# Gas-phase Hydrogen Chloride-catalysed Decomposition of Some Cyclic Alcohols

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The gas-phase thermal decomposition of cyclopentanol, cyclohexanol, and cycloheptanol catalysed by hydrogen chloride in a seasoned Pyrex reaction vessel has been studied in a static system between 693 and 773 K. The reactions are homogeneous. The rate constants ($k_2$) are defined respectively by the Arrhenius equations (i)—(iii)

$$k_2 = 10^{13.36 \pm 0.12} \exp -(36\,143 \pm 388)/RT \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1} \quad \text{(i)}$$

$$k_2 = 10^{13.41 \pm 0.16} \exp -(38\,927 \pm 529)\ RT \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1} \quad \text{(ii)}$$

$$k_2 = 10^{12.31 \pm 0.18} \exp -(32\,254 \pm 613)/RT \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1} \quad \text{(iii)}$$

where $R$ = 1.987 cal mol$^{-1}$ K$^{-1}$.† The activation energies show a decrease with increasing ring-strain energy changes. The significance of this is discussed.

THE gas-phase decompositions of alcohols catalysed by hydrogen halides have received a good attention by Stimson and his co-workers.[1-5] However, most of the work deals with the decomposition of tertiary alcohols. The only work on secondary alcohols is that on propan-2-ol [3,6] and butan-2-ol.[5] More recently Trenwith [7] has reported the uncatalysed decomposition of propan-2-ol. In this work we report the catalysed decomposition of cyclic secondary alcohols ($C_5$—$C_7$) and attempt to find the effect of the ring size on the rate of elimination of water following the work of Dakubu and Holmes on the decomposition of cycloalkyl chlorides,[8] for which the rate sequence is cyclohexyl < cyclopentyl < cycloheptyl.

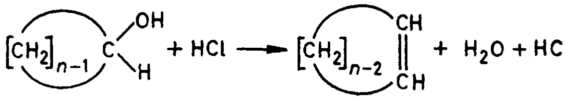
## EXPERIMENTAL

*Materials.*—Cyclopentanol and cycloheptanol, obtained from Aldrich, had $n_D{}^{20}$ 1.452 1, b.p. 141 °C and $n_D{}^{20}$ 1.476 0, b.p. 180 °C, respectively. Cyclohexanol, from Koch–Light, had $n_D{}^{20}$ 1.462 5, b.p. 161 °C. G.l.c. analysis of the compounds showed that each had purity >99.5%. Hydrogen chloride was prepared from hydrochloric acid and concentrated sulphuric acid.

*Procedure.*—All the catalysed decompositions were carried out in reaction vessels which had been seasoned by the decomposition products of allyl bromide.[9] The rate of dehydration was followed by measurement of the rate of pressure increase in a static system. This procedure is representative of the reaction because g.l.c. analysis of the hydrocarbons, using peak areas to calculate the amounts (4M 10% Carbowax 20M on 60—100 mesh Chromosorb W), showed that in the case of cycloheptanol, the only hydrocarbon produced is cycloheptene. (The presence of water was only qualitatively established.) In the case of cyclopentanol and cyclohexanol however, the decomposition products are the cycloalkenes and water only up to *ca.* 40% decomposition. Beyond this percentage, the decomposition products of the alkenes were observed. Cyclopentene [10] decomposes to cyclopentadiene and hydrogen (which was considered to be formed because of the formation of uncondensable gases) while cyclohexene [11] gives traces of several products *e.g.* ethylene, cyclohexa-1,3-diene, and buta-1,3-diene. The ratio of the final ($P_f$) to the initial ($P_0$) pressure is between 2.40—2.70 for the $C_5$ and $C_6$ alcohols. This also indicates further decomposition of the cycloalkenes formed. The $P_f : P_0$ ratio for cycloheptanol however was always *ca.* 2, indicating no further decomposition.

## RESULTS AND DISCUSSION

In all the catalysed reactions, the stoicheiometry of dehydration may be represented by equation (1), and



(1)

the reactions follow the rate equation (2). In all cases

$$-\mathrm{d}[\text{alcohol}]/\mathrm{d}t = k_2[\text{alcohol}][\text{HCl}] \quad (2)$$

the runs are first order in alcohol and the first-order rate coefficients are proportional to the hydrogen chloride concentration, to within 1% over the range 26—180 Torr at all temperatures. Uncatalysed dehydration was insignificant at the temperatures the studies were done. All rate coefficients were calculated from plots of log ($2P_0 - P_t$) against $t$, $P_t$ being the total pressure less that of hydrogen chloride at time $t$. Such plots were usually carried out up to *ca.* 40% decomposition as this is the region where analytical (g.l.c.) and pressure measurements are in agreement. (In the case of cycloheptanol, the fall off starts at *ca.* 70% decomposition). The values of rate coefficients calculated as above were in good agreement with calculations based on gradients of $P_t$ *versus* $t$ curves.

The reactions are all homogeneous between 693 and 773 K since rates of dehydration in unpacked ($s/v$ 0.95 cm$^{-1}$) and packed ($s/v$ 4.3 cm$^{-1}$) vessels never differed by >1%; *i.e.*, they agreed within experimental error.

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† 1 cal = 4.187 J.

[1] A. Maccoll and V. R. Stimson, *J. Chem. Soc.*, 1960, 2836.

[2] K. G. Lewis and V. R. Stimson, *J. Chem. Soc.*, 1960, 3087.

[3] R. A. Ross and V. R. Stimson, *J. Chem. Soc.*, 1960, 3090.

[4] V. R. Stimson and E. J. Watson, *J. Chem. Soc.*, 1961, 1392.

[5] R. L. Failes and V. R. Stimson, *J. Chem. Soc.*, 1962, 653.

[6] J. A. Barnard, *Trans. Faraday Soc.*, 1960, **56**, 72.

[7] A. B. Trenwith, *J.C.S. Faraday I*, 1975, 2405.

[8] M. Dakubu and J. L. Holmes, *J. Chem. Soc.* (*B*), 1971, 1040.

[9] A. Maccoll, *J. Chem. Soc.*, 1955, 965.

[10] C. A. Wellington and W. D. Walters, *J. Amer. Chem. Soc.*, 1961, **83**, 4888.

[11] S. V. Smith and A. S. Gordon, *J. Amer. Chem. Soc.*, 1960, **65**, 1124.

For all three compounds, over the temperature range 693—703 K, additions of cyclohexene as large as those providing a ratio $P_i : P_0$ up to 1.5 led to rate reductions of, at most, 5%. Thus, the reaction can be regarded as essentially molecular. The variation of the rate coefficients with temperature is shown in Table 1, and by the method of least squares, leads to the Arrhenius equations (3)—(5) where $R = 1.987$ cal mol$^{-1}$ K$^{-1}$ for cyclopentanol, cyclohexanol, and cycloheptanol, respectively.

TABLE 1

Variation of rate constants with temperature

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | Cyclopentanol | | | |
| $T$/K | 693.2 | 709.0 | 726.2 | 735.0 | 741.0 | 749.8 | 753.0 |
| No. of runs | 5 | 4 | 4 | 5 | 4 | 3 | 5 |
| $k_2$/s$^{-1}$ cm$^3$ mol$^{-1}$ | 91.18 | 166.7 | 299.3 | 390.9 | 520.3 | 688.0 | 999.2 |
| | | | | Cyclohexanol | | | |
| $T$/K | 693.2 | 717.0 | 739.8 | 746.0 | 754.0 | 759.0 | 769.2 |
| No. of runs | 3 | 3 | 6 | 2 | 2 | 6 | 3 |
| $k_2$/s$^{-1}$ cm$^3$ mol$^{-1}$ | 13.7 | 35.9 | 79.3 | 109.0 | 135.8 | 160.7 | 225.9 |
| | | | | Cycloheptanol | | | |
| $T$/K | 639.2 | 716.0 | 723.8 | 741.0 | 747.0 | 757.0 | 766.0 |
| No. of runs | 2 | 3 | 2 | 6 | 4 | 4 | 4 |
| $k_2$/s$^{-1}$ cm$^3$ mol$^{-1}$ | 136.6 | 301.8 | 404.1 | 617.8 | 766.3 | 1 019 | 1 253 |

$$k_2 = 10^{13.36 \pm 0.12} \exp\,(-36\,143 \pm 388) \text{ cal mol}^{-1}/RT \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1} \quad (3)$$

$$k_2 = 10^{13.41 \pm 0.16} \exp\,(-38\,927 \pm 529) \text{ cal mol}^{-1}/RT \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1} \quad (4)$$

$$k_2 = 10^{12.31 \pm 0.18} \exp\,(-32\,254 \pm 613) \text{ cal mol}^{-1}/RT \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1} \quad (5)$$

From the results so far, it is concluded that the hydrogen chloride catalysed dehydration of the three cycloalcohols is homogeneous and bimolecular, and first order with respect to the alcohol.

Table 2 shows the activation energies of the cycloalcohols, propan-2-ol, isopropyl chloride, and some cycloalkyl chlorides. The activation energy of the propan-2-ol was estimated from the data of Stimson and Ross [3] on the HBr-catalysed dehydration and relative rates of the HBr- and HCl-catalysed dehydrations at 440 °C (25 : 1). We assumed the value of $3.0 \times 10^{12}$ cm$^3$ s$^{-1}$ mol$^{-1}$ for the $A$ factor purely on intuitive grounds by inspection of the $A$ factors for HBr- and HCl-catalysed dehydrations of some alcohols.[1-4,6]

The results in Table 2 indicate significant decrease in activation energy in the sequence isopropyl ≈ cyclohexyl > cyclopentyl > cycloheptyl. These changes are in the same sequence as the strain energy changes $\Delta E_s$ in going from cycloalkanes to cycloalkenes. Dakubu and Holmes [8] have observed similar trends in the dehydrochlorination reactions of cycloalkyl chlorides.

TABLE 2

Activation energies for catalysed (HCl) dehydration of some alcohols and dehydrochlorination of some alkyl chlorides

| | Alcohol $E_a$/kcal mol$^{-1}$ | Chloride $E_a$/kcal mol$^{-1}$ | $\Delta E_s{}^{8,15}$/ kcal mol$^{-1}$ |
|---|---|---|---|
| Isopropyl | 39.3 [a] | 50.5[12] | |
| Cyclohexyl | 38.9 [b] | 50.1[13] | 0.0 |
| Cyclopentyl | 36.1 [b] | 48.3[14] | 1.8 |
| Cycloheptyl | 32.3 [b] | 43.6[8] | 2.4 |

[a] Estimated. [b] This work.

The differences ($\Delta E_a$) between the activation energy of propan-2-ol and the cycloalcohol are 0.4, 3.2, and 7.0 kcal mol$^{-1}$ for $C_6$, $C_5$, and $C_7$, respectively. Similar values for the dehydrochlorination reactions are 0.4, 2.2, and 6.9 kcal mol$^{-1}$. The magnitudes of the differences for the dehydrations and dehydrochlorinations are very similar even though the mechanisms for the two processes are different. Dakubu and Holmes [8] have suggested that there are two possible ways that the strain energy can affect the activation energy: (i) that owing to the strain, the energy of the ground state of the cyclo-compound relative to the transition state is increased, hence the lowering of the activation energy; or (ii) the presence of the strain in the ring facilitates the attainment of the geometry required by the transition state.

Now the geometry required will depend on the mechanism operative, and hence on the energy contribution from the ring, which may be different for different mechanisms. The similarities therefore of the magnitude of $\Delta E_a$ values for the dehydration and dehydrochlorination reactions, irrespective of the different mechanisms, seem to favour the first possibility for the part played by the strain energy.

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[12] D. H. R. Barton and A. J. Head, *Trans. Faraday Soc.*, 1950, **46**, 114.

[13] E. S. Swinbourne, *J. Chem. Soc.*, 1960, 4668.

[14] E. S. Swinbourne, *Austral. J. Chem.*, 1958, 314.

[15] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968, p. 179.