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THE HYDROLYSIS OF 3-PHENYLSYDNONE

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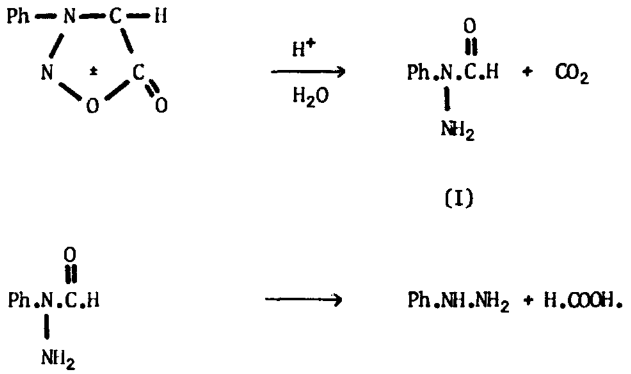
3-Phenylsydnone hydrolyses in the presence of hydrochloric acid to form phenylhydrazine, formic acid and carbon dioxide (3,4). The results of ^{15}N-labelling experiments by Staley and Clarke (5) ruled out the possibility of N→N aryl migration during hydrolysis and were consistent with the mechanism of hydrolysis suggested earlier by Baker and Ollis (6):



Zotova and Yashunskii have recently repeated (7) the isolation of the elusive unstable acylhydrazine intermediate I, earlier reported without experimental detail by Kenner and Mackay (8) but subsequently disputed by others (c.f.5). The Russian workers also concluded, however, that the increase in the rate of hydrolysis of 3-phenylsydnone in aqueous dioxan caused by the addition of hydrochloric acid was not due to acid catalysis but to the specific reaction of the sydnone with undissociated hydrogen chloride molecules.

This conclusion was held to be supported by the fact that hydrolysis could not be observed in aqueous solution, where hydrochloric acid is completely dissociated. The observation of a reaction in aqueous dioxan and the increase in the rate of this hydrolysis with increasing dioxan content was thought to parallel the well known tendency of hydrochloric acid to be incompletely dissociated in solvents of low dielectric constant. No reaction could

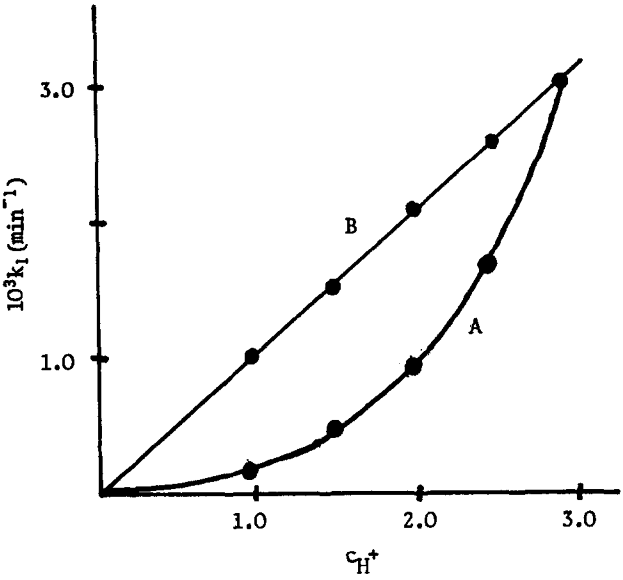


Figure 1. First-order rate coefficients, k_1, for the hydrolysis of 3-phenylsydnone in water at 50°.
A, HCl; B, HCl + LiCl.

be observed in the presence of perchloric or sulphuric acids in aqueous dioxan at the temperature used (20°). The catalytic effect of perchloric acid and sulphuric acid on the hydrochloric acid-catalysed reaction was attributed to a common-ion repression of the dissociation of hydrochloric acid, thereby increasing the concentration of undissociated hydrogen chloride.

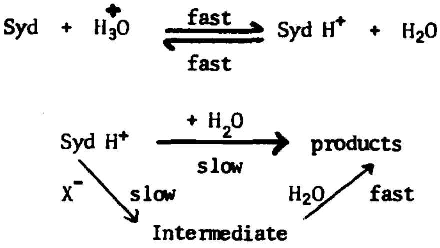
We wish to question the validity of these conclusions and now report further experimental data on this reaction in both water and aqueous dioxan.

By raising the temperature to 50° it is possible to observe the hydrolysis of 3-phenylsydnone in water. The variation of rate of hydrolysis (9) with concentration of hydrochloric acid is shown in Figure 1. (A). Kinetic data (not shown here) at low acid concentrations shows that the rate of hydrolysis in both hydrochloric acid and hydrobromic acid at first increases linearly with acid concentration but above _ca_ 1.0 Molar increases more rapidly than does acid concentration. In mixtures of hydrochloric acid and lithium chloride, (Figure 1, B) or hydrobromic acid and lithium bromide (not shown), at constant halide ion concentration (2.90 _M_), the rate is directly proportional to stoicheiometric acidity. The increase in rate obtained under these conditions must be due to acid catalysis. A similar linear dependence of rate on acid concentration at constant halide ion concentration was observed in 40% dioxan-water at 25°.

The values obtained for the kinetic deuterium solvent effect ($k_1^{D_2O}/k_1^{H_2O} = 2.6$ and 2.9 for HCl and HBr in water at 50°, 3.0 and 2.3 in 40% dioxan at 25°) are characteristic (10) of reactions which proceed by a pre-equilibrium proton transfer, i.e. specific hydrogen ion catalysis occurs.

The effectiveness of halogen acids in catalysing the hydrolysis fell in order of decreasing nucleophilic power of the acid anion, i.e. $HBr > HCl$. This is further illustrated by the effect of added salts on the hydrochloric acid-catalysed reaction. The effect of added perchlorate anions on the rate is approximately linear in salt concentration and presumably arises from a primary salt effect. The effect of added halides, however, is far too large to be ascribed solely to a simple salt effect and suggests halide ion participation in the rate-determining step. Similar specific anion catalysis has been observed for the hydrolysis of diazosulphones (11), diazoketones (12,13), and sulfite esters (14).

Our observations suggest the following mechanism for the hydrolysis of sydnones:



(X=Cl or Br)

When water is the most reactive nucleophile present the reaction proceeds immeasurably slowly as indicated by the apparent absence of any reaction when perchloric acid is added. The reaction which occurs readily in the presence of halide ions must involve the formation of a halo-intermediate which rapidly decomposes in water to the observed products. It is also just possible to detect a reaction in aqueous sulphuric acid (5.0 Molar at 50°).

The similar kinetic behaviour observed in both water and 40% dioxan suggests that the hydrolysis proceeds by the same mechanism in both solvents. Molecular orbital calculations (15) of the electron distribution in 3-methylsydnone predict protonation on the number 2 N-atom. In a kinetic study of the hydrochloric acid-catalysed hydrolysis of some alkyl sydnones Garrett(16) also assumed protonation on nitrogen. He did not, however, examine the role of chloride ion in the rate-determining step.

Further work is in progress to elucidate the detailed mechanism of hydrolysis of the sydnone ring.

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