The Hydrolysis of Hydrogen Cyanide in Acetic Acid Solutions with Mineral Acids as Catalysts[1]

BY VERNON K. KRIEBLE, FREDERICK C. DUENNEBIER AND EDWARD COLTON

In 1930 E. R. Blanchard working in this Laboratory made a few determinations on the rate of hydrolysis of hydrogen cyanide in 50 and 75% acetic acid solutions using hydrochloric acid as the catalyst at 30°.

Normality	50% Acetic $k \times 10^4$	75% Acetic $k \times 10^4$
2	7	102
3	33.4	458
4	124	1590

These rates were approximately forty times faster in the 50% acetic acid solution and six hundred times faster in the 75% acetic acid solution than those reported by Krieble and McNally[2] for a 2 N hydrochloric acid. These results suggested the desirability of studying this hydrolysis in more concentrated acetic acid as a solvent and this paper gives and discusses the data of such an investigation.

Preparation of Materials and Methods of Procedure

Hydrogen Cyanide.—It was prepared according to the method of K. Ziegler.[3] The gas was dried by passing it through two towers filled with calcium chloride and then condensed to a liquid which was immediately dissolved in acetic acid. Previous experiments had shown that hydrogen cyanide could be kept for months without any sign of hydrolysis, decomposition or polymerization.

Acetic Acid.—The acid was prepared by heating glacial acetic acid at the boiling point for one hour with 10 g. of chromium trioxide per liter of acid and enough acetic anhydride to take up the water. The resulting mixture was distilled in an all-glass still, the first and last fractions being rejected. A product containing 99.97% acetic acid by weight was obtained.

Acetic Anhydride.—The C. P. grade of the General Chemical Company was used. It was distilled before using, rejecting the fractions distilling above or below the 137.3–138.8° range.

Experimental Procedure.—The rates reported in this paper were based on the disappearance of hydrogen cyanide. The initial solution was made up from three standard solutions. For example, the initial solutions for the study of hydrolysis in 50% acetic acid were made up as follows: (a) 50% acetic acid by weight, prepared by adding the correct amount of water to a known weight of analyzed acetic acid. (b) Sulfuric acid in 50% acetic acid, prepared by adding glacial acetic acid to a known weight of analyzed sulfuric acid until the ratio of water to acetic acid in the solution was 1:1 by weight. Where hydrochloric acid
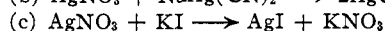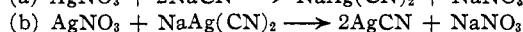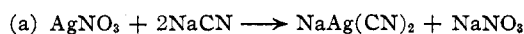
was the catalyst a solution of this acid in glacial acetic acid was diluted with water until the ratio of acetic acid and water was 1:1. (c) Approximately 5% hydrogen cyanide in 50% acetic acid, prepared by adding anhydrous hydrogen cyanide directly to 50% acetic acid. The same procedure could be followed for any other acetic acid–water ratio. Where the hydrolysis was carried out in 100% acetic acid, solutions (b) and (c) were made up in glacial acetic and (a) was glacial acetic.

To carry out a hydrolysis experiment a certain amount of solution (b) containing the catalyst was run from a weight buret into a stoppered Erlenmeyer flask cooled with ice and water. Knowing the weight of solution (b) and its concentration in hydrochloric or sulfuric acid it was possible to calculate the amounts of (a) and (c) that had to be added to bring the final strength of the solution to the molality of the catalyzing acid desired and at the same time to have a suitable amount of hydrogen cyanide present. The concentration of hydrogen cyanide varied from 0.1 to 1 mole—the actual amount present in any experiment does not affect the rate constant of hydrolysis.

The ice cold solution prepared above was then filled into ampoules which had previously been marked and weighed. They were filled from a dropping funnel, the stem of which was bent up into the form of a U and fitted with a small piece of rubber tubing. An ampoule was placed into the rubber tube and filled by applying slight pressure to the solution in the dropping funnel. Without removing the ampoule the upper end was sealed with a small hand torch. The ampoule was then removed and inverted into an ice-bath and the other end sealed. The ampoules were immediately placed into a thermostat maintained within ±0.1° of the temperature indicated in the table. After the ampoules had time to attain the temperature of the bath one was removed, quickly dried, weighed and emptied into ice cold water. The solution was immediately neutralized in an ice-bath and analyzed. The concentration of hydrogen cyanide found was taken as the initial amount present. At suitable time intervals ampoules were removed from the bath and treated in the same way.

For the faster rates the reacting solution was placed in a buret instead of ampoules. The buret was surrounded by a condenser jacket and ice water from a large reservoir of ice, salt and water was pumped through it, maintaining an even temperature in the buret. In this way samples could be taken quickly and treated as described above.

The hydrogen cyanide was determined by titrating the neutralized solution with standard silver nitrate (0.02 normal) in the presence of ammonia and potassium iodide according to the method developed by Sharwood.[4] The reactions involved are as follows

   (a) $AgNO_3 + 2NaCN \longrightarrow NaAg(CN)_2 + NaNO_3$
   (b) $AgNO_3 + NaAg(CN)_2 \longrightarrow 2AgCN + NaNO_3$
   (c) $AgNO_3 + KI \longrightarrow AgI + KNO_3$

(1) Original manuscript received August 20, 1942.

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

(3) Gilman, "Organic Syntheses," Vol. 1, p. 307.

(4) Sharwood, THIS JOURNAL, **19**, 400 (1897).

The presence of ammonia prevents the precipitation of silver cyanide (b) but does not prevent the precipitation of silver iodide (c) when the second reaction is complete. The first appearance of a permanent yellow turbidity is therefore the end-point. The presence of salts such as sodium acetate or a slight excess of sodium hydroxide does not affect the titration of hydrogen cyanide.

The velocity constants recorded are based on a first-order reaction with respect to hydrogen cyanide with the hour as the unit of time.

TABLE I

Temperature 45°C.

H_2SO_4 Molality	Solvent	$k \times 10^4$
1.86	50% Acetic acid	4.94
1.98	50% Acetic acid	5.28
3.87	50% Acetic acid	21.5
5.85	50% Acetic acid	75.9
2	95% Acetic acid	166
4	95% Acetic acid	835
6	95% Acetic acid	2010
6.75	99.5% Acetic acid	3790
6.72	83% Acetic acid + 17% Acetic anhyd.	4690

TABLE II

Temperature 0°C.

HCl		$k \times 10^4$
0.8	95% Acetic acid	414
1.45	95% Acetic acid	4360
1.65	95% Acetic acid	9330
1.75	95% Acetic acid	12400
2.65	95% Acetic acid	125000
2.80	95% Acetic acid	250000
1.15	100% Acetic acid	4520
1.35	100% Acetic acid	9410
1.75	100% Acetic acid	37600
2.18	100% Acetic acid	149000
2.45	100% Acetic acid	306000

TABLE III

Temperature 10°C.

HCl		$k \times 10^4$
0.85	95% Acetic acid	2320
1.45	95% Acetic acid	22000
1.65	95% Acetic acid	38700
1.70	95% Acetic acid	61500
2	95% Acetic acid	234000
1	100% Acetic acid	22300
1.25	100% Acetic acid	44000
1.55	100% Acetic acid	110000
1.75	100% Acetic acid	183000
1.85	100% Acetic acid	312000

Discussion.—That the rates of hydrolysis of hydrogen cyanide in various concentrations of acetic acid as a solvent should be much faster than in water is not surprising. That the relative rates between corresponding concentrations of hydrochloric acid and sulfuric acid should be far greater than in aqueous solutions, however,

TABLE IV

TEMPERATURE 0°C.

Glacial acetic acid mixed with the following percentages of acetic anhydride.

HCl	Acetic anhydride, %	$k \times 10^4$
1.10	10	2140
1.12	26	1730
1.15	35	1490
1.42	11	4120
1.40	20	3500
1.40	31	2450
1.77	12	9600
1.81	22	8240
1.85	30	7320
2.23	9	51900
2.25	20	49200
2.30	30	46700

would probably not have been predicted. Nor would the very rapid increase in rate, where hydrochloric acid is the catalyst, with relatively small increase in concentration, been predicted.

Hantzsch and Geidel[5] on the basis of physical measurements claim that the first reaction with hydrochloric or sulfuric acid on organic nitriles is to form an imino-hydrinium salt which is practically completely ionized in strong acid solutions. The nitrilium salt then adds water to form an imidohydrinium salt

(1) $RCN + HCl \longrightarrow [RCNH]^+Cl^-$

(2) $[RCNH]^+Cl^- + H_2O \longrightarrow [RCOHNH_2]^+Cl^-$
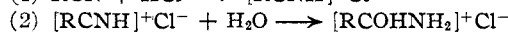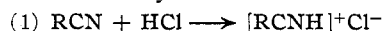
If this is the case then the rate of reaction would be controlled by the second reaction since the first consists in adding a proton to a base which should be instantaneous. Since hydrochloric acid would form the same cation as sulfuric acid the difference in rates for the same concentration of the two acids as well as the difference in rates between two concentrations of the same acid should be proportional to the acidities of these solutions. That such is not the case for the action of sulfuric acid on hydrogen cyanide in aqueous solution was pointed out by Krieble and Peiker.[6] Nor does this relationship hold for either sulfuric or hydrochloric acid on organic nitriles according to Krieble and Noll.[7]

In previous communications from this Laboratory it has been pointed out that there is a close relationship between the activity of the hydrochloric acid molecule a_2 and the rates of hydrolysis for both hydrogen cyanide and organic nitriles in aqueous solution. The activity of hydrochloric acid in acetic acid solutions has not been deter-

(5) Hantzsch and Geidel, Ber., **64B**, 667 (1931).

(6) Krieble and Peiker, THIS JOURNAL, **55**, 2326 (1933).

(7) Krieble and Noll, ibid., **61**, 560 (1939).

mined, but the vapor pressure of hydrochloric acid in acetic acid solutions has been measured at 25° by Rodebush and Ewart.[8] Unfortunately these measurements were not carried out for concentrations where most of our measurements were made. If the assumption is made that solutions of hydrochloric acid in water and in acetic acid which have the same partial vapor pressure of hydrochloric acid also have the same activity, then the activity of hydrochloric acid in acetic acid can be determined. By plotting the vapor pressures of hydrochloric acid in acetic acid and the vapor pressure of hydrochloric acid in water where the pressures of hydrochloric acid are of the same order of magnitude on the same plot, it was possible to read off corresponding concentrations which had identical vapor pressures. By interpolating the activities of Lewis and Randall[9] for aqueous solutions it at once gave the activity for a solution of hydrochloric acid in acetic acid.

All the rates in acetic acid where hydrochloric acid was the catalyst were measured at 0 and 10° while the aqueous solutions previously reported were measured at 65°. However, in a thesis by A. L. Peiker[10] there are rate constants recorded for a 2.07 molal solution at 35° of 0.000375, at 45° of 0.0014 and 65° of 0.0145. In order to bring the rates in acetic acid and in water to the same temperature at which the activities were measured, namely 25°, use was made of the Arrhenius equation. From the data at 0 and 10° in acetic acid the activation energy was calculated to have an average of 27,000 calories and from the data at 35 and 45° in water the activation energy was calculated to be 25,400 calories. On the basis of these activation energies the rate constant for a 1.02 molal solution in acetic acid at 25° would be 42.4 and in water 1.13×10^{-5} or they would have a ratio $k_{(CH_3COOH)}/k_{(H_2O)}$ of 3.8×10^6 while the ratio of the activities of hydrochloric acid $a_{2(CH_3COOH)}/a_{2(H_2O)}$ is 1.4×10^6. For a 2.07 molal solution the ratio of $k_{(CH_3COOH)}/k_{(H_2O)}$ is 7.9×10^6 while the ratio of activities $a_{2(CH_3COOH)}/a_{2(H_2O)}$ is 5.4×10^5. This is considered an excellent agreement because Rodebush and Ewart report that their vapor pressure results for 3 and 5% hydrochloric acid

solutions are only approximate, and it is on these results that we had to depend for the extrapolation for the activities in acetic acid. It is therefore logical to assume that the reason hydrochloric acid is several million times better as a catalyst when dissolved in acetic acid than when dissolved in water is because of the fact that the activity of both ions or the activity of the molecule has been stepped up correspondingly. This suggests that the controlling reaction in acetic acid solutions just as in aqueous solutions is the addition of the hydrochloric acid molecule to the hydrogen cyanide molecule. If this is the case, then the velocity constant should fall off as the reaction proceeds unless the hydrochloric acid is continually regenerated through a second reaction. The velocity constant, however, does not fall off appreciably; for example, where the concentration of hydrogen cyanide was 0.82 mole and the hydrochloric acid 1.15 moles, k is 0.042 when 22.5% of hydrogen cyanide has disappeared, 0.045 when 48.9% is gone and 0.043 when 82% is gone. In an aqueous solution any addition compound between hydrogen cyanide and hydrochloric acid would react with water, but in 100% acetic acid there should be no water. Colson[11] has shown that in the presence of a nitrile hydrochloric acid reacts with acetic acid to form acetyl chloride and water and the water is immediately taken up by the nitrile to form an amide. If this happens with hydrogen cyanide, then hydrochloric acid would be tied up as acetyl chloride and again the velocity constant should fall off. Even when the solvent contains a considerable quantity of acetic anhydride the velocity still remains remarkably constant.

Table IV, however, shows very conclusively that acetic anhydride does not help the hydrolysis of hydrogen cyanide. For the four concentrations of hydrochloric acid studied the rates have fallen from one-half to one-tenth of what they were in glacial acetic acid. For any hydrochloric acid concentration the more acetic anhydride added the slower the rate. According to S. S. Nametkin, L. Ya. Bryusova and A. I. Fedoseeva[12] hydrochloric acid readily reacts with acetic anhydride to form acetyl chloride which may cause the reduction in hydrolysis of hydrogen cyanide.

It has always been difficult in our hydrolytic

(8) Rodebush and Ewart, THIS JOURNAL, **54**, 419 (1932).

(9) "Thermodynamics." McGraw-Hill Book Co., Inc., New York, N. Y., first edition, 1923.

(10) Presented to the Graduate Committee, Trinity College, June, 1927.

(11) Colson, *Ann. chim. phys.*, [7] **12**, 250 (1897).

(12) S. S. Nametkin, L. Ya. Bryusova and A. I. Fedoseeva, *J. Applied Chem.* (U. S. S. R.), **12**, 1698 (1939).

studies to correlate the velocity constants with any of the other physical properties of sulfuric acid, such as ionization, activity or acidity and the present series in Table I is no exception. Hall and Spengeman[13] have recently measured the acidity function H_0 of sulfuric acid dissolved in acetic acid. According to Hammett $H_0 + \log k$ is a constant when the velocity depends on the acidity of the solution. The velocity constant for the disappearance of hydrogen cyanide, however, is not in close agreement with this. For a 2 molal solution $H_0 + \log k$ is -5.10 for a 4 molal solution -5.38 and for a 6 molal solution -5.62.

It is worth noting that the rate of disappearance of hydrogen cyanide keeps on increasing as the amount of water decreases—in fact the fastest rate appears in the presence of anhydrous acetic acid containing acetic anhydride. This is just the reverse of what happened with hydrochloric acid. Russell and Cameron[14] found a great increase in acidity for sulfuric acid dissolved in glacial acetic acid when acetic anhydride is added to such a solution. So, in spite of the fact that the rates of hydrolysis do not strictly follow Hammett's acidity function, the acidity of the solution does influence these rates.

We are continuing the investigation, especially the study of the hydrolysis of organic nitriles in

(13) Hall and Spengeman, THIS JOURNAL, 62, 2487 (1940).
(14) Russell and Cameron, ibid., 60, 1345 (1938).

organic solvents and the hydrolysis of substituted amides and of amides of acids other than carboxylic.

Summary

A study has been made of the hydrolysis of hydrogen cyanide in various concentrations of acetic acid, glacial acetic acid, and acetic acid containing as much as 33% of acetic anhydride using hydrochloric acid and sulfuric acid as catalysts.

It has been shown that the rates of hydrolysis increase rapidly as the concentration of water in the solvent decreases. For sulfuric acid the rate is most rapid in glacial acetic acid containing acetic anhydride. For hydrochloric acid glacial acetic, without the addition of acetic anhydride, is the best solvent. Hydrochloric acid is a very much better catalyst than sulfuric acid and hydrolyzes hydrogen cyanide several million times faster in acetic acid than it does in water. This rate is very sensitive to small changes in concentration of hydrochloric acid.

For hydrochloric acid the rate varies as the square of the mean ion activity or as the activity of the molecule of the acid. It has not been possible to correlate the rates of hydrolysis where sulfuric acid is the catalyst with any physical property of its solutions.

The Crystal Structure of Magnesium Carbide

BY M. A. BREDIG[1]

In connection with a study of the formation of calcium and magnesium metal and of their carbides by reduction of the oxides with carbon in a vacuum, the crystal structures of some of the carbides MeC_2 such as MgC_2, CaC_2, SrC_2 and BaC_2 were discussed.[2a,b] A very satisfactory powder X-ray diagram of magnesium acetylide was produced,[2a] careful consideration of which showed that this carbide was not isotypic with the tetragonal forms of the other three carbides. Its structure appeared to be of lower symmetry, and could therefore not be determined by means of powder X-ray patterns, the only ones avail-

(1) Address: Vanadium Corporation of America, New York, N. Y.
(2a) H. H. Franck, M. A. Bredig and Kin-Hsing Kou, Z. anorg. allgem. Chem., 232, 75 (1937).
(2b) M. A. Bredig, J. Phys. Chem., 46, 801 (1942).

able, since single crystals could not be prepared.

In contradiction to this finding, W. H. C. Rueggeberg[3] recently has proposed the values 4.86 and 5.67 Å. for the constants a_0 and c_0 of a tetragonal lattice of magnesium carbide, analogous to tetragonal calcium carbide (1). The experimental evidence consists of the—rather unsatisfactory—agreement of the measured spacings of four weak, or very weak, X-ray lines with spacings, calculated from those lattice constants. The deviations of the experimental figures from the calculated values range from 1.6 to 4.3%, that is more than 2 to 5 times the experimental error which is expected even if no particular care is applied in preparing and measuring the X-ray pattern.

(3) W. H. C. Rueggeberg, THIS JOURNAL, 65, 602 (1943).