[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Hydrolysis of Cyanamide in Acid Solution[1a,b]

BY MILLER J. SULLIVAN[2] AND MARY L. KILPATRICK

Cyanamide hydrolyzes, in an aqueous acid solution, to give urea; the identity of the product was established by Hetherington and Braham,[3] who also showed the reaction to be of the first order with respect to cyanamide. The only extensive investigation of the effect of acids, prior to the present one, is that of Grube. Grube and Motz,[4] and Grube and Schmid,[5] studied the reaction in nitric acid solution, the acid concentration ranging from 0.05 to 5 *N*. They found the rate to increase steadily with increase in acid concentration, their results conforming to the equation

$$\log (k_{\mathrm{obs.}}/N_{\mathrm{HNO_3}}) = A + BN_{\mathrm{HNO}}$$

where $k_{\mathrm{obs.}}$ is the first-order constant, $N_{\mathrm{HNO_3}}$ the normality of the nitric acid, and A and B are constants. At the lowest acid concentrations Grube and Motz detected a decrease in $k_{\mathrm{obs.}}$ with time. This they attributed to the fact that urea is a stronger base than cyanamide, in consequence of which the hydrogen-ion concentration would decrease as the reaction progresses. They determined the equilibrium constant

$$K_1 = [\mathrm{NH_2CN{\cdot}H^+}]/[\mathrm{NH_2CN}][\mathrm{H^+}]$$

(the symbol $\mathrm{H^+}$ is used throughout this paper, for brevity, to denote the solvated hydrogen ion) and as they expected, found it smaller than the equilibrium constant

$$K_2 = [\mathrm{(NH_2)_2CO{\cdot}H^+}]/[\mathrm{(NH_2)_2CO}][\mathrm{H^+}]$$

With acid in excess over cyanamide, Grube and Motz detected no trend in $k_{\mathrm{obs.}}$. Grube and Schmid studied the effect of various nitrates, the acid concentration being kept constant at 0.25 *N*. In every case, the salt accelerated the reaction.

Grube concluded from these findings that the hydrolysis of cyanamide is an example of hydrogen–ion catalysis, with a large linear salt effect. This conclusion was accepted by Hammett and Paul,[6] who used the hydrolysis of cyanamide as an illustration of specific hydrogen-ion catalysis, their criterion being conformity to the relationship

$$H_0 + \log k_{\mathrm{obs.}} = \text{constant}$$

where H_0 is the acidity function of Hammett.

Our results indicate that the hydrolysis of cyanamide in acid solution is a two-stage protolysis, the rate-determining step being the reaction between the cation of cyanamide, $\mathrm{NH_2CN{\cdot}H^+}$, and any bases present. Before the experimental work is presented, it should be mentioned that our progress was retarded by the specificity of action of the halogen acids, which appear to form unhydrolyzable, or difficultly hydrolyzable, complexes with cyanamide.

Experimental

The hydrolysis of cyanamide to urea is accompanied by a contraction (*ca.* 9 cc. per mole of cyanamide) which we made use of to follow the reaction dilatometrically.

Cyanamide.—Through the courtesy of the American Cyanamid Company a carefully purified sample of cyanamide was obtained for which the following analysis was reported:

Anal. Calcd. for $\mathrm{NH_2CN}$: N, 66.64. Found: N (titration), 65.38, N (Kjeldahl), 64.95, N (dicyanodiamide), 0.09.

Since experiments performed with the above sample, and with a sample prepared by us, gave consistent results, the above sample was used without further purification. During the course of the work the m. p. remained 43–44°, and checks upon the analysis by the silver titration continued in good agreement.

Dilatometers.—The experiments with a low initial concentration of cyanamide (0.045 *M* or less) were performed in dilatometers like that described by Brönsted, Kilpatrick and Kilpatrick.[7] These are called the "large" dilatometers. All other experiments were carried out in sealed[7] dilatometers.

Nitric Acid as Catalyst

In these experiments the initial cyanamide concentration was 0.25 *M*, twice that used by Grube, and at low acid concentrations $k_{\mathrm{obs.}}$ decreased as the reaction progressed. To utilize the results at the low acid concentrations, it was necessary to consider the effect upon the rate of reaction of the basic nature of cyanamide and urea.

Calculation of Rate.—Let it be assumed the activity-coefficient ratios $f_{\mathrm{NH_2CN{\cdot}H^+}}/f_{\mathrm{NH_2CN}}f_{\mathrm{H^+}}$ and $f_{\mathrm{(NH_2)_2CO{\cdot}H^+}}/f_{\mathrm{(NH_2)_2CO}}f_{\mathrm{H^+}}$ remain unity over the range of acid concentration employed. Let it be assumed that equilibrium is maintained between $\mathrm{NH_2CN}$ and $\mathrm{NH_2CN{\cdot}H^+}$, and between $\mathrm{(NH_2)_2CO}$ and $\mathrm{(NH_2)_2CO{\cdot}H^+}$.

If $\mathrm{NH_2CN}$ is the reactive species, and the rate-determining step is the reaction between $\mathrm{NH_2CN}$ and $\mathrm{H^+}$, one has

$$v = k'[\mathrm{NH_2CN}][\mathrm{H^+}]\frac{f_{\mathrm{NH_2CN}}f_{\mathrm{H^+}}}{f_{\mathrm{NH_2CN{\cdot}H^+}}} = k[\mathrm{NH_2CN}][\mathrm{H^+}] \quad (1)$$

since the ionic strength remains constant during an experiment. Setting

$$z = [\mathrm{NH_2CN}] + [\mathrm{NH_2CN{\cdot}H^+}] \quad (2)$$

---

[1] (a) Abstracted from the dissertation of Miller J. Sullivan presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirement for the degree of Doctor of Philosophy, November, 1943. (b) This work was originally directed by Martin Kilpatrick, who since January, 1943, has been on leave of absence from the University of Pennsylvania. (c) Presented at the Spring Meeting of the Philadelphia Section of the American Chemical Society, June 13, 1945.

[2] Present address: The Socony-Vacuum Oil Company, Paulsboro, N. J.

[3] Hetherington and Braham, THIS JOURNAL, **45**, 824 (1923).

[4] Grube and Motz, *Z. physik. Chem.*, **118**, 145 (1925).

[5] Grube and Schmid, *ibid.*, **119**, 19 (1926).

[6] Hammett and Paul, THIS JOURNAL, **56**, 830 (1934).

[7] Brönsted, Kilpatrick and Kilpatrick, *ibid.*, **50**, 428 (1928).

equation (1) becomes

$$-\frac{dz}{dt} = \frac{k[H^+]z}{1 + K_1[H^+]} \qquad (3)$$

Let a be the initial stoichiometric concentration of cyanamide, b, that of nitric acid, in moles per liter. Provided a is not too high relative to b, $[H]^+$ may be represented, with sufficient accuracy, as a linear function of the fraction of substrate remaining

$$[H^+] = [H^+]_\infty + \{[H^+]_0 - [H^+]_\infty\} z/a = D + \{C - D\}z/a \qquad (4)$$

and (3) may be integrated, yielding

$$k = (2.303/t)\ [K_1 \log a/z + (1/D) \log \{(1/C)[D\,a/z + C - D]\}] \qquad (5a)$$

If the acid concentration is so high that the relative change in $[H^+]$ during the course of the reaction is slight, and a satisfactory first-order constant is obtained, one may write $[H^+]_{av} = (1/2)\{[H^+]_0 + [H^+]_\infty\}$ = constant, and from (3) it follows that

$$k = \{(1 + K_1[H^+]_{av})/[H^+]_{av}\}(2.303/t) \log a/z = \{(1 + K_1[H^+]_{av})/[H^+]_{av}\}k_{obs.} \qquad (5b)$$

If $NH_2CN{\cdot}H^+$ is the reactive species, and the rate-determining step is the reaction between $NH_2CN{\cdot}H^+$ and a water molecule, one has in place of (1)

$$v = \bar{k}'[NH_2CN{\cdot}H^+][H_2O]f_{NH_2CN\cdot H^+}f_{H_2O}/f_{NH_2CN\cdot H^+,H_2O} = \bar{k}[NH_2CN{\cdot}H^+] \qquad (6)$$

and upon proceeding as before, obtains equations identical with (5a) and (5b) except that k is replaced by $\bar{k}K_1$.

Experimental Results.—The results of all the experiments at 25 and 30° are collected in Table I. For nitric acid concentrations above 0.5 N, the cyanamide concentration remaining *ca.* 0.25 M, $k_{obs.}$ was computed from the dilatometer readings by Guggenheim's method, and k was obtained from $k_{obs.}$ by (5b). For the lower acid concentrations, k was computed by (5a), with $a/z = (V_0 - V_\infty)/(V_t - V_\infty)$. The values[8] 0.244 and 1.31 were employed for K_1 and K_2, respectively. The unit of time is the minute.

To illustrate the need for using (5a), the experiment with 0.1220 N acid, at 25°, will serve. As the reaction progressed from 10 to 91% of completion, $k_{obs.}$ decreased steadily from 21.8×10^{-5} to 19.7×10^{-5}; on the other hand, k computed from (5a) showed no trend, and its average deviation was 0.6%.

It is of interest to compare the dilatometric velocity constants at 25° with the analytic constants of Grube and Schmid. Over the range of acid concentration of the experiments of Table I, the difference in $k_{obs.}$ runs from +6% (the dilatometric being greater) at the lowest concentration, to −3% at the highest. At the two lowest acid concentrations, the dilatometric first-order constant was taken as $k[H^+]_{av}/(1 + K_1[H^+]_{av})$ where k is from the last column of Table I.

TABLE I

THE EFFECT OF NITRIC ACID UPON THE RATE OF HYDROLYSIS OF CYANAMIDE

HNO_3, N	$[H^+]_{av}$	$10^5\ k_{obs.}$	$10^5\ k$ by (5b)	$10^5\ k$ by (5a)
Temperature, 25.00°; cyanamide, 0.254 M				
0.1220	0.1048			196.3
.2507^a	.2221			204.0
.5947^b	.5320	111.9	237.6	239.9
.9994^a	.9216	216.4	287.6	291.6
1.490^a	1.394	376.3	361.7	
1.977	1.848	582.6	457.5	
2.512	2.370	899.6	599.1	
3.003	2.850	1262^c	750.7	
3.486	3.326	1736^c	945.4	
3.881	3.715	2215	1137	
Temperature, 30.00°; cyanamide, 0.254 M				
0.1220	0.1048			332.4
.2507	.1983			354.2
.9994^a	.9216	375.3	497.5	
1.490^a	1.394	651.6	626.4	
1.977	1.848	1004^a	788.3	
2.512	2.370	1531	1020	
3.003	2.850	2145^c	1276	
3.486	3.326	2966^c	1615	
3.881	3.715	3776	1938	

^{a} Cyanamide, 0.214 M. ^{b} 0.243 M. ^{c} Average of two experiments.

In Fig. 1 the logarithm of k is plotted against N_{HNO_3}

$$\text{at } 25°, \log k = \bar{3}.2586 + 0.2056\,N_{HNO_3} \qquad (7a)$$

$$\text{at } 30°, \log k = \bar{3}.4927 + 0.2042\,N_{HNO_3} \qquad (7b)$$

The electrolyte effect of nitric acid upon the rate of hydrolysis of cyanamide is about the same as that of hydrochloric acid upon the rate of inversion of sucrose.

In Table II is shown the energy of activation

$$E_A = \frac{2.303\,RT_1T_2}{T_1 - T_2} \log (k_{T_1}/k_{T_2})$$

computed from the second-order constants given in columns 4 and 5 of Table I. It will be seen that any systematic variation of E_A with acid concentration lies within the experimental error. If the ratio of first-order constants, rather than second-order, is employed to determine E_A very similar values are found.

To test the effect of temperature upon E_A, additional experiments were carried out, at three convenient acid concentrations, at 25, 30, 35 (34.17), and 40°, and E_A at the mid-point of each

---

(8) Grube and Motz[4] determined K_1 at 25° by measurement of the rate of hydrolysis of methyl acetate in 0.5 N hydrochloric or sulfuric acid solution, with and without added cyanamide; the average of their results is 0.227. and if the experiments with sulfuric acid are omitted, 0.244. The figure for K_2 was selected after comparing the values reported by Walker, *Z. physik. Chem.*, **4**, 321 (1889), Walker and Wood, *J. Chem. Soc.*, **83**, 484 (1903), and Grube and Motz,[4] with values obtained by the authors. All were determined by a kinetic method. The effect of temperature upon K_2, over the range from 25 to 40°, appears to lie within the experimental error of the measurements.

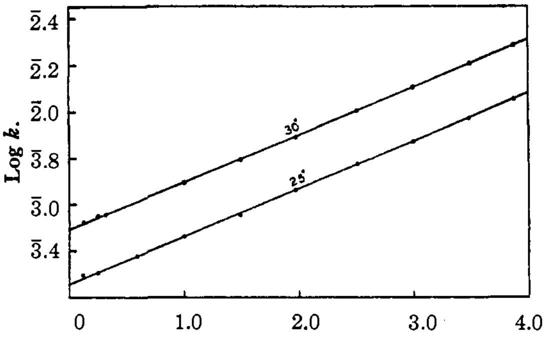

Fig. 1.—The effect of nitric acid.

five-degree interval was computed from the ratio of first-order constants for a given solution. Below are listed the average value of E_A

at 27.50°, 19,670 cal.
at 32.08°, 19,287 cal.
at 37.08°, 19,617 cal.

Any change of E_A with temperature, over this range, lies within the experimental error.

TABLE II

THE EFFECT OF NITRIC ACID UPON THE ENERGY OF ACTIVATION

N_{HNO_3}	E_A, cal., at 27.50°	N_{HNO_3}	E_A, cal., at 27.50°
0.1220	18,900	2.512	19,100
.2507	19,800	3.003	19,040
.9994	19,760	3.486	19,220
1.490	19,710	3.881	19,140
1.977	19,530		
		Mean	19,356 ± 306 cal.

Hydrochloric Acid as Catalyst.—With hydrochloric acid it was possible to use the large dilatometers, and to reduce the cyanamide concentration to 0.045 *M*. Good conformity to the first-order law was found when the data were plotted by Guggenheim's method. Table III gives the results obtained; it also gives the results of two experiments in perchloric acid. The change in $k_{obs.}$ with N_{HCl} is shown by the upper curve of Fig. 2.

TABLE III

THE EFFECT OF HCl UPON THE RATE OF HYDROLYSIS OF CYANAMIDE

NH_2CN, 0.045 *M*, *N* acid	25.00°		30.00°	
	$10^5\ k_{obs.}$	$10^5\ k_{obs.}/N_{acid}$	$10^5\ k_{obs.}$	$10^5\ k_{obs.}/N_{acid}$
0.0959	....	...	28.41	296.4
.2474	44.21	178.7	76.91	310.9
.6010	117.0	194.7	203.3	338.3
.9820	199.6	203.3	340.1	346.3
1.330	267.8	201.4	468.6	352.3
1.613	296.6	183.9	518.2	321.3
1.822	296.4	162.7	521.4	286.2
2.066	269.4	130.4	474.8	229.8
2.246	....	...	432.7	192.7
2.665	155.0	58.2	289.2	108.5
2.935	108.7	37.0	200.6	68.3

THE EFFECT OF $HClO_4$ UPON THE RATE OF HYDROLYSIS OF CYANAMIDE

0.4844[a]			149.0	307.6
.4979			152.2	305.7

(a) Cyanamide, 0.036 *M*.

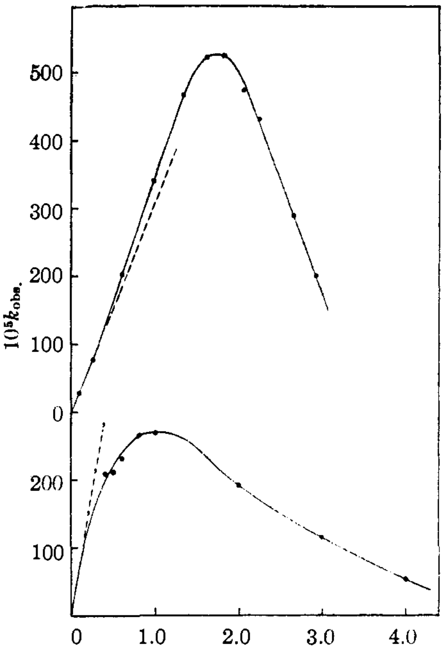

Fig. 2.—The effect of HCl at 30°, upper curve, HCl solution; lower curve, HCl–NaCl solutions.

At high concentrations the effect of hydrochloric acid is very different from that of nitric. Thus, at 30°:

For 1.00 *N* acid, $k_{obs.}$ = 375 × 10^{-5} with HNO_3, 340 × 10^{-5} with HCl
For 1.98 *N* acid, $k_{obs.}$ = 1004 × 10^{-5} with HNO_3, 496 × 10^{-5} with HCl
For 3.00 *N* acid, $k_{obs.}$ = 2145 × 10^{-5} with HNO_3, 201 × 10^{-5} with HCl

The great difference in rate suggests that perhaps a side reaction, with formation of a different product than urea, is going on in solutions of hydrochloric acid. The volume changes observed with nitric and with hydrochloric acid were, however, almost the same over the whole range of concentration, which makes the occurrence of a side reaction improbable.

A number of experiments were next carried out to determine the effect of change in concentration of cyanamide, and of addition of sodium chloride. With 0.25 *M* cyanamide somewhat higher rates were obtained than with 0.045, but the same general behavior was observed. The addition of 1 mole of sodium chloride, at 1 *N* acid, caused an increase in rate, but the addition of a second mole caused a decrease, and at higher acid concentrations, a decrease accompanied each addition.

These findings suggested the set of experiments at constant chloride concentration given in Table IV.

TABLE IV

THE EFFECT OF HYDROCHLORIC ACID UPON THE RATE OF HYDROLYSIS OF CYANAMIDE AT CONSTANT CHLORIDE CONCENTRATION

	0.254 M cyanamide		$N_{HCl} + N_{NaCl} = 4.0$	
	$10^5 k_{obs}$		$10^5 k_{obs}/N_{HCl}$	
N HCl	30.00°	40.00°	30.00°	40.00°
0.3965[a]	208.5	...	525.9	.....
.500	210.5	604.7	421.0	1209
.600	232.0	681.1	387.1	1135
.800	265.0	789.6	331.2	987.0
1.000	268.5	658.9	268.5	858.9
2.000[b]	192.5	589.5	96.25	294.8
3.000	115.8	352.2	38.60	117.4
4.000[b]	54.11	187.7	13.53	46.92

° Cyanamide, 0.040 M. [b] 0.214 M.

The first-order constant in the salt–acid mixtures is shown as the lower curve of Fig. 2. The maximum occurs at a lower acid concentration than in the case of the pure acid solutions (upper curve, Fig. 2). In the salt–acid mixtures the ratio k_{obs}/N_{HCl} decreases steadily, and its logarithm changes linearly with N_{HCl} (*cf.* Fig. 3).

$$\text{At } 30°, \log (k_{obs}/N_{HCl}) = \bar{3}.860 - 0.432 N_{HCl} \quad (8a)$$

$$\text{At } 40°, \log (k_{obs}/N_{HCl}) = \bar{2}.298 - 0.407 N_{HCl} \quad (8b)$$

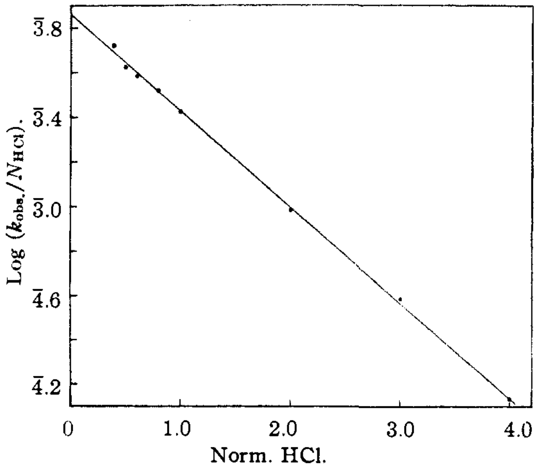

Fig. 3.—Experiments with constant halide concentration.

Like the velocity constants, the energy of activation shows a marked difference in concentrated solutions of nitric and hydrochloric acid. The first-order constants from Table III were used in computing the values of E_A given in Table V

TABLE V

THE EFFECT OF HCl UPON THE ENERGY OF ACTIVATION

HCl, N	E_A, cal., at 27.50°	HCl, N	E_A, cal., at 27.50°
0.2474	19,870	1.822	20,110
.6010	19,830	2.066	20,340
.9820	19,370	2.665	22,390
1.330	20,080	2.935	21,990
1.613	20,030		

E_A thus increases from *ca.* 19,700 cal. below 1 N acid to *ca.* 22,000 cal. at 3 N.

Hydrobromic Acid as Catalyst.—The results obtained with hydrobromic acid are in general similar to those with hydrochloric, as may be seen by comparing Fig. 4 below with Fig. 2 (upper curve). In hydrobromic acid solution the maximum in $k_{obs.}$ occurs at 3.2 N, while in hydrochloric it occurs at 1.7 N acid.

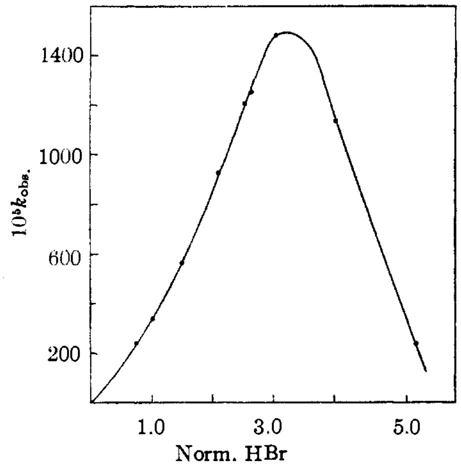

Fig. 4.—The effect of HBr at 30°.

In Table VI are given the velocity constants obtained with hydrobromic acid as catalyst, together with the corresponding values of the energy of activation.

TABLE VI

THE EFFECT OF HYDROBROMIC ACID UPON THE RATE OF HYDROLYSIS OF CYANAMIDE AND UPON THE ENERGY OF ACTIVATION

Cyanamide, 0.254 M

	$10^5 k_{obs.}$		
HBr, N	30.00°	25.00°	E_A, cal. at 27.50°
1.010	337.6	201.7	18,450
1.499°	556.4	333.8	18,980
2.097[a]	926.8	540.4	19,360
2.534°	1207	700.0	19,560

	$10^5 k_{obs.}$		
HBr, N	40.00°	30.00°	E_A, cal. at 35.00°
0.7492	639.7	239.2	18,540
2.642	3514	1254	19,420
3.038	4140	1481	19,380
4.027	3396	1136	20,640
5.178	815.6	237.3	23,280

[a] Cyanamide, 0.214 M.

E_A thus increases by 5000 cal. over the range of acid concentration used.

Trichloroacetic Acid as Catalyst.—In Table VII are given the results obtained at 30° with trichloroacetic acid as catalyst. At the end of each run, the solution was tested for chloride ion; the test was always negative.

In Fig. 5 k_{obs} is plotted (as the solid curve) against the acid concentration. Although the figure shows some erraticalness in the results at

TABLE VII

THE EFFECT OF CCl_3COOH UPON THE RATE OF HYDROLYSIS OF CYANAMIDE

Temperature, 30.00°; cyanamide, 0.254 *M*

CCl_3COOH, *N*	$10^5 k_{obs}$	CCl_3COOH, *N*	$10^5 k_{obs}$
0.2497	97.2	2.040[b]	1415
0.4928	222.9	2.497	1624
1.022	568.7	2.905	2017
1.487[a]	960.2	3.971	2602

[a] Cyanamide, 0.214 *M*. [b] 0.191 *M*.

the high acid concentrations, good first-order lines were obtained. These experiments were carried out under the same conditions as the experiments with nitric acid, and the volume changes were the same. The broken curve of Fig. 5 represents k_{obs} with nitric acid as catalyst. The curves intersect just below 3 *N*; at lower acid concentrations, the rate is greater in trichloroacetic, at higher, the rate is greater in nitric acid solution.

Experiments at Low Hydrogen-Ion Concentration

It appeared that cyanamide hydrolyzed at about the same rate in dilute solutions of acid. To test this point further, a set of experiments was carried out in 0.05 *N* acid solution, in the sealed dilatometers, at 35°. Readings were taken over twelve days, or five times the half-time of the reaction, and *k* was computed by (5a), the same values of K_1 and K_2 being used in the computation of $[H^+]_0$ and $[H^+]_\infty$, as were used at the lower temperatures. The results are shown in Part A of Table VIII. In a given experiment, the average deviation of the values of *k* from the mean was 0.4%. The figures in the last two columns show that the strong acids in 0.05 *N* solution are equally effective catalysts. It may be mentioned that, as computed from equation (7a) and E_A, *k* in 0.05 *N* nitric acid solution is 537×10^{-5}.

TABLE VIII

EXPERIMENTS AT LOW HYDROGEN-ION CONCENTRATION

A. In 0.05 *N* acid solution at 35.00°

Acid	Moles per liter Acid	Moles per liter NH_2CN	$[H^+]_0$	$[H^+]_\infty$	$10^5 k$	10^5 ($k_{obs.}$) av.
HCl	0.05070	0.254	0.0478	0.0385	527	22.5
HNO_3	.05028	.254	.0474	.0382	530	22.4
$C_6H_5SO_3H$	.05111	.107	.0498	.0451	528	24.8
HBr	.05055	.131	.0490	.0435	513	23.4

B. In buffer solution at 30.00°

Acid	Mols per liter Acid	Mols per liter Na Salt	Mols per liter NH_2CN	$k_{obs.} \times 10^5$	$[H^+]$	$k_{obs.}/[H^+]$
$HCCl_2COOH$	0.503	0.988	0.044	92.7	0.0302[a]	0.0307
$HCCl_2COOH$	.993	.988	.045	164.4	.0580[a]	.0283
CH_3COOH	2.44	.499	.040	2.1 2.9	.00016[b]	.13 .18

[a] Calculated[9] from $K = 6.5 \times 10^{-2}$. [b] Calculated[10] from $K = 3.3 \times 10^{-5}$.

It may be asked whether the hydrolysis of urea affected the determination of the rate of hydrolysis of cyanamide in the slow experiments of Table VIII. No change in volume was observed when a solution 0.04 *M* in urea and 0.03 *N* in hydrochloric acid was allowed to stand for twenty-four hours at 30° in the bulb of the large dilatometer.

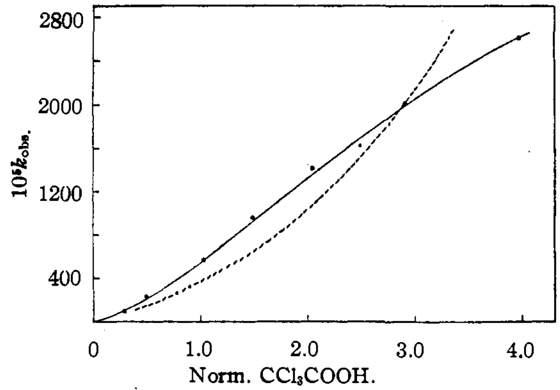

Fig. 5.—The effect of trichloroacetic acid at 30°; ——— CCl_3COOH; - - - - HNO_3.

The first two lines of part B of the table give the results of two experiments carried out in dichloroacetic acid–sodium dichloroacetate buffer solution, at 30°. For these experiments excellent lines were obtained when the data were plotted by Guggenheim's method. There was during the reaction in the more alkaline buffer some formation of chloride by hydrolysis of the dichloroacetate ion; the amount formed was small, however, and it appeared to be without effect upon the course of the reaction. In order to estimate *k* it was necessary to select values of the dissociation constant of the acid in the buffer solutions; these were taken[9] as 6.5×10^{-2}. Although the estimation of the hydrogen-ion concentration is very rough, it is unlikely that the true value of the ratio

$$k_{obs} (1 + K_1[H^+])/[H^+] \approx k_{obs}/[H^+]$$

is much less than the value given in the last column of the table, *i. e.*, 0.03. In *N* nitric acid solution *k* is 0.005, and the six-fold increase upon going to the buffer solutions is too large to attribute to difference in the effect of the medium.

An even greater increase in the ratio $k_{obs}/[H^+]$ is exhibited by the experiment in acetic acid–sodium acetate buffer solution, the last experiment in Table VIII. Here k_{obs} was estimated from dilatometer readings extending over a period of a week, and an infinity reading calculated from the amount of cyanamide taken. The two values of k_{obs} correspond to infinity readings calculated from the largest, and the smallest, contraction per mole of cyanamide previously observed. The dissociation constant of acetic acid was taken as 3.3×10^{-5}, its value[10] in 0.5 molal sodium chloride solution. In 0.5 *N* nitric acid solution, *k* is 0.004; in the buffer solution, the ratio $k_{obs.}/[H^+]$ is about forty times as large.

Discussion

Two questions must be considered in any explanation of the experimental results: (1) Why does the rate exhibit a maximum in hydrochloric,

---

[9] See the values given by Harned and Hawkins (THIS JOURNAL, **50**, 85 (1928)) in sodium chloride and bromide solution.

[10] Harned and Hickey, *ibid.*, **59**, 1284 (1937).

and in hydrobromic, but not in nitric acid solution? (2) Why is the reaction so fast in solutions of trichloroacetic acid, and in the dichloroacetate and acetate buffers?

(1) To achieve practically complete conversion to the acid form, for a base with equilibrium constant of the order of 10^{-1}, is not possible in aqueous solution. Nevertheless, with a halogen acid as catalyst, the rate of hydrolysis of cyanamide reaches a maximum, which lies at 1.7 N in hydrochloric, and at 3.2 N in hydrobromic acid solution. If one assumes that the rate-determining step is the reaction between $NH_2CN{\cdot}H^+$ and a water molecule, and attributes the existence of the maximum to change in the classical equilibrium constant K_1 with change in medium from nitric to hydrochloric or hydrobromic acid solution, one must accept a thousand-fold increase in K_1. Nor does it appear helpful to assume an equilibrium between amino and imino forms[11] of the substrate, since it becomes necessary to postulate that the effect of the halogen acids upon the position of equilibrium is quite different from that of nitric acid. The suggestion that the decrease in rate, beyond the maximum, is due to decrease in the activity of water,[11] also fails to fit the present case, since the decrease in activity occurs in nitric acid solution, as well as in hydrochloric, and hydrobromic.

The most probable explanation of the maximum rate appears to be the formation of an unhydrolyzable complex between substrate and acid. This explanation was put forward by Benrath[12] and by Taylor[13] to account for the maximum rate observed in the acid hydrolysis of acetamide. Cyanamide dihydrochloride, $NH_2CN{\cdot}2HCl$, or chloroformamidine hydrochloride,[14] is a stable compound in the solid state. In dilute solution it must be largely broken up, however, since Hantzsch and Vagt[15] found the molar conductance of a $^1/_{30}$ M solution to be practically that of two moles of hydrochloric acid.

The kinetic data lend support to this hypothesis. Let it be assumed that there are present in hydrochloric acid solution the unhydrolyzable complexes $NH_2CN{\cdot}HCl{\cdot}H^+$ and $NH_2CN{\cdot}HCl$; possibly higher complexes, such as $NH_2CN{\cdot}HCl{\cdot}2H^{++}$, are also present. Let

$$(K_3)_0 = [NH_2CN{\cdot}HCl{\cdot}H^+]/[NH_2CN{\cdot}H^+][H^+][Cl^-]f_{H^+}f_{Cl^-} = K_3/f^2 \quad (9a)$$

$$(K_4)_0 = [NH_2CN{\cdot}HCl]/[NH_2CN][H^+][Cl^-]f_{H^+}f_{Cl^-} = K_4/f^2 \quad (9b)$$

where the activity coefficients of $NH_2CN{\cdot}HCl{\cdot}H^+$ and $NH_2CN{\cdot}H^+$, and of $NH_2CN{\cdot}HCl$ and NH_2CN, are taken as equal. If the concentration of acid is high relative to that of cyanamide, so that $[H^+]$ and $[Cl^-]$ may be considered constant during an experiment, and if one proceeds as in the derivation of equations (5), one obtains

$$k_{obs} = k[H^+]/\{1 + K_1[H^+] + K_1K_3[H^+]^2[Cl^-] + K_4[H^+][Cl^-]\} \quad (10)$$

An equation of the same form, but with k replaced by $\bar{k}K_1$, results if the rate-determining step is taken as the reaction between $NH_2CN{\cdot}H^+$ and a water molecule, and with this understanding (10) may be employed interchangeably.

Were there no salt effect upon k, it would be expected that the ratio $k_{obs.}/[H^+]$ would decrease with increasing acid concentration over the whole range. The experiments with nitric acid, however, lead one to believe that there exists a positive salt effect of considerable magnitude, and it therefore seems reasonable to explain the maximum observed when $k_{obs.}$ is plotted *vs.* N_{HCl} by saying that below the maximum, the increasing concentration of the hydrogen ion and the positive salt effect predominate while above it complex formation predominates.

The extent of complex formation probably decreases with rise of temperature, and it is not surprising that the measured energy of activation changes with change in concentration of hydrochloric acid. One has at a given acid concentration

$$\frac{\partial \ln k_{obs.}}{\partial T} = \frac{E_A}{RT^2} = \frac{1}{k}\frac{\partial k}{\partial T} - \frac{[H^+]\dfrac{\partial K_1}{\partial T} + [H^+]^2[Cl^-]\left\{K_1\dfrac{\partial K_3}{\partial T} + K_3\dfrac{\partial K_1}{\partial T}\right\} + [H^+][Cl^-]\dfrac{\partial K_4}{\partial T}}{1 + K_1[H^+] + K_1K_3[H^+]^2[Cl^-] + K_4[H^+][Cl^-]} \quad (11)$$

Taking $\partial K_3/\partial T$ and $\partial K_4/\partial T$ as negative, and $\partial K_3/\partial N_{HCl}$ and $\partial K_4/\partial N_{HCl}$ as positive, which will be the case when $N_{HCl} > 0.5$, it can be shown that $\partial E_A/\partial N_{HCl}$ will be positive.[16]

In pure hydrochloric acid solution k_{obs}/N_{HCl} first increases, then decreases, with increase in N_{HCl}, while in the acid-salt mixtures it decreases steadily (*cf.* Tables III and IV); $k_{obs.}$, on the other hand, exhibits a maximum in both cases. This is readily explained provided one makes certain assumptions concerning the salt effects.

Let it be assumed that in pure acid solution the effect of hydrochloric acid upon the second-order constant is the same as that of nitric acid, *i. e.*, let it be assumed that at 30° (7b) is applicable. Let it be assumed that in the acid–salt mixtures

$$\log k = \bar{3}.8600 + 0.0278\ N_{HCl} \quad (12)$$

---

[11] Krieble and Holst, THIS JOURNAL, **60**, 2976 (1938).

[12] Benrath, *Z. anorg. allgem. Chem.*, **151**, 53 (1926).

[13] Taylor, *J. Chem. Soc.*, 2741 (1930).

[14] Johnson and Sprague, THIS JOURNAL, **61**, 176 (1939).

[15] Hantzsch and Vagt, *Ann.*, **314**, 366 (1900).

[16] In this connection, it is of interest to consider the decrease in E_A with increase in N_{HCl} observed in the hydrolysis of propionitrile by Ravinovitch, Winkler and Stewart (*Can. J. Research*, **B20**, 121 (1942)), who concluded that "for reactions in which real changes in the parameters of the Arrhenius equation occur with change in catalyst concentration, apparent relations between reaction rate and other factors such as mean ion activity, acidity function, salt effect, etc., probably do not represent fundamental analysis of the factors influencing the reaction." The constancy of E_A with nitric acid as catalyst, in the hydrolysis of cyanamide, and its increase with increase in acid concentration with hydrochloric acid, or hydrobromic, as catalyst, is an argument against relegating the "other factors" to a minor position

where $\bar{3}.8600$ is the intercept of the line of Fig. 3, and 0.0278 is the slope found by Duboux,[17] who measured the rate of inversion of sucrose in sodium chloride–hydrochloric acid mixtures 3.5 N in chloride. When the acid is present in large excess over cyanamide

$$[H^+] = N_{HCl} = x$$

and one may write

$$\ln k = a + bx$$

where b is larger for the pure acid case, and smaller for the case of the mixtures, and positive for both cases. Change in K_1 with change in medium will be neglected; the change in K_3 and K_4 is determined by the change in the mean activity coefficient of the ions of hydrochloric acid. Since

$$\frac{dk}{dx} = bk, \text{ and } \lim_{x \longrightarrow 0} \left(x\frac{dK_3}{dx}\right) \text{ or } \left(x\frac{dK_4}{dx}\right) = 0$$

it follows from (10) that

$$\left(\frac{d\ (k_{obs}/x)}{dx}\right)_{x=0} = k(b - K_1) \text{ for the pure acid} \quad (13a)$$

$$\left(\frac{d\ (k_{obs}/x)}{dx}\right)_{x=0} = k(b - K_1 - 4K_4) \text{ for the mixtures} \quad (13b)$$

For the pure acid case, k is the second-order constant at infinite dilution, and is obtained from equation (7b); b is the slope from (7b). Putting in the numerical values, one has

$$\left(\frac{d\ (k_{obs}/x}{dx}\right)_{x=0} = 311 \times 10^{-5}\{2.303\ (0.2042) - 0.2444\} = 70 \times 10^{-5}$$

In Fig. 6, k_{obs}/N_{HCl} for the pure acid solutions, at 30°, is plotted as a function of N_{HCl}. The slope of the broken line is 75×10^{-5}. In drawing the curve, the most dilute point was disregarded, since here the cyanamide concentration was half the acid concentration; however, if the initial slope is taken as the slope of the line through the two most dilute points, it is $95 \cdot \times 10^{-5}$. The experimental slope is thus of the expected sign and magnitude.

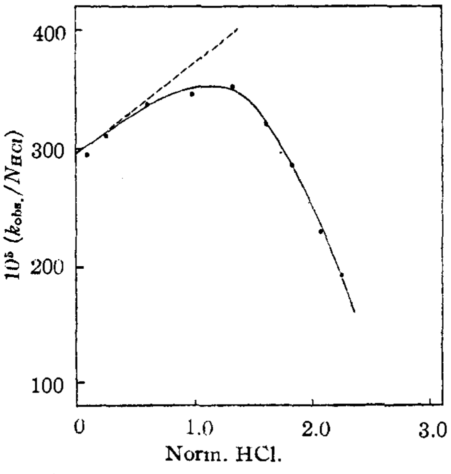

Fig. 6.—The effect of HCl upon $k_{obs.}/N_{HCl}$ in HCl solutions at 30°.

For the mixtures, k and b are obtained from (12). Putting in the numerical values, one has

$$\left(\frac{d\ (k_{obs}/x}{dx}\right)_{x=0} = 725 \times 10^{-5}\{2.303\ (0.0278) - 0.244 - 4K_4\}$$

In Fig. 7 k_{obs}/N_{HCl} for the mixtures, at 30°, is plotted as a function of N_{HCl}. The upper broken line of Fig. 7 has the slope computed from the equation above with K_4 set equal to zero, -130×10^{-5}. From the steeper slope of the curve it follows that, if the assumptions made are good, 4 K_4 cannot be neglected in comparison to K_1. The curve drawn has an initial slope of -580×10^{-5}; introducing this into the equation above, and solving for K_4, one obtains $K_4 = 0.16$ in 4 N sodium chloride solution, and $(K_4)_0 = K_4/f^2 = 0.06$.[18] For the acid–salt mixtures, then, the initial slope of the curve is of the expected sign, and its magnitude indicates either that K_4 is not negligibly small or that K_1 is as large as 3.5 (0.244) in 4 N sodium chloride solution.

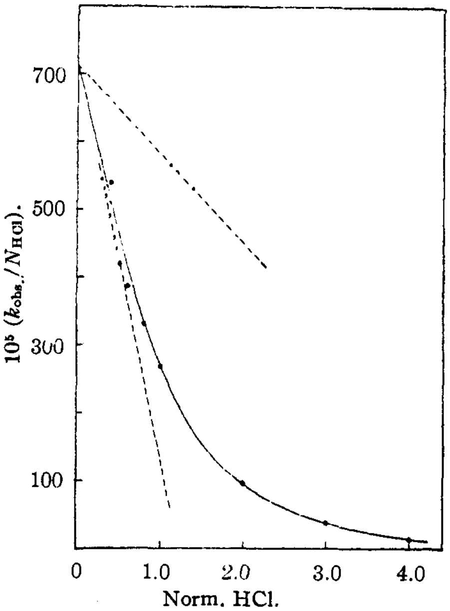

Fig. 7.—The effect of HCl upon $k_{obs.}/N_{HCl}$ in HCl–NaCl solutions at 30°.

Turning now to the first-order constant, one obtains from (10)

$$\left(\frac{d\ (k_{obs})}{dx}\right)_{x=0} = k \quad (14)$$

and upon proceeding as before, one finds

$k = 311 \times 10^{-5}$ for the pure acid solutions and
$k = 725 \times 10^{-5}$ for the mixtures

---

[17] Duboux, *Helv. Chim. Acta*, **21**, 236 (1938).

[18] By interpolation of the data of Hawkins (THIS JOURNAL, **54**, 4480 (1932)) it was found that $\log f = 0.1958 + 0.03223\ N_{HCl}$ in solutions 4 N in chloride, at 25°.

In both cases it is expected that the initial slope of the k_{obs} *vs.* N_{HCl} curve will be positive; it is also expected that the initial slope will be greater in the case of the mixtures. The upper broken line of Fig. 2 is drawn with a slope of 311×10^{-5}, the lower, with a slope of 725×10^{-5}, and one sees that the initial slopes observed agree well with the calculated. It is of interest to compare the effect of 4 N sodium chloride upon the reaction with the effect of 4 N sodium nitrate. Grube and Schmid found the following values of k_{obs}/N_{HNO_3} at 25°

159×10^{-5} for a solution 0.25 N in HNO_3

383×10^{-5} for a solution 0.25 N in HNO_3 and 4 N in $NaNO_3$

Thus the increase in rate caused by the presence of sodium chloride is of the same magnitude as that caused by the presence of sodium nitrate.

An estimate of the magnitude of K_3 may be made in the following fashion. By rearrangement of (10), one has

$$(K_4)_0 + K_1(K_3)_0[H^+] = 1/f^2\{k/k_{obs}[Cl^-] - (1 + K_1[H^+])/[H^+][Cl^-]\} = u$$

and upon plotting u *vs.* $[H^+]$ expects a line of slope $K_1(K_3)_0$ and intercept $(K_4)_0$ provided no higher complexes are formed, and provided k and K_1 are correctly taken. The points for the acid–salt mixtures, up to 2 N acid, were found to lie on a line of slope 0.45 and intercept 0.04 and, at higher acid concentrations, to lie above it. The experiments were not designed for the evaluation of equilibrium constants, but the results do indicate that K_3 is larger than K_4, and that higher complexes are probably present in the strongly acid solutions.

(2) The hydrolysis of cyanamide in trichloroacetic acid solution was found to be more rapid than expected for a reaction catalyzed specifically by the hydrogen ion, since

$$[H^+]_{HNO_3}/[H^+]_{CCl_3COOH} = 1.7 \text{ at } 0.5\ N\text{, and } 2.0 \text{ at } 1\ N \text{ acid}^{19}$$

and

$$(k_{obs})_{HNO_3}/(k_{obs})_{CCl_3COOH} < 1$$

And as has already been pointed out, greater disparity was found in the case of the dichloroacetate and acetate buffers.

On the assumption that the molecular acid HX catalyzes the hydrolysis, as well as the hydrogen ion, and on the assumption that the rate-determining step is the reaction between the cyanamide molecule and the catalyst, one has

$$k_{obs} = [1/(1 + K_1[H^+])]\{k[H^+] + k_{HX}[HX]\} \quad (15)$$

where k is the second-order constant for the hydrogen–ion catalyzed reaction, k_{HX} that for the reaction catalyzed by the acetic acid molecule, or the di- or trichloroacetic acid molecule. When catalytic constants for the molecular acids were computed by (15) from the data of Tables VII and VIIIB, the catalytic constant for the trichloroacetic acid molecule was found about twice as great as that for the hydrogen ion, which at once cast doubt upon the mechanism suggested. In addition, the stability of an aqueous solution of cyanamide argues against the existence of general acid catalysis. Buchanan and Barsky[20] found that solutions of cyanamide prepared from calcium cyanamide and sulfuric acid, and just acid to methyl red, suffered practically no change in concentration over a period of several months, and Grube and Kruger[21] found no change, over the period of observation of five days, in the concentration of an aqueous solution of cyanamide kept at 50°.

On the assumption that the anion of the acid HX catalyzes the hydrolysis, as does the water molecule functioning as a base, and on the assumption that the rate-determining step is the reaction between the cyanamide cation and the catalyst, one has

$$k_{obs} = [K_1[H^+]/(1 + K_1[H^+])]\{k_{H_2O}[H_2O] + k_{X^-}[X^-]\} \quad (16)$$

where k_{X^-} is the second-order constant for the reaction with the anion of the acid. In nitric acid solution the only base present is presumably water. It is not possible to decide, from the results in nitric acid solution, whether the hydrolysis proceeds *via* the cation, or *via* the molecule of cyanamide; the latter interpretation yields

$$v = k[NH_2CN][H^+] \text{ and } k_{obs} = k[H^+]/(1 + K_1[H^+])$$

and the former yields

$$v = \bar{k}[NH_2CN{\cdot}H^+] \text{ and } k_{obs} = \bar{k}K_1[H^+]/(1 + K_1[H^+])$$

where $\bar{k} = k_{H_2O}[H_2O]$ and $\bar{k}K_1 = k$. In Table IX are shown the values of k_{X^-} computed by (16) from the data of Tables VII and VIIIB. It was assumed, in making the calculation, that there was no medium effect of the undissociated acid upon k. For the buffer solutions k was calculated from the equation

$$\log k = \bar{3}.4927 + 0.1021\ N_{X^-} \quad (17a)$$

the salt effect being taken as equal to half that of nitric acid; for the trichloroacetic acid solutions, k was calculated from the equation

$$\log k = \bar{3}.4927 + 0.2042\ N_{X^-} \quad (17b)$$

the salt effect of the dissociated trichloroacetic acid being taken as equal to that of nitric acid. In the case of the experiments in trichloroacetic acid solution, where the initial cyanamide concentration was 0.254 M, it was necessary to compute the average values of the hydrogen- and trichloroacetate-ion concentrations; this was done by a graphic method, with $K_1 = 0.244$, $K_2 = 1.31$, and K as given in the table.

It will be seen from Table IX that the catalytic constants stand in the order of the basic strength of the anions, that for the acetate ion being great·

---

[19] The values of $[H^+]_{CCl_3COOH}$ were computed from K as given by the formula $\log K = \log (K)_0 + \sqrt{\mu}/(1 + \sqrt{\mu})$ where μ is the ionic strength; $(K)_0$ was taken as 0.2 (Hall, *Chem. Rev.*, **8**, 191 (1931)).

[20] Buchanan and Barsky, THIS JOURNAL, **52**, 195 (1930)

[21] Grube and Kruger, *Z. physik. Chem.*, **86**, 65 (1913).

TABLE IX

EFFECT OF ANION BASES UPON THE HYDROLYSIS OF CYANAMIDE

Anion X^-	K	Moles per liter H^+	Moles per liter X^-	$k_{obs} \times 10^5$	$k \times 10^5$	k_{X^-}
CH_3COO^-	3.3×10^{-5}	0.000161	0.499	2.1 2.9	350	1.0 1.4
$HCCl_2COO^-$	6.5×10^{-2}	.0302	1.018	92.7	395	0.109
$HCCl_2COO^-$	6.5×10^{-2}	.0580	1.046	164.4	398	.097
					Mean	0.103
CCl_3COO^-	0.39	.154	.179	97.2	338	.0725
CCl_3COO^-	.45	.269	.309	222.9	360	.0696
CCl_3COO^-	.52	.474	.535	568.7	400	.0719
					Mean	0.0714

est. In the absence of catalysis by the acetate ion, the rate expected for the experiment in the acetate buffer would be

$$k_{obs} = k[H^+]/(1 + K_1[H^+]) = 5.6 \times 10^{-7} \text{ min.}^{-1}$$

which corresponds to a half-time of 850 days. The observed half-time is *ca.* twenty days. Although the experiments were carried out in solutions of differing ionic strength, and concentration of undissociated acid, the catalytic constants for the three anion bases conform roughly to the Brönsted relation, as Table X shows.

TABLE X

CONFORMITY TO THE BRÖNSTED RELATION

$$k_B/q \doteq 0.025\ (p/qK)^{0.31}$$

Catalyst	p	q	K	$(k_B)_{calcd.}$	$(k_B)_{obs.}$
CH_3COO^-	1	2	1.75×10^{-5}	1.2	1.0 1.4
$HCCl_2COO^-$	1	2	3.32×10^{-2}	0.12	.10
CCl_3COO^-	1	2	0.20	.067	.071
H_2O	1	1	55.5	.0073	.00023

It will be observed that the catalytic constant for the water molecule, $k_{H_2O} = (311 \times 10^{-5})/(0.244)(55.5) = 2.3 \times 10^{-4}$, is considerably smaller than the value calculated from the Brönsted equation to which the constants for the three singly charged anions conform. If k_{H_2O} is obtained from the value of k in 0.5 N nitric acid solution, instead of that at infinite dilution, it becomes 2.9×10^{-4} but remains well below $(k_{H_2O})_{calcd.}$ It is probably true that the charge type of the basic catalyst is important in the hydrolysis of cyanamide, just as it is in the decomposition of nitramide. Since the exponent in the Brönsted relation for the hydrolysis of cyanamide is small, it is to be expected that of two catalysts of the same basic strength the one having the fewer negative charges will be the less effective,[22] and consequently it is not surprising that k_{H_2O} is low. It will be of interest to determine k_{NH_3}, and evaluate the parameters of the Brönsted relation for uncharged bases from k_{H_2O} and k_{NH_3}. It will also be of interest to measure the rate in buffer systems where the base is a doubly charged anion, and when greater catalytic effectiveness may be expected.

Summary

1. In nitric acid solution, the rate of hydrolysis of cyanamide increases steadily with increase in acid concentration, and the measured energy of activation shows no change with change in acid concentration.

2. In hydrochloric and in hydrobromic acid solution, the rate increases to a maximum, and thereafter drops off, as the acid concentration increases. The energy of activation increases by 2000 cal. with increase in concentration of hydrochloric acid from 1 to 3 N, and by 5000 cal. with increase in concentration of hydrobromic acid from 1 to 5 N. This is believed due to formation of unhydrolyzable complexes between substrate and acid. Experiments carried out in sodium chloride–hydrochloric acid solutions 4 N in chloride can be similarly explained.

3. In trichloroacetic acid solution, and in dichloroacetate and acetate buffers, the hydrolysis is more rapid than is anticipated from the hydrogen-ion concentration. The higher rate is believed due to catalysis by the anion of the acid, the reaction being

$$NH_2CN{\cdot}H^+ + X^- \longrightarrow$$

and concurrently

$$NH_2CN{\cdot}H^+ + H_2O \longrightarrow$$

which is the sole reaction in the solution of a strong acid. The same situation may perhaps exist in the acid hydrolysis of amides.

PHILADELPHIA, PA.

RECEIVED MARCH 26, 1945

---

[22] Pedersen, *J. Phys. Chem.*, **38**, 581 (1934).