The Mechanism of Thermal Eliminations. Part 16.[1] Rate Data for Pyrolysis of 2-(2-Hydroxyethyl)pyridine; Prediction of Elimination Rates

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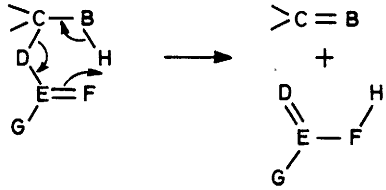
Rates of thermal decomposition of 2-(2-hydroxyethyl)pyridine have been measured between 625.2 and 690.5 K. It undergoes a unimolecular first-order elimination to give formaldehyde and 2-methylpyridine according to the rate equation $k = 9.016 \times 10^{11}\, e^{-178060/RT}\, s^{-1}$ (R = 8.312 J K^{-1} mol^{-1}). A cyclic six-membered transition state is therefore indicated and the decomposition parallels that for β-hydroxy-alkenes. 2-(2-Hydroxyethyl)pyridine eliminates 23.0 times faster at 600 K than its isomer 2-ethoxypyridine. However, analysis of the literature data shows that interchange of the two groups attached to the α-carbon, and which participate in the elimination, produces widely varying changes in reactivity though in general the hydroxy-compounds are more reactive than their isomers. The difference in reactivity of a given pair of isomers is approximately dependent upon the elimination rate of either of them. This suggests it may be possible to predict the rates of gas-phase elimination of compounds not yet studied under kinetic conditions.

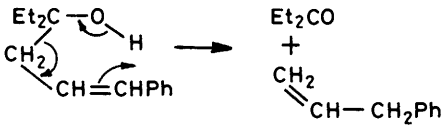
In the general cyclic transition state (I) for a wide range of thermal eliminations, the effects of interchange of D and F have been measured and discussed in a number of studies. Thus amides (I; D = NH, F = O)[2] are much less reactive than iminoethers (I; D = O, F = NH),[3] ketones (I; D = CH_2, F = O)[4] are much less reactive than vinyl ethers (I; D = O, F = CH_2),[5] and thiolesters (I; D = S, F = O)[6] are much less reactive than thionesters (I; D = O, F = S),[6] the reactivity differences being of the order of 10^5. By contrast, the effects of interchanging B and D have not been considered, though examination of the literature shows that it is possible to deduce the effect in one case (see Discussion section).

Some years ago we showed that the pyrolysis of β-hydroxy-alkenes, *e.g.* (II), proceeded *via* a six-membered transition state.[7] Just as it is possible to replace the double bond in esters with the 1,2-aromatic π-bond of pyridine and obtain an analogous elimination, so it is possible similarly to replace the double bond of hydroxy-alkenes, giving compounds such as 2-(2-hydroxyethyl)pyridine. The latter is thus the isomer of 2-ethoxypyridine whereby the groups B and D have been interchanged. A non-kinetic study of the thermal stability of 2-(2-hydroxyethyl)pyridine by Goldman[8] showed that it eliminated formaldehyde to give 2-methylpyridine, and he proposed the six-centre cyclic mechanism (III). The reaction was accompanied by *ca.* 1% of dehydration (a four-centre process) and this appears to be surface catalysed. 2-(2-Hydroxyethyl)pyrazine also underwent a similar elimination, and to approximately the same extent. A recent study of the decomposition of substituted 2-(2-hydroxyethyl)pyrazines (in solvents)[9] indicated that very little charge is developed at the α-carbon, which parallels the previous observation for β-hydroxy-alkenes.[10]

In order to confirm or otherwise the cyclic transition state proposed for the elimination we have determined the Arrhenius parameters and in so doing have evaluated the effect of the B–D interchange which has indicated the possibility of predicting elimination rates for compounds not yet studied.



(I)



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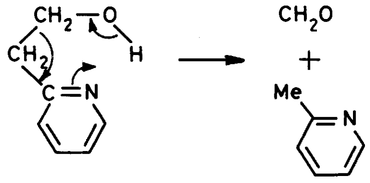
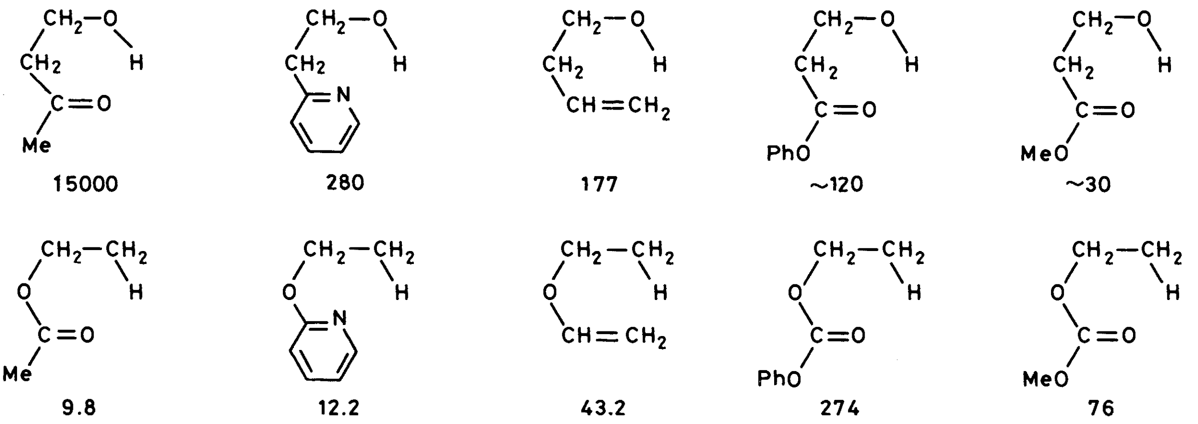


(III)

Results and Discussion

Initial kinetic studies with 2-(2-hydroxyethyl)pyridine were not very encouraging. The compound was evidently prone to surface-catalysed elimination as shown by non-reproducibility of rates, and scatter on the Arrhenius plot. Furthermore, the kinetic form was curious, runs showing an initial fast reaction which then settled down to an excellent first-order form. A large number of kinetic runs (*ca.* 50) were performed in order to solve the problem. Two commercial sources of 2-(2-hydroxyethyl)pyridine were used and one tended to give lower rate coefficients than the other, though no differences in them could be detected by n.m.r. We initially assumed that the alcohol was hygroscopic and a run carried out with added water did indeed give a faster rate, *i.e.* the fast portion of the runs could be due to reaction of the hydrogen-bonded species, assuming that there was insufficient water present to bond to each molecule. However we also observed that the alcohol turned yellow quite rapidly in the presence of air, which might be due to formation of the *N*-oxide. The alcohol was therefore fractionally distilled and the distillate certainly gave lower coefficients, but on standing in air it gave higher ones. Thus to obtain good kinetics, runs were always carried out on freshly distilled material, *i.e.* pyrolysed within 1 h of collection. With this method, not only was the fast initial portion of the runs absent or almost entirely so, but in the latter cases, runs first order throughout could be obtained by



$k_{rel.}$	1531	23.0	4.1	0.44	0.39
$k_{rel.(corr.)}$[a]	4593	69.0	12.3	~1.32	~1.17

[a] Corrected for the different number of β-hydrogens

Scheme. Rate coefficients ($10^6k/\mathrm{s}^{-1}$ at 600 K) for thermal elimination.

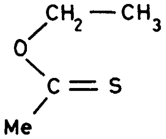
Rate data for pyrolysis of 2-(2-hydroxyethyl)pyridine

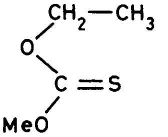
T/K	$10^3k/\mathrm{s}^{-1}$	$\log(A/\mathrm{s}^{-1})$	$E/\mathrm{kJ\ mol}^{-1}$	Correlation coefficient
625.2	1.10	11.955 ± 0.1	178.06 ± 1.4	0.998 90
638.8	2.63			
654.9	6.01			
668.6	10.85			
681.6	20.4			
690.5	29.2			

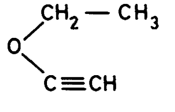
carrying one out immediately after evacuating the reactor following the preceding run. This suggested that the first portion of the runs was surface catalysed, but it seemed unlikely that this was dehydration since there was no reason for this to be reduced simply on distillation of the alcohol. In this way the minimum set of rate coefficients obtained from good first-order runs gave a linear Arrhenius plot as shown by the correlation coefficient.

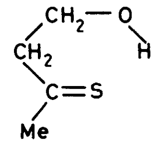
The rate data are given in the Table and the log A value is within the range obtained for β-hydroxy-alkenes,[7,10] and almost exactly that calculated,[11] providing strong support for the proposed cyclic mechanism (III). The rate coefficient at 600 K is $280 \times 10^{-6}\ \mathrm{s}^{-1}$ (*cf.* $12.2 \times 10^{-6}\ \mathrm{s}^{-1}$ for 2-ethoxypyridine[12]) so that the alcohol is 25 times more reactive. These results are compared in the Scheme with the literature results for vinyl ethers[5] *versus* hydroxy-alkenes.[10] The Scheme also gives unpublished results[13] for hydroxy-ketones and hydroxy-esters *versus* esters[14] and carbonates,[1] respectively. The data for the hydroxy-ketones and hydroxy-esters are preliminary ones, but even if they are in error by ±50%, it makes no difference to the general conclusions which are as follows.

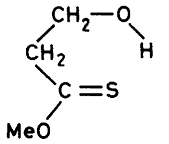
(i) Compared with interchange of D and F, interchange of D and B produces a rate change which can vary from being very large to trivial. In the transition state both the α-C–D and β-B–H bonds are partially broken, and we have previously shown that a lower polarity in both these bonds produces a lower reaction rate.[14,15] Thus moving the electronegative oxygen from D to B can substantially compensate for the loss of α-C–D polarity through an increase in β-B–H polarity.

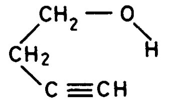

(IV)
$10^6\ k/\mathrm{s}^{-1}$ 1830


(V)
$10^6 k/\mathrm{s}^{-1}$ 3350


(VI)
$10^6\ k/\mathrm{s}^{-1}$ *ca* 25


(VII)
$10^6\ k/\mathrm{s}^{-1}$ *ca* 5


(VIII)
$10^6\ k/\mathrm{s}^{-1}$ *ca* 1


(IX)
$10^6\ k/\mathrm{s}^{-1}$ 460

When oxygen is at D, breaking of the α-C–D bond is the most important rate-determining step, and when it is at B, breaking of the B–H bond and hence nucleophilic attack upon it must likewise become the most important step. The net result of the interchange of B and D will then largely depend on the nucleophilicity of the attacking group F and the balance of bond energies in forming the F–H bond and breaking the B–H bond.* Because the breaking of the B–H bond is very rate determining for the hydroxy-compounds, but not so for their isomers, there is a wide variation in the elimination rates for the top row of compounds in the Scheme, and only a small variation of rates for the compounds in the bottom row.

(ii) The hydroxy-compounds are all more reactive per β-hydrogen than their isomers, the statistically corrected ratios varying from 4 593 to 1.17. Interestingly, this ratio decreases with decreasing reactivity of the hydroxy-compound in a

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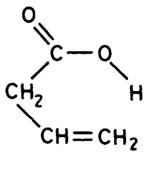
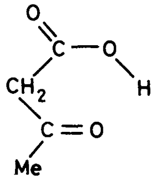
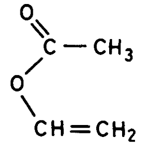
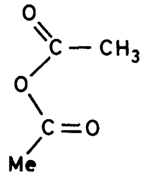
* A referee has suggested that interchanging B and D can also affect the nucleophilicity of the E=F bond. Our view is that nucleophilic attack only becomes important when there is a non-polar group at D, and such a group would be unlikely to have any significant effect upon this nucleophilicity.


(X)


(XI)


(XII)


(XIII)

fairly regular way which suggests that we may be able to predict the elimination rates for compounds not yet studied. (Prediction of gas-phase elimination rates should become increasingly possible as understanding grows regarding the factors involved.) Thus from the rate coefficients for elimination at 600 K of ethyl thionacetate (IV),[16] ethyl methyl thioncarbonate (V),[17] and but-3-ynol (IX)[18] the rate coefficients for pyrolysis of the hydroxy-thioketone (VII), hydroxy-thionester (VIII), and ethyl ethynyl ether (VI) are predicted to be approximately as shown.

(iii) A parallel to the present results is also found in the fact that βγ-alkenoic acids[19] (X) and β-keto-acids[20] (XI) are more reactive than vinyl acetate[13,21] (XII) and acetic anhydride[22] (XIII) respectively, though precise values for the relative reactivities are not known, and there is evidence that the latter two compounds may in fact pyrolyse *via* their enol forms.[13]

It is tempting to suggest that the correlations found here can be equally well applied to the analogues with nitrogen and sulphur at B or D, leading to further predictions of rates. We hope in due course to obtain results directed towards that end.

Experimental

2-(2-Hydroxyethyl)pyridine (Aldrich) was fractionally distilled before each set of kinetic runs (as described in the Results section), the fraction boiling at 170 °C at 100 mmHg being collected.

Kinetic Studies.—The general (static) method involving a stainless steel reactor with pressure-sensing diagram has been described previously along with the method for deactivating the surface.[23] Samples of 2-(2-hydroxyethyl)pyridine (*ca.* 70—200 μl) were injected into the reactor using a gas-tight syringe, in the normal way. A large number of runs were carried out for reasons given in the Results and Discussion, and at any temperature we used only the minimum rate coefficients provided they could be duplicated to ±2%; these values then fell on a linear Arrhenius plot. Within the variation in sample size noted above, rate coefficients were reproducible. This is widely regarded as a satisfactory test for the absence of surface catalysis but has in our view lost validity because of the large number of published papers claiming rate coefficients invariant with sample size, yet whose data have since been shown to be affected by surface catalysis. Our experience is that linearity of Arrhenius plots is a more reliable indicator of the absence of surface effects; surface catalysis diminishes in importance as the temperature is raised so that curved plots, concave upwards, are always obtained if non-homogeneity occurs.

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Received 2*nd August* 1982; *Paper* 2/1334