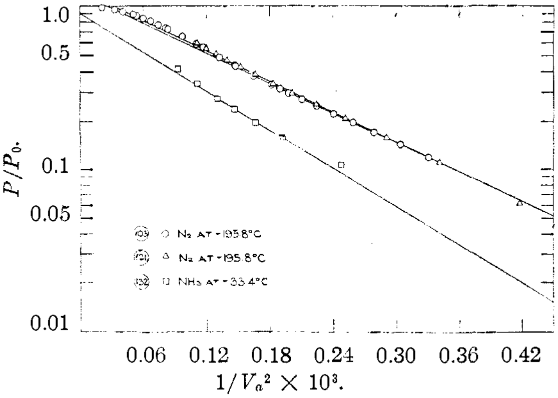

Fig. 4.—Nitrogen and ammonia adsorption by catalyst H-G according to Harkins–Jura equation.

"k" constant for ammonia. This is best accomplished by careful ammonia adsorption measurements on a non-porous titanium oxide sample of known area (BET or HJ "absolute" method). However, since the BET and HJ areas are in excellent agreement for nitrogen on the H-G catalyst a preliminary value of "k" for ammonia at liquid ammonia temperatures is calculated from the nitrogen area of H-G and the slope of the ammonia HJ plot. The value obtained is 3.46. It is assumed in the calculation of "k" that pore structure and surface composition factors are not significant.

Acknowledgment.—The authors wish to thank Mr. E. C. Herthel and Mr. J. W. Teter for their interest and advice, Mr. M. F. L. Johnson and Mr. J. Melik for suggestions and assistance, Miss Sarah Siebenmorgen for calculating and plotting, and Mr. R. D. Duncan for preparing the figures. The authors are also grateful to Dr. P. H. Emmett for his valuable criticism of the original manuscript.

Summary

Adsorption–desorption isotherms of ammonia on a high area supported cobalt catalyst at liquid ammonia temperatures have been studied and are compared with those obtained using nitrogen at liquid nitrogen temperatures. The results are discussed with respect to surface area values, hysteresis characteristics, pore volumes, pore radii and heats of adsorption. Experimental methods for the ammonia studies are described along with an outline of possible explanations for the slow rate of approach to adsorption equilibrium. Adsorption data obtained with the two adsorbates are quite similar except for the failure of the desorption branch of the ammonia isotherm to rejoin the adsorption curve. The Brunauer–Emmett–Teller and Harkins–Jura area values calculated from the nitrogen isotherms of this study differ by less than two per cent.

EAST CHICAGO, INDIANA RECEIVED SEPTEMBER 3, 1946

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

A Mechanism for the Hydrolysis of Cyanamide in Acid Solution

BY MARY L. KILPATRICK

The mechanism here proposed for the hydrolysis of cyanamide in acid solution is offered with the view that it may throw light upon some of the anomalies which have been observed in the hydrolysis of nitriles. It is based upon kinetic measurements with water as solvent, already reported,[1] and upon unpublished results obtained in this Laboratory with alcohol as solvent.[2] In water, the product of solvolysis is urea, in alcohol, the salt of the alkyl isourea.[3] The results of the kinetic measurements are summarized below.

With water as solvent: (i) The rate of hydrolysis of cyanamide is the same in dilute solutions of various strong acids, very different in concentrated solutions. (ii) In nitric acid solution, the rate increases continuously as the acid concentration increases, and the measured energy of activation shows no change with acid concentration. (iii) 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 with acid concentration in both cases. (iv) In trichloroacetic acid solution, and in dichloroacetate and acetate buffers, the hydrolysis is more rapid than is anticipated from the hydrogen ion concentration. The catalytic constant for the trichloroacetic acid molecule, calculated on the assumption of general acid catalysis, is greater than that for the hydrogen ion; consequently the data are to be interpreted rather as basic catalysis of the cation of cyanamide.

With methyl or ethyl alcohol as solvent: (v) The solvolysis is more rapid than in water. For instance, in 0.1 N hydrochloric acid solution, at 30°, the formation of methyl isourea hydrochloride is *ca.* 150 times, and that of ethyl isourea hydrochloride 50 times, as fast as the formation of urea in the aqueous acid solution. (vi) The rate drops off with increasing concentration of hydrochloric acid at quite low acid concentrations, and since

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[1] Sullivan and Kilpatrick, THIS JOURNAL, **67**, 1815 (1945).

[2] M. J. Sullivan, unpublished work.

[3] Stieglitz and McKee, *Ber.*, **33**, 810, 1518 (1900); McKee, *Am. Chem. J.*, **26**, 209 (1901).

no reaction takes place in the absence of acid, the maximum must occur at a much lower concentration of hydrochloric acid in alcohol than in water. The addition of lithium chloride retards the reaction.

The Raman spectrum of cyanamide[4] indicates that in cyanamide (solid, molten, dissolved) there are at least two molecular forms in equilibrium, one certainly the amide $H_2NC{\equiv}N$, the second probably the diimide $HN{=}C{=}NH$, and possibly a third, perhaps an associated molecule.[5] On the other hand, the Raman spectrum of cyanamide dihydrochloride[4] shows no $C{\equiv}N$ line, and this, together with the fact that the infrared absorption spectrum of monoethylol cyanamide hydrochloride[6] shows a pronounced $C{=}N$ band, may be taken as indicating conversion of $C{\equiv}N$ to $C{=}N$ in cyanamide dihydrochloride. Since the Raman spectrum of cyanamide dihydrochloride was obtained from a solution of cyanamide in an excess of concentrated aqueous hydrochloric acid, it appears that an appreciable quantity of molecular cyanamide no longer exists in a solution containing much hydrochloric acid. A dilute aqueous solution of the dihydrochloride, however, has the conductance of two moles of hydrochloric acid[7] and is therefore largely dissociated.

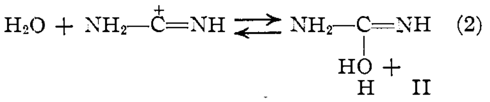
It has been remarked that the compounds of cyanamide with hydrogen chloride and bromide, $NH_2CN{\cdot}2HCl$ and $NH_2CN{\cdot}2HBr$, possess a unique stability. Drechsel,[8] who prepared them, wrote their formulas with one mole of acid attached to the CN group, one to the NH_2. The formation of the dihydrochloride from cyanamide and hydrochloric acid in ethyl alcohol is fast in comparison with the formation of ethyl isourea hydrochloride,[9] and in water fast in comparison with the formation of urea.[7] The only other reported compound of cyanamide with an acid is that with hypochlorous acid,[10] which on warming to room temperature rapidly decomposes.

The following path is proposed for the hydrolysis of cyanamide in acid solution

$$NH_2CN + A \rightleftharpoons B + [NH_2C{\equiv}\overset{+}{N}H \longleftrightarrow NH_2{-}\overset{+}{C}{=}NH \longleftrightarrow \overset{+}{N}H_2{=}C{=}NH] \quad (1)$$

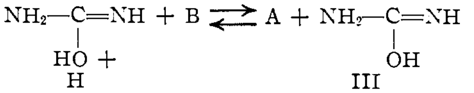
I

where A is an acid, B its conjugate base. Some of the cation may have the structure $\overset{+}{N}H_3C{\equiv}N$ rather than the structure represented by I.



$$H_2O + NH_2{-}\overset{+}{C}{=}NH \rightleftharpoons NH_2{-}\underset{\underset{H}{HO^+}}{\underset{|}{C}}{=}NH \quad (2)$$

II

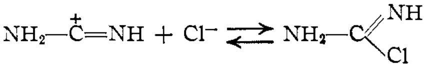


$$NH_2{-}\underset{\underset{H}{HO^+}}{\underset{|}{C}}{=}NH + B \rightleftharpoons A + NH_2{-}\underset{OH}{\underset{|}{C}}{=}NH \quad (3)$$

III

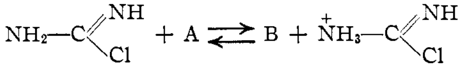
I, II, and III were given by Hammett[11] as probable intermediates in the acid hydrolysis of cyanamide. Conversion of isourea (III) to urea is achieved by a pair of protolytic reactions which must occur very rapidly since isourea does not exist as such, but only as its O-substituted derivatives; moreover, the reaction in alcohol stops at the stage of the alkyl isourea, yet is of measurable speed. Step (1) is rejected as rate-determining because of the rapidity of formation of cyanamide dihydrochloride, and because of the relative order of effectiveness of nitric and trichloroacetic acids in hydrolyzing cyanamide, and the assumption is made that equilibrium is immediately established between cyanamide and cation. Step (2) is rejected as rate-determining because its rate depends on the concentration of I, which is governed by the hydrogen-ion concentration; were (2) rate-determining, we should have specific hydrogen-ion catalysis. Step (3) remains as rate-determining, which means that II, the hydrated cation, splits out a molecule of water with much greater frequency than it yields a proton to an approaching base.

It is proposed that in hydrochloric or hydrobromic acid solution the concentration of the reactive ion I is diminished by formation of unhydrolyzable (IV, V) or difficultly hydrolyzable (VI) complexes, thus



(4)

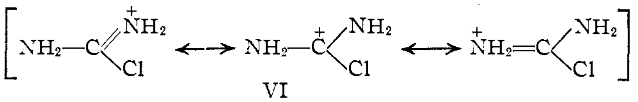
IV



(5)

V

or



VI

Equilibria (4) and (5) are assumed to be established rapidly. Although a monohydrochloride is not known in the solid state, formation of V (or VI) may be expected to proceed stepwise by way of IV. The structure of the cation of the dihydrochloride appears to be an open question; structure V (Drechsel's) will not add a water molecule at the carbon atom by coördination, but, on the other hand, although the resonating structure VI possesses a carbenium ion form, its terminal forms are identical, which makes for stability. The kinetic data do not permit a choice between V and VI, for if a large part of the substrate is present as VI in hydrochloric acid solution, and if VI hydrolyzes much more slowly than I, the over-all rate of reaction will be slow.

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(4) Kahovec and Kohlrausch, *Z. physik. Chem.*, **37B**, 421 (1937).

(5) See also Hunter and Rees, *Nature*, **153**, 284 (1944).

(6) Barnes, Liddell and Williams, *Ind. Eng. Chem., Anal. Ed.*, **15**, 659 (1943).

(7) Hantzsch and Vogt, *Ann.*, **314**, 366 (1900).

(8) Drechsel, *J. prakt. Chem.*, [2] **11**, 315 (1875).

(9) Pinck and Hetherington, *Ind. Eng. Chem.*, **18**, 629 (1926).

(10) Manguin and Simon, *Compt. rend.*, **170**, 998 (1920).

(11) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 340.

TABLE I

EFFECT OF VARIOUS ACIDS ON THE HYDROLYSIS OF NITRILES

A. m = molality acid. $T = 65°$

Nitrile	Acid	$k_{\text{obs.}} \times 10^3$ hr.$^{-1}$				
		$m = 1$	$m = 2$	$m = 4$	$m = 6$	$m = 8$
HCN	HCl	1.75	13.3	250	2000[a]	
HCN	HBr	0.91	2.2	29	420	
HCN	H_2SO_4	1.45	4.0	12	22[a]	
CH_3CN	HCl		0.60	2.07	7.7	38.7
CH_3CN	HBr		.59	1.89		
CH_3CN	H_2SO_4		.85	2.65	6.04	10.60
CH_3CH_2CN	HCl			3.6	14.4	78.4
CH_3CH_2CN	H_2SO_4			4.6	9.1	
$CH_3CH(OH)CN$	HCl			28	259	1022
$CH_3CH(OH)CN$	H_2SO_4			6.1	17.5	
CH_2OHCH_2CN	HCl			1.85	6.6	
CH_2OHCH_2CN	H_2SO_4			2.7	6.3	

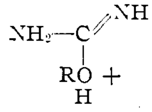
B. M = molarity acid. $T = 65°$

Nitrile	Acid	$k_{\text{obs.}} \times 10^3$ hr.$^{-1}$[b]				
		$M = 1$	$M = 4$	$M = 9.43$	$M = 10.13$	$M = 13.01$
CH_3CH_2CN	HCl	1.1	12		13,500	
CH_3CH_2CN	HBr	1.1	10			
CH_3CH_2CN	H_2SO_4	1.1		720		
CH_3CH_2CN	HNO_3	1.0	10			250

[a] Extrapolated. [b] Calculated from the Arrhenius equation.

The kinetic data are in agreement with the mechanism outlined. Consider first the results obtained with water as solvent. In nitric acid solution increasing the concentration of acid increases the concentration of I, and a steady increase in rate results. Water functions as the base in step (3). There is no indication of a maximum rate, *i.e.*, there appears to be no tendency to form $NH_2CN \cdot HNO_3$ or $NH_2CN \cdot HNO_3 \cdot H^+$. In trichloroacetic acid solution, similarly, the concentration of I increases with the hydrogen ion concentration; here, the trichloroacetate ion functions as a base in step (3), as well as the water molecule. In hydrochloric acid solution the rate of formation of urea is the same, at low acid concentrations, as in nitric acid solution, since the reaction proceeds *via* I. With increasing concentration of hydrochloric acid IV and V (or VI) begin to form, the fraction of substrate present as I is reduced, and the rate drops off. The same explanation applies in the case of hydrobromic acid; here the tendency toward formation of complexes is less than in the case of hydrochloric acid, and a higher acid concentration is required to produce the maximum rate. In regard to the effect of temperature, it is to be expected that the measured energy of activation will increase with increasing concentration of hydrochloric or hydrobromic acid if the extent of complex formation decreases with rise in temperature.[1]

Consider now the results obtained with alcohol as solvent. The greater speed in alcohol is expected because of the greater acid strength of the ion as compared to II, the base conjugate to VII being an ether, the base conjugate to II, an alcohol. The fact that the rate in alcohol drops off with increasing concentration of hydrochloric acid at quite low acid concentrations, while without acid no reaction occurs, is compatible with a greater tendency toward formation of IV and V (or VI) in alcohol than in water.



VII

Hydrolysis of Nitriles

The strong acids are as specific in their effect on the hydrolysis of aliphatic nitriles as they are on the hydrolysis of cyanamide, but whereas hydrochloric is least effective in hydrolyzing cyanamide, it is in concentrated solution most effective in hydrolyzing nitriles. This is apparent from an examination of Table I. In Part A of Table I are given the first-order velocity constants obtained by Krieble and Peiker[12] for the hydrolysis of hydrogen cyanide, and by Krieble and Noll[13] for the hydrolysis of aceto-, propio-, α-hydroxypropio- and β-hydroxypropionitrile. In Part B of the table are given a few values of the rate of hydrolysis of propionitrile in hydrochloric acid solution,[14] and in hydrobromic, sulfuric and nitric acid solution,[15] calculated from the data of Winkler and his co-workers.

The table shows that, at 4 molal, hydrochloric acid is much the most effective in hydrolyzing hydrogen cyanide and α-hydroxypropionitrile,

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(12) Krieble and Peiker, THIS JOURNAL, **51**, 3368 (1929).

(13) Krieble and Noll, *ibid.*, **61**, 560 (1939); the results for cyanoacetic acid are omitted because of evidence of a side reaction, and all results at acid concentrations higher than 8 molal are omitted because the hydrolysis of the amide affects the measured rate.[14,15]

(14) Rabinovitch, Winkler and Stewart, *Can. J. Research*, **B20**, 121 (1942).

(15) McLean, Rabinovitch and Winkler, *ibid.*, **B20**, 168 (1942).

and that, for the other nitriles, its superiority does not appear until higher acid concentrations are reached.

Winkler and his co-workers determined the parameters A and E of the Arrhenius equation

$$k = k_{\text{obs.}}/M_{\text{acid}} = Ae^{-E/RT} \qquad (6)$$

for the hydrolysis of propionitrile in hydrochloric, hydrobromic, sulfuric and nitric acid solution,[14,15] and for the hydrolysis of hydrogen cyanide and of acetonitrile in hydrochloric acid solution.[16] They found that, although the equation holds, at a given acid concentration, over the range of temperature investigated, the parameters A and E in every case change with change in acid concentration. Their extreme values of A and E for propionitrile are as follows:

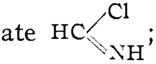
For 1 M HCl, E = 25,600 and for 10.13 M, 18,900 cal.
For 1 M HCl, log A = 10.04 and for 10.13 M, 8.78
For 1 M HBr, E = 25,700 and for 7.68 M, 22,600 cal.
For 1 M HBr, log A = 10.1 and for 7.68 M, 9.5
For 1 M H_2SO_4, E = 25,700 and for 9.43 M, 23,000 cal.
For 1 M H_2SO_4, log A = 10.1 and for 9.43 M, 10.2
For 1 M HNO_3, E = 26,700 and for 13.01 M, 20,700 cal.
For 1 M HNO_3, log A = 10.7 and for 13.01 M, 8.1

where "log" is the logarithm to the base 10, and time is in seconds. The great part of the change in A and E occurs when $M_{\text{acid}} > 4$.

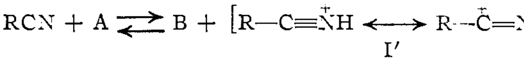
In addition to these rates in aqueous solution, there are available measurements by Krieble, Duennebier, and Colton[17] on the rate of solvolysis of hydrogen cyanide in acetic acid as solvent, in the presence of hydrochloric or sulfuric acid. The product is presumably the salt of formimidoacetate.[18] In the absence of the mineral acid, the solution of hydrogen cyanide in glacial acetic acid is stable[19]; in its presence, hydrogen cyanide disappears in accordance with the first-order law. The reaction is very much faster in acetic acid as solvent than it is in water; thus for a solution 1 molal in hydrochloric acid, at 25°

$$(k_{\text{obs.}})_{CH_3COOH}/(k_{\text{obs.}})_{H_2O} = 4 \times 10^6$$

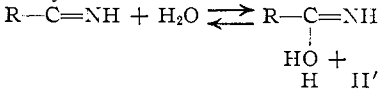
and for a 2 molal solution, 8×10^6. The difference in effectiveness of hydrochloric and sulfuric acids is much greater in acetic acid than it is in water.

The specificity of the strong acids is attributed by McLean, Rabinovitch and Winkler[15] to variation of the parameters of the Arrhenius equation with acid concentration. On the other hand, Krieble and McNally,[20] and Krieble and Peiker, attribute the superior effectiveness of hydrochloric acid over sulfuric, in hydrolyzing hydrogen cyanide, to the formation of the reactive intermediate  $HC\langle^{Cl}_{NH}$; since they found the rate of hydrolysis in hydrochloric acid solution proportional to the activity of the acid, they consider the formation of the intermediate to be the rate-determining step. The same explanation is offered by Krieble, Duennebier and Colton for their results in acetic acid as solvent. The results of Krieble on the hydrolysis of hydrogen cyanide are interpreted by Hammett[21] as indicating that the reaction is composite, depending at high acidities on the reaction of the anion of the acid, as well as of a proton, while at lower acidities a reaction with H_3O^+ predominates.

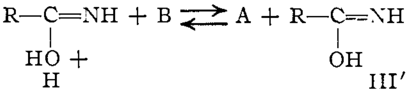
If the hydrolysis of the nitrile proceeds by the path given for cyanamide, one has



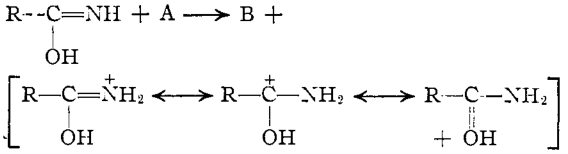
$$RCN + A \rightleftharpoons B + \left[R{-}C{\equiv}\overset{+}{N}H \longleftrightarrow R{-}\overset{+}{C}{=}NH\right] \quad \underset{\text{I}'}{} \qquad (7)$$



$$R{-}\overset{+}{C}{=}NH + H_2O \rightleftharpoons \underset{\substack{HO+\\ H}}{R{-}C}{=}NH \quad \text{II}' \qquad (8)$$

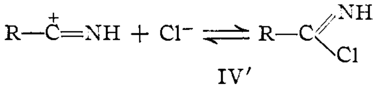


$$\underset{\substack{HO+\\ H}}{R{-}C}{=}NH + B \rightleftharpoons A + \underset{OH}{R{-}C}{=}NH \quad \text{III}' \qquad (9)$$

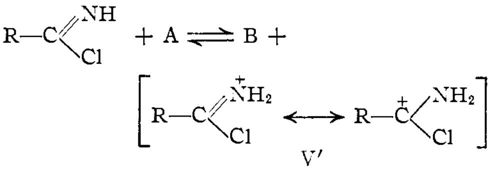


$$\underset{OH}{R{-}C}{=}NH + A \longrightarrow B + \left[\underset{OH}{R{-}C}{=}\overset{+}{N}H_2 \longleftrightarrow \underset{OH}{R{-}\overset{+}{C}}{-}NH_2 \longleftrightarrow \underset{+\,OH}{R{-}\overset{\|}{C}}{-}NH_2\right] \qquad (10)$$

which by loss of a proton yields the amide. This path will be referred to as Path A. By analogy with cyanamide, its rate-determining step would be (9), and it might be expected to show general basic catalysis. If hydrochloric acid adds to the nitrile in solution, one has (*cf.* (4) and (5))

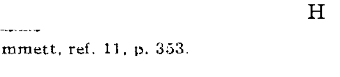


$$R{-}\overset{+}{C}{=}NH + Cl^- \rightleftharpoons R{-}C\langle^{NH}_{Cl} \quad \text{IV}' \qquad (11)$$



$$R{-}C\langle^{NH}_{Cl} + A \rightleftharpoons B + \left[R{-}C\langle^{\overset{+}{N}H_2}_{Cl} \longleftrightarrow R{-}\overset{+}{C}\langle^{NH_2}_{Cl}\right] \quad \text{V}' \qquad (12)$$

Here IV′ is of the type of IV and V′ of the type of VI; however, V′ does not exhibit the symmetrical resonance of VI and may be expected to be much more reactive than VI. Addition of water to V′, followed by removal of a proton, the splitting out of chloride ion, and removal of a second proton, would yield the amide; in the scheme below, the splitting out of chloride is considered irreversible



$$R{-}\overset{+}{C}\langle^{NH_2}_{Cl} + H_2O \rightleftharpoons \underset{\substack{HO+\\ H}}{R{-}C}\langle^{NH_2}_{Cl} \qquad (13)$$

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[16] Rabinovitch and Winkler, *Can. J. Research*, **B20**, 221 (1942).

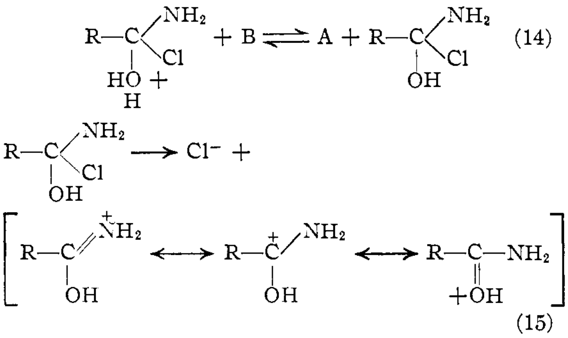
[17] Krieble, Duennebier and Colton, THIS JOURNAL, **65**, 1479 (1943).

[18] See Krieble and Smellie, *C. A.*, **40**, 1868 (1946).

[19] Krieble and Smellie, THIS JOURNAL, **67**, 690 (1945).

[20] Krieble and McNally, *ibid.*, **51**, 3368 (1929).

[21] Hammett, ref. 11, p. 353.

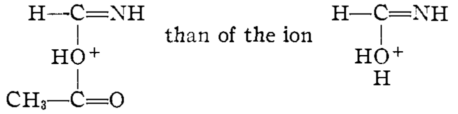


(14)

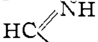
(15)

The existence in solution of V′ thus opens up a new path (Path B) to the amide. Path B includes (7), (11), (12) and the subsequent reactions mentioned. Although given for the case of hydrochloric acid, reaction *via* Path B may be expected to occur wherever the anion of the acid adds to the cation of the nitrile.

This mechanism is readily applicable to acetic acid as solvent. On the assumption that most of the reaction in the presence of sulfuric acid goes by Path A, the faster rate of solvolysis of hydrogen cyanide in acetic acid than in water may be attributed to the greater acid strength of the ion



$$\begin{matrix} H\text{—}C\text{=}NH \\ | \\ HO^+ \\ | \\ CH_3\text{—}C\text{=}O \end{matrix} \quad \text{than of the ion} \quad \begin{matrix} H\text{—}C\text{=}NH \\ | \\ HO^+ \\ H \end{matrix}$$

The fact that certain addition compounds of nitriles with mineral acids react readily with water is an indication that hydrolysis may occur *via* Path B. Gautier[22] prepared a crystalline hydrochloride of hydrogen cyanide for which he gave the formula $HCN{\cdot}HCl$; dissolved in water, it dissociated partially into its components, but at the same time rapid hydrolysis occurred. It has since been shown that Gautier's hydrochloride was probably a mixture of the sesquichloride, $2HCN{\cdot}3HCl$, and its decomposition product $2HCN{\cdot}HCl$.[23] The formimidochloride, , has not been isolated, but its existence in ethereal solution is indicated as an intermediate in the formation of formamidodichloride, $NH_2\text{-}CHCl_2$, which itself exists in solution as an intermediate in the formation of the sesquichloride.[24] Gautier's hydrochloride of acetonitrile has been shown to be acetamidodichloride, $CH_3CCl_2NH_2$, a crystalline compound melting at 6° with decomposition into acetimidochloride, acetonitrile, and hydrogen chloride.[25] Gautier prepared also a hydrochloride of propionitrile; it was slower to form, and less readily hydrolyzed, than the hydrochloride of hydrogen cyanide. Crystalline addition compounds of hydrogen cyanide with sulfuric and phosphoric acid are known with formulas $HCN{\cdot}H_2SO_4$[26] and $HCN{\cdot}H_3PO_4$,[27,26] respectively. The former is characterized by its extreme deliquescence in moist air and its reactivity with water and alcohol. In the presence of excess sulfuric acid it hydrolyzes quantitatively to ammonia and formic acid. The rate of its formation from the two components was measured by Cobb and Walton in sulfuric acid as solvent; at 0° the first-order reaction has a half-time of 71.5 minutes in 100% sulfuric acid, and of 224 min. in acid containing 3.8% of water. No reaction was detected between hydrogen cyanide and acetic, formic, metaphosphoric, perchloric (60%), or selenous acid.

The Kinetics of the Composite Reaction in Aqueous Solution

It is assumed in what follows, by analogy with cyanamide, that the equilibrium

$$RCN + H_3O^+ \rightleftharpoons RCN{\cdot}H^+ + H_2O$$

is established with great rapidity. In order to include concentrated acid solutions, the equilibrium constant

$$(K)_0 = \frac{[RCN{\cdot}H^+][H_2O]}{[RCN][H_3O^+]}\frac{f_{RCN\cdot H^+}\, f_{H_2O}}{f_{RCN}\, f_{H_3O^+}} = K\frac{f_{RCN\cdot H^+}\, f_{H_2O}}{f_{RCN}\, f_{H_3O^+}} \qquad (16)$$

is employed, rather than the customary expression from which the factor $[H_2O]f_{H_2O}$ is omitted; for a reaction of this type the classical equilibrium constant is expected to change, with electrolyte concentration, in accordance with the equation

$$\log K = \log(K)_0 + \beta\mu \qquad (17)$$

where μ is the ionic strength, and β a constant for a given electrolyte.

When species II′ and III′ of equations (8) and (9) are considered to be reactive intermediates present at very low, and constant, concentrations, and when the reactant is considered to be $RCN{\cdot}H^+ = I'$, application of Christiansen's method yields for the rate of reaction by Path A

$$v_A = \frac{k_8k_9k_{10}[RCN{\cdot}H^+][H_2O][B]}{k_9k_{10}[B] + k_{-8}k_{10} + k_{-8}k_{-9}} \qquad (18)$$

where each velocity constant is numbered for the equation to which it applies, a positive number denoting reaction from left to right, a negative, the reverse. If k_9k_{10} [B] $\ll k_{-8}k_{10}+k_{-8}k_{-9}$, *i.e.*, if the hydrated cation splits out water with much greater frequency than it reacts with the base, and if $k_{10} \gg k_{-9}$, this becomes

$$v_A = (k_8/k_{-8})k_9[RCN{\cdot}H^+][H_2O][B] = K_8k_9[RCN{\cdot}H^+][H_2O][B] \qquad (19a)$$

or if several bases are present

$$v_A = K_8[RCN{\cdot}H^+][H_2O]\sum(k_9)_i[B_i] \qquad (19b)$$

Equation (19b) may be written as

$$v_A = K_8K[RCN][H_3O^+]\sum(k_9)_i[B_i] \qquad (20)$$

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[22] Gautier, *Ann. chim. phys.*, [4] **17**, 129 (1869).

[23] Hinkel and Dunn, *J. Chem. Soc.*, 1834 (1930).

[24] Hinkel and Watkins, *ibid.*, 407 (1940).

[25] Hinkel and Treharne, *ibid.*, 866 (1945).

[26] Cobb and Walton, *J. Phys. Chem.*, **41**, 351 (1937).

[27] Berger and Olivier, *Rec. trav. chim.*, **46**, 600 (1927).

or, letting

$$z = [\mathrm{RCN}] + [\mathrm{RCN{\cdot}H^+}] \qquad (21a)$$

$$\text{and } (k_9')_i = K_8(k_9)_i \qquad (21b)$$

as

$$v_A = (Kz[\mathrm{H_3O^+}]/\{1 + K[\mathrm{H_3O^+}]/[\mathrm{H_2O}]\})\sum(k_9')_i[B_i] \qquad (22)$$

An equation of this form was found applicable to the hydrolysis of cyanamide. In the aqueous solution of a strong acid the only base present is water, and by analogy with cyanamide the electrolyte effect on the velocity constant is expressed as

$$\log (k_9')_{\mathrm{H_2O}} = \log k_9' = \log (k_9')_0 + b\mu \qquad (23)$$

where b is a positive constant, for a given electrolyte.

On applying Christiansen's method to Path B one obtains

$$v_B = k_{11}k_{12}k_{13}k_{14}k_{15}[\mathrm{RCN{\cdot}H^+}][\mathrm{Cl^-}][\mathrm{A}][\mathrm{H_2O}]/D \qquad (24)$$

where

$$D = k_{12}k_{13}k_{14}k_{15}[\mathrm{A}][\mathrm{H_2O}] + k_{-11}k_{13}k_{14}k_{15}[\mathrm{H_2O}] + k_{-11}k_{-12}k_{14}k_{15}[\mathrm{H_2O}] + k_{-11}k_{-12}k_{-13}k_{15} + k_{-11}k_{-12}k_{-13}k_{-14}\ [\mathrm{A}] \qquad (25)$$

Krieble and his co-workers found the rate-determining step in the hydrolysis of hydrogen cyanide in hydrochloric acid solution to be the formation of formimidochloride, and an examination of the expressions above shows that if the first term in the denominator preponderates

$$v_B = k_{11}[\mathrm{RCN{\cdot}H^+}][\mathrm{Cl^-}] \qquad (26)$$

The electrolyte effect on k_{11} is expressible, according to Brönsted, as

$$k_{11} = (k_{11})_0\, f_{\mathrm{RCN{\cdot}H^+}}\, f_{\mathrm{Cl^-}}/f_{\mathrm{RCN{\cdot}H^+,\,Cl^-}} \qquad (27)$$

and from (16) and (27) it follows that, if f_{RCN} and $f_{\mathrm{RCN{\cdot}H^+,\,Cl^-}}$ cancel

$$v_B = (K)_0(k_{11})_0[\mathrm{RCN}][\mathrm{H_3O^+}][\mathrm{Cl^-}]f_{\mathrm{H_3O^+}}f_{\mathrm{Cl^-}}/[\mathrm{H_2O}]f_{\mathrm{H_2O}} \qquad (28)$$

For a base as weak as hydrogen cyanide $z \approx [\mathrm{RCN}]$, and if $[\mathrm{H_2O}]\,f_{\mathrm{H_2O}}$ changes only slightly, the first-order constant will be approximately proportional to the activity of the hydrochloric acid.

It remains to examine the assumption that the first term in the denominator of v_B preponderates. The first term contains the factor k_{12} which the remaining terms all lack, and if k_{12} is very much greater than any other k, the first term will preponderate. If this is so, it follows that, when $[\mathrm{H_3O^+}]$ is not very small, the equilibrium

$$\mathrm{RCN{\cdot}HCl} + \mathrm{H_3O^+} \rightleftharpoons \mathrm{RCN{\cdot}HCl{\cdot}H^+} + \mathrm{H_2O}$$

is displaced far toward the right, in which connection it may be of significance that acetamidodichloride is more stable than acetimidochloride.[25]

The velocity constants given in Table I indicate that in hydrochloric acid solution the hydrolysis of propionitrile occurs chiefly by Path A when $M_{\mathrm{HCl}} < 4$, and that at higher acid concentrations reaction by Path B may contribute to the over-all rate. If this is so, the critical increment E obtained by Winkler and his co-workers will be expected to change with acid concentration. Now E may change with acid concentration even if hydrolysis proceeds solely by Path A, as the following considerations show; for simplicity, a weakly basic substrate is chosen, for which $\{1 + K\ [\mathrm{H_3O^+}]/[\mathrm{H_2O}]\} \approx 1$, so that

$$k_{\mathrm{obs.}} = KK_8[\mathrm{H_3O^+}](k_9)_{\mathrm{H_2O}}\ [\mathrm{H_2O}] \qquad (29)$$

when hydrolysis occurs in the solution of a strong acid. Since

$$\left(\frac{\partial \ln k_{\mathrm{obs.}}}{\partial T}\right)_{M_{\mathrm{acid}}} = \frac{E_{\mathrm{obs.}}}{RT^2} = \left(\frac{\partial \ln (k_9)_{\mathrm{H_2O}}}{\partial T} + \frac{\partial \ln K}{\partial T} + \frac{\partial \ln K_8}{\partial T}\right)_{M_{\mathrm{acid}}} = \frac{1}{RT^2}\{E_9 + \Delta H + \Delta H_8\} \qquad (30)$$

and

$$\left(\frac{\partial E_{\mathrm{obs.}}}{\partial M_{\mathrm{acid}}}\right)_T = \left(\frac{\partial}{\partial M_{\mathrm{acid}}}\{E_9 + \Delta H + \Delta H_8\}\right)_T \qquad (31)$$

it is clear that change in $E_{\mathrm{obs.}}$ with acid concentration can be brought about by change in one or more of the terms within the braces, in especial, by change in ΔH and ΔH_8 with acid concentration. No change in $E_{\mathrm{obs.}}$ was found for the hydrolysis of cyanamide in nitric acid solution over the measured range ($M_{\mathrm{acid}} < 4$), and only slight change for the hydrolysis of propionitrile in hydrochloric acid solution up to 2 or 3 M, but for higher concentrations of hydrochloric acid there was a pronounced decrease in $E_{\mathrm{obs.}}$ for propionitrile. While this decrease can be attributed to change in $[E_9 + \Delta H + \Delta H_8]$ with acid concentration, as well as to reaction by Path B, the superior effectiveness of hydrochloric acid over sulfuric in hydrolyzing hydrogen cyanide and α-hydroxypropionitrile indicates that reaction by Path B, as well as by Path A, probably occurs when propionitrile hydrolyzes in hydrochloric acid solutions more concentrated than 4M.

From (20) and (28) the over-all rate for the hydrolysis of propionitrile in hydrochloric acid solution is

$$v_A + v_B = [\mathrm{RCN}](Kk_9'[\mathrm{H_3O^+}][\mathrm{H_2O}] + (K)_0(k_{11})_0\, a_{\mathrm{HCl}}/a_{\mathrm{H_2O}} \qquad (32)$$

Setting

$$[\mathrm{RCN}] = z/\{1 + K[\mathrm{H_3O^+}]/[\mathrm{H_2O}]\}$$

the first-order constant is

$$\frac{v_A + v_B}{z} = \frac{K(k_9')[\mathrm{H_3O^+}][\mathrm{H_2O}] + (K)_0(k_{11})_0\, a_{\mathrm{HCl}}/a_{\mathrm{H_2O}}}{\{1 + K[\mathrm{H_3O^+}]/[\mathrm{H_2O}]\}} \qquad (33)$$

Table II shows the result of applying (33) to the kinetic data of Rabinovitch, Winkler and Stewart.

The equilibrium constant $(K)_0$ at 59.6° was estimated by taking the value at 25° as (55.4) × (0.16) = 8.78,[28] and assuming ΔH for the reaction

$$\mathrm{CH_3CH_2CN} + \mathrm{H_3O^+} \longrightarrow \mathrm{CH_3CH_2CN{\cdot}H^+} + \mathrm{H_2O}$$

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[28] Hall, THIS JOURNAL, **52**, 5124 (1930).

TABLE II

THE HYDROLYSIS OF PROPIONITRILE IN HYDROCHLORIC ACID SOLUTION

$T = 59.6°$, $(K)_0 = 2.53$

M_{HCl}	$\log \frac{a_{HCl}}{a_{H_2O}}$	$v_A/z + v_B/z$ hr.$^{-1}$ Obsd.	Calcd., $\beta = 0$	Calcd., $\beta = -0.1$
0.509	$\bar{1}.18$	0.00026	0.00026	0.00026
1.00	$\bar{1}.85$	.00058	.00061	.00060
2.00	0.72	.0015	.0017	.0017
4.00	1.97	.0067	.0083	.0080
4.55	2.29	.012	.013	.013
5.02	2.57	.017	.020	.020
6.48	3.42	.10	.096	.093
8.47	4.52	1.2	.95	1.0
10.13	5.43	8.3	6.8	8.0

to be −7105 cal., the same as for the corresponding reaction of aniline.[29] To obtain the constants b and $(k'_9)_0$ in equation (23), necessary for the evaluation of k'_9, reaction by Path B was assumed negligible in comparison to that by Path A for $M_{HCl} \leq 2$. The ratio a_{HCl}/a_{H_2O} was assumed to be the same at 59.6° as at 25°, for which temperature figures are given in the second column of the table.[30]

The values of the first-order constant in the fourth column of the table were obtained by taking β in equation (17) as zero, and $(k_{11})_0$ as 1.60×10^{-5} liter/mole/hour; those in the fifth column, by taking β as −0.100, and $(k_{11})_0$ as 1.23×10^{-5}. This very rough computation shows that in hydrochloric acid solution hydrolysis probably takes place by two paths, and that, in consequence, the parameters of the Arrhenius equation

$$k = k_{obs.}/M_{acid} = Ae^{-E/RT}$$

have no theoretical significance.

Acknowledgment.—The writer wishes to express her appreciation of stimulating discussions with Professors E. C. Wagner and Martin Kilpatrick.

Summary

A mechanism has been proposed to account for the fact that, of the strong acids, the halogen acids are least effective in hydrolyzing cyanamide, but are most effective in hydrolyzing the aliphatic nitriles. In the case of the nitriles, hydrolysis probably occurs by two paths in the solution of a halogen acid; the kinetic equations set up giving the rate of reaction by each path are supported by the experimental results of Rabinovitch, Winkler and Stewart on the hydrolysis of propionitrile. The mechanism is in harmony with the experimental results of Krieble and his co-workers.

PHILADELPHIA, PA. RECEIVED AUGUST 12, 1946

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[29] Pedersen, *Kgl. Dansk Videnskab. Selskab.*, **14**, No. 9, 3 (1937).

[30] "International Critical Tables," Vol. VII, p. 233.

[CONTRIBUTION FROM PULP MILLS RESEARCH PROJECT, UNIVERSITY OF WASHINGTON]

Oxidation Potentials of Some Compounds Related to Vanillin

BY D. M. RITTER

The ease with which phenols are oxidized to the corresponding free radicals can be considered a measure of how readily electrons are removed from a specific point in the molecule. The oxidation potential is related to the availability of electrons at that point, and thus to the general distribution of electron density throughout the molecule. Fieser[1] has demonstrated that, though the over-all oxidation of phenols is irreversible, the reaction occurs in steps of which one, the electron transfer, appears to be a reversible process. Certain groups were found to alter the ease with which electrons are removed from phenols. This property, shared by electron-attracting groups such as the nitro group, is a characteristic found not only in the phenols, but is also a property of substituents in compounds of the quinone–hydroquinone types which form reversible oxidation-reduction systems. Conversely, groups such as methoxyl, which repel electrons, lower the normal potentials and the related critical oxidation potentials (E_c) of phenolic substances.[2]

For several reasons determination of the critical oxidation potentials of guaiacyl derivatives should prove interesting. Vanillin and other *p*-hydroxyaldehydes undergo carbonyl addition reactions at retarded rates.[3,4] The similarly lowered reactivity of other guaiacyl derivatives may possibly be ascribed to the influence on the class B side chain reactions of electron-repulsion by the *p*-hydroxyl substituent. Vanillin was found to possess a higher potential (E_c = 1.080 v.) than guaiacol (E_c = 0.868 v.), indicating the displacement of electrons toward the side chain which should retard reaction with nucleophilic reagents. The extent to which electron donation by the hydroxyl group has occurred should be reflected in the oxidation potentials and these should thus furnish a means of predicting the side chain reactivity of other guaiacyl derivatives.

In addition to such considerations concerning side chain reactivity vanillin is only a fair antioxidant. Correlations between antioxidant efficiency and critical oxidation potentials for pro-

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[1] Fieser, THIS JOURNAL, **52**, 5204–5241 (1930).

[2] Fieser and Fieser, "Organic Chemistry," D. C. Heath and Company, Boston, 1944, p. 729.

[3] Vavon and Montheard, *Bull. soc. chim.*, **7**, 551, 560 (1940).

[4] Geissman, "Organic Reactions," vol. 2, John Wiley and Son, New York, N. Y., 1944, p. 94.