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ON THE RATE MAXIMA OBSERVED IN THE ACID-HYDROLYSIS OF SOME ALKYLHYDROXAMIC ACIDS

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Abstract. Rate maxima seen in the acid-hydrolysis of 2,2-dimethyl- and phenylacetohydroxamic acids are discussed in terms of acid-base equilibria, transition state formation and the different acidity functions that control these steps.

Maxima have been observed for plots of observed rate constant (k_{obs}) versus acid concentration in the acid-hydrolysis of a wide variety of substrates, including arylhydroxamic acids[1]. These maxima are usually attributed to the existence of an A-2 mechanism, with an acid-base pre-equilibrium step. Mane and Jagdale also offer this explanation in their work on the acid-hydrolysis of acetohydroxamic acid and similar compounds[2]. However they present no evidence for the proposed acid-base equilibrium. Since there are other situations which can give rise to rate maxima[1], it was thought necessary to investigate more closely the acid-hydrolysis of some alkylhydroxamic acids. Accordingly, we report the results of a preliminary investigation into the acid-catalysed hydrolysis of 2,2-dimethylacetohydroxamic (I) and phenylacetohydroxamic acid (II)[3] in aqueous sulphuric acid.

A rate maximum is observed in each case (Fig 1) and both substances are shown conclusively to be involved in an acid-base equilibrium as indicated by a study of their uv spectra in sulphuric acid solutions of concentrations up to 10 M.

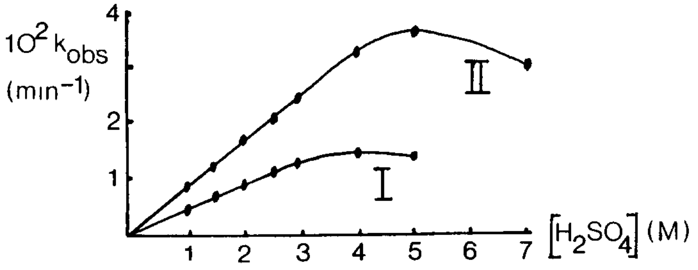
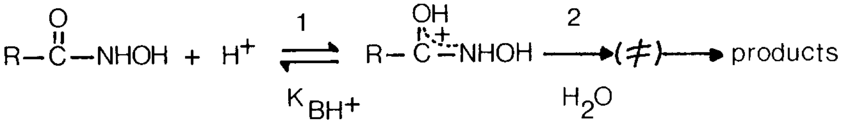


Figure 1
Rate Profile for the Hydrolysis of I and II in H_2SO_4 at 49.8°

Analysis of the equilibrium data by both a conventional acidity function method[4] and by Carpentier's method[5] indicates that I and II are Hammett bases for the amide acidity function H_A (^4H in Carpentier's terminology): the acid-base equilibrium is governed by the amide acidity function. Thus a plot of logI versus H_A for both I and II is linear with a slope of unity and pK_{BH^+} is -1.50 and -1.55 respectively. Similarly, a plot of $1/(A-A_B)$ versus $1/h_A$ is also linear and pK_{BH^+} is calculated as -1.40 and -1.66 respectively.

Analysis of the kinetic data below the acidity function value corresponding to pK_{BH^+} (below 3.0 M - H_2SO_4) was carried out by plotting log k_{obs} against H_x (various acidity functions)[6]. These plots are linear with unit slope only for the ketone acidity function ([5]H in Carpentier's terminology). This implies that the transition state formation from the conjugate acid in the rate-limiting step is controlled by this acidity function and not by H_A. In a recent analysis of the rate maxima which exist in the acid-hydrolysis of benzamides, Carpentier and co-workers have proposed that the rate maxima occur because the acid-base pre-equilibrium step and the transition state formation step are governed by different acidity functions[7]. In particular the acidity function controlling the transition state formation increases less rapidly than the acidity function governing the acid-base equilibrium, with increasing acid concentration.

Consideration of the results of this preliminary investigation, in the light of Carpentier's approach, points to the operation of an A2 - type mechanism (equ 1) in which the substrates are significantly protonated in the more concentrated acid solutions, in broad agreement with Mane and Jagdale.



$$R-\overset{O}{\overset{\|}{C}}-NHOH + H^+ \underset{K_{BH^+}}{\overset{1}{\rightleftharpoons}} R-\overset{OH}{\overset{\vdots +}{C}}\cdots NHOH \xrightarrow[H_2O]{2} (\neq) \longrightarrow \text{products}$$

(equ.1)

In particular the rate maxima can be considered a direct result of steps 1 and 2 being controlled by the amide acidity function and the ketone acidity function respectively.

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REFERENCE AND NOTES

1 A J Buglass, K Hudson and J G Tillett, J Chem Soc (B), 1971, 123.

2 B S Mane and M H Jagdale, React kinet Cat lett, 1977, 6, 417.

3 N-hydroxy-2,2-dimethylpropanamide and N-hydroxy-2-phenylethanamide, respectively.

4 K Yates, J B Stevens and A R Katritzky, Can J Chem, 1964, 42, 1957.

$$pK_{BH^+} = \log (A - A_B)/(A_{BH^+} - A) + H_x \ (= \log I + H_x)$$

A_B, A_{BH^+} and A are respectively the absorbance of the base, its conjugate acid and a mixture of the two at a particular value of H_x.

5 P Lemetais and J M Carpentier, J Chem Research, 1981 (S) 282; (M) 3369

$$1/(A - A_B) = 1/(A_B - A_{BH^+}) + K_{BH^+}/(A_B - A_{BH^+})h_x$$

The symbols have the same meaning as for ref 4; $H_x = -\log h_x$.

6 Monitored by the Fe(III) complexation method described in ref 1; λ_{max} = 520 nm.

7 P Lemetais and J M Carpentier, J Chem Research, 1983, (S) 34; (M) 0358.

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