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THE HYDROLYSIS OF SOME 3-ALKYLSYDNONES

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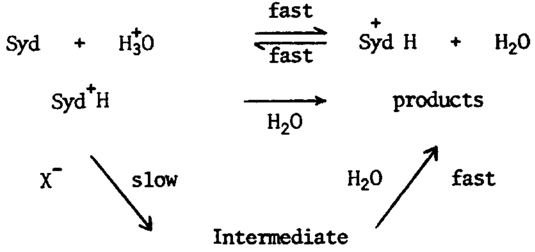
It has been shown recently (1) that the hydrolysis of 3-arylsydnones catalysed by hydrochloric acid involves both specific hydrogen ion catalysis and nucleophilic catalysis. The following mechanism was proposed:-



(X = Cl or Br)

Nucleophilic catalysis in which anions possessing nucleophilic properties compete with the solvent for the conjugate acid of the substrate has also been observed in the hydrolysis of diazoketones (2), diazosulphones (3), dialkyl sulphites (4), methyl toluene-p-sulphinate (5), and ethylene episulphoxide (6). The unique feature of the hydrolysis of 3-arylsydnones, however, is that when water is the most reactive nucleophile present the reaction proceeds immeasurably slowly. Hydrolysis can only be detected in the presence of a strong nucleophile such as Cl^- or Br^-.

We now report quite different behaviour for the hydrolyses of some 3-alkylsydnones. The kinetic forms observed for the hydrolysis of 3-t-butylsydnone (I) and 3-furfurylsydnone (II) are very similar (7). Both hydrolyse by a pH-independent mechanism (i.e. "neutral" hydrolysis) as well as by an acid catalysed pathway. Their rates of hydrolysis have been studied mainly in water as solvent.

The values obtained for the kinetic deuterium solvent effect ($\underline{k}_1^{D_2O}/\underline{k}_1^{H_2O}$ = 1.73 and 1.79 for I and II respectively in water at 60° with $HClO_4$) are characteristic of reactions which (8) proceed by a pre-equilibrium proton transfer. The rate of hydrolysis in perchloric acid (shown in the Figure for I) at first increases linearly with acid concentration but above ca. 0.5 molar

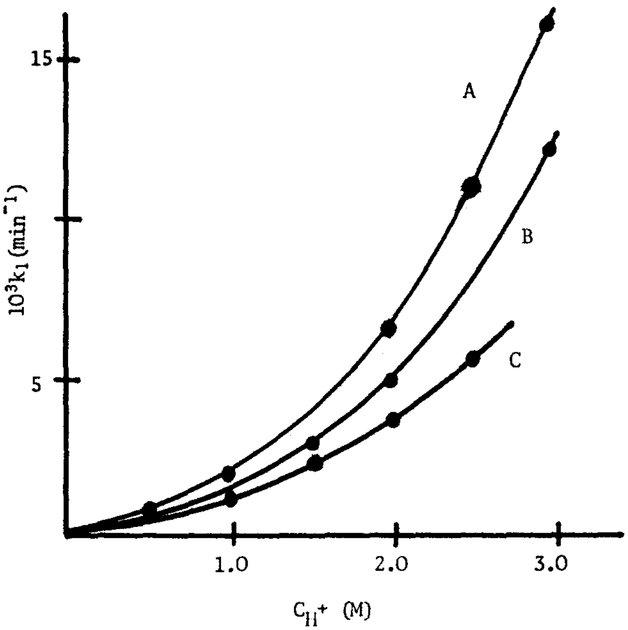


Figure. First-order rate coefficients, k_1, for the hydrolysis of 3-t-butylsydnone (I) in water at 75.0°.
A, $HClO_4$; B, H_2SO_4; C, HCl.

acid, increases much more rapidly. The slopes of the Hammett plots (log $\underline{k}_1$ versus $-H_0$) are 0.87 and 0.98 for I and II. This could be interpreted as evidence for an A-1 mechanism on the basis of the simple Zucker-Hammett hypothesis (9). However, in mixtures of perchloric acid and lithium perchlorate at constant ionic strength, the rate of hydrolysis is directly proportional to stoicheiometric acidity (data not shown) suggesting an A-2 mechanism. These conflicting predictions of the Zucker-Hammett hypothesis, admittedly relating to somewhat different conditions, indicate the unreliability of this criterion in the present instance.

The most striking feature of the effect of different acids on the hydrolysis of I and II is the order of effectiveness of the acids, viz., $HClO_4 > H_2SO_4 >$ HBr > HCl (Figure). This is in marked contrast to their effect on the hydrolysis of 3-phenylsydnone which was related to the nucleophilic power of the acid anion. This important difference suggests that there might be a change in mechanism on going from 3-aryl-substituted to 3-alkyl-substituted sydnones.

In a recent study of electrolyte effects on the acid catalysed hydrolysis of esters, Bunton and his co-workers (10) suggested the generalization that for A-1 reactions the catalytic effect of acids decreases in the order $HClO_4 > HCl \sim H_2SO_4$, whereas for A-2 reactions the relative order is $H_2SO_4 > HCl \sim HBr > HClO_4$. On the basis of this criterion the order of effectiveness of acids on the hydrolysis of I and II suggests that both hydrolyse by an A-1 mechanism.

Further information about the mechanism of hydrolysis can be obtained from the effect of added salts. Lithium perchlorate and lithium chloride have a similar effect on the acid catalysed hydrolysis at relatively low concentrations of added salt (< 2.0 molar), but above this the perchlorate begins to exert a larger effect. This is consistent with the relative effects of added salts on A-1 reactions as determined by Bunton et al. (10).

The Bunnett w values (11) for the hydrolysis of I and II are approximately zero, and are therefore consistent with an A-1 mechanism. Further confirmation of this is provided by the values of the entropies of activation (I, + 8.9 e.u.; II, -1.72 e.u.) which are in the range usually associated with a unimolecular process (12).

The rate of hydrolysis of II in dioxan-water decreases with increasing dioxan content. This is in accord with the observation by Garrett (13) that the rate of hydrolysis of t-octylsydnone in aqueous ethanol also decreases with decreasing polarity of the solvent. Thus the solvent effects in the present case are also consistent with an A-1 mechanism.

The evidence available suggests that the acid catalysed hydrolysis of 3-t-butylsydnone (I) and 3-furfurylsydnone (II), in marked contrast to that of 3-arylsydnones, follows an A-1 mechanism which can be generalised as follows:-

$$\begin{aligned}
\mathrm{Syd} + \mathrm{H_3\overset{+}{O}} &\underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{Sy\overset{+}{d}\,H} + \mathrm{H_2O} \\
\mathrm{Syd^{+}H} &\xrightarrow{\text{slow}} [\text{Intermediate}] \\
[\text{Intermediate}] &\xrightarrow[\mathrm{H^+,\ H_2O}]{\text{fast}} \text{products}
\end{aligned}$$

Garrett previously studied (13) the hydrochloric acid catalysed hydrolysis of a series of 3-alkylsydnones. He did not examine the role of halide ion in the hydrolysis or attempt to elucidate the mechanism in any detail. His data shows, however, that there is a change in log A values about half-way along the series t-octyl, t-butyl, furfuryl, iso-propyl, propyl and methyl. This suggests that there might be a change in mechanism and that the hydrolysis of the last three compounds might proceed by an A-2 mechanism. Further work is in progress to investigate this point and to see whether the hydrolyses of these compounds exhibit nucleophilic catalysis like their 3-aryl-substituted analogues.

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