - (210\,000 \pm 1\,800)\ \mathrm{J\ mol}^{-1}/RT\ln 10$$

The Arrhenius parameters are not altered significantly by the weighted procedure, which indicates that all the rate constants have approximately the same percentage errors; this is, of course, the assumption of the normal non-weighted procedure. In fact for this particular set of data the per-

Rate constants for the decomposition of DHP *

Temp./°C	329.84	335.55	340.16	346.79
$10^4k/\mathrm{s}^{-1}$	1.934 ±0.019	2.794 ±0.022	3.78 ±0.027	5.641 ±0.030
Temp./°C	355.58	361.79	366.86	371.64
$10^4k/\mathrm{s}^{-1}$	10.30 ±0.05	14.24 ±0.07	21.45 ±0.08	28.19 ±0.09
Temp./°C	375.56			
$10^4k/\mathrm{s}^{-1}$	35.32 ±0.11			

* Errors quoted are standard deviations.

centage errors are greatest at the lowest temperatures, probably owing to problems associated with drift in the output of the pressure transducer for the relatively long runs.

A series of runs was carried out at 330.22 °C in which the progress of the reaction was monitored by g.l.c. analysis of the butadiene produced. These runs yielded a rate constant of $(2.073 \pm 0.220) \times 10^{-4}\ s^{-1}$. In view of the scatter of the data, this is in good agreement with the rate constant calculated from the Arrhenius equation, *viz.* $1.94 \times 10^{-4}\ s^{-1}$.

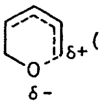
Another series of runs was carried out at 329.62 °C in a reaction vessel filled with glass tubes to give it a surface to volume ratio 14 times greater than that of the unpacked reaction vessel. Once again the extent of reaction was monitored by g.l.c. analysis of the butadiene formed. The rate constant obtained in this way was $(1.887 \pm 0.066) \times 10^{-4}\ s^{-1}$, in very good agreement with that calculated for the unpacked vessel using the Arrhenius equation. This almost exact agreement is, of course, fortuitous but it is clear that there can be no appreciable heterogeneous component of the reaction.

DISCUSSION

The conclusions of the earlier work on *cis*-2,6-dimethyl-3,6-dihydro-2*H*-pyran are fully supported by the present study on the unsubstituted DHP, that is, the reaction is unimolecular and concerted. The possibility of a diradical intermediate of the type (A) can be ruled out on energetic grounds, since we estimate the energy required to break the appropriate bond in DHP as 276 kJ mol^{-1}, 68 kJ mol^{-1} *more* than the observed energy of activation. (This estimate is based on group additivity and should be reliable to ± 10 kJ mol^{-1}.)

(A)

However, even though a diradical intermediate can be dismissed, it is still possible to distinguish between concerted synchronous and non-synchronous processes. We favour the latter and expect the rupture of the oxygen–carbon bond to lead that of the carbon–carbon bond. A similar situation has been suggested for the activated complex involved in the thermal decompositions of the 3,4-dihydro-2*H*-pyrans.[6] In those molecules some polar character was postulated for the complex and we feel it possible that this is also true for the present compound. We therefore suggest an activated complex of the type (B).



(B)

The *A* factor for the decomposition, which corresponds to a small positive entropy of activation of just over 14 J K^{-1} mol^{-1}, is very reasonable for a concerted process leading to a fragmentation reaction. One would expect a value close to zero for a concerted isomerization and an appreciably larger value if a fully developed diradical were involved. (Such a diradical would have two relatively unhindered internal rotations not present in the reactant.) In fact the value is within the range (8—21 J K^{-1} mol^{-1}) that has been obtained from studies on the pyrolysis of 3,4-dihydro-2*H*-pyran [7] and its derivatives.[6]

The relative rates of decomposition of the 3,4-dihydro-2*H*-pyran and the 3,6-dihydro-2*H*-pyran at 350 °C are 1 : 4. The higher rate for the compound studied in the present work is entirely due to its lower energy of activation for decomposition. More information about the nature of the activated complex should be obtainable by observing the effect of substituents on the rate parameters. Thus a substituent on C-2 would be expected to have a major effect if it stabilized or destabilized a positive charge centre, whereas the same substituent elsewhere in the ring would be expected to have only a minor effect. At present, there do not appear to be data on singly substituted molecules, but rate data are available for *cis*-2,6-dimethyl-3,6-dihydro-2*H*-pyran.[1] At about 350 °C this compound decomposes some 4 times *faster* than the unsubstituted molecule, and the effect is entirely due to a reduction in the energy of activation. We interpret this result largely in terms of the stabilization of the activated complex by the 2-methyl substituent, while nevertheless being aware that there could also be a small stabilization due to the 6-methyl substituent, and even a destabilization of the reactant by methyl—methyl repulsion (this latter effect is likely to be very small indeed in the pseudo-equatorial configuration of the reactant.[1]) A more definitive result could be expected from a study of simple 2-alkyl and 2-alkoxy compounds, and we hope to carry out the necessary work.

We thank Miss Ruth Pottinger for carrying out some of the initial studies. We also thank the S.R.C. for a studentship.

[9/152 *Received*, 31*st January*, 1979]

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