Thermal Conversion of 2-Ethoxypyridine into 2-Pyridone; an Analogue of Ester Pyrolysis

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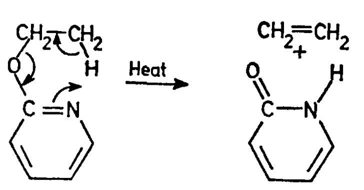
Summary 2-Ethoxypyridine undergoes thermal elimination of ethylene to give 2-pyridone *via* a 6-centred cyclic process which is a nitrogen analogue of ester pyrolysis.

At temperatures above *ca.* 400 °C, 2-ethoxypyridine pyrolyses rapidly in a clean first order homogeneous and unimolecular reaction to give 2-pyridone and ethylene. The elimination rate (measured in a stainless steel reactor with a deactivated surface[1]) is unaffected by a 5-fold change in initial pressure, and gives a stoicheiometry of 2·0. Kinetic data obtained over a 50 °C range (Table) give an excellent Arrhenius plot (correlation coefficient = 0·99975). The log A factor is typical for a reaction having a semi-concerted 6-centred cyclic transition state which must therefore be (I), and the reaction (1) is thus the nitrogen analogue of carboxylate ester pyrolysis [reaction (2); X = Y = O, R = alkyl]. This is the first kinetic study of this type of reaction in which aromatic π-electrons participate. A large number of compounds including carboxylic esters, carbonates, thiocarbonates, carbamates, enol ethers, thioacetates, and amides, *i.e.* X, Y = O, S, NH, or CH_2; R = alkyl, OR′, SR′, NHR′, undergoes pyrolysis according to equation (2); permutations indicate that 64 types of compound should undergo this elimination though relatively few have so far been shown to do so. In general, interchange of X and Y produces a large change in the elimination rate, either because of the energy change accompanying the change from –X–C=Y to X=C–Y– on going from reagents to products,[2] or because electron withdrawal by X (which favours polarisation of the C_α–X bond, the primary step of the elimination[3]) makes this group less able to form a Y–H bond when substituted at the position Y.

Table. Pyrolysis of 2-ethoxypyridine.

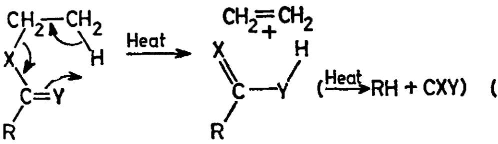
T/°C	$10^3k/s^{-1}$	log (A/s^{-1})	E/kJ mol^{-1}
441·8	8·08, 7·89	12·22[a]	195·94[a]
433·0	5·42, 5·25		
420·5	2·92, 2·95		
406·7	1·40, 1·42		
392·2	0·698, 0·696		

[a] For ethyl acetate pyrolysis, log A = 12·5 s^{-1} and $E_{atc.}$ = 200·0 kJ mol^{-1} (R. Taylor, *J.C.S. Perkin II*, 1975, 1025).



(I)

(1)



(2)

Pyrolysis of carboxylic acid amides (X = NH, Y = O, R = alkyl) proceeds relatively slowly (much more slowly than that of acetate for example), attributable to the low polarity of the –C_α–NH bond. Thus the pyrolysis of iminoethers (X = O, Y = NH, R = alkyl) could be expected to be fast (and faster than for acetates). No study of these has been reported save an observation that $Bu^sOC(Ph){:}NPh$ is unstable.[4] The example which we now report can be regarded as related to imino ether pyrolysis, differing in that the third bond to nitrogen forms part of an aromatic ring. Although nucleophilic attack at the β-hydrogen involves delocalizing a pair of π-electrons out of the aromatic ring the reaction is still relatively fast and indeed the elimination rate is identical to that of ethyl acetate at **419** °C, which suggests that imino ether pyrolysis (in which the electron pair is not initially conjugated) should be considerably faster.

It is tempting to suggest that the pyrolysis of the ethoxy ethers of carbocyclic aromatic compounds (*e.g.* phenetole) reported many years ago to give ethylene and phenols[5] proceeds by the same mechanism (which is thus the aromatic analogue of vinyl ether pyrolysis). However preliminary experiments over a 50 °C range show that phenetole pyrolysis is partly zeroth order, and gives non-reproducible kinetics and consequently a very poor Arrhenius plot ($E_{act.}$ *ca.* 190 kJ mol^{-1}). A free-radical reaction is therefore at least partly involved. The reaction is *ca.* 7 times slower than the pyrolysis of 2-ethoxypyridine, which would be expected if there is a component of the mechanism analogous to (I), since the aromatic π-electrons involved in the cyclic transition state are more polarised (and in the required direction) in 2-ethoxypyridine.

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[1] R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1397.

[2] C. H. De Puy and C. A. Bishop, *Tetrahedron Letters*, 1963, 239.

[3] S. de Burgh Norfolk and R. Taylor, *J.C.S. Perkin II*, 1976, 280, and earlier papers in this series.

[4] K. B. Wiberg and B. L. Rowland, *J. Amer. Chem. Soc.*, 1955, **77**, 2207.

[5] E. Bamberger, *Ber.*, 1886, **19**, 1818 (we thank a referee for drawing our attention to this and related papers).