[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

THE HYDROLYSIS OF HYDROGEN CYANIDE BY ACIDS[1]

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In 1909 Walker and Krieble[2] investigated the hydrolytic action of aqueous solutions of hydrochloric and sulfuric acids on amygdalin. Their experiments showed that when strong aqueous solutions of these acids were used their hydrolytic action was quite different. Hydrochloric acid attacked the nitrile group first while sulfuric acid showed little tendency to attack this group but readily removed the two glucose radicals with the formation of mandelonitrile. These experiments were the first ones, so far as we know, which showed radical differences between like concentrations of these acids in regard to their catalytic power on hydrolysis. The present investigation was undertaken to determine whether this is a characteristic peculiar to amygdalin or whether it is general for nitriles.

This communication takes up the hydrolysis of the simplest of all nitriles—hydrogen cyanide. The results with other nitriles will be treated in a future publication. Our results show that there is a marked difference in the rate at which hydrochloric, sulfuric and hydrobromic acids catalyze the hydrolysis of hydrogen cyanide and that the rate for hydrochloric acid increases very rapidly with an increase in concentration of this catalyst.

Preparation of Material and Method of Procedure

Preparation of Hydrogen Cyanide.—This substance was prepared by the usual methods of treating either sodium or potassium cyanide with moderately concentrated sulfuric acid and distilling off the nitrile. By adding a drop of dilute sulfuric acid to the distillate the hydrogen cyanide could be kept for several months without any appreciable change in appearance or concentration. The solution was standardized by either Liebig's soluble cyanide method or by the gravimetric method using the insoluble silver salt.

Procedure.—The hydrolysis was carried out in several different ways. The most satisfactory one was to mix cold standardized hydrogen cyanide with cold standardized acid in a beaker surrounded with salt and ice. From this beaker a series of pyrex test-tubes was filled. These tubes were then sealed off as near as possible to the liquid or else closed with a rubber stopper which was tied down to make a gas tight seal. It is obvious that it is necessary to have the tubes as nearly full as possible to reduce to a minimum the evaporation of the hydrogen cyanide into the air space. We found that our results were the same irrespective of the container used. The tubes were then placed in a constant temperature bath regulated to 0.1 °. Tubes were taken out at various time intervals and analyzed for ammonium formate.

Method of Following the Hydrolysis.—The hydrolysis of hydrogen cyanide is usually expressed

$$HCN + H_2O = HCONH_2 \quad (1)$$

$$HCONH_2 + H_2O = HCOONH_4 \quad (2)$$

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[1] Read at the meeting of the American Chemical Society in Richmond, Virginia, April, 1927.

[2] Walker and Krieble, *J. Chem. Soc.*, **85**, 1369 (1909).

We were interested in the first reaction but we did not follow it directly. Experiments to be described later showed that the rate of the second reaction can be considered to be infinitely greater than the first, making it possible to follow the first by estimating the ammonium salt.[3] This was done by the well-known Folin aspiration method. Aliquot portions of the solution were pipetted into large pyrex test-tubes and an excess of sodium carbonate was added. Air freed of ammonia was sucked through this solution and then through standard acid. The excess acid was titrated and the amount of ammonium salt present calculated.

Experimental Results

Figure 1 shows the action of 5 *N* hydrochloric and 5 *N* sulfuric acid containing 4% amygdalin at 25° in so far as the hydrolysis of the nitrile group in amygdalin is concerned. These results agree with those reported by Walker and Krieble, namely, that hydrochloric acid attacks the nitrile group much more readily than sulfuric acid.

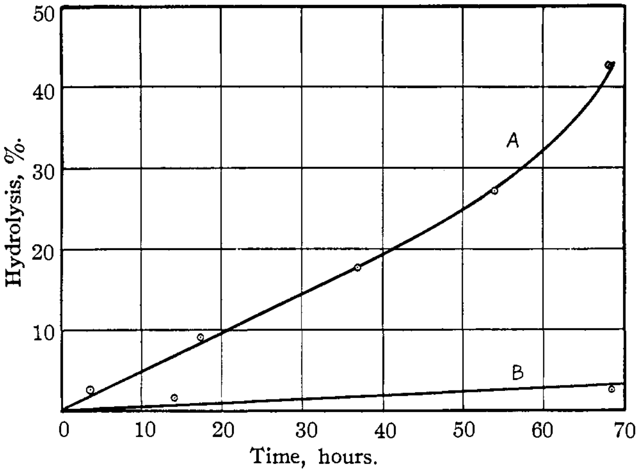

Fig. 1.—The hydrolysis of amygdalin at 25°. A, 5 *N* HCl used as catalyst; B, 5 *N* H_2SO_4 used as catalyst.

In Fig. 2 we have the action of the same acids at the same concentration and temperature on hydrogen cyanide.[4] Here the difference in rates between these two acids is even more striking than with amygdalin. These two sets of experiments show that the nitrile hydrolysis does not follow the hydrogen-ion concentration of the solution in which the hydrolysis takes place. This conclusion is confirmed by examining a comparison of the rates of hydrolysis with different concentrations of hydrochloric acid. In Fig. 3 we have a comparison of 1.95 *N*, 3.92 *N*, 5.88 *N* and

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[3] Subsequent experiments by Mr. Blanchard showed that practically the same values are obtaineed when the disappearance of hydrogen cyanide is measured.

[4] The acid solutions in all of the experiments with hydrogen cyanide contained 0.7 moles of HCN per liter.

7.84 *N* hydrochloric acid solutions on hydrogen cyanide at 30°. The concentration of the acid has increased four-fold while the hydrogen-ion concentration has not increased that much but the time necessary to hydrolyze 25% of the hydrogen cyanide has increased a thousand-fold. We have studied the same reaction at 45°. The results are given in Fig. 4. The relative rates at this temperature for the various acid concentrations are similar to those at 30°. The temperature coefficient between 30 and 45° and between 45 and 65° is about 5. In Fig. 5 we have the comparison of 4 *N* hydrochloric acid and 4 *N* hydrobromic acid at 45°. Here we have two acids equally dissociated as measured by conductivity or by the lowering of the freezing point but the rate of hydrolysis where the hydrochloric

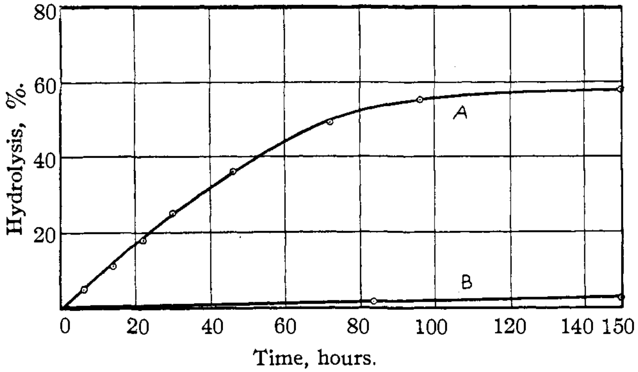

Fig. 2.—The hydrolysis of HCN at 25°. A, 5 *N* HCl used as catalyst; B, 5 *N* H_2SO_4 used as catalyst.

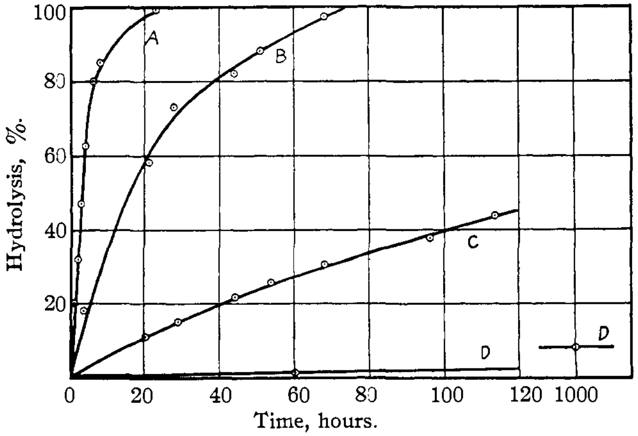

Fig. 3.—The hydrolysis of HCN at 30°. A, 7.84 *N* HCl used as catalyst; B, 5.88 *N* HCl; C, 3.92 *N* HCl; D, 1.95 *N* HCl.

acid is the catalyst is very much greater. This is in marked contrast with the hydrolysis of the corresponding amide. Figure 6 shows the rate of hydrolysis of formamide in the presence of 2 *N* hydrochloric acid and 2 *N* hydrobromic acid at 25°. In this case they are equally efficient as catalysts, as one would expect if the catalysis is due to the hydrogen ion. When the time required to hydrolyze 25% of hydrogen cyanide to formamide is compared with the time to hydrolyze 25% of formamide to ammonium formate in Figs. 3 and 6 the ratio is found to be 1400 hours to 6 minutes. The second molecule of water is therefore added on 14,000 times more rapidly than the first. These results on amide hydrolysis agree with those of other investigators, and when compared with the nitrile hydrolysis show conclusively that the mechanism for the two must be different.

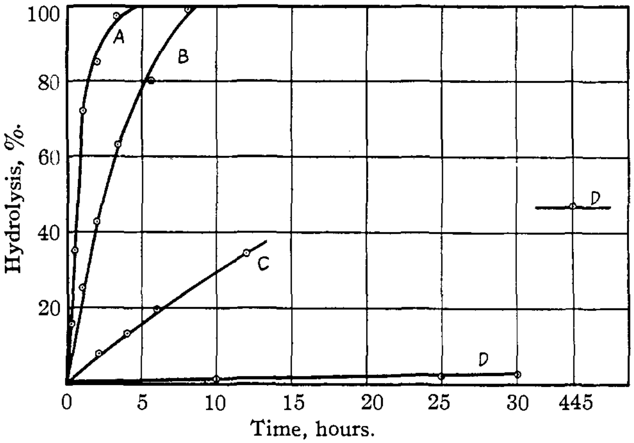

Fig. 4.—The hydrolysis of HCN at 45°. A, 7.84 *N* HCl used as catalyst; B, 5.88 *N* HCl; C, 3.92 *N* HCl; D, 1.95 *N* HCl.

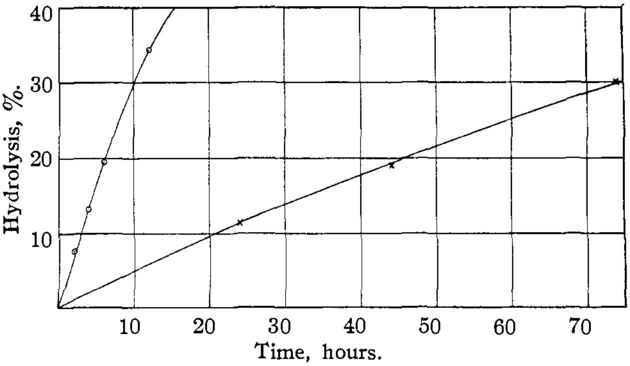

Fig. 5.—⊙, 4 *N* HCl at 45°; ×, 4 *N* HBr at 45°.

Discussion of Results

No other hydrolytic reaction has been revealed in the literature where the rate went up so rapidly with increase in concentration. Blanksma[5] observed that in the transformation of acetylchloraminobenzene to *p*-chloro-acetanilide with hydrochloric acid as a catalyst the velocity changed as the square of the concentration of the hydrochloric acid.

Maass and Sivertz,[6] in studying the addition of hydrochloric acid to propylene, observed that the excess acid acted as a catalyst and that the rate increased very rapidly with small increases in concentration. These reactions are not hydrolytic reactions and, therefore, not of the same type described in this communication.

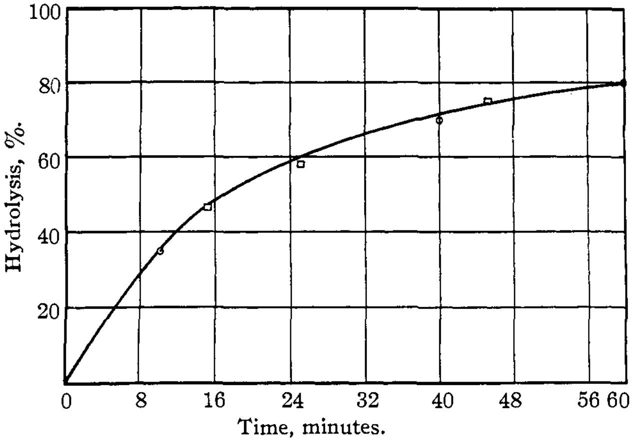

Fig. 6.—The hydrolysis of $HCONH_2$ at 25°. □, 2 *M* HCl used as catalyst; ⊙, 2 *M* HBr used as catalyst.

A study of the change in rate with change in acid concentration in Fig. 3 shows that it is of the same order of magnitude as the change of activity of the undissociated hydrochloric acid molecule as indicated by electromotive-force measurements in the literature. To make more suitable the graphical representation of this relationship in Fig. 7 between velocity constants and the activities we plotted the logarithm of the velocity constants[7] for hydrochloric acid concentrations of 1.95, 3.92, 5.88 and 7.84 *N* as abscissa against the logarithm of the activities[8] for undissociated hydrochloric acid of the same concentrations. The velocity constants were calculated as described below from the data of experiments carried out

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[5] Blanksma, *Rec. trav. chim.*, **21**, 366 (1902); **22**, 290 (1902).

[6] Maass and Sivertz, This Journal, **47**, 2883 (1925).

[7] Actually the logarithm of $K \times 10^5$ was plotted, which merely shifts the origin.

[8] The values for the activities used are those 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.

at 30, 45 and 65°. If the relationship were exact a straight line would be obtained.

This close relationship between the velocity of this reaction and the activity of the hydrogen chloride molecule calculated from physical measurements is remarkable. The literature does not record another like it so far as we know.[9] It suggests a combination between hydrogen cyanide and hydrogen chloride. That such a combination takes place in non-aqueous solutions is well known. A compound $2HCN \cdot 3HCl$ has been isolated in an ethyl acetate solution.[10] That an iminoformyl chloride $ClC{=}NH$ can also be formed is pretty well proved by Gattermann's reaction for the synthesis of aldehydes[11]

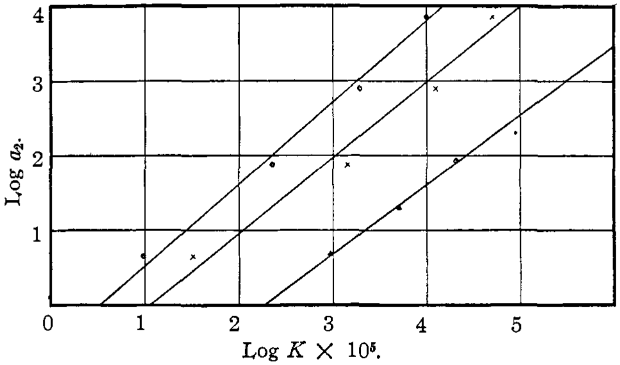
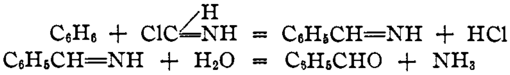
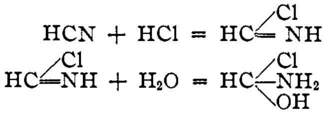


Fig. 7.—⊙, 30°; ×, 45°; △, 65°.



$$C_6H_6 + ClC(H){=}NH = C_6H_5CH{=}NH + HCl$$
$$C_6H_5CH{=}NH + H_2O = C_6H_5CHO + NH_3$$

Gautier[12] isolated a compound $HCN \cdot HCl$ by passing anhydrous hydrogen chloride into hydrogen cyanide at 35 to 40°. He found it to be a very unstable compound which decomposed spontaneously when added to water, producing formic acid. We, therefore, propose that the hydrolysis to the amide takes place through the following series of reactions



$$HCN + HCl = HC(Cl){=}NH \quad (1)$$
$$HC(Cl){=}NH + H_2O = HC(Cl)(OH){-}NH_2 \quad (2)$$

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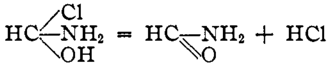
[9] Maass and Hiebert, This Journal, **46**, 299 (1924), found that the decomposition of hydrogen peroxide was catalyzed by the undissociated hydrogen chloride molecule. Their velocity constant, however, did not vary with the activity of the hydrogen chloride molecule.

[10] N. S. Sidgwick, "The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, **1910**, p. 199.

[11] Gattermann, *Ber.*, **31**, 1149, 1765 (1898); *Ann.*, **347**, 347 (1906); **357**, 313 (1907).

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



$$\mathrm{HC}\begin{smallmatrix}\diagup\mathrm{Cl}\\ -\mathrm{NH_2}\\ \diagdown\mathrm{OH}\end{smallmatrix} = \mathrm{HC}\begin{smallmatrix}-\mathrm{NH_2}\\ \diagdown\!\!\diagdown\mathrm{O}\end{smallmatrix} + \mathrm{HCl} \qquad (3)$$

Gautier found that his hydrogen chloride–hydrogen cyanide compound decomposed with almost explosive violence, so that Reactions 2 and 3 are very fast compared with 1. So the rate of hydrolysis is controlled by the rate of addition of hydrogen chloride to hydrogen cyanide, which in turn is a function of the number of hydrogen chloride molecules present in such a state that they can enter into the reaction. As the hydrogen chloride is only momentarily combined, its concentration for any given set of conditions is a constant; and as the amount of water present is very large, the reaction can for practical purposes be considered a monomolecular reaction. In Table I we have recorded the velocity constants for a few of our experiments calculated on the basis of a monomolecular reaction.

Table I

Velocity Constants

3.92 *N* HCl at 30°			7.84 *N* HCl at 30°		
Time, hours	% Hydrolyzed	*K*	Time, hours	% Hydrolyzed	*K*
4.08	1.9	0.0020	1	20.85	0.1015
21.13	10.75	.0023	1.91	32.92	.1010
28.33	14.87	.0024	2.71	46.96	.1011
48.33	21.7	.0024	4.26	69.50	.1220
53.75	25.6	.0024	5.65	78.33	.1175
68.12	31.15	.0024	6.88	82.99	.1118

We believe that the mechanism with hydrobromic acid as a catalyst is similar to that with hydrochloric acid. It is interesting to note that in non-hydrolytic reactions, hydrobromic acid has frequently been found to be more reactive than hydrochloric acid. Maass and Sivertz[13] found that hydrobromic acid added on to propylene 200 times faster than hydrochloric acid did. Acree and Johnson,[14] in studying the transformation of acetylchloro-aminobenzene to *p*-chloro-acetanilide, found that hydrobromic acid was 1000 times more effective than hydrochloric acid.

Whether sulfuric acid reacts in the same way as the halogen acids we shall be better able to say after we have studied it more thoroughly.[15]

Summary

The rates of hydrolysis of amygdalin and hydrogen cyanide when catalyzed by hydrochloric and sulfuric acids have been quantitatively studied. It is found that for 5 *N* concentrations hydrochloric acid hydrolyzes amygdalin ten times faster than sulfuric. For hydrogen cyanide the difference is even greater.

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[13] Ref. 6, p. 2888.

[14] Acree and Johnson, *Am. Chem. J.*, 38, 274 (1907).

[15] Recent experiments by Mr. Peiker seem to show that the rate of hydrolysis passes through a minimum when the concentration of sulfuric acid is increased.

When the concentration of hydrochloric acid was varied from 1.95 N to 7.84 N, the velocity in the hydrogen cyanide hydrolysis increased about 1000 times. It is pointed out that this increase in velocity corresponds to the increase in activity for corresponding concentrations of the undissociated hydrogen chloride molecule as measured by electromotive force methods, and it is suggested that this increase in velocity is due to an increase in the concentration of activated hydrogen chloride molecules.

A 4 N hydrochloric acid solution is more than 6 times as effective in hydrolyzing hydrogen cyanide as a corresponding hydrobromic acid solution.

A tentative mechanism for the hydrolysis of hydrogen cyanide is proposed.

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A METHOD OF COUPLING ORGANIC RADICALS BY MEANS OF THE GRIGNARD REAGENT[1]

BY JOHN H. GARDNER AND P. BORGSTROM

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The coupling of organic radicals by the action of heavy metal salts on organomagnesium compounds has been studied by a number of investigators.[2] However, the use of silver halides for this purpose has not been investigated, although Gilman and Kirby studied the action of certain Grignard reagents on silver cyanide. They observed the coupling of the organic radicals, the cyanide radical reacting as a halogen.[3]

We have investigated the application of the reaction of Grignard reagents with silver bromide to the preparation of symmetrical biaryls and bialkyls. A few preliminary experiments with cuprous chloride failed to give promising results. The bromide was selected in place of the chloride, as dry silver bromide is so little sensitive to light that it may be used in a fairly well lighted room.

The advantage of silver bromide over other heavy metal salts lies in the fact that it is easily prepared pure and dry. Its cost is compensated for by the fact that it can be recovered readily and almost completely. We have found the laboratory accumulation of silver residues a cheap and satisfactory source of silver bromide.[4]

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[1] The major part of this work was done while one of us (G.) was a National Research Fellow in Chemistry.

[2] Gilman and Parker, THIS JOURNAL, **46**, 2823 (1924), give a very complete review of the literature; see also Moyer and Adams, *ibid.*, **51**, 630 (1929).

[3] Gilman and Kirby, *Rec. trav. chim.*, **48**, 155 (1929).

[4] We are indebted to Mr. C. F. Brown of West Virginia University for the working up of silver residues into the bromide used in the early part of this work.