[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF TRINITY COLLEGE AND MCGILL UNIVERSITY]

The Hydrolysis of Hydrogen Cyanide by Acids. II

BY VERNON K. KRIEBLE AND ALFRED L. PEIKER

Krieble and McNally[1] have shown that the hydrolysis of hydrogen cyanide is an excellent reaction for studying the catalytic effect of concentrated mineral acids because the velocity is not too great to be measured even in concentrated acid solutions and the rate can easily be followed by determining the hydrolytic product, namely, ammonium formate. They pointed out that the rate of hydrolysis of hydrogen cyanide with mineral acids was quite different from what one would expect from the hydrogen-ion concentration of the solution. With hydrochloric acid for concentrations from 1.95 to 7.84 *N*, the velocity increased in the same order as the activity of the undissociated molecule. This suggested that the molecule of hydrochloric acid was the effective catalyst. There were also a few experiments reported with hydrobromic acid and sulfuric acid as catalysts; in each case the velocity constants were very much lower than those obtained with hydrochloric acid for equivalent concentrations. There were not enough experiments, however, to draw any general conclusions.

In the present communication the results of a more extended investigation of the hydrolysis of hydrogen cyanide with mineral acids are given.

Procedure and Preparation of Materials.—The preparation of hydrogen cyanide and the method of carrying out the hydrolysis were the same as those described in the paper to which reference has just been made.

Hydrolysis Follows Monomolecular Reaction.—A wide variation in hydrogen cyanide concentration with the same acid concentration was investigated and the velocities calculated by the usual monomolecular formula. The results are given in Table I.

TABLE I

Concn. HCN, *M*	Concn. HCl, *M*	Temp., °C.	$K \times 10^3$	Concn. HCN, *M*	Concn. HCl, *M*	Temp., °C.	$K \times 10^3$
0.8	2.07	65	15.2	2.5	2.07	65	15.1
1.0	2.07	65	15.6	0.8	2.07	45	1.50
1.5	2.07	65	14.2	2.0	2.07	45	1.40
2.0	2.07	65	14.7	2.5	2.07	45	1.39

Reaction Velocities with Hydrochloric, Hydrobromic and Sulfuric Acids at 65°

The velocity constants for hydrochloric acid increase rapidly with increase in acid concentration. Column 4 of Table II shows that they go up much faster than the activity of the hydrogen ion. In column 6 of the table the velocity constants are divided by the activity of the undissociated hydrochloric acid molecule. If this is the only catalyst involved, this

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(1) Krieble and McNally, THIS JOURNAL, **51**, 3368 (1929).

TABLE II

Concn. HCl, *M*	$K \times 10^3$	a[a]	$\frac{K \times 10^3}{a}$	a_2[a]	$\frac{K \times 10^3}{a_2}$
0.302	0.29	0.232	1.3	0.0538	5.4
.505	.57	.385	1.5	.1482	3.8
1.02	1.80	.832	2.2	.6918	2.6
2.07	15.20	2.19	6.9	4.786	3.1
3.17	95.00	4.52	21.0	20.420	4.6
4.30	359.00	8.71	41.0	75.800	4.7
5.52	1260.00	16.59	75.9	275.400	4.6

[a] The activities of the hydrogen ion and the undissociated hydrochloric acid molecule are the interpolated values as given by Lewis and Randall for 25°, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 336.

TABLE IIa

Concn. HBr, *M*	$K \times 10^3$	Concn. H_2SO_4, *M*	$K \times 10^3$
0.30	0.29	0.508	0.62
.50	.46	1.03	1.50
1.03	.94	1.57	2.50
2.12	2.80	2.11	4.40
3.25	8.50	2.68	5.50
4.45	47.00	3.25	8.70
5.74	292.00	3.82	10.80
7.13	1640.00	5.49	19.60

ratio should be a constant. As a first approximation this seems to be the case. The agreement is not so good at the lower concentrations. This is to be expected, as it is likely that the non-ionized molecule is not the only catalyst and that the effect of other factors would relatively be more marked at the lower concentrations where the velocity is small. It is at these concentrations that it is more difficult to get reliable velocity constants because it requires several hundred hours to produce appreciable hydrolysis. It must also be remembered that the activities of hydrochloric acid were measured at 25° and without any cyanide present. The relationship which Krieble and McNally had pointed out from 2 to 9 molal then holds fairly well down to 0.3 molal.

Table IIa shows that the velocity constants also increase rapidly with hydrobromic acid as the concentration increases, although Fig. 1 illustrates that the increase is not nearly so rapid as with hydrochloric acid especially at the lower concentrations. That hydrobromic acid should be so much poorer than hydrochloric acid as a catalyst is most surprising, especially as Hantzsch and Weissberger[2] found it more active in the hydrolysis of cane sugar. They found that hydrobromic acid was more active at all concentrations and at 4 *N* the difference was approximately 60%. On the other hand, Taylor[3] reports that in the hydrolysis of acetamide hydrochloric acid is more active than hydrobromic acid but the

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(2) Hantzsch and Weissberger, *Z. physik. Chem.*, **125**, 251 (1927).

(3) Taylor, *J. Chem. Soc.*, 2743 (1930).

difference is only about 20% at 4 *N*. This would indicate that at the higher concentrations of these acids it is impossible to predict how they will behave as catalysts in hydrolytic reactions.

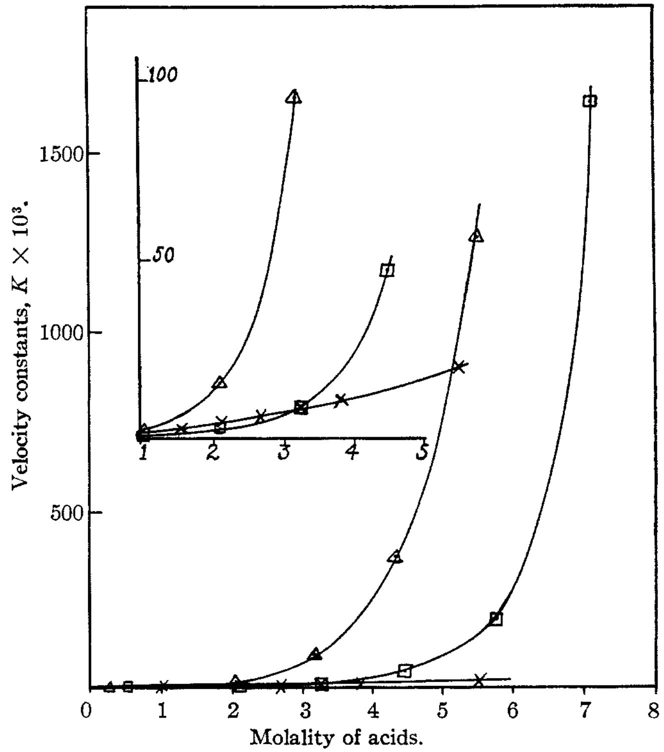

Fig. 1.—Plot of velocity constants $K \times 10^3$ against molality of acids: △, HCl; ⊡ HBr; ×, H_2SO_4.

A few reactions were carried out at 45° with both acids. The results of these experiments along with the results obtained at 65° for the same acid concentrations are given in Table III.

TABLE III

Molal concn. of acid	Temp., °C.	$K \times 10^3$	Comparison of $K \times 10^3$ at 45 and 65°	
			$\frac{4.33\ HCl}{2.07\ HCl}$	$\frac{4.45\ HBr}{2.12\ HBr}$
2.07 HCl	45	1.53		
4.33 HCl	45	35.00	24.7	
2.07 HCl	65	15.20		
4.33 HCl	65	359.00	24.0	
2.12 HBr	45	0.27		
4.45 HBr	45	4.85		18.2
2.12 HBr	65	2.80		
4.45 HBr	65	47.00		16.6

Table III shows that the relative difference in rates between two concentrations of an acid is independent of the temperature. It also shows that the temperature coefficient is considerably higher than that for unsubstituted ester hydrolysis but is much less than that for cane sugar hydrolysis.

Sulfuric acid is a very poor catalyst for hydrogen cyanide hydrolysis in concentrated solutions when compared with hydrochloric acid and hydrobromic acid, especially when the basis of comparison is normality rather than molality. By reducing the molal to normal concentrations in Table II and then interpolating them, it is found that a 5 *N* hydrochloric acid solution is 230 times as effective, and a 5 *N* hydrobromic acid solution 54 times as effective as the corresponding sulfuric acid solution. In terms of molality, however, the difference is not so large as is shown graphically in Fig. 1. The activity of sulfuric acid as a catalyst increases surprisingly little with increase in concentration. This would suggest that the undissociated molecule plays a far less important role as a catalyst than it did in hydrochloric acid for instance.[4]

Reaction Velocities of Hydrochloric and Hydrobromic Acids in the Presence of Neutral Salts.—The results of our experiments seemed to indicate that the undissociated molecule of hydrochloric and hydrobromic acid was the principal catalyst in the hydrolysis of hydrogen cyanide. If this is true then it should be possible to increase the velocity very materially by adding salts to the acids particularly in the higher concentrations of acid where a small shift in concentration makes a large difference in the velocity. That this is the case is shown in Table IV, which gives the results for two different salt concentrations on hydrochloric and hydrobromic acids varying in strength from 0.3 to 2 normal at 65°.

In the last column of Part 1 of the table we have the ratio of the velocity constants of the acids without salts K_A to those with salts $K_A + S$. The salts almost invariably cause an increase in the rate of reaction, the only apparent exceptions being in cases where the velocity is very slow and therefore difficult to determine accurately. Irrespective of the amount of salt added the biggest increase comes in the strongest acid solutions. A

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(4) Since this article was written we have noticed the paper by Hammett and Deyrup [THIS JOURNAL, **54**, 2721 (1932)] on the Acidity Function of Sulfuric and Perchloric Acids. They find that the acidity function H_0 of sulfuric acid, which they determined by means of indicators, parallels in many cases the reaction velocity k when the acid acts as a catalyst. They express this relationship by the equation $H_0 + \log k = \text{constant}$. By interpolating their values we were able to obtain the acidity function for the concentrations of sulfuric acid which we used in this work and thus apply the equation to the velocity constants which we obtained. The results are given in the following table.

Concn. H_2SO_4, M	H_0	$\log (K \times 10^3)$	$H_0 + \log K$	Concn. H_2SO_4, M	H_0	$\log (K \times 10^3)$	$H_0 + \log K$
0.508	+0.53	−1.7924	+0.32	2.68	−0.89	0.7404	−0.14
1.03	+ .14	.1761	+ .31	3.25	−1.19	.9395	− .25
1.57	− .23	.3979	+ .16	3.82	−1.59	1.0334	− .56
2.11	− .57	.6434	+ .07	5.49	−2.37	1.2923	−1.08

The rates of reaction in this case do not seem to parallel the acidity function very closely.

TABLE IV

Acid concn.	Salt concn.	$K \times 10^3$	$\frac{K_A + S}{K_A}$	Acid concn.	Salt concn.	$K \times 10^3$
	Part 1				Part 2	
0.3 N HCl	2 N NaCl	0.46	1.64	0.3 N HCl	2 N KCl	0.41
.5 N HCl	2 N NaCl	0.97	1.83	1.0 N HCl	2 N KCl	5.20
1.0 N HCl	2 N NaCl	5.00	2.78	2.0 N HCl	2 N KCl	48.00
2.0 N HCl	2 N NaCl	72.00	4.83	0.5 N HCl	0.5 N KCl	0.51
0.5 N HCl	0.5 N NaCl	0.48	0.91	1.0 N HCl	0.5 N KCl	2.80
1.0 N HCl	0.5 N NaCl	2.80	1.41	2.0 N HCl	0.5 N KCl	16.00
2.0 N HCl	0.5 N NaCl	25.30	1.70	0.3 N HBr	2 N KBr	0.29
0.3 N HBr	2 N NaBr	0.39	1.34	0.5 N HBr	2 N KBr	0.49
.5 N HBr	2 N NaBr	0.61	1.35	1.0 N HBr	2 N KBr	1.50
1.0 N HBr	2 N NaBr	1.99	2.60	2.0 N HBr	2 N KBr	6.40
2.0 N HBr	2 N NaBr	8.29	2.92	0.5 N HBr	0.5 N KBr	0.41
0.5 N HBr	0.5 N NaBr	0.36	0.80	1.0 N HBr	0.5 N KBr	1.10
1.0 N HBr	0.5 N NaBr	1.10	1.17	2.0 N HBr	0.5 N KBr	3.00
2.0 N HBr	0.5 N NaBr	3.39	1.21			

2 N solution of hydrochloric acid becomes nearly five times as active by adding its equivalent of sodium chloride to it. This is to be expected if the undissociated molecule is the active catalyst. The salt represses the dissociation of the acid and, therefore, increases the concentration of the undissociated molecule, a slight shift of which, however, in low acid concentrations has relatively little effect on the velocity, but as the concentration of the acid increases a slight change makes a big difference in the velocity. This is amply illustrated by Table II and Fig. 1. The table shows that bromides in hydrobromic acid behave in the same way although the effect is not quite so great. Apparently temperature has little effect on the influence of salts on the activity of acids because the ratio of the velocity constant for a 2 N hydrochloric acid solution and a 2 N sodium chloride solution to a 2 N acid solution is 5.2 at 35°, 5.1 at 45° and 4.83 at 65°. For hydrobromic acid the ratio is 2.6 at 45° and 2.92 at 65° for corresponding concentrations of acid and salt. Taylor and Close[5] observed a similar relationship in the effect of chlorides on hydrochloric acid as a catalyst in lactone formation.

In Part 2 of Table IV we have the results of a number of experiments which were carried out with potassium chloride instead of sodium chloride. For acid concentrations of 1 N or less the results are about the same, but at higher concentrations the velocity constants are always lower with potassium chloride. This is similar to what other investigators have found in regard to these salts in homogeneous catalysis.

Summary and Conclusions

1. The rate of hydrolysis of hydrogen cyanide is independent of the concentration of hydrogen cyanide.

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[5] Taylor and Close, *J. Phys. Chem.*, **29**, 1085 (1925).

2. Velocity constants for the hydrolysis of hydrogen cyanide using various concentrations of hydrochloric and hydrobromic acids as catalysts have been determined at 45 and 65°. The velocity goes up very rapidly with increase in concentration of acid. The conclusion is drawn that the principal catalyst is the undissociated acid molecule.

3. The results obtained with sulfuric acid at 65° show this acid to be a poor catalyst compared with the other two acids, especially at the higher concentrations.

4. The relative difference in velocity between two acid concentrations is independent of the temperature.

5. The addition of sodium and potassium chlorides to hydrochloric acid and of sodium and potassium bromides to hydrobromic acid increases the velocity very markedly. In some cases the increase is five fold.

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The Preparation of Acetate and Phosphate Buffer Solutions of Known *P*H and Ionic Strength

BY ARDA ALDEN GREEN

A systematic study of the dissociation constant of acetic acid[1] and of the second dissociation constant of phosphoric acid[2] in the presence of their salts was undertaken by Cohn and by Cohn, Heyroth and Menkin in terms of recent theories of electrolyte solutions. The equilibria in mixtures of CH_3COOH and CH_3COONa up to 2 molar, and of K_2HPO_4 and KH_2PO_4 in concentrations as high as 1.2 molar phosphate, were described. It has been found advisable to extend the concentration limit of the phosphates also to two molar solutions in order to study the behavior of proteins in concentrated electrolytes.[3,4,5,6] The electromotive force measurements in this concentrated range have been carried out both with the hydrogen electrode and with the glass electrode.

The interpolation tables and graphs presented in the earlier communications from this Laboratory have been replaced in use by a system better adapted to facilitate the preparation of solutions of known *P*H, concentration and ionic strength. These are given in terms of the mole fractions of salt required to yield a given *P*H, whereas in the previous theoretical treatment the activity coefficients at given mole fractions were calculated.

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(1) Cohn, Heyroth and Menkin, THIS JOURNAL, **50**, 696 (1928).
(2) Cohn, *ibid.*, **49**, 173 (1927).
(3) Cohn and Green, *J. Biol. Chem.*, **78**, 32 (1928).
(4) Green, *ibid.*, **93**, 517 (1931).
(5) Green, *ibid.*, **93**, 495 (1931).
(6) Florkin, *ibid.*, **87**, 629 (1930).