The Acid-catalysed Hydrolysis of Benzonitrile

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The hydrolysis of benzonitrile has been carried out in sulphuric, perchloric, and hydrochloric acids over a wide range of acidities and temperatures. Analysis of these data by Zucker–Hammett, Bunnett, and Bunnett–Olsen criteria, and inverse solvent deuterium isotope effects are consistent with a mechanism involving equilibrium *N*-protonation, followed by rate-limiting attack of water on carbon.

EARLY investigations made on the acid-catalysed hydration of nitriles and hydrogen cyanide by Krieble [1] and Winkler [2] and their associates, established that the hydrolytic actions of mineral acids were quite different, that increasing acid concentration caused a large increase in rate, and that activation energies tended to decrease with increasing acid concentration. Two investigations [1c,3] have been made on the effects of substituents, but the only detailed mechanistic studies have been concerned with the hydroysis of cyanamide.[4,5] We report below our results for the hydrolysis of benzonitrile over an extensive range of acidities and temperatures in hydrochloric, sulphuric, and perchloric acids. Deuterium isotope effects have been measured and the data obtained have been applied to various criteria of reaction mechanism in an attempt to elucidate the role of water in the rate-determining step.

RESULTS AND DISCUSSION

Table 1 summarizes the results obtained for the hydrolysis of benzonitrile in acid solutions. (The values of c_{H^+} are calculated in terms of complete ionisation of the relevant acids.) The value of $pK_{AH^+} = -10.45$ [6] indicates that benzonitrile is a very weak base, and the equations applicable to hydrolysis of weak bases have been used in the application of the data in Table 1 to the criteria of mechanism which follow. Where the data are available, values of H_0 and a_w appropriate to the temperature of the rate measurements have been substituted into the equations of criteria of mechanism. This method has been described previously.[7]

Table 2 summarizes the results for hydrolysis in D_2SO_4 and DCl, together with the ratio $k_{\psi(D)}/k_{\psi(H)}$ calculated from comparison with the rates in H_2SO_4 and HCl respectively. These values, which are greater than unity, indicate that water acts as a nucleophile in the rate-determining step and that the mechanism involves specific hydrogen ion catalysis.

Table 3 shows the results of plotting the Zucker–Hammett relationship $\log_{10} k_\psi$ against $-H_0$. The correlation coefficients are generally very good, particularly when hydrochloric acid is the catalyst, and this agreement is indicative of specific hydrogen ion catalysis.[8] It is interesting to note that while the slopes for

TABLE 1

Hydrolysis of benzonitrile in concentrated solutions of mineral acids

t/°C	110·6	100·1	90·0	80·5	70·2	25·0
			$10^5 k_\psi$/s^{-1}			
c_{H^+}/M^{-1} Sulphuric acid						
17·76		2400				
16·65		1960	1440	959	345	8·51
15·40		1550				
14·07		1050	580	407	147	1·51
12·75		754				
11·48	962	430	145	74·5	26·4	0·20
10·30		207				
9·16	234	85·5	33·2	14·0	5·85	0·060
7·11	74·5	31·4	15·7	3·41	1·28	
5·31	23·0	11·5	3·04	1·55	0·43	
3·73	8·26	2·58	1·69	0·35	0·10	
2·32	2·34	1·25	0·73	0·11		
1·09	0·44	0·17	0·10			
0·52		0·077				
c_{H^+}/M^{-1} Perchloric acid						
11·60		655	270	87·5	30·7	
11·09		399				
10·33		153				
9·13	188	71·2	29·6	11·0	3·30	
8·01		20·9				
6·98	32·2	12·2	5·53	1·71	0·66	
6·02		6·26				
5·15	7·24	3·61	1·35	0·36		
3·58	1·29	0·55	0·16	0·093		
2·23	0·57	0·30	0·073			
1·05	0·27	0·11	0·036			
0·51		0·037				
c_{H^+}/M^{-1} Hydrochloric acid						
12·05		1100	635	496	140	
10·90		662	252	165	49·0	
10·40		486				
9·40	467		83·0	33·6	18·5	
8·80		141				
7·65	70·5	36·5	13·6	4·75	1·87	
6·04	22·4	9·85	2·88	1·27	0·37	
5·30		5·02				
4·42	7·28	2·63	1·09	0·33	0·12	
3·70		1·53				
2·85	3·36	1·17	0·35	0·081		
2·15		0·90				
1·55		0·43				

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[1] (*a*) V. K. Krieble and J. G. McNally, *J. Amer. Chem. Soc.*, 1929, **51**, 3368; (*b*) V. K. Krieble and A. L. Peiker, *ibid.*, 1933, **55**, 2326; (*c*) V. K. Krieble and C. I. Noll, *ibid.*, 1939, **61**, 560; (*d*) V. K. Krieble, F. C. Duennebier, and E. Colton, *ibid.*, 1943, **65**, 1479.

[2] (*a*) B. S. Rabinovitch, C. A. Winkler, and A. R. P. Stewart, *Canad. J. Research*, 1942, **20B**, 121; (*b*) J. D. McLean, B. S. Rabinovitch, and C. A. Winkler, *ibid.*, p. 168; (*c*) B .S. Rabinovitch and C. A. Winkler, *ibid.*, p. 221.

[3] D. Karve and D. V. Gharpure, *J. Univ. Bombay*, 1939, **8**, 139.

[4] (*a*) M. J. Sullivan and M. L. Kilpatrick, *J. Amer. Chem. Soc.*, 1945, **67**, 1815; (*b*) M. L. Kilpatrick, *ibid.*, 1947, **69**, 40.

[5] B. R. Mole, J. P. Murray, and J. G. Tillett, *J. Chem. Soc.*, 1965, 802.

[6] M. Liler and D. Kosanovic, *J. Chem. Soc.*, 1958, 1084.

[7] (*a*) C. A. Bunton, S. J. Farber, A. J. G. Milbank, C. J. O'Connor, and T. A. Turney, *J.C.S. Perkin II*, 1972, **1869**; (*b*) J. W. Barnett and C. J. O'Connor, *ibid.*, p. **2378**; (*c*) C. R. Smith and K. Yates, *J. Amer. Chem. Soc.*, 1971, **93**, 6578; (*d*) D. W. Farlow and R. B. Moodie, *J. Chem. Soc.* (*B*), 1971, 407.

[8] K. J. Pedersen, *J. Phys. Chem.*, 1934, **38**, 581.

Zucker–Hammett plots are approximately unity for hydrochloric acid, for sulphuric and perchloric acids the slopes are only half this value. The results are thus similar to those obtained by Deno *et al.*[9] for the acid dependence of the hydrolysis of acrylonitrile. Over the range 25·5—85·0% *w*/*w* H_2SO_4 their data showed that to within 10—30% $d\log_{10} k = -dH_0$.

TABLE 2

Deuterium isotope effect on the hydrolysis of benzonitrile at 100·1 °C

Acid	c_{D^+}/M^{-1}	$10^5 k_\psi$/s^{-1}	$k_{\psi(D)}/k_{\psi(H)}$
D_2SO_4	5·15	18·2	1·60
D_2SO_4	9·16	174	1·75
DCl	4·64	5·31	1·97
DCl	5·86	15·8	1·98

TABLE 3

Analysis of rate data for hydrolysis of benzonitrile by use of Zucker–Hammett ($\log_{10} k_\psi$ *vs.* $-H_0$) hypothesis

Acid	Sulphuric		Perchloric		Hydrochloric	
t/°C	Slope	Correln. coefft.	Slope	Correln. coefft.	Slope	Correln. coefft.
110·6	0·707	0·990	0·603	0·993	0·904	0·993
100·1	0·553	0·973	0·517	0·988	0·914	0·997
90·0	0·577	0·984	0·541	0·985	0·976	0·998
80·5	0·578	0·989	0·478	0·990	1·11	0·999
70·2	0·554	0·988	0·397	0·999	1·09	0·995
25·0	0·472	0·997				

TABLE 4

Analysis of rate data for hydrolysis of benzonitrile by use of Bunnett *w* and *w** relationships

Acid	Sulphuric		Perchloric		Hydrochloric		
t/°C	*w*	Correln. coefft.	*w*	Correln. coefft.	Correln. coefft. for *w* plot	*w**	Correln. coefft.
110·6	1·37	0·993	2·00	0·986	0·584	−3·69	0·994
110·1	1·24	0·995	2·06	0·996	0·816	−3·52	0·995
90·0	1·15	0·991	1·97	0·993	0·381	−3·82	0·997
80·5	1·04	0·996	1·99	0·999	0·942	−4·45	0·998
70·2	1·01	0·998	2·08	0·999	0·664	−4·26	0·993
25·0	0·87	0·981					

Krieble and Noll[1c] found that the Zucker–Hammett relationship did not hold for the hydrolysis of hydrocyanic acid or other nitriles they studied, but straight lines of non-unit slope were obtained using sulphuric acid as the catalyst. Using hydrochloric acid a straight line was obtained only for the substrate hydrogen cyanide. The data for hydrolysis of cyanamide[10] in nitric acid ($\leqslant$5M) exhibits unit slope, and Rabinovitch *et al.*[2a] obtained a linear relation of slope 0·9 for the hydrolysis of propionitrile in hydrochloric acid up to 5M, but deviations from linearity occurred at higher concentrations.

Table 4 gives the slopes (*w* values) and correlation coefficients for the Bunnett *w* plot[11a] of ($\log_{10} k_\psi + H_0$) against $\log_{10} a_w$ for the data in sulphuric and perchloric acids. For the data in hydrochloric acid only the correlation coefficients for the *w* plot are given, but both the slopes (*w** values) and correlation coefficients of the Bunnett *w** plot[11a] ($\log_{10} k_\psi - \log_{10} c_{H^+}$) against $\log_{10} a_w$ are tabulated.

Table 5 gives the slopes (ϕ values), intercepts ($\log_{10} k_2°$), and correlation coefficients for the plots of the standard formulation of the Bunnett–Olsen kinetic linear free-energy relationship[11b] ($\log_{10} k_\psi + H_0$) against ($H_0 + \log_{10} c_{H^+}$) for the data in sulphuric and perchloric acids, and the slopes [($1 - \phi$) values], intercepts ($\log_{10} k_2°$), and correlation coefficients for the plots of the original formulation of the kinetic l.f.e.r. ($\log_{10} k_\psi - \log_{10} c_{H^+}$) against ($-H_0 - \log_{10} c_{H^+}$), which has the same *y*-co-ordinate as the Bunnett *w** plot, for the data in hydrochloric acid.

The data for sulphuric and perchloric acids fit a Bunnett *w* plot with excellent correlation; in both cases the value of *w* lies in the region of water acting as a nucleophile in the rate-determining step. For the same two acids correlation with the standard formulation of Bunnett and Olsen's kinetic l.f.e.r. is reasonable, and generally the values of ϕ obtained lie in the region of water acting as a nucleophile, *i.e.* <0·56.

When hydrochloric acid is the catalysing acid the data do not fit the Bunnett *w* plot, but do fit the Bunnett *w** plot with excellent correlation. The value of *w** obtained is less than −2 and is therefore suggestive of water acting as a nucleophile in the rate-determining step (although the classification of *w** values[11a] is not clearly defined).

TABLE 5

Analysis of rate data for hydrolysis of benzonitrile by use of the Bunnett–Olsen linear free energy relationship

Acid	Sulphuric			Perchloric			Hydrochloric		
t/°C	$-\log_{10} k_2°$	ϕ	Correln. coefft.	$-\log_{10} k_2°$	ϕ	Correln. coefft.	$-\log_{10} k_2°$	$(1 - \phi)$	Correln. coefft.
110·6	5·32	0·379	0·971	5·83	0·482	0·998	5·52	0·885	0·987
100·1	5·49	0·532	0·975	6·11	0·555	0·993	5·93	0·896	0·996
90·0	5·92	0·502	0·985	6·61	0·528	0·987	6·48	0·971	0·997
80·5	6·44	0·480	0·987	6·89	0·568	0·995	7·16	1·13	0·999
70·2	6·85	0·496	0·986	7·00	0·636	1·000	7·56	1·11	0·993
25·0	8·75	0·559	0·997						

Since the Bunnett *w* plots for benzonitrile in hydrochloric acid were curved, we did not expect the standard formulation of the kinetic l.f.e.r. to give linear plots and this was true. On the other hand, the original formu-

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[9] N. C. Deno, T. Edwards, and C. Perizzolo, *J. Amer. Chem. Soc.*, 1957, **79**, 2108.

[10] G. Grube and G. Schmid, *Z. Physik Chem.*, 1926, **119**, 19.

[11] (*a*) J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973, 4978; (*b*) J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1917.

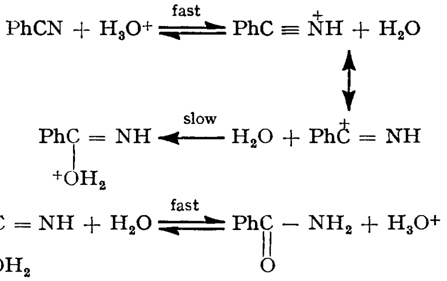
lation of the kinetic l.f.e.r., which has the same y coordinate as the Bunnett w^* plot, gave very good correlations. These results in hydrochloric acid are analogous to those found for the inversion of sucrose[12] in sulphuric, perchloric, and hydrochloric acids in which there was excellent correlation for the Bunnett w^* plots and for the plots of the original formulation of the kinetic l.f.e.r.

For the hydrolysis of benzonitrile by hydrochloric acid the original formulation of the kinetic l.f.e.r. gives a slope $(1 - \phi) = ca.\,0{\cdot}9$. Therefore $\phi = ca.\,0{\cdot}1$ and this value is in the region of water acting as a nucleophile in the rate-determining step.

Generally the values of ϕ, w, and w^* obtained in this investigation indicate that water acts as a nucleophile in the slow rate-determining step. Bunnett[11] emphasises, however, that mechanistic interpretation of w and ϕ values for reactions of weakly basic substrates is fraught with uncertainty.

As we have found previously for the hydrolysis of N-acetylsulphanilic acid[7b] values of w decrease whilst those of ϕ increase with decreasing temperature.

Mechanism.—In spite of the apparent anomaly of the data in hydrochloric acid when applied to the Bunnett hydration parameter treatment, compared with those in sulphuric and perchloric acids, the results in the deuteriated acids indicate that the role of water is unaffected by the nature of the mineral acid and acts as a nucleophile in the rate-determining step. The hydrolysis of benzonitrile can be considered to occur by the following mechanism (Scheme 1):



SCHEME 1

i.e. a rapid pre-equilibrium protonation to form a mesomeric cation is followed by slow nucleophile attack of a water molecule on the carbonium ionic form of the protonated intermediate.

The kinetic isotope effect (Table 2) supports this mechanism. D_3O^+ Is a considerably stronger acid in D_2O than H_3O^+ is in H_2O; the fast pre-equilibrium will therefore be shifted to the right in the deuteriated solvents, producing a greater concentration of the protonated species which is the reactant in the slow step of the reaction. Since benzonitrile is a very weak base whose tendency to protonate is small, such an increase in the concentration of the protonated species would cause an increase in the rate, and this was observed.

Temperature Effect.—Table 6 gives the values of the Arrhenius parameters E_a, $\log_{10} A$, and $\Delta S^‡$ as a function of molarity of acid and as mole %. At low concentrations of sulphuric acid E_a decreases. For perchloric acid only a small decrease in E_a is observed, while for hydrochloric acid E_a decreases markedly as the acidity increases. A similar decrease in E_a with increasing acidity was observed by Rabinovitch and Winkler[2] for the acid-catalysed hydrolysis of some aliphatic nitriles.

TABLE 6

Arrhenius parameters for the hydrolysis of benzonitrile

c_{H^+}/M^{-1}	Mole %	E_a / kcal mol^{-1}	$\log_{10} A/s^{-1}$	$\Delta S^‡$ (at 100·1 °C) / cal deg^{-1} mol^{-1}
		Sulphuric acid		
1·09	2·0	28·0	10·8	−12
2·32	4·4	28·2	11·6	−8
3·73	7·3	28·3	12·1	−6
5·31	10·9	26·8	11·7	−6
7·11	15·5	25·4	11·4	−9
9·16	21·6	24·0	11·1	−11
11·48	30·1	22·5	10·8	−12
14·07	42·3	19·7	9·7	−17
16·65	62·3	16·6	8·2	−24
		Perchloric acid		
1·05	2·0	28·4	10·6	−13
2·23	4·3	27·8	10·7	−12
3·58	7·2	27·4	10·8	−12
5·15	10·7	26·5	11·1	−10
6·98	15·3	25·2	10·9	−11
9·13	21·3	25·2	11·6	−8
11·60	29·6	25·2	12·6	−4
2·85	5·2	30·8	13·1	−1
4·42	8·0	27·0	11·3	−10
6·04	11·0	26·3	11·3	−9
7·65	14·1	24·4	10·8	−12
9·40	17·5	22·0	10·5	−15
10·90	20·2	20·1	9·6	−17
12·05	22·6	14·9	6·7	−30

These variations are in the same direction as those found by Leininger and Kilpatrick for the hydrolysis of sucrose[13] and ethylal[14] in concentrated hydrochloric acid. These latter results were interpreted in terms of a variation of the heat content of the activated intermediate with acid concentration, determined principally by the heat of dilution of the hydronium ion, H_3O^+. Such a decrease of solvation could therefore account for an activation energy decrease with increasing acid concentration. This explanation appears analogous to an earlier conclusion[15] that the Arrhenius parameters depend on the internal volume change for the reaction, and particularly on the relative solvation of reactants and activated complex.

The trends observed in the variation in entropy of activation for hydrochloric and sulphuric acids are somewhat similar to those outlined above for the variation in activation energies.

All species in solution are solvated so that in dilute

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[12] J. W. Barnett and C. J. O'Connor, *J. Chem. Soc.* (*B*), 1971 1163.

[13] P. M. Leininger and M. Kilpatrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2891.

[14] P. M. Leininger and M. Kilpatrick, *J. Amer. Chem. Soc.*, 1939, **61**, 2510.

[15] R. A. Ogg and O. K. Rice, *J. Chem. Phys.*, 1937, **5**, 140.

acid the intermediate species in the proposed mechanism (Scheme 1) is, in fact, $(\mathrm{PhC}\overset{+}{\mathrm{N}}\mathrm{H})(\mathrm{H_2O})_n$. As the acid concentration increases the water molecules of solvation will be gradually replaced by molecules of acid. The transition state will resemble the protonated intermediate and, in view of the known stabilisation of carbonium ions by acid media, it does not seem unreasonable that the energy requirements of the transition state solvated by acid will be less than those of the water solvated transition state.

Spectral Changes with Acid Concentration.—The method of Flexser *et al.*[16] is commonly used in the determination of basicity constants. This involves measuring the change in absorbance with varying acidity at a particular wavelength, and plotting the logarithm of the indicator ratio I against the appropriate acidity function, H,

i.e.
$$\begin{aligned} H &= \mathrm{p}K_{\mathrm{AH^+}} + \log_{10}\frac{c_{\mathrm{A}}}{c_{\mathrm{AH^+}}} \\ &= \mathrm{p}K_{\mathrm{AH^+}} - \log_{10} I \end{aligned}$$

Benzonitrile exhibits such a change in absorbance with changing acidity in sulphuric, hydrochloric, and perchloric acids, even in the region of relatively weak acid concentration ($\lambda_{\max.}$ and $\varepsilon_{\max.}$ both increase with increasing acidity).

If the difference in extinction coefficients at two selected wavelengths is plotted against the appropriate acidity function, the point of inflexion of the sigmoid curve so obtained is said to give the value of the acidity function at half protonation.[17] When such a plot was made for the benzonitrile data, using the H_0 acidity function, the H_0 values for the point of inflexion obtained were as follows: $\mathrm{HClO_4}$ (−3·8), $\mathrm{H_2SO_4}$ (−3·5), and HCl (−3·7).

Previous workers [6] have shown that benzonitrile is a very weak base, and the results of their conductometric studies showed that benzonitrile is not half-protonated until 99·8% $\mathrm{H_2SO_4}$; further, Arnett [18] used their results and calculated a value of $\mathrm{p}K_{\mathrm{AH^+}} = -10{\cdot}45$. The Raman [19] and proton magnetic resonance [20] studies of Deno and his co-workers have confirmed these conductometric results.

If this alternate evidence on the basicity constant of benzonitrile were not available, the observed change in absorbance, which is found even at low acid concentrations where no protonation occurs, could be misinterpreted in terms of benzonitrile being a moderate base having an H_0 value at half protonation of *ca.* −3·7. The methods of Davis and Geissman,[17] and Flexser *et al.*[16] must therefore be treated with caution when applied to protonation studies.

It is possible that the observed change in spectra for benzonitrile is due to a variation in the degree of hydrogen bonding. The interaction between a nitrile, RC≡N, and a Bronsted–Lowry acid, H–Y, leading to a hydrogen-bonded complex could be represented by the equation: [21]

$$\mathrm{R{-}C{\equiv}N\!:} + \mathrm{H{-}Y} \rightleftharpoons \mathrm{R{-}C{\equiv}N\!:\,.\,.\,H{-}Y}$$

Addition complexes RCN,*n*HX and 2RCN,*n*HX have indeed been isolated, *e.g.* the hydrochloride of propionitrile prepared by Gautier,[22] and the compounds of hydrocyanic acid with sulphuric and phosphoric acids with formulae $\mathrm{HCN,H_2SO_4}$ [23] and $\mathrm{HCN,H_3PO_4}$ [23,24] respectively.

EXPERIMENTAL

Materials.—Concentrated AnalaR sulphuric, perchloric, and hydrochloric acids were standardised against sodium hydroxide, and were diluted with deionised water by weighing to give solutions of the required percentage composition. Each dilution was then standardised against sodium hydroxide.

DCl (Merck., 99% D) and $\mathrm{D_2SO_4}$ (Merck., 99% D) were diluted with $\mathrm{D_2O}$ (B.D.H., 99·7% D).

Benzonitrile (B.D.H.) was purified by distillation (b.p. 191 °C).

Apparatus.—Hydrolysis reactions at all temperatures except 25 °C were carried out in oil-baths maintained at the required temperature (±0·1 °C), by using a Gallenkamp contact thermometer, Klaxon stirrer, and a heating element. The hydrolyses at 25 °C were carried out using a water-bath maintained at 25·0 °C (±0·1 °C) by use of a Tecam (Techne, Cambridge) temperature unit.

The analyses of the hydrolyses were carried out spectrophotometrically using a Unicam SP 800A recording spectrophotometer. A Cary 14 spectrophotometer was used for the measurement of the variation in spectra with varying acid concentration. The spectra were recorded from *ca.* 210 to 240 nm.

Measurement of Reaction Rates.—Benzonitrile (*ca.* 10^{-3} g) was dissolved in 10 ml of the appropriate acid. Aliquots (1 ml) were sealed in ampoules and placed in the appropriate temperature bath. Samples were removed after heating for *ca.* 0, ¼, ½, ¾, 1, 1½, 2 times the half-life of the reaction, and an infinite time sample was removed after heating for 8—10 times the half-life. The hydrolysis reaction was quenched by plunging the sample into a solid $\mathrm{CO_2}$–ethanol slurry. After the completion of a run, the samples were thawed and aliquots (1 ml) of the solution were then diluted with deionised water to 10 ml and analysed spectrophotometrically. The time taken to dilute and analyse the samples at room temperature is insignificant compared with the rate of hydrolysis at this temperature.

The hydrolysis was followed by observing the change in absorbance at 223 nm, an isosbestic point between benz-

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[16] L. A. Flexser, L. P. Hammett, and A. Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103.

[17] C. T. Davis and T. A. Geissman, *J. Amer. Chem. Soc.*, 1954, **76**, 3507.

[18] E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 233.

[19] N. C. Deno and M. J. Wisotsky, *J. Amer. Chem. Soc.*, 1963, **85**, 1735.

[20] N. C. Deno, R. W. Gaugler, and M. J. Wisotsky, *J. Org. Chem.*, 1966, **31**, 1967.

[21] J. Grundnes and P. Klaboe, 'The Chemistry of the Cyano Group,' ed. Z. Rappoport, Interscience–John Wiley, London, 1970, p. 136.

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[23] A. W. Cobb and J. H. Walton, *J. Phys. Chem.*, 1937, **41**, 351.

[24] G. Berger and S. C. J. Olivier, *Rec. Trav. chim.*, 1927, **46**, 600.

amide and benzoic acid. By using this isosbestic point, absorbance changes are a measure of conversion of nitrile into amide only, without interference from any subsequent conversion of amide to acid. The isosbestic point at 223 nm was found to be constant, irrespective of changes in acid concentration. In concentrated acid solutions another isosbestic point also exists at 257 nm, but in more dilute acid solutions it shifts to a lower wavelength and is, therefore, unsuitable for following the hydrolysis of benzonitrile to benzamide.

The absorbance at 223 nm is proportional to the concentration of nitrile and amide. Beer's law is obeyed and thus the decrease in absorbance can be used to measure the kinetics of the reaction. Under the experimental conditions the plot of $\log_{10}(A_t - A_\infty)$ *vs.* t (where A_t and A_∞ are the absorbances of the aliquots at time t and at infinite time respectively) gives a value of k_ψ, the pseudo-first-order rate constant for hydrolysis. Agreement was generally very good (±2%) and the average value of k_ψ is quoted in Table 1. For the slower runs the accuracy decreased to ±5% and these rates are quoted to only 2 significant figures in Table 2.

Least-squares analyses were carried out on an IBM 1130 computer.

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