+5° (*c* 0.05, $CHCl_3$); ir (KBr) 2400, 1760, 1270, 1190, 1030, 990, 820, 540 cm^{-1}; nmr ($CDCl_3$); 0.89 (s, C-18 CH_3), 1.05 (s, C-19 CH_3), 3.76 [d, $J = 12$ Hz, $P(O)(OCH_3)$], 6.81 [d, $J = 694$ Hz, P(O)H)], 4.30 (m, C-3α H), 2.48 (double m, C-4 protons), and 5.42 (m, C-6 H). *Anal.* Calcd for $C_{20}H_{31}O_4P$: C, 65.56; H, 8.52; P, 8.45. Found: C, 65.90; H, 8.32; P, 8.36.

Registry No.—**2**, 33066-23-8; **6**, 33066-24-9; **7**, 13913-60-5.

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The Kinetics and Mechanism of the Decomposition of Potassium Cyanide in Aqueous Alkaline Medium. Hydrolysis of the Simplest Nitrile, HCN

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Cyanide ion is known to decompose slowly in aqueous alkaline solution to yield formate ion and ammonia.[2] In acidic medium the products are formic acid and ammonium ion.[3] In connection with some earlier studies[4] involving aqueous cyanide solutions, we sought to determine the extent and pathway by which this decomposition competed with the reactions under investigation.

$$CN^- + 2H_2O \xrightarrow{OH^-} HCO_2^- + NH_3$$

Krieble[3,5,6] studied the rate of decomposition of hydrogen cyanide in various strongly acidic media. Noting that aqueous cyanide solutions used in electroplating lost strength with "an apparent regularity" upon standing, Leftin[7] found that solutions about 0.25 *N* in cyanide lost about 0.000240 *N*/day in cyanide concentration at room temperature. This loss was nearly constant over a period of 180 days. Other workers[8,9] also have discussed the loss of cyanide from electroplating solutions.

In a more definitive study Ricca and D'Amore determined the rate of the decomposition in aqueous solutions through which a stream of CO_2-free air was passed to remove HCN, formed in the hydrolysis of cyanide ion, and the ammonia resulting from the decomposition itself.[2,10] The first-order rate constants for the disappearance of cyanide ion at 30, 50, and 80° were found to be 0.122×10^{-6}, 0.366×10^{-6}, and 2.72×10^{-6} sec^{-1}, respectively. Addition of a 30-fold excess of NaCl was found to retard the rate of the reaction.

More recently, several studies have dealt with the hydrolysis and polymerization of HCN in aqueous solution as a means for removal of HCN from crude coal gas[11] and as a possible means of formation of purine precursors under primitive earth conditions.[12,13]

We present here the results of a more extensive kinetic study of this decomposition and the mechanistic implications of these results.

Results

Experimental procedure differed from that of Ricca and D'Amore in that no air was passed through the solutions during the course of the reaction. Instead, the reaction was carried out under a nitrogen atmosphere in tightly stoppered flasks. Potassium hydroxide was added to suppress the polymerization of HCN, the pH being adjusted to a value of 11 or greater for all runs.[14]

The overall decomposition was found to be cleanly first order with respect to the cyanide ion concentration throughout the range of temperatures and concentrations studied. That the rate was independent of the concentration of hydroxide ion was shown by comparison of the volume of titrant used in simultaneous runs at 33.1 and 49.5° in which the concentration of hydroxide ion was varied. At 49.5°, for example, simultaneous runs 0.0680 and 0.0340 *M* in KOH required the same volume of titrant, within experimental error, over more than 60% of the reaction.

Effects of added salt and of changes in solvent polarity were also observed. Addition of a tenfold excess of KNO_3 resulted in a small but significant decrease in the overall rate. This effect is the same as was observed earlier for added NaCl.[10] A marked increase in rate was observed when the solvent polarity was diminished by the addition of small amounts of ethanol. The overall rate constants for the decomposition under various conditions are presented in Table I.

Discussion

The kinetic data clearly preclude a reaction mechanism involving direct attack of hydroxide ion upon cyanide ion in the rate-determining step, or one in which two or more hydroxide ions are consumed before the slow step in the reaction. Two reaction pathways are consistent with these data, one involving the direct attack of water upon cyanide ion in the rate-determining step (eq 1), and the other the rapid hydrolysis of

$$CN^- + H_2O \xrightarrow[\text{slow}]{k_b} [\text{activated complex}] \xrightarrow[\text{fast}]{\text{rel}} \text{products} \quad (1)$$

cyanide ion to HCN (eq 2), with subsequent attack of

$$CN^- + H_2O \overset{K_h}{\rightleftarrows} HCN + OH^- \quad (2)$$

hydroxide ion upon the HCN in the rate-determining step (eq 3).

$$HCN + OH^- \xrightarrow[\text{slow}]{k_a} \begin{bmatrix}\text{activated}\\ \text{complex}\end{bmatrix} \xrightarrow[\text{fast}]{\text{rel}} \text{products} \quad (3)$$

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[14] Below pH 10 polymerization of HCN competes with hydrolysis, and at high cyanide concentrations and low pH becomes the predominant reaction pathway.[11,13]

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF POTASSIUM CYANIDE[a]

Temp, °C	Reaction conditions	$k \times 10^7$, sec^{-1}	Standard deviation
33.1	0.181 M KOH	0.274	0.020
49.5	0.0680 M KOH	1.97	0.09
60.0	0.0680 M KOH	5.86	0.09
	0.0667 M KOH 4.9% in KNO_3	5.38	0.17
	No added KOH	6.09	0.12
65.0	0.0680 M KOH	10.07	0.16
	0.0616 M KOH, 8.05% in ethanol	14.61	0.15
	0.0551 M KOH, 16.4% in ethanol	16.76	0.25

[a] Initial concentration of KCN was 0.05 M in all cases.

The rate expression for this process can be derived as follows.[15]

$$\frac{\mathrm{d[activated\ complex]}}{\mathrm{d}t} = k_s[\mathrm{HCN}][\mathrm{OH}^-] \qquad (4)$$

$$[\mathrm{HCN}] = K_h[\mathrm{CN}^-]/[\mathrm{OH}^-] \qquad (5)$$

$$\frac{\mathrm{d[activated\ complex]}}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{CN}^-]}{\mathrm{d}t} \qquad (6)$$

$$-\frac{\mathrm{d}[\mathrm{CN}^-]}{\mathrm{d}t} = k_sK_h[\mathrm{CN}^-] \qquad (7)$$

Qualitatively, it can be seen that, in the initial rapid hydrolysis (eq 2), an increase in $[\mathrm{OH}^-]$ results in a corresponding decrease in [HCN]. Since the overall rate is actually dependent upon the product, $[\mathrm{HCN}][\mathrm{OH}^-]$, no change in rate should occur as $[\mathrm{OH}^-]$ is varied.

If the former mechanism, in which cyanide ion and water participate directly in the rate-determining step (eq 1), were operative, the overall rate constants, k, would be pseudo first order, since water would be in large excess. The second-order rate constants, k_b, therefore can be obtained by dividing the values of k by the concentrations of water at the respective temperatures.

In the case of the second pathway in which there is attack of hydroxide ion upon HCN, the overall rate constants, k, would in effect be the product, k_sK_h. The second-order rate constants, k_s, can be found by dividing each of the overall rate constants by the appropriate hydrolysis constant, K_h. The values of K_h for cyanide ion at different temperatures were obtained by use of the empirical relationship, $\log K_h$ (mol/l.) $= -2.274 - 757.2/T$ (°K), obtained by Marshall and Moelwyn-Hughes.[16] Calculated values of k_b, K_h, and k_s are presented in Table II.

TABLE II

CALCULATED VALUES OF k_b, K_h, AND k_s

Temp, °C	33.1[a]	49.5[b]	60.0[b]	65.0[b]
$K_h \times 10^5$, mol/l.[c]	1.79	2.39	2.84	3.07
$k_b \times 10^{10}$, M^{-1} sec^{-1}	4.96	35.9	107	185
$k_s \times 10^3$, M^{-1} sec^{-1}	1.53	8.24	20.6	32.8

[a] Run in 0.181 M KOH. [b] Run in 0.0680 M KOH. [c] Calculated from $\log K_h$ (mol/l.) $= 2.274 - 757.2/T$ (°K), ref 16.

A comparison of the values of k_b and k_s indicates clearly that the reaction pathway involves attack of hydroxide ion upon HCN in the rate-determining step, since k_s is on the order of 10^6k_b. Using the tabulated values of k_s the average activation energy, E_a, was found to be 19.7 kcal/mol (standard deviation 0.6). Similarly, values of k_b yielded a value of 23.3 kcal/mol (standard deviation 0.7). It should be noted that the former value, obtained from k_s, is consistent with those for a host of other reactions in which an ion and a neutral molecule are involved in the rate-determining step, whereas the higher value from k_b is not.[17]

Effects of added salt upon reactions involving an ion and a neutral molecule participating in the rate-determining step are usually small.[18,19] The small, negative salt effect of both added KNO_3 and NaCl on the overall rate of the decomposition, then, is not inconsistent with either mechanism. The more marked increase in rate which occurs as the solvent polarity is reduced is also consistent with the two mechanisms.[20]

The exact reaction pathway following k_s, is, of course, subject to speculation, although it is likely that formamide is an intermediate. Amides are known to be rapidly hydrolyzed intermediates in the alkaline hydrolysis of nitriles, the initial attack upon the nitrile being the slower step.[23] That formamide is an intermediate is feasible, since the rate constant for the alkaline hydrolysis of formamide[24] at 17° is 1.24×10^{-3} M^{-1} sec^{-1}, whereas k_s calculated at 17° is 8.18×10^{-4} M^{-1} sec^{-1}.

Summary

The spontaneous decomposition of cyanide ion in alkaline medium is believed to follow the reaction pathway

$$\mathrm{CN}^- + \mathrm{H_2O} \underset{\text{rapid}}{\overset{K_h}{\rightleftharpoons}} \mathrm{HCN} + \mathrm{OH}^-$$

$$\mathrm{HCN} + \mathrm{OH}^- \xrightarrow[\text{slow}]{k_s} [\text{activated complex}] \longrightarrow$$

$$\mathrm{HCONH_2} \xrightarrow[\text{fast}]{\text{rel}} \mathrm{HCO_2}^- + \mathrm{NH_3}$$

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[15] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 193-196.

[16] B. W. Marshall and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 7119 (1965).

[17] Reference 15, p 148.

[18] Reference 15, pp 151-152.

[19] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 186.

[20] However, if the effect of added salt upon k_s in the second pathway is to be determined, the effect upon K_h must be known. Unfortunately, little is known about the latter, although it is known that added NaCl increases K_h slightly, and KNO_3 "salts in" KCN, which would have the same effect. Sodium chloride also "salts in" HCN.[21] An increase in K_h, since the overall rate, k, is decreased, would result in an even larger decrease in k_s than is indicated by the small decrease in k. Since the activated complex would exhibit charge dispersal, solvation of the activated complex, as compared to that of the reactants (HCN and OH^-), would be less in a medium of greater ionic strength.

It is also necessary to determine how a reduction in solvent polarity would affect K_h in the second pathway. Since the hydrolysis of cyanide ion is isoelectric, and the change in solvent polarity is small, the effect should be negligible.[22] The increased overall rate, therefore, would be primarily the result of an increase in k_s.

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At lower temperatures the decomposition is very slow, the rate increasing by a factor of about three for each 10° rise in temperature. This decomposition can become important, especially at higher temperatures in systems in which cyanide ion is undergoing another reaction, particularly if this reaction is itself fairly slow. There is at least one instance in the literature in which only approximations as the kinetics could be made owing to the lack of rate data on the decomposition of cyanide.[16] Also, there are undoubtedly instances in which this reaction was ignored as being insignificant in kinetic studies.

Experimental Section

General.—J. T. Baker "Analyzed" Reagent KCN was used in the experiments without further purification.

Kinetics.—The progress of the reaction was followed by titration of aliquots of the reaction mixture with standard $AgNO_3$ solution, KI being used as the indicator.[25] The presence of KNO_3 or ethanol in the reaction mixture did not interfere with this method of analysis.

Solutions were prepared using CO_2-free distilled water, stored under nitrogen, and protected from atmospheric CO_2 by trapping the vent with Ascarite. Stock solutions of KOH were prepared in large quantities and standardized; the KCN solutions were prepared from these KOH stock solutions immediately prior to each run.

Runs were made in triplicate under a nitrogen atmosphere in tightly stoppered 125-ml flasks. An initial volume of 100 ml of reaction mixture 0.05 *M* in KCN was used in each instance. The mixtures were prepared from stock solutions kept in the thermostated bath and were reimmersed in the bath immediately after preparation. After 1 hr, and at suitable intervals thereafter, 10-ml aliquots were withdrawn and titrated, the nitrogen in the flasks being replenished each time. The first point obtained after mixing was taken as $t = 0$ in the calculation of the rate constants. Determinations were made until the reactions were 55–80% complete, except for the runs at 33.1°, which were followed to only 16% completion. Runs of different mixture compositions made at the same temperature were carried out simultaneously in order that comparison of differences in rate could be made without regard to small variations in temperature over the course of the experiments.

Errors.—Titrations were read to ±0.02 ml (initial volume of titrant consumed was about 5 ml) and the average volumes of titrant, having a standard deviation of 0.03 ml or less, were used in calculation of the point-by-point rate constants. Each value of k reported in Table I is the average of all of the individual rate constants obtained in a given run. Individual rate constants obtained early in the reaction showed more scatter than those obtained later on, proably because of the very small differences in titre observed initially. The large standard deviation in k obtained at 33.1° is no doubt a reflection of this, since the reaction at this temperature was so slow. Since the accuracy of the values of K_h is uncertain, errors in k_s have not been reported.

Although it was possible to control temperatures to ±0.05°, it is doubtful that this value was realized because of the long duration of the kinetic runs. A value of ±0.1° would probably be a better estimate.

Registry No.—Potassium cyanide, 151-50-8; hydrocyanic acid, 74-90-8; potassium hydroxide, 1310-58-3.

Acknowledgments.—We wish to thank Professor G. Myron Arcand for many helpful discussions. Partial support of this project from the National Science Foundation and the Idaho State University Research Programs Committee is also gratefully acknowledged.

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A Simple, Comprehensive Correlation of Organic Oxidation and Ionization Potentials

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We have been interested in developing new and useful organic electrooxidations. The sublime goal of this work is of course the ability to predict the products and rates of reactions for any oxidation. The most fundamental data needed for such predictions are the oxidation potentials of the reactants and possible products. One must know if the reactant will give up one or more electrons in the accessible potential range and if the possible products will survive the potential necessary to oxidize the reactant. It would, therefore, be useful to have an equation to predict oxidation potentials. This equation should be simple, use readily accessible input data, and provide oxidation potentials for a wide variety of species. We describe such an equation using ionization potentials (IP) as the only input data. Extensive tabulations of IP are available,[1-3] and photoelectron spectroscopy should provide a burgeoning source of data.[4]

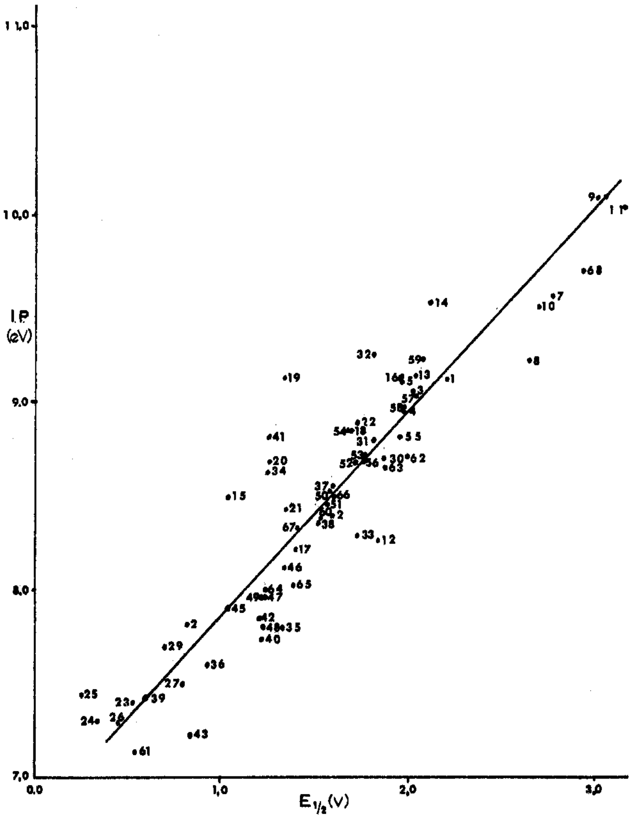

Figure 1.—Plot of vertical IP *vs.* $E_{1/2}$. Numbers refer to Table I.

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