216. *Conductometric Investigation of the Rate of Hydrolysis of Nitriles in 100% Sulphuric Acid.*

By (Miss) M. Liler and Dj. Kosanović.

The electrical conductivities of the solutions of acetonitrile and benzonitrile in 100% sulphuric acid at 25° decrease with time to a limiting value, owing to a decrease in the concentration of the highly mobile HSO_4^- ions which results from the reactions, $RCN + 2H_2SO_4 = R{\cdot}CO{\cdot}NH_2 + H_2S_2O_7$ (1), or $R{\cdot}CNH^+ + HSO_4^- + H_2SO_4 = R{\cdot}CO{\cdot}NH_3^+ + HS_2O_7^-$ (2), with subsequent solvolysis of the $HS_2O_7^-$ ion. Calculation of the first-order reaction rate constants from the electrical conductivity changes gives values increasing with concentration. Second-order reaction rate constants, corresponding to equation (2), are calculated to be: acetonitrile, $k = 8{\cdot}01 \times 10^{-2}$ kg. mole^{-1} min.$^{-1}$ (in the range 0·15—0·43 mole kg.$^{-1}$); benzonitrile, $k = 3{\cdot}54 \times 10^{-1}$ kg. mole^{-1} min.$^{-1}$ (in the range 0·07—0·19 mole kg.$^{-1}$); both independent of concentration. A possible reaction mechanism is discussed.

On the basis of electrical conductivity values for $t = 0$, obtained by extrapolation, the degrees of dissociation and the basic dissociation constants for the two nitriles have been obtained: acetonitrile $K_b = 0{\cdot}157$; benzonitrile $K_b = 0{\cdot}076$.

The only previous investigation of the behaviour of nitriles in sulphuric acid was made cryoscopically by Hantzsch [1] in 1909. He found that nitriles ionise as bases in sulphuric acid, the molecular weights obtained being about 70% of their normal values, in contrast to the majority of organic oxygen compounds, whose molecular weights in sulphuric acid he found to be about 50% of their normal values. On the basis of these results Hammett [2] classified nitriles as substances which are practically completely ionised in sulphuric acid,

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[1] Hantzsch, *Z. phys. Chem.*, 1909, **65**, 41.

[2] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., New York and London, 1940, p. 47.

behaving as simple strong bases. This is probably the reason why the attention of later investigators in this field has been diverted from nitriles, and the fact which arises from Hantzsch's investigations, that the nitriles are *not* strong bases in sulphuric acid, like a number of organic oxygen compounds, remained obscured. The weaker basicity of nitriles than of most oxygen bases has however, been observed, recently in some other investigations also.[3] The aim of the present investigation was originally to show that conductometrically, as well as cryoscopically, it can be proved that the nitriles are weak bases in sulphuric acid. In view of Hantzsch's finding [1] that the nitriles are regenerated when their solutions in sulphuric acid are poured into water, we expected to obtain constant electrical conductivity values for these solutions. However, our preliminary experiments showed that the electrical conductivities of the solutions of acetonitrile in sulphuric acid decrease with time, reaching finally a limiting value, which means that nitriles undergo some chemical change in sulphuric acid at a measurable rate. We have assumed that this is hydrolysis represented by the equation:

$$RCN + 2H_2SO_4 = R{\cdot}CO{\cdot}NH_2 + H_2S_2O_7 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

with subsequent ionisation of both reaction products, or

$$R{\cdot}CNH^+ + HSO_4^- + H_2SO_4 = R{\cdot}CO{\cdot}NH_3^+ + HS_2O_7^- \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

accompanied by the solvolysis of the $HS_2O_7^-$ ion. In the course of this reaction the concentration of highly conducting HSO_4^- ions is reduced and the conductivity therefore decreases. A careful examination of the changes of electrical conductivity with time has shown that first-order, as well as second-order, reaction rate constants can be calculated from them.

The rate of hydrolysis of nitriles has hitherto been investigated only for aqueous solutions [4] where they give, first, amides, then acids. In dilute acid solutions hydrolysis of amides is several times faster than that of nitriles, whereas in concentrated acid solutions this relation is reversed. Amides can be obtained by dissolving nitriles in 96% sulphuric acid, which means that the amides are not hydrolysed in this medium (see, however, ref. 5). Previous investigations have shown that acetamide and benzamide in 100% sulphuric acid ionise as strong simple bases and remain otherwise unchanged.[6] Therefore the simplest nitriles—acetonitrile and benzonitrile—were chosen for these investigations.

The applicability of the conductometric method for following the kinetics of a reaction depends on whether or not the changes of electrical conductivity are a known function of the decreasing concentration of reactants and the increasing concentration of the products, the most favourable dependence being a linear one. It is well known that in dilute solutions of bases in sulphuric acid and in dilute oleum the changes of electrical conductivity with concentration of the dissolved bases or sulphur trioxide are approximately linear, except in the region of the minimum corresponding to 100% sulphuric acid, owing to the self-dissociation of sulphuric acid.[7] Since reactions (1) or (2) occur, however, at relatively considerable ionic concentrations in sulphuric acid, it is a reasonable assumption that the self-dissociation of sulphuric acid will not affect the linearity of electrical conductivity changes with concentration in the course of the reaction. In fact, the concentration-dependence of the initial and the final value of electrical conductivity of the solutions of acetonitrile (in the range of 0·15—0·43 mole kg.$^{-1}$) and of benzonitrile

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[3] Lemaire and Lucas, *J. Amer. Chem. Soc.*, 1951, **73**, 5198; Pratt and Matsuda, *ibid.*, 1953, **75**, 3739; Tsubomura, *Bull. Chem. Soc. Japan*, 1954, **27**, 445.

[4] Krieble and Noll, *J. Amer. Chem. Soc.*, 1939, **61**, 560; Rabinovich, Winkler, and Stewart, *Canad. J. Res.*, 1942, **20**, *B*, 121; Rabinovich and Winkler, *ibid.*, p. 221; Remick, "Electronic Interpretations of Organic Chemistry," Chapman and Hall, Ltd., London, 1949, p. 422; Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1956, pp. 299—300.

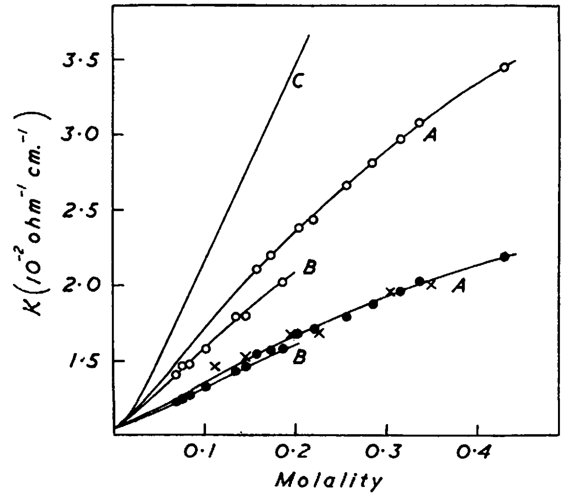
[5] Duffy and Leisten, *Nature*, 1956, **178**, 1242.

[6] Hantzsch, *Z. phys. Chem.*, 1907, **61**, 257; Oddo and Scandola, *Gazzetta*, 1909, **39**, I, 569; Tutundžić, Liler, and Kosanović, *Bull. Soc. chim. Beograd*, 1954, **19**, 225.

[7] Gillespie and Wasif, *J.*, 1953, 204.

(in the range of 0·07—0·19 mole kg.$^{-1}$) in sulphuric acid is approximately linear (Tables 3 and 4, p. 1088, and Figure). Therefore it is justifiable to use the changes of electrical conductivity with time to evaluate the changes of concentration of the nitriles in the course of the reaction.

We considered, however, that it was necessary to confirm the correctness of our assumption that the final values of electrical conductivities represent in fact the conductivities of amides in dilute oleum of equivalent concentration of sulphur trioxide. The first indication that this is so is that the solutions of benzonitrile, which is immiscible with water, give a layer of nitrile when poured into water 10—20 minutes after dissolution, but not after the completion of the reaction (when κ_∞ is reached) in agreement with the solubility of the amide in water. It has been observed also that after completion of the reaction the solutions evolve much more sulphur trioxide vapour than does 100% sulphuric acid itself. Final evidence was obtained by measuring the electrical conductivity of solutions of acetamide in dilute oleum of equivalent trioxide concentration. The trioxide content of the dilute oleum was estimated on the basis of electrical-conductivity values of dilute oleum given by Gillespie and Wasif.[7] An equivalent quantity of the amide was then dissolved in a weighed quantity of the oleum, and the electrical conductivity was measured again. The results are given in Table 7 (p. 1090). It was found that the electrical conductivity of the oleum was lowered by dissolution of the amide, as expected, because the equilibrium



Initial and final values of electrical conductivity of acetonitrile and benzonitrile in sulphuric acid.

A, *Acetonitrile.*
B, *Benzonitrile.*
C, $KHSO_4$.
×, *Acetamide in dilute oleum.*
○, *Initial.*
●, *Final.*

$$H_2SO_4 + H_2S_2O_7 \rightleftharpoons H_3SO_4^+ + HS_2O_7^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

is replaced by

$$CH_3{\cdot}CO{\cdot}NH_2 + H_2S_2O_7 \rightleftharpoons CH_3{\cdot}CO{\cdot}NH_3^+ + HS_2O_7^- \quad . \; . \; . \; . \; . \quad (4)$$

in which the ions of high mobility $H_3SO_4^+$ do not participate any more. The final conductivity is due to the solvolysis of $HS_2O_7^-$ ions:

$$HS_2O_7^- + H_2SO_4 \rightleftharpoons HSO_4^- + H_2S_2O_7 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

which gives a certain concentration of highly mobile HSO_4^- ions.[8] The equilibrium (4) is very probably shifted completely to the right, because the amides are ionised as strong bases in sulphuric acid (Hantzsch, and Oddo and Scandola [6]) and should be surely even more so in the presence of the stronger pyrosulphuric acid. The values of the electrical conductivities of acetamide in dilute oleum of equivalent concentration are also shown

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[8] Gillespie and Wasif, *J.*, 1953, 209.

in the Figure: within the limits of experimental error they correspond very well to the final values of electrical conductivity of the solutions of acetonitrile in sulphuric acid, which means that the final state is in fact a solution of the amide in dilute oleum. Similar conductometric evidence for the reaction of the acetic and benzoic anhydride in sulphuric acid was given by Flowers, Gillespie, and Wasif [9] by dissolving acetic acid and benzoic acid in dilute oleum.

In this way it has been proved that in 100% sulphuric acid solutions acetonitrile and benzonitrile undergo hydrolysis and that the rate constants calculated on the basis of electrical-conductivity changes represent the rate constants for hydrolysis of these nitriles in 100% sulphuric acid.

The results for the changes of electrical conductivity with time are given for two representative experiments with acetonitrile and benzonitrile in Tables 1 and 2. Since sulphuric acid is present in large excess, reaction (1) can be treated as a first-order reaction. The corresponding rate constants have been calculated from the equation

$$k_{\mathrm{I}} = \frac{2{\cdot}303}{t}\log\frac{a}{a-x} = \frac{2{\cdot}303}{t}\log\frac{\kappa_0-\kappa_\infty}{\kappa_t-\kappa_\infty} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

on the assumption that the conductivity decreases linearly with the concentration of the nitrile and that the total change of electrical conductivity in the course of the reaction is proportional to the initial concentration of the nitrile. This assumption is approximately correct, as can be seen from the Figure. However, the first-order rate constants obtained show in most experiments a trend to decrease with time, and the mean values of the rate constants show a definite increase with the concentration of the nitrile (Tables 3 and

TABLE 1. *Rate of hydrolysis of acetonitrile in 100% sulphuric acid on the basis of conductivity data.*

a_0 = 0·3359 mole kg.$^{-1}$, Temp. = 25°.

t (min.)	κ_t (10^{-2} ohm^{-1} cm.$^{-1}$)	10^2k_{I} (min.$^{-1}$)	[HSO$_4^-$]	a_t	β	10^2k_{II} (kg. mole^{-1} min.$^{-1}$)
0	(3·070)	—	0·1690	0·336	—	—
10	2·957	1·02	0·1605	0·303	0·255	6·66
20	2·857	1·07	0·1525	0·271	0·253	6·61
30	2·770	1·08	0·1460	0·243	0·245	6·93
40	2·695	1·07	0·1400	0·219	0·246	7·05
50	2·627	1·06	0·1350	0·198	0·244	7·19
60	2·569	1·05	0·1300	0·179	0·246	7·12
71	2·513	1·04	0·1260	0·161	0·243	7·25
∞	2·011					

k_{I} (mean) = 1·06 × 10^{-2} k_{II} (mean) = 6·98 × 10^{-2}

TABLE 2. *Rate of hydrolysis of benzonitrile in 100% sulphuric acid on the basis of conductivity data.*

a_0 = 0·1420 mole kg.$^{-1}$, Temp. = 25°.

t (min.)	κ_t (10^{-2} ohm^{-1} cm.$^{-1}$)	10^2k_{I} (min.$^{-1}$)	[HSO$_4^-$]	a_t	β	$10k_{\mathrm{II}}$ (kg. mole^{-1} min.$^{-1}$)
0	(1·790)	—	0·0730	0·1420	—	—
10	1·727	2·02	0·0687	0·1160	0·166	2·95
20	1·669	2·16	0·0645	0·0920	0·170	3·18
31	1·611	2·37	0·0603	0·0681	0·172	3·62
40	1·582	2·32	0·0583	0·0560	0·171	3·62
50	1·558	2·24	0·0568	0·0463	0·169	3·55
60	1·533	2·29	0·0550	0·0359	0·170	3·73
70	1·514	2·31	0·0536	0·0281	0·170	3·82
∞	1·446					

k_{I} (mean) = 2·28 × 10^{-2} k_{II} (mean) = 3·50 × 10^{-1}

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[9] Flowers, Gillespie, and Wasif, *J.*, 1956, 607.

4). This can be understood if the reaction is in fact a second-order one, as represented by equation (2).

TABLE 3. *The initial and final values of electrical conductivity and rate constants for solutions of acetonitrile.*

a_0 (mole kg.$^{-1}$)	κ_0 (10^{-2} ohm^{-1} cm.$^{-1}$)	κ_∞	$10^2 k_{\text{I}}$ (min.$^{-1}$)	β	$10^2 k_{\text{II}}$ (kg. mole^{-1} min.$^{-1}$)
0·1573	2·100	1·532	0·90	0·274	10·18
0·1722	2·191	1·561	0·88	0·278	9·90
0·2032	2·370	1·667	0·90	0·268	8·06
0·2206	2·425	1·706	1·00	0·250	7·48
0·2572	2·649	1·782	0·98	0·256	7·65
0·2840	2·800	1·858	1·04	0·256	7·62
0·3164	2·964	1·951	1·13	0·248	7·67
0·3359	3·070	2·011	1·06	0·246	6·98
0·4296	3·440	2·182	1·26	0·225	7·05

k_{II} (mean) $= 8{\cdot}01 \times 10^{-2}$

TABLE 4. *The initial and final values of electrical conductivity and rate constants for solutions of benzonitrile.*

a_0 (mole kg.$^{-1}$)	κ_0 (10^{-2} ohm^{-1} cm.$^{-1}$)	κ_∞	$10^2 k_{\text{I}}$ (min.$^{-1}$)	β	$10 k_{\text{II}}$ (kg. mole^{-1} min.$^{-1}$)
0·0708	1·400	1·218	1·48	0·184	3·48
0·0765	1·460	1·242	1·68	0·206	3·71
0·0845	1·470	1·260	1·78	0·174	3·82
0·1024	1·570	1·322	1·78	0·168	3·48
0·1358	1·780	1·420	2·12	0·187	3·43
0·1420	1·790	1·446	2·28	0·170	3·50
0·1876	2·012	1·569	2·64	0·173	3·36

k_{II} (mean) $= 3{\cdot}54 \times 10^{-1}$

Treatment of electrical conductivity changes in order to calculate the second-order constants has to take into account the fact that the $HS_2O_7^-$ ions formed in the reaction according to the equation (2) are solvolysed [equation (5)], regenerating in this way a certain amount of HSO_4^- which has taken part in the reaction. This means that the change of HSO_4^- concentration during the reaction is less than the corresponding change of the nitrile concentration. We have assumed that this change is proportional to the change of the nitrile concentration, the proportionality constant being less than unity. The rate of the reaction is then given by

$$\mathrm{d}x/\mathrm{d}t = k_{\text{II}}\,(a - x)\,(b - \beta x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $(a - x) = a_t$ is the actual concentration of the nitrile, calculated as $a_0(\kappa_t - \kappa_\infty)/(\kappa_0 - \kappa_\infty)$, and $(b - \beta x) = [HSO_4^-]$ is the actual concentration of HSO_4^- ions, calculated on the basis of electrical conductivity values, by taking the corresponding concentration c_s of a strong base ($KHSO_4$[10]) and using the equation:

$$[HSO_4^-] = c_s/2 + \sqrt{(c_s^2/4 + K_{\text{ap}})}$$

where $K_{\text{ap}} = 2{\cdot}2 \times 10^{-4}$ (25°) is the autoprotolysis constant of sulphuric acid (the procedure suggested by Gillespie and Solomons [11]); x is the concentration of the amide formed, calculated as $a_0(\kappa_0 - \kappa_t)/(\kappa_0 - \kappa_\infty)$, and β is the proportionality constant defined as $(b - [HSO_4^-])/x$. By integrating this differential equation (7) the values of the second-order rate constant can be obtained:

$$k_{\text{II}} = \frac{1}{t} \cdot \frac{1}{b - \beta a} \ln \frac{a(b - \beta x)}{b(a - x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In order to calculate k_{II} the value of β must be found. The values of β for all the experiments proved to be reasonably constant, as can be seen from the Tables 1 and 2 for the

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[10] Gillespie and Wasif, *J.*, 1953, 221.

[11] Gillespie and Solomons, *J.*, 1957, 1796.

two representative experiments. In this way the assumption made in deriving the differential equation (7) is justified and the integral equation (8) may be used to find the values of the rate constants. Whether the overall concentration or the concentration of the ionised nitrile is introduced in this equation does not make much difference. The degree of ionisation of the nitrile no doubt changes with the concentration and with the changes occurring in the solvent during the reaction, but these changes are probably not very substantial, since the nature of the medium does not change appreciably.

The results for the second-order rate constants are given for acetonitrile and benzonitrile in Tables 3 and 4 respectively. The values for the rate constants for the hydrolysis of acetonitrile decrease somewhat with concentration, whereas those for benzonitrile are very satisfactorily constant. We believe therefore that the conductometric method which we have described offers a simple means for the investigation of the hydrolysis of a number of nitriles in 100% sulphuric acid. This would give data for the elucidation of electronic effects in these reactions, which are at present not at all clear (cf. Hine[4]). The only condition for the applicability of the method to a given nitrile is that it does not react with sulphuric acid in any other way and that the amide which is formed remains unchanged in dilute oleum. This condition is probably fulfilled by most saturated aliphatic and aromatic nitriles, which may also be substituted by groups which do not react with sulphuric acid or show only simple basic ionisation. Investigation of the temperature coefficients of the rate of hydrolysis by the conductivity method should present no difficulties.

The fact that the second-order law is so well applicable to the nitrile hydrolysis in sulphuric acid suggests that the reaction probably proceeds by a bimolecular mechanism. The higher rate obtained for the hydrolysis of benzonitrile than of acetonitrile indicates that the rate-determining step is attack on positively charged carbon of the nitrile group by negative HSO_4^- ions:

$$\mathrm{R{\cdot}C{\vdots}NH^+ + HSO_4^- = R{\cdot}CO{\cdot}NH_2 + SO_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

It is probable that the ionised nitrile reacts, because the structure of the nitrile $\mathrm{R{\cdot}C{\vdots}N} \longleftrightarrow \mathrm{R{\cdot}C^+{\vdots}N^-}$ after ionisation has a definite excess of positive charge on the carbon $\mathrm{R{\cdot}C^+{\vdots}NH}$. The nature of the radical directly influences the donor ability of the nitrile, an aromatic radical causing, through its inductive influence, a higher positive charge on the carbon. The resonance transfer of the positive charge from the α-carbon atom to the benzene ring does not seem to be able to diminish this charge very much, since benzonitrile is a weaker base and reacts faster than acetonitrile. The HSO_4^- ions are also likely to be more reactive than the H_2SO_4 molecules, since the negative charge on the oxygen atoms is greater. Owing to the high dielectric constant of sulphuric acid, long-range electrostatic attraction between the ionised nitrile molecules and HSO_4^- ions is probably negligible, but the probability that a sulphuric acid molecule in the vicinity of the positive $\mathrm{R{\cdot}C{\vdots}NH^+}$ ion will lose one of its protons increases with increasing HSO_4^- ion concentration in the solution. This provides a possible explanation for the increase in the rate produced by increasing HSO_4^- ion concentration, in spite of the fact that the sulphuric acid molecules are present at any given moment in large excess around the positive nitrile ions.

Finally, the values of electrical conductivity for $t = 0$ (Tables 5 and 6), which are electrical conductivities of the nitriles in sulphuric acid, give the conductometric confirmation of the cryoscopic results of Hantzsch.[1] The line *C* in the Figure represents the electrical conductivity of potassium hydrogen sulphate,[10] which according to cryoscopic investigations shows 100% basic ionisation.[12] It can be seen that the values of electrical conductivities of the nitriles are considerably lower, indicating that the nitriles are incompletely ionised as bases in sulphuric acid. Using the procedure described by Gillespie and Solomons,[11] we have calculated the degrees of dissociation and the basic dissociation constants of these two nitriles. The values obtained are given in Tables

[12] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.

TABLE 5. *Basic dissociation constant of acetonitrile in 100% sulphuric acid.*

a_0 (mole kg.$^{-1}$)	κ_0 (10^{-2} ohm^{-1} cm.$^{-1}$)	α	K_b
0·1573	2·100	0·598	0·143
0·1722	2·191	0·587	0·147
0·2032	2·370	0·567	0·153
0·2206	2·425	0·542	0·143
0·2572	2·649	0·533	0·158
0·2840	2·800	0·524	0·165
0·3164	2·964	0·507	0·166
0·3359	3·070	0·502	0·171
0·4296	3·440	0·461	0·170

K_b (mean) $= 0·157 \pm 0·014$

TABLE 6. *Basic dissociation constant of benzonitrile in 100% sulphuric acid.*

a_0 (mole kg.$^{-1}$)	κ_0 (10^{-2} ohm^{-1} cm.$^{-1}$)	α	K_b
0·0708	1·400	0·579	0·0630
0·0765	1·460	0·595	0·0734
0·0845	1·470	0·545	0·0604
0·1024	1·570	0·527	0·0644
0·1358	1·780	0·508	0·0744
0·1420	1·790	0·493	0·0710
0·1876	2·012	0·464	0·0774

K_b (mean) $= 0·069 \pm 0·009$

TABLE 7. *Electrical conductivity of solutions of acetamide in dilute oleum of equivalent concentration.*

κ (oleum) (10^{-2} ohm^{-1} cm.$^{-1}$)	1·520	1·681	1·864	1·966	2·211	2·306
Concn. (mole kg.$^{-1}$)	0·112	0·145	0·195	0·226	0·305	0·350
κ (amide in oleum) (10^{-2} ohm^{-1} cm.$^{-1}$)	1·457	1·521	1·668	1·678	1·949	1·996

5 and 6. The basic dissociation constants of the two nitriles are reasonably constant and are comparable in magnitude with those of nitrotoluenes.[11]

EXPERIMENTAL

Materials.—Sulphuric acid was prepared according to Kendall and Carpenter.[13] Its m. p. was 10·4° and κ_{25} was $1·05 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$.

Acetonitrile. A " B.D.H. laboratory reagent " was treated with phosphoric oxide and then distilled. It had m. p. −41°, d_4^{25} 0·7768.[14, 15]

Benzonitrile. A product from Dr. Fraenkel and Dr. Landau, Berlin, of m. p. −13·3°,[15] was not purified.

Acetamide. Material from E. Merck, Darmstadt, was recrystallised from benzene, then having m. p. 80·0°.

Method.—The measurements of electrical conductivity were carried out as previously described.[16] The solutions were prepared in the following way. Sulphuric acid (usually 15—20 g.) was weighed into a small glass-stoppered bottle, which was then kept in a water-thermostat at 25° ± 0·05° together with the empty electrical conductivity cell. After about 15 min. the bottle was taken out, and its weight quickly checked. The desired quantity of the nitrile was then added from a 1 ml. pipette, the mixture shaken, and the zero time noted. The bottle was then weighed again, and the mixture immediately poured into the conductivity cell in the thermostat. The whole procedure of preparing the solution lasted usually not more than 3—4 min. Electrical conductivity was measured after 10 min., then at 10 min. intervals. Values of electrical conductivity for $t = 0$ were found by graphical and numerical extrapolation of the curves. The final values of electrical conductivity were measured after 24 hr. and remained afterwards unchanged. Since the work was performed with relatively small quantities of sulphuric acid and the addition of the nitriles was made with an ordinary pipette, it is possible that the exclusion of moisture was not perfect in some experiments, which would account for the variations of the conductivity values themselves as well as of the reaction rate constants.

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INSTITUTE OF CHEMISTRY, BELGRADE, YUGOSLAVIA. [*Received, September 9th,* 1957.]

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[16] Tutundžić and Liler, *Bull. Soc. chim. Beograd*, 1953, **18**, 521.