

THE HYDROLYSIS OF PHENYLHYDROXAMIC ACID IN CONCENTRATED AQUEOUS SODIUM HYDROXIDE

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Phenylhydroxamic acid undergoes hydrolysis in concentrated NaOH via a complex mechanism: a maximum is observed in the plot of k_o versus $[NaOH]$ which is attributed to the existence of one or more pre-equilibria influencing the rate-limiting step.

Hydroxamic acids are known to undergo hydrolysis in acidic, neutral and alkaline media.¹⁻⁴ The reactions in aqueous NaOH, however, have been studied mainly at either low ionic strength or in conditions of constant ionic strength.¹⁻³ An outstanding feature of these studies is the existence of a linear dependence of the pseudo first order rate constant (k_o) on $[NaOH]$, and for alkylhydroxamic acids even at high $[NaOH]$.⁴ Our preliminary investigation of the hydrolysis of phenylhydroxamic acid⁵ (I) in aqueous NaOH solutions of relatively high ionic strength has revealed a more complex dependence of k_o on $[NaOH]$. A rate maximum is observed at about 3.5M-NaOH (Fig. 1). The most likely cause of this maximum is either the superimposition of a large negative salt effect on the rate of alkaline hydrolysis or the existence of a pre-equilibrium situation. The first possibility can be discounted since a positive salt effect on the rate of alkaline hydrolysis of I is observed. Moreover, a rate maximum is also observed for the alkaline hydrolysis of I at constant ionic strength (Figs. 2 and 3).

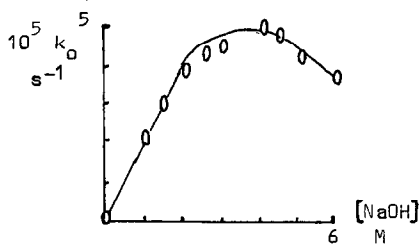


Fig. 1. Hydrolysis of I in aq. NaOH (80°)

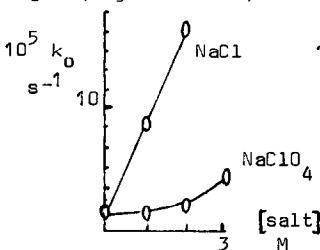


Fig. 2. Hydrolysis of I with added salts ($[NaOH] = 3M, 80^\circ$)

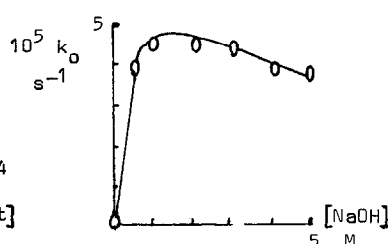
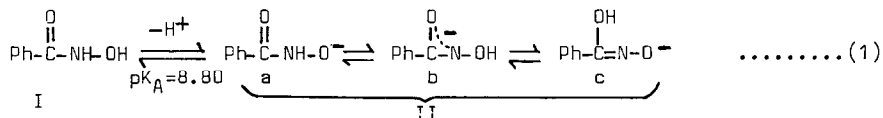


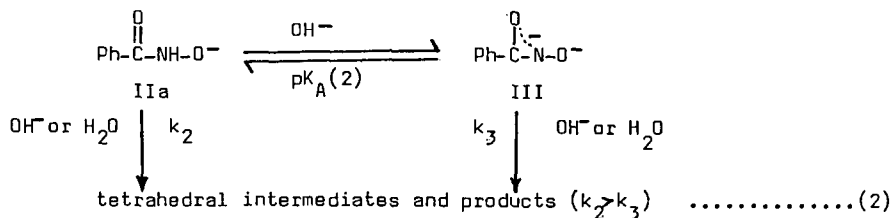
Fig. 3. Hydrolysis of I at constant μ ($[NaOH] = 5M, 80^\circ$)

It seems more likely that a pre-equilibrium is the cause of the rate maximum. Even at the lower concentrations used in this study the substrate will exist almost entirely as the anion (II).⁶ Hence any pre-equilibrium will involve one or more of the hydroxamate tautomers (eq. 1).



Spectroscopic studies⁷ of arylhydroxamates in aqueous solution suggest that the major tautomers are IIa and IIb, and that solid phenylhydroxamate salts exist largely as IIa.^{8,9} One possible pre-equilibrium could involve the anion tautomeric equilibrium in eq. 1. A shift in the position may occur, at high $[NaOH]$, from IIa to the probably less reactive IIb. The latter's hydration requirements are probably less and hence this tautomer may predominate in solutions where

hydration is restricted. A more likely explanation, however, is that a second ionisation occurs in solutions of high $[\text{NaOH}]$ - see eq. 2. A study of the uv/visible spectra of II in NaOH solutions up to a concentration of 12M suggests that this may indeed be the case: A plot of $\log_{10} I$ against the H_2 -acidity function^{10,11} is linear with a gradient of 1.08 and hence the intercept on the H_2 -axis at 15.8 can reasonably be expected to represent the thermodynamic pK_A value for the ionisation of II. From the value of $pK_A(2)$ it can be deduced that considerable ionisation occurs in solutions of NaOH concentrations where the rate maximum is observed. The hydroxamate dianion (III) is likely to be less reactive toward nucleophilic attack (eq. 2).



Hence k_0 begins to decrease when the concentration of dianion becomes significant and a rate maximum is observed.

In conclusion, as there is no direct evidence for the formation of a dianion (other than correlation of \log_{10} with H_2), we propose that the observed rate maximum is the direct result of the operation of one or more pre-equilibria. Work is in progress on ring substituted derivatives of I to clarify the issue and initial results indicate the existence of rate maxima.

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