

1024. *N-Substituted Heterocyclic Cations. Part IV.* Rates and Equilibria in the Reactions of the N-Cyano-quinolinium and -isoquinolinium Ions in Dilute Aqueous Acids. Some Salt Effects on the Acidity Function H_R .*

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The equilibria between the *N*-cyano-quinolinium and -isoquinolinium ions and their corresponding pseudo-bases have been studied and shown to be dependent upon the acidity function H_R . The effect of salts on one of these equilibria has been used to evaluate the effect of salts on the acidity function. The hydrolysis of the two ions occurs through the hydrolysis of the cyano-groups of the pseudo-bases; in the case of the isoquinoline pseudo-base, the intermediate *N*-carbamoylisoquinolinium ion has been isolated as the fluoroborate. In sulphuric acid there is additional nucleophilic catalysis of the hydrolysis of the *N*-cyanoquinolinium ion by bisulphate ion.

PREVIOUSLY¹ some differences in the chemistry of the *N*-cyano-quinolinium and -isoquinolinium ions have been explored. One unexplained difference was the isolation of *N*-carbamoylisoquinolinium fluoroborate in the reaction of the *N*-cyanoisoquinolinium ion with fluoroboric acid; in the corresponding reaction of the *N*-cyanoquinolinium ion no such intermediate was obtained. We have explored in detail the reaction of the two ions in acidic solution, with particular reference to the nature of the hydrolyses and the equilibria, if any, between the ions and their pseudo-bases.

The N-Cyanoquinolinium Ion.—Spectrophotometry in aqueous perchloric and sulphuric acid showed that up to three heterocyclic species are present in detectable amounts at any concentration of acid considered in this work. These are the *N*-cyanoquinolinium ion (I), its pseudo-base 1-cyano-1,2-dihydro-2-hydroxyquinoline (II), and their hydrolysis product, the quinolinium ion (III). Equilibrium between the *N*-cyanoquinolinium ion and its pseudo-base was established immediately at any acidity, but the protonated quinolinium ion always formed at a measurable rate.

Equilibria. The equilibrium concentrations of the *N*-cyanoquinolinium ion and its pseudo-base were determined spectrophotometrically by using the longest wavelength band of the ion (λ_{\max} 365 m μ); in this region absorption by the pseudo-base and other species is negligible. The ratios of the equilibrium concentrations of the *N*-cyano-

TABLE 1.

HClO ₄ (M)	0.62	0.86	1.23	1.74
$-H_R$	0.43	0.78	1.29	1.88
$\log X^*$ (± 0.03)	-0.42	-0.11	0.31	0.84

* $X = [\text{QCN}^+]/[\text{QCNOH}]$.

TABLE 2.

H ₂ SO ₄ (M)	1.94	1.59	1.39	1.25	1.06	0.78
$-H_R$	1.56	1.20	1.02	0.89	0.71	0.38
$\log X^*$ (± 0.03)	0.83	0.42	0.21	0.115	-0.07	-0.36

* $X = [\text{QCN}^+]/[\text{QCNOH}]$.

quinolinium ion (for simplicity in equations referred to as QCN⁺) and its pseudo-base (referred to as QCNOH) determined in different concentrations of aqueous perchloric acid at 22° are shown in Table 1. They may be expressed by eqn. (1) where H_R † is the acidity function defined by eqn. (1a) for an equilibrium of the type $R^+ + H_2O \rightleftharpoons ROH + H^+$ and measured by Deno *et al.*² by using a series of triarylmethylcarbonium ions (R⁺) in perchloric acid as indicators, the term pK_{ROH} having been determined separately.

$$\log[\text{QCN}^+]/[\text{QCNOH}] = -0.86H_R - 0.79 \quad (1)$$

$$H_R = pK_{ROH} - \log[R^+]/[ROH] \quad (1a)$$

* Part III, Johnson, *J.*, 1964, 200.

† H_R is sometimes referred to as J_0^4 and C_0 .

¹ M. D. Johnson, *J.*, 1962, 283; M. D. Johnson and J. H. Ridd, *J.*, 1962, 291; M. D. Johnson, *J.*, 1964, 200.

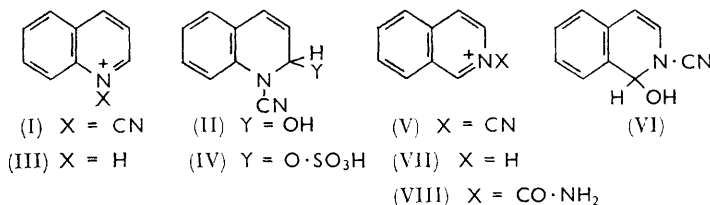
² N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Petersen, *J. Amer. Chem. Soc.*, 1959, **81**, 2345, 6535.

The ratios of the concentrations of the *N*-cyanoquinolinium ion and its pseudo-base at various concentrations of aqueous sulphuric acid are shown in Table 2 and can be expressed by eqn. (2).

$$\log[\text{QCN}^+]/[\text{QCNOH}] = -0.99H_R - 0.77 \quad (2)$$

where H_R is the acidity function defined by eqn. (1a) but determined in aqueous sulphuric acid.³

The N-cyanoisoquinolinium Ion.—Spectrophotometry of the reaction of the *N*-cyanoisoquinolinium ion in aqueous perchloric acid showed that up to four heterocyclic species are present in detectable amounts at any concentration of acid. These are the *N*-cyanoisoquinolinium ion (V), its pseudo-base, 2-cyano-1-hydroxy-1,2-dihydroisoquinoline (VI), and their hydrolysis products, the isoquinolinium ion (VII) and the *N*-carbamoyliso-



quinolinium ion (VIII), whose structure is discussed later. Equilibrium between the *N*-cyanoisoquinolinium ion and its pseudo-base was attained immediately at each concentration of acid, but the overall hydrolysis always occurred at a measurable rate.

Equilibria. The measurement of the ratios of the equilibrium concentrations of the *N*-cyanoisoquinolinium ion (referred to in equations as isoQCN⁺) and its pseudo-base (isoQCNOH) in aqueous perchloric acid was hindered by the rapid hydrolysis of the *N*-cyanoisoquinolinium ion to the *N*-carbamoylisoquinolinium ion and by possible

TABLE 3.

HClO ₄ (M)	-H _R	log Y* (±0.03)	HClO ₄ (M)	-H _R	log Y* (±0.03)
1.12	1.12	-0.71 ^a	2.40	2.64	0.48 ^a
1.39	1.5	-0.37 ^a	2.50	2.74	0.61 ^a
1.60	1.73	-0.13 ^a	1.69	1.85	0.08 ^b
1.89	2.08	0.04 ^a	2.00	2.17	0.17 ^b
2.05	2.24	0.21 ^a	2.31	2.53	0.37 ^b

* Y = [isoQCN]/[isoQCNOH].

^a By extrapolation method at 400 mμ. ^b By isosbestic point method at ca. 360 mμ.

uncertainties in medium effects on spectra, but these difficulties were overcome by using two methods, described later, which led to the same results.

The results obtained at 22° are shown in Table 3 and can be expressed by eqn. (3). The

$$\log\{[\text{isoQCN}^+]/[\text{isoQCNOH}]\} = -0.81H_R - 1.62 \quad (3)$$

deviation of the slopes derived from eqns. (1) and (3) from unity implies that the equilibria involving (a) the *N*-cyano-cations, and (b) the triarylmethylcarbonium ions do not have exactly the same dependence upon perchloric acid concentration.

Since pK_{ROH} is defined (eqn. 1a) as the value of H_R at which $[\text{R}^+] = [\text{ROH}]$, the value of $pK_{\text{ROH}} = -0.86 \pm 0.1$ for the *N*-cyanoquinolinium ion can be obtained by reference to eqns. (1) and (2); similarly $pK_{\text{ROH}} = -2.0 \pm 0.1$ for the *N*-cyanoisoquinolinium ion can be obtained from eqn. (3). These values are not significantly altered by a temperature difference of several degrees. The *N*-cyanoisoquinolinium ion is therefore the stronger acid, but both *N*-cyano-cations are enormously stronger acids than the corresponding *N*-methyl cations ($pK > 12$), thus indicating the extremely large electron-withdrawing

³ N. C. Deno, J. J. Jaruzelski, and A. Sahriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

effect of the cyano-group when attached to nitrogen, and the wide range of pK_{ROH} values possible in this field.

Hydrolysis of the N-Cyano-cations.—The hydrolysis of the *N*-cyanoquinolinium ion to the quinolinium ion was studied over a wide range of acid concentration. In up to 6*M*-perchloric acid the disappearance of the *N*-cyanoquinolinium ion followed first-order kinetics over at least three half-lives, and the rate coefficients were independent of the initial concentration of the *N*-cyano-ion. In greater than 6*M*-perchloric acid, and in sulphuric acid, only initial rates were measured, but the first-order rate coefficients were also insensitive to the initial concentration of the *N*-cyano-ion. For any particular value of H_{R} , H_0 (defined below), or stoichiometric acidity, the observed rate coefficient, k_{obs} (sec^{-1}), at 30° for the hydrolysis in sulphuric acid (Table 4) is greater than that for perchloric acid (Table 5). The significance of this rate difference is discussed later, but

TABLE 4.

H_2SO_4 (M)	$\log k_{\text{obs}}$ (± 0.01)	$\log k_{\text{b}}$	$\log (k_{\text{b}} - k_{\text{a}})$	$-H_0$	$[\text{HSO}_4^-]$	$\log [\text{HSO}_4^-] - H_0$
0.650	-2.41	-2.30	-2.60	0.05	0.47	-0.28
0.791	-2.34	-2.18	-2.45	0.12	0.56	-0.13
1.13	-2.08	-1.78	-1.97	0.34	0.81	0.25
1.46	-2.05	-1.55	-1.73	0.52	1.02	0.53
1.81	-2.06	-1.31	-1.51	0.74	1.24	0.83
2.42	-2.12	-0.88	-1.08	1.07	1.62	1.38
2.96	-2.25	-0.57	-0.77	1.34	1.98	1.64
4.25	-2.57	0.40	0.30	1.93	2.90	2.39
5.23	-2.94	0.97	0.88	2.36	3.64	2.92
5.85	-3.05	1.43	1.35	2.65	4.10	3.26
8.00	-3.40	3.21	3.17	3.85	6.2	4.64
11.95	-4.37	6.71	6.73	5.84	11.1	6.88

TABLE 5.

HClO_4 (M)	$\log k_{\text{obs}}$ (± 0.01)	$\log k_{\text{a}}$	$-H_0$	HClO_4 (M)	$\log k_{\text{obs}}$ (± 0.01)	$\log k_{\text{a}}$	$-H_0$
0.62	-2.89	-2.75	-0.08	2.51	-2.95	-1.35	1.02
0.862	-2.79	-2.52	0.12	3.53	-3.31	-0.83	1.49
1.23	-2.70	-2.38	0.37	4.55	-3.61	-0.20	1.99
1.54	-2.73	-2.00	0.54	5.20	-3.84	0.24	2.36

it is important that the values of k_{obs} reach a maximum in each acid at $H_{\text{R}} = -1.1 \pm 0.3$, *i.e.*, at the value of H_{R} corresponding to the pK_{ROH} of the *N*-cyanoquinolinium ion. Since the acidity function $-H_{\text{R}}$ increases faster than the acidity function $-H_0$ with stoichiometric acid concentration in this region of acidity, the existence and position of the maximum shows that the overall reaction rate is dominated by the change in the equilibrium concentrations of the *N*-cyanoquinolinium ion and its pseudo-base (a function of $-H_{\text{R}}$), rather than by the change in rate associated with one of the species (probably a function of water activity and/or acidity function H_0). The rate coefficients k_{a} , which relate to reaction through the pseudo-base, are given by k_{obs}/f , where f is the fraction of the *N*-cyano-species present in the pseudo-base form at each particular concentration of perchloric acid. They are assembled in Table 5, and are a function of the acidity function H_0 as shown in eqn. (4); where H_0 is defined⁴ by eqn. (5) and calculated from the equilibrium concentrations of the protonated and unprotonated forms of a series of aromatic amines at different acid concentrations; the term pK_{a} refers to the amine in question.

$$\log k_{\text{a}} = -1.24H_0 - 2.66 \quad (4)$$

$$-H_0 = \log[\text{ArNH}_3^+]/[\text{ArNH}_2] - pK_{\text{a}} \quad (5)$$

⁴ M. A. Paul and F. A. Long, *Chem. Revs.*, 1957, 57, 1.

The slope, but not the linearity, of the plot derived from eqn. (4) is markedly dependent on the slope derived from eqn. (1); *e.g.*, for a slope of 0.78 from eqn. (1), the slope derived from eqn. (4) becomes unity. The implications of eqn. (4) are discussed later.

The hydrolysis of the *N*-cyanoisoquinolinium ion in perchloric acid occurs in two stages. In the first, the *N*-cyanoisoquinolinium ion (V; $\lambda_{\text{max.}}$ * 297, 306.5, 381 μ ; $\log \epsilon$ 3.84, 3.89, 3.70) is hydrolysed to the *N*-carbamoylisoquinolinium ion (VIII; $\lambda_{\text{max.}}$ * 286, 295, 358 μ ; $\log \epsilon$ 3.61, 3.51, 3.59) with isosbestic points at 242, 261.5, 284, 314, and 360 μ in 6.1M-perchloric acid. In the second stage the *N*-carbamoylisoquinolinium ion changes to the isoquinolinium ion (VII; $\lambda_{\text{max.}}$ 266, 274 333 μ ; $\log \epsilon$ 3.17, 3.18, 3.51) with isosbestic points at 231, 262, 300, and 339 μ in 3M-perchloric acid. In 8—12M-perchloric acid the two stages are distinct, but at lower acidities the second reaction intrudes upon the first.

The first-order rate coefficients (k_{obs} , sec.^{-1}) at 25° for the formation of the *N*-carbamoylisoquinolinium ion, which were independent of the initial concentration of the *N*-cyanoisoquinolinium ion, passed through a maximum at $-H_{\text{R}} = 1.8 \pm 0.2$, *i.e.*, at the value of H_{R} corresponding to the $\text{p}K_{\text{ROH}}$ of the *N*-cyanoisoquinolinium ion. By similar reasoning to that used for the *N*-cyanoquinolinium ion, it follows that the overall rate is dominated by the equilibrium between the *N*-cyanoisoquinolinium ion and its pseudo-base. The rate coefficients k_{a} , which relate to reaction through the pseudo-base, are the observed rate coefficients divided by the mole fraction of the pseudo-base present at each acid concentration. They are shown in Table 6 and are a function of the acidity function H_0 as shown in eqn. (6). The similarity between eqns. (4) and (6) suggests that the hydrolyses

$$\log k_{\text{a}} = -1.0H_0 - 2.22 \quad (6)$$

of the *N*-cyano-quinolinium and -isoquinolinium ions follow the same mechanism. The equations show that the transition states each involve the *N*-cyano-cation and at least one molecule of water, but they do not discriminate between the following possibilities: protonation of the pseudo-base or some isomer of the pseudo-base, or reaction of water with the *N*-cyano-cation.

TABLE 6.

HClO ₄ (M)	$\log k_{\text{obs}} (\pm 0.01)$	$\log k_{\text{a}}$	$-H_0$
5.85	-3.00	0.63	2.74
4.34	-2.52	-0.41	1.89
2.64	-1.99	-1.13	1.08
1.79	-1.91	-1.56	0.67
0.862	-2.28	-2.21	-0.06
0.624	-2.54	-2.50	-0.20

TABLE 7.

HClO ₄ (M)	$\log k_{\text{e}} (\pm 0.01)$	$-H_0$
2.86	-3.41	1.17
1.75	-2.65	0.66
1.45	-2.53	0.49
1.14	-2.28	0.32
0.775	-1.92	-0.11
0.485	-1.59	-0.31

A choice between these mechanisms can be made from a consideration of the rate of hydrolysis of cyanamide. The data of Sullivan and Kilpatrick⁵ show that the rate of hydrolysis of cyanamide at 25° and at 30° has a similar magnitude and dependence on H_0 (eqns. 7 and 8) as have the corrected rate coefficients k_{a} and k_{d} for the pseudo-bases (eqns. 4 and 6). The pseudo-bases are themselves substituted cyanamides, and as it has been

$$\log k = -0.92H_0 - 2.84 \quad (25^\circ) \quad (7)$$

$$\log k = -0.91H_0 - 2.59 \quad (30^\circ) \quad (8)$$

shown that alkyl and aryl substituents have little effect on the rate of hydrolysis of cyanamide,⁶ it may be concluded that the *N*-cyano-cations are hydrolysed through the acid-catalysed hydrolysis of the cyano-group of the pseudo-bases. Bunnett⁷ has interpreted

* Wavelength maxima are here quoted for 12M-perchloric acid: for 6M and lower concentrations of acid the values are slightly different.

⁵ M. J. Sullivan and M. L. Kilpatrick, *J. Amer. Chem. Soc.*, 1945, **67**, 1815.

⁶ T. Mukaiyama, S. Ohishi, and H. Takamura, *Bull. Chem. Soc. Japan*, 1954, **27**, 416.

⁷ J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4978.

the data on cyanamide in terms of a nucleophilic attack of water on the protonated cyano-group, because plots of $\log k + H_0$ against $\log a_{\text{H}_2\text{O}}$ have slopes of approximately unity (which represents in effect the order of reaction with respect to water). Similar plots for the *N*-cyano-ions are not meaningful because their slopes would be markedly dependent, like those of eqns. (4) and (6), on the rather imprecise slopes of eqns. (1) and (3), respectively.

The corrected rate constants k_b for the hydrolysis of the *N*-cyanoquinolinium ion in sulphuric acid (Table 4), which are the observed rate coefficients divided by the fraction of the *N*-cyano-species present as the pseudo-base at each acid concentration, are greater, and rise more steeply with increasing acid concentration, than the corrected rate coefficients k_a (Table 5) in perchloric acid. This enhanced reactivity is far too great to be due to changes in the water activity, and must be due to catalysis by some species derived from the sulphuric acid, probably bisulphate ion.* Such catalysis could be brought about by (i) formation of the pseudo-base ester (IV) which would react similarly to the pseudo-base, or (ii) nucleophilic catalysis of the acid-catalysed hydrolysis of the pseudo-base.

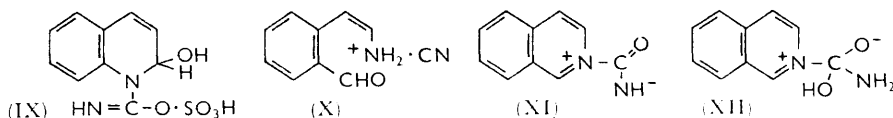
The formation of the ester (IV) cannot be the whole cause of the rate difference, because calculations show that irrespective of the rate of reaction of the ester and the value of the equilibrium constant K (eqn. 9), the rate profile could not be the same as that observed.

$$K = [\text{HSO}_4^-][\text{QCN}^+]/[\text{Ester (IV)}] \quad (9)$$

Nucleophilic catalysis of the acid-catalysed hydrolysis of the pseudo-base by bisulphate ion would follow the rate expression (10) where k_c is the rate coefficient for the catalysed

$$k_b = k_a + k_c[\text{HSO}_4^-]h_0 \quad (10)$$

reaction, and h_0 is $\text{antilog}(-H_0)$. The bisulphate ion catalysis is confirmed by the linearity and unit slope of a plot of $\log(k_b - k_a)$ against $\log[\text{HSO}_4^-] - H_0$ up to $-H_0 = 2.7$. Above this value the slope increases, but this deviation can be accommodated because (a) the values of k_a involve greater extrapolation of eqns. (1) and (2) than can be justified, and (b) reaction through the ester (IV) may well be significant at higher acid concentration. This catalysis by bisulphate ion is further evidence in favour of the acid-catalysed hydrolysis of the pseudo-base, because similar catalysis has been observed in the hydrolysis of cyanamide and its derivatives;⁶ the intermediate (IX) is envisaged.



Hydrolysis of the N-Carbamoylisoquinolinium Ion.—The *N*-carbamoylisoquinolinium ion was isolated as the fluoroborate, which is unstable in the presence of traces of moisture and changes rapidly to isoquinolinium fluoroborate. It has a characteristic infrared spectrum with a very strong carbonyl absorption at 1795 cm^{-1} ; all samples also absorbed at 2270 cm^{-1} , but this peak, the intensity of which varied from sample to sample, and increased in intensity during measurement of the spectrum in a Nujol mull, was due to the liberation of cyanate ion. The analysis, spectra, and mode of formation indicated either the *N*-carbamoylisoquinolinium ion or an open-chain ion (X). The latter was ruled out because (a) there is no sign of proton loss even in dilute acid, and (b) it is doubtful whether the carbonyl stretching frequency of an aromatic aldehyde could be as high as 1795 cm^{-1} . The first-order rate coefficients (k_a , sec^{-1}) at 25° for the hydrolysis of the *N*-carbamoylisoquinolinium ion to the isoquinolinium ion were independent of the initial concentration

* All data on species present in sulphuric acid are taken from reference 8.

⁶ T. F. Young, L. F. Maranville, and H. M. Smith, "The Structure of Electrolyte Solutions," ed. W. J. Hamer, John Wiley, New York, 1959, p. 35.

of the reactant and decreased with increasing acidity. The results are shown in Table 7 and can be expressed by equation (11). This is consistent with a slow decomposition of

$$\log k_c = 1.14H_0 - 1.98 \quad (11)$$

the conjugate base (XI) of the *N*-carbamoylisoquinolinium ion to cyanic acid and isoquinoline, or less likely, the nucleophilic displacement of isoquinoline by water (or hydroxide ion) with the formation of unstable carbamic acid, *via* the intermediate (XII). In either case cyanate ion would be formed, and its formation was confirmed by the isolation of a complex cyanate when the *N*-carbamoylisoquinolinium ion was decomposed in an aqueous solution of pyridine and cupric ion. The alternative mechanism involving the reaction of the pseudo-base of the *N*-carbamoylisoquinolinium ion can be ruled out because of the stability of *NN*-disubstituted ureas⁶ (the pseudo-base being such a compound) in dilute acid. As no evidence could be obtained for the presence of the *N*-carbamoylquinolinium ion, it must be very much less stable than the *N*-carbamylisoquinolinium ion, but the reason for this is not apparent.

APPENDIX

Effect of Added Salts on H_R .—The effect of added salts on the ratio $[QC\dot{N}^+]/[QCNOH]$ was also studied, and the values of H_R for each salt concentration were calculated using

TABLE 8.

HClO ₄ (M)	0.125	0.25	0.34	0.44	0.55	0.74	1.04	0.75	1.05
log X^d	-0.59	-0.31	-0.07	0.15	0.23	0.50	0.81	0.24	0.30
- H_R^a	-0.83	-0.40	-0.14	0.10	0.29	0.62	1.05	0.64	1.05
- H_R^b	0.23	0.56	0.84	1.09	1.19	1.50	1.96	1.20	1.27
ΔH_R^c	1.07	0.96	0.98	0.99	0.90	0.88	0.81	0.56	0.22
LiClO ₄ (M)	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.25	0.63

^a Value of H_R for acid concentration in absence of salt. ^b Value of H_R calculated from log X^d using equation (1). ^c $\Delta H_R = H_R^a - H_R^b$. ^d $X = [QC\dot{N}^+]/[QCNOH]$.

eqn. (1) for perchloric acid and (2) for sulphuric acid. The results obtained for added lithium perchlorate in perchloric acid, assembled in Table 8, show that the salt effect ΔH_R is not markedly dependent upon acid concentration, but varies approximately linearly with salt concentration ($\Delta H_R \approx 0.5$ per mole l.⁻¹). This salt effect is in accord with the results of Perrin and Westheimer⁹ for added sodium perchlorate, but is some 2.3 times greater than the effect of sodium perchlorate* on H_0 ($\Delta H_0 \approx 0.21$ per mole l.⁻¹ in 0.5M-

TABLE 9.

HClO ₄ (M)	0.253	0.348	0.445	0.553	0.747	0.746	1.045
log X^d	-0.036	-0.14	0.01	0.16	0.47	0.23	0.27
- H_R^a	-0.40	-0.13	0.10	0.29	0.63	0.63	1.05
- H_R^b	0.50	0.76	0.93	1.10	1.47	1.19	1.23
ΔH_R	0.90	0.89	0.83	0.81	0.84	0.56	0.18
NaBr (M)	1.88	1.88	1.88	1.88	1.88	1.25	0.626

^{a b c d} See Table 8.

perchloric acid¹⁰). The ratio $\Delta H_R/\Delta H_0 = 2.3$ is very similar to the corresponding ratio ($\Delta H_R/\Delta H_0 = 2.5$) for the change in acidity functions on increasing acid concentration in the absence of salts. This indicates that the larger rate of increase of H_R than H_0 with increasing acid concentration may be due mainly to the salt effect of perchloric acid itself.

The results in Table 9 show that added sodium bromide has almost the same effect as lithium perchlorate. As expected, the addition of tetraethylammonium bromide has the

* A study of the literature suggests that the difference between the salt effects on H_0 of sodium and lithium salts is less than 15%.

⁹ C. Perrin and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1963, **85**, 2773.

¹⁰ B. C. Challis and J. H. Ridd, *J.*, 1962, 5208.

TABLE 10.

H ₂ SO ₄ (M)	1.94	1.16	
log X ^d	0.47	-0.45	
-H _R ^a	1.56	0.78	^a ^d As in Table 8. ^e Value of -H _R calculated from
-H _R ^e	1.25	0.32	log [QC ⁺ N]/[QCNOH] by use of eqn. (2).
ΔH _R	-0.31	-0.46	
Et ₄ N ⁺ Br ⁻ M	1.19	1.76	

opposite effect on H_R (Table 10), but because of a lack of suitable data for the effect of this salt on H_0 , comparison is not appropriate.

EXPERIMENTAL

Materials.—1-Cyano-1,2-dihydro-2-hydroxyquinoline and 2-cyano-1,2-dihydro-1-hydroxyisoquinoline were prepared as described previously.¹ Perchloric acid was AnalaR, *d* 1.72. Sodium bromide and tetraethylammonium bromide were AnalaR and lithium perchlorate was Hopkin and Williams Reagent grade, recrystallised from water. Acid solutions were standardised by titration against standard alkali, and bromide solutions by Volhard titrations. Sulphuric acid was AnalaR reagent, *d* 1.84.

N-Carbamoylisoquinolinium fluoroborate. 2-Cyano-1-hydroxy-1,2-dihydroisoquinoline (0.94 g., 0.006 mole) was dissolved in fluoroboric acid (42%, 70 ml.). After 90 min. at room temperature, the solution was cooled in ice and the precipitate was filtered off, washed with ether, and dried (P₂O₅). The product, N-carbamoylisoquinolinium fluoroborate (0.282 g., 32%) lost weight slowly, even when kept over drying agents, the loss of weight in the formation of isoquinolinium fluoroborate being 16.9% (Calc. 17.7%) (Found: C, 47.3; H, 3.6; F, 28.5; N, 10.2. C₁₀H₉BF₄N₂O requires C, 46.4; H, 3.5; F, 29.4; N, 10.8%).

Identification of Cyanate Ion.—A fresh sample of N-carbamoyl isoquinolinium fluoroborate was added to an aqueous solution of copper sulphate (1 mol.) and pyridine (1 mol.). The pale blue precipitate was isolated and purified and shown to be identical with that obtained in the reaction of potassium cyanate with the same solution.¹¹

Equilibrium Studies.—The equilibrium concentrations of the N-cyano-cations and their pseudo-bases were measured by the dilution with water of a solution of the pseudo-base in concentrated acid (*i.e.*, a solution of the cation) to the appropriate acidity and by extrapolating the observed optical density back to zero time of dilution of the solution, and comparing the resulting optical density (O.D.₀) with that of the pure cation (O.D._{max}) at the same concentrations. Thus [cation]/[pseudo-base] = O.D.₀/(O.D._{max} - O.D.₀). For the N-cyanoquinolinium ion, the measurements were carried out at 365 mμ; for the N-cyanoisoquinolinium ion at 400 mμ and also at the isobestic point, in the region of 360 mμ, between the spectra of the N-cyano- and N-carbamoyl-isoquinolinium ions. The isobestic point had to be determined at each acid concentration, for it varied because of the presence of the pseudo-base, but the extrapolation procedure was simplified because the optical density was invariant with time until the second stage of the reaction became apparent.

Rate Measurements.—The rates of the decompositions were measured by the change in optical density of the solutions as functions of time. For the N-cyanoquinolinium ion, measurements were carried out at 365 mμ at 30 ± 0.2°. For the first stage of the hydrolysis of the N-cyanoisoquinolinium ion, measurements were carried out at 300 mμ at 25 ± 0.2°, *i.e.*, at the isobestic point between the spectra of the N-carbamoylisoquinolinium and isoquinolinium ions. For the hydrolysis of the N-carbamoylisoquinolinium ion, measurements were made at 360 mμ at 25 ± 0.2°, after dilution of the N-carbamoylisoquinolinium ion in 36% perchloric acid, made *in situ* from the N-cyanoisoquinolinium ion, and also by following the rate of hydrolysis after completion of the first stage of hydrolysis of the N-cyanoisoquinolinium ion at each acidity.

Rate coefficients were evaluated by standard methods.

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¹¹ E. L. Martin and J. McClelland, *Analyt. Chem.*, 1951, **23**, 1519.