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THE HYDROLYSIS OF AMIDES IN DILUTE ACID

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PREVIOUSLY available kinetic studies of the hydrolysis of aliphatic amides in dilute acid are due to Willems and Bruylants[2] and de Roo and Bruylants[3]. Bolton and Henshall[4] have noted significant differences between the Arrhenius parameters deduced from Bruylants' work and those which apply in hydrolyses catalysed by a cation-exchange resin.

As a preliminary to other studies of amide hydrolysis some of Bruylants' work has been re-examined and shown to be in serious error. The following second order rate constants were obtained for acetamide at 75·0° by (a) Bruylants and co-workers; (b) the present authors using three different catalysing acids:

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[2] M. Willems and A. Bruylants, Bull. soc. chim. Belges, **60**, 191 (1951).

[3] de Roo and A. Bruylants, ibid. **63** 140 (1954).

[4] P. D. Bolton and T. Henshall, J. Chem. Soc. 1226 (1962).

	(a) Bruylants	(b) Present Study			
	H_2SO_4 (0·05 N)	HCl (0·1 N)	HCl (0·05 N)	HClO (0·1 N)	HNO_3 (0·1 N)
$10^4.k_2$ (l.mole^{-1}sec.$^{-1}$)	4·70	10·5	10·4	10·2	10·0

Similar discrepancies were found at other temperatures and with other substrates.

Bruylants and co-workers determined rates by Nessler analysis for ammonia. We have used direct titration with dilute NaOH using a recording potentiograph (Metrohm E336) to plot the first differential of E.M.F. from a glass electrode cell *vs* titrant volume. This method allows simultaneous and independent analysis of both carboxylic acid and ammonium ion. In other respects our experimental techniques were identical with those of Bruylants.

As catalysing acid Bruylants used H_2SO_4 (initially 0·05 N) Using the same acid we were able to duplicate their results approximately if we assumed complete dissociation of the H_2SO_4. This assumption is untenable. If the incompleteness of the second stage of ionization of sulphuric acid is taken into account by calculating instantaneous hydrogen ion concentrations (obtained from extrapolation of literature values of the ionization of H_2SO_4[5]) then the same hydrolysis results gave second-order rate constants agreeing with those found in HCl and the other completely ionized acids. Similar errors do not appear to be present in Bruylants' work in alkaline solutions, and other workers have produced results

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[5] M. Kerker, *J. Amer. Chem. Soc.* **79** 3664 (1957).

in general agreement with these[6].

This revision of the rate constants for the homogeneous systems brings the entropy of activation (calculated at 55°) and energy of activation for resin catalysis and homogeneous catalysis to equality within probable experimental error (e.g. for acetamide E_a = 19·6 Kcals.; ΔS^* = −18·2 e.u. in dilute acid. cf E_a = 19·9 Kcals.; ΔS^* = −18·0 e.u. resin catalysed).

The experimental results for the resin catalysed amide hydrolysis quoted above require to be treated by the method described by Bolton and Henshall[4]. This analysis will lower the entropy of activation below that of an equivalent homogeneous system, and bring it into agreement with Hammett's general theory of resin catalysis[7]. From the revised values for homogeneous hydrolyses, however, the activation energy of acetamide hydrolysis in dilute acid is now shown to be approximately equal to that found in 4·0 M acid[8]. That portion of the evidence quoted by Bolton and Henshall in support of their approach which depended on the reported variation of activation energy with acid concentration must now be considered invalid.

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[6] J. Packer, A.L. Thomson and J. Vaughan, J. Chem. Soc. 2601 (1955).

[7] S. A. Bernhard and L. P. Hammett, J. Amer. Chem. Soc. 75, 1798, 5834 (1953).

[8] B. S. Rabinovitch and C. A. Winkler, Canad. J. Res. 20B,73 (1942).