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Kinetics and Mechanism of Ozonation of Free Cyanide Species in Water

Mirat D. Gurol* and William M. Bremen[†]

Civil Engineering Department and Environmental Studies Institute, Drexel University, Philadelphia, Pennsylvania 19104

■ The reaction rates of ozone with free cyanide species were determined by a stopped-flow spectrophotometer in the pH range 2.5–12.0. The direct reaction of molecular ozone and the free radical reactions which contribute to the overall reaction were identified. A reaction mechanism consistent with the observations was proposed. The rate constant for the direct reaction of molecular ozone with cyanide ion was calculated to be 2600 ± 700 M^{-1} s^{-1}. Batch and bubble-column experiments indicated stoichiometric conversion of cyanide to cyanate and an ozone consumption of 1.2 ± 0.2 mol/mol of oxidized cyanide.

Introduction

Oxidation of aqueous cyanide by ozone has been the subject of numerous studies (*1–8*) partly because of the potential application of this process for the treatment of cyanide-bearing wastewaters. The readers are referred to the paper by Zeelvalkink et al. (*7*) for a complete literature review on this subject. Previous ozonation studies, which were performed while continuously contacting gaseous ozone with water under dynamic conditions, generated several different rate equations that combined the kinetics of chemical reactions and the kinetics of ozone absorption, and were therefore empirical and system specific.

Additionally, in earlier studies very little attempt was made to identify the reactive species and to understand the reaction mechanism and the effect of pH on the mechanism and the kinetics of the reactions. For example, Zeelvalkink et al. (*7*), who conducted the experiments at pH 11.8 under dynamic conditions, proposed without experimental verification a free radical mechanism in which hydrogen cyanide, HCN, reacts with the radical O_2^-·, which is a product of self-decomposition of ozone.

On the basis of the accumulated literature on ozone chemistry, it can be postulated that the cyanide species, HCN and CN⁻, may react directly by molecular ozone, as well as by the hydroxyl radical, OH·, which may be pro-

duced upon hydroxide ion initiated decomposition of ozone (*9*), and as an intermediate product of the reaction of cyanide species with molecular ozone. The decomposition of ozone is strongly catalyzed by the hydroxide ion (*10–12*). Therefore, the rate of OH· formation, as well as cyanide speciation, is determined by the pH of water. Figure 1 depicts possible reaction pathways for cyanide oxidation by ozone.

The present study was designed to investigate the kinetics and the mechanism of the reaction between free cyanide species and ozone at various pH values between pH 2.5 and 12.0. To be able to eliminate the kinetics of mass transfer of ozone from the gaseous phase to the dissolved phase in water, the experiments were conducted by mixing cyanide and ozone solutions under quiescent conditions. Since the reactions were very fast, a stopped-flow spectrophotometer was used for mixing the solutions and for observation of the reaction rate. Cyanide was kept in excess to maintain pseudo-order conditions for ozone, as described by Hoigne and Bader (*13*). The stoichiometric relations among the reactants and the products were investigated in a beaker and in a bubble column.

Cyanate was produced as an intermediate of ozonation of cyanide and was further oxidized at a slow rate to nitrate and carbon dioxide. The reactions of cyanate with ozone is the subject of a forthcoming publication (*14*). The present paper is restricted to the first step of cyanide oxidation.

Experimental Methods

Solutions. Ozone was produced from oxygen by a Welsbach Model T-408 ozone generator. The gas stream was bubbled through a washing bottle filled with a 500-mL solution. The temperature of the contents of the bottle was kept at 20 °C by circulating water at constant temperature through a water jacket around the bottle. The details of this experimental setup were given elsewhere (*15, 16*).

All solutions were made with glass-distilled and deionized water. Ozone solution was prepared with 0.03 M

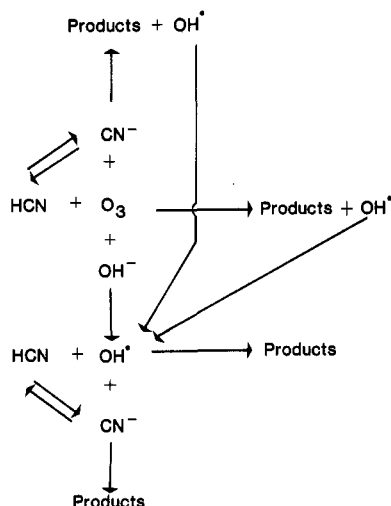[†]Present address: Versar Inc., Springfield, VA 22151.

Figure 1. Possible reaction pathways for ozonation of free cyanide species.

sodium sulfate to have an ionic strength of 0.01; the pH was adjusted to 2.5 with dilute sulfuric acid in order to minimize ozone loss by decomposition. Ozone gas was bubbled through this solution in the washing bottle until equilibration. Ozone solution was kept as stock (20–30 mg/L ozone) for subsequent use in batch studies. Cyanide solutions (10–24000 mg/L) were prepared by dissolving sodium cyanide in 0.01 M phosphate buffers. Phosphate salts were used throughout the pH range 2.5–12.0 in order to eliminate varying salt effects on the reaction kinetics and mechanism. The pH remained within ±0.1 pH unit of the adjusted pH over the reaction period. The pH of the cyanide solutions was adjusted by dilute sodium hydroxide or sulfuric acid to a value predetermined by mixing the ozone solution at pH 2.5 with an equal volume of the cyanide solution to obtain the desired pH in the mixture. This procedure simulated the equal-volume mixing in the stopped-flow spectrophotometer.

In order to investigate the reaction mechanism, some experiments were repeated by using 0.05 M carbonate buffer or 0.1–0.2 M *tert*-butyl alcohol (TBA) in phosphate buffer, as proposed by Hoigne and Bader (*9*).

The concentration of ozone in stock solutions and in the gas phase was measured by the potassium iodide, KI, method (*17*). In ozonated cyanide solutions, ozone was measured by both the KI and the indigo (*18*) methods which yielded very similar results, indicating the absence of any interference by the reaction products. Cyanide and cyanate were measured, respectively, by titration with silver nitrate (*17*) and by acid hydrolysis (*17*).

Kinetic Analysis. Kinetic studies were performed in a Durrum Model 110 stopped-flow spectrophotometer (Dionex Corp., Sunnyvale, CA) in which solutions of cyanide and ozone were mixed in a 20-mm light path, 0.063-mL cuvette with a dead time of less than 2 ms. The reaction temperature was maintained constant at 20 ± 0.1 °C. The concentration of ozone was monitored by measurement of the absorption of UV light at 260 nm. Absorption by cyanide and the buffer salts at this wavelength was negligible. The data of absorption vs. time were recorded by a Tektronix Model 5115 storage oscilliscope and then were either traced manually on a graph paper or photographed by a Polaroid camera attached to the oscilliscope screen. The experiments were repeated several times, usually using different time scales, to ensure reproducibility.

The general rate expression for the reaction of ozone with cyanide can be expressed as

$$-\frac{d[O_3]}{dt} = k[CN_T]^n[O_3]^m \qquad (1)$$

where $[O_3]$ and $[CN_T]$ are the concentrations of ozone and the total cyanide and k is the reaction rate constant. Kinetic studies were performed in at least 5-fold and up to 1300-fold stoichiometric excess of total cyanide. Under such conditions, eq 1 becomes

$$-\frac{d[O_3]}{[O_3]^m} = k_{obsd} \qquad (2)$$

where

$$k_{obsd} = k[CN_T]^n \qquad (3)$$

As will be shown, the order of the reaction with respect to ozone is one. Hence, the integrated form of eq 2 becomes

$$\ln (A/A_0) = k_{obsd}t \qquad (4)$$

where A and A_0 are the absorption at time t and zero, respectively, and are directly proportional to the concentration of ozone in water. The function $\ln (A/A_0)$ was plotted as a function of time, according to eq 4; the pseudo-first-order rate constant, k_{obsd}, was determined from the slope of the straight line drawn by using a linear regression model.

The reaction order with respect to total cyanide, n, was determined by plotting $\log k_{obsd}$ vs. $\log [CN_T]$, according to the following equation for various pH values.

$$\log k_{obsd} = \log k + n \log [CN_T] \qquad (5)$$

The reaction rate constants, k, were obtained from the intercept of the linear-regression lines.

The rate of self-decomposition of ozone at several pH values was determined by a similar procedure. For this case, the cyanide solution was replaced by a buffer solution.

Stoichiometric Analysis. To determine the molar consumption of ozone and the production of cyanate per mole of cyanide oxidized, solutions containing known concentrations of ozone and cyanide (cyanide being in stoichiometric excess) were mixed rapidly in a beaker. After ozone was consumed completely, cyanate and the remaining cyanide concentrations were measured as described above.

Bubble-Column Experiments. In the batch method described above, due to the limited solubility of ozone in water, relatively small amounts of cyanide were oxidized which yielded low amounts of cyanate to detect. Therefore, ozonation experiments were repeated in a bubble column into which ozone was fed continuously at a flow rate of 0.5 L/min. The applied ozone dosage was 19 mg/min. During the course of the ozonation of cyanide solutions, two sets of samples were taken at various time intervals. The first set of samples was analyzed for ozone residual, and the other set was used to measure the cyanide and the cyanate concentrations. Concentration of ozone in the effluent gas was continuously monitored with a UV spectrophotometer, which was calibrated at 260 nm with the KI method.

Results and Discussion

Kinetics of Ozone Disappearance. Kinetic experiments were performed with the stopped-flow spectrophotometer for initial cyanide concentrations of 1.9×10^{-4}–0.46 M (5–12000 mg/L), and ozone concentrations of 1.0×10^{-4}–3.1×10^{-4} M (5–15 mg/L) in the pH range 2.5–12.0. Figure 2 shows a photograph of the typical curves obtained with phosphate buffer at pH 11.2 in the absence and presence of cyanide for the same initial ozone concentra-
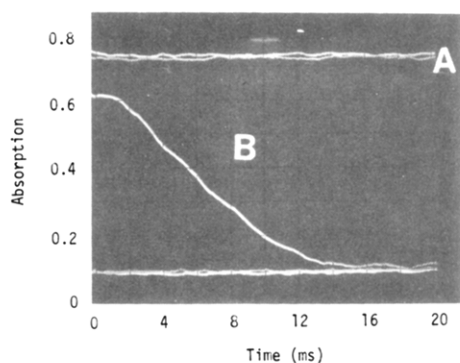
Figure 2. Decay of UV absorption by ozone with time at 260 nm and pH 11.2 in phosphate solutions containing (A) no cyanide and (B) 3.8 × 10⁻³ M total cyanide.
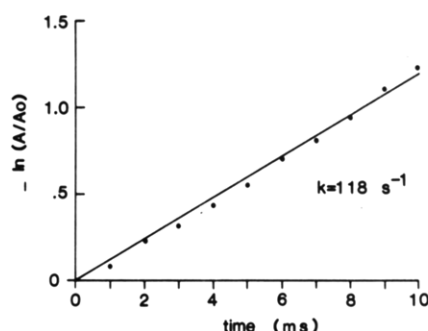

Figure 3. Pseudo-first-order plot for ozone decay at pH 11.2 in the presence of 3.8×10^{-3} M total cyanide.

Figure 4. Observed pseudo-first-order rate constant for ozone decay vs. total cyanide concentration on log scales.

tion. In the presence of 3.8×10^{-3} M cyanide, the reaction was completed within 12 ms, following pseudo-first-order reaction kinetics with a rate constant of 118 s⁻¹, as shown in Figure 3. In the absence of cyanide, it took 45 s for ozone to disappear by self-decomposition, yielding a decomposition rate constant of 0.88 s⁻¹. Assuming that the decomposition is initiated by a reaction step that is first order with respect to both ozone and the hydroxide ion (11, 12), the second-order rate constant for the decomposition of ozone is calculated as 560 M⁻¹ s⁻¹, which is consistent with the rate constant reported by Forni et al. (12) as 540 ± 20 M⁻¹ s⁻¹. This and similar results at other pH values indicated that the rate of hydroxide ion initiated decomposition of ozone in the absence of cyanide is negligible compared to the rate of the reaction of ozone with cyanide ion.

Effect of pH. The pseudo-first-order rate constants observed in the presence of different concentrations of excess cyanide, k_{obsd}, were plotted in Figure 4 as a function of total cyanide concentration, [CN$_T$], according to eq 5, for pH values 11.2, 9.5, and 7.0. For equal concentrations of [CN$_T$], k_{obsd} increased with increasing pH, reaching a value of approximately 1000 s⁻¹ at pH 11.2 for a [CN$_T$] value of 0.25 M. This rate, which corresponds to a half-life of 0.7 ms, is about the maximum that can be observed by the stopped-flow instrument used in this study.

According to Figure 4, the dependence of k_{obsd} on [CN$_T$] varies with pH. An statistical analysis for 95% confidence interval ($p = 0.95$) yields the following rate expressions for pH values of 11.2, 9.5, and 7.0, respectively.

$$-d[O_3]/dt = (2600 \pm 700)[CN_T]^{0.55\pm0.06}[O_3] \quad (6)$$

$$-d[O_3]/dt = (2700 \pm 850)[CN_T]^{0.83\pm0.14}[O_3] \quad (7)$$

$$-d[O_3]/dt = (550 \pm 200)[CN_T]^{1.06\pm0.10}[O_3] \quad (8)$$

The rate expressions are first order with respect to ozone. The rate also shows a first-order dependence on cyanide

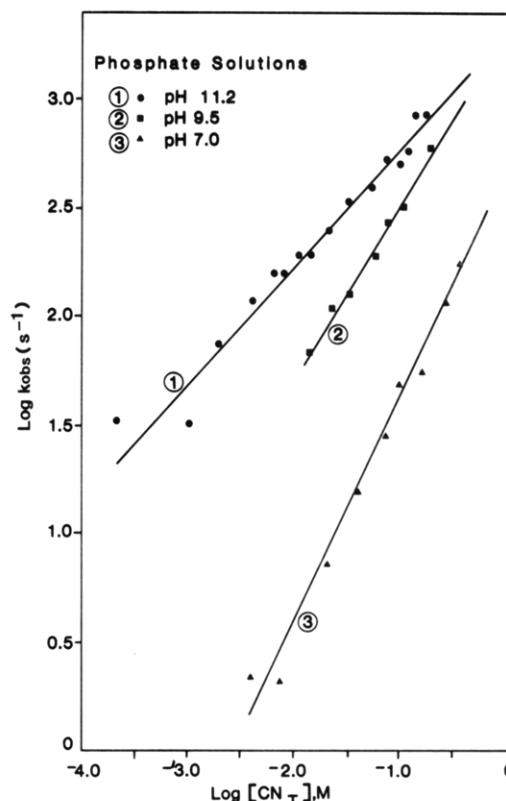at neutral pH; however, the order decreases with increasing pH. Furthermore, the rate equations for pH 11.2 and 9.5 have the same intercept, i.e., the same pseudo-first-order rate constant for a [CN$_T$] of 1.0 M.

Stoichiometry. Results of 17 experiments conducted at pH 11.2 and 7.0 by mixing the solutions of ozone and cyanide in a beaker, as described under Experimental Methods, showed that 1.2 ± 0.2 mol of ozone is consumed for each mole of cyanide oxidized. This is in agreement with previous observations (4, 5) in semi-batch reactors. The slight deviation of the stoichiometric ratio from one can be attributed to the reaction of ozone with free radicals, as will be described in the following section. Oxidation of 1 mol of cyanide produced 1 mol of cyanate. The stoichiometric results observed at the two pH values were not significantly different from each other, as also confirmed by the bubble-column experiments.

Effect of TBA and Carbonate. Kinetic experiments conducted in the presence of cyanide at pH 2.5, where hydroxide ion initiated decomposition of ozone is negligible (10) and cyanide is primarily in the form of HCN, showed that the reaction of molecular ozone with HCN is very slow. Since the rates of removal of ozone and of cyanide increase with increasing pH, ozone appears to be reacting primarily with the cyanide ion. However, the reaction of ozone with cyanide ion does not conform to a simple and bimolecular elementary reaction of ozone; the pH-dependent and fractional reaction order with respect to cyanide in eq 6–8 suggest that the contribution of radical reactions to the oxidation of cyanide species might be significant.

In order to differentiate between the molecular and radical reactions of ozone, *tert*-butyl alcohol (TBA) and carbonate were used as scavengers of hydroxyl radical, OH·, as suggested by Hoigne and Bader (9, 13). TBA and carbonate, when present at sufficient concentrations, can trap the OH· and apparently eliminate its further chain
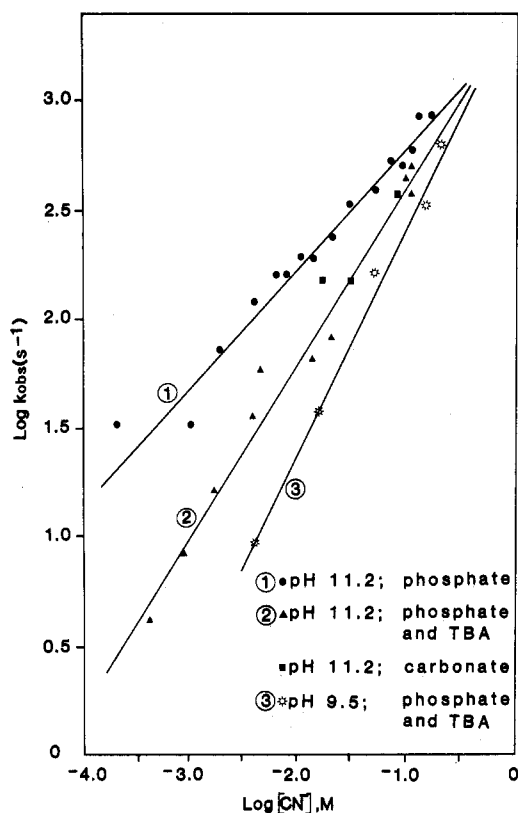
Figure 5. Observed pseudo-first-order rate constant for ozone decay vs. cyanide ion concentration on log scales in the presence of TBA (0.1–0.2 M) and carbonate (0.05 M).
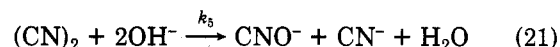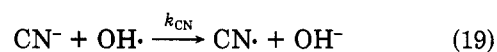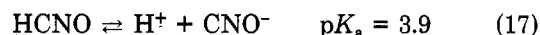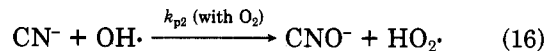
reactions with ozone and other solutes.

The results of the experiments conducted at pH 11.2 in the presence of 0.1–0.2 M TBA with 0.01 M phosphate buffer, and 0.05 M carbonate alone, are presented in Figure 5 together with the results obtained with phosphate buffer alone at the same pH. In the presence of TBA and carbonate, the rate of ozone disappearance reduced significantly, and the order of the reaction with respect to cyanide ion increased from 0.55 ± 0.06 to 0.86 ± 0.16 (the slop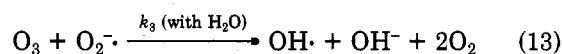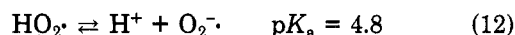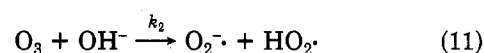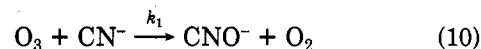es of lines 1 and 2, respectively, in Figure 5 for $p = 0.95$). Experiments repeated at pH 9.5 in the presence of the same amounts of TBA also reduced the rate and increased the reaction order from 0.83 ± 0.14 (line 2, Figure 4) to 1.06 ± 0.09 (line 3, Figure 5). These observations are in agreement with the expectations that the free radical reactions contribute significantly to the overall rates of removal of ozone and cyanide and that if the radical reactions could be eliminated, the molecular reaction of ozone with cyanide ion may be described by a rate expression which is first order with respect to both ozone and cyanide ion.

It should be noted that increasing the concentration of TBA from 0.1 to 0.2 M (from 7500 to 15 000 mg/L) did not affect the results since these concentrations were already very much in excess.

Although the reaction rate of ozone with cyanide was affected significantly by TBA and carbonate ion, similar experiments in the absence of cyanide showed that the rate of ozone decomposition was insensitive to TBA and carbonate. This was probably due to the presence of sufficient amounts of phosphate in water (0.01 M) which is also an effective radical scavenger. It is obvious that the rate of formation of hydroxyl radical is much faster in the presence of cyanide than it is in the absence of cyanide; i.e., cyanide promotes the chain reaction by entering into radical generation reactions.

Mechanism. Some of the experimental results which have helped to postulate a reaction mechanism for the ozonation of cyanide can be summarized as follows: (1) Ozone molecule reacts primarily with the cyanide ion; its reaction with hydrogen cyanide is negligible. (2) A free radical reaction, as well as the direct reaction of ozone with cyanide ion, contributes to the overall disappearance of ozone. (3) Upon oxidation of 1 mol of cyanide ion, slightly more than 1 mol of ozone is consumed and 1 mol of cyanate is produced. (4) The rate of hydroxide ion initiated decomposition of ozone is negligible compared to the rate of overall disappearance of ozone. (5) Cyanide promotes the formation of free radicals. Furthermore, as the concentration of cyanide ion increases, the difference in the k_{obsd} values observed with and without TBA (or carbonate), i.e., the contribution of the free radical reactions to the overall rate, becomes smaller (Figure 5).

In light of these observations, the following reaction sequences can be suggested:

$$O_3 + CN^- \xrightarrow{k_1} CNO^- + O_2 \qquad (10)$$

$$O_3 + OH^- \xrightarrow{k_2} O_2^- \cdot + HO_2 \cdot \qquad (11)$$

$$HO_2 \cdot \rightleftarrows H^+ + O_2^- \cdot \qquad pK_a = 4.8 \qquad (12)$$

$$O_3 + O_2^- \cdot \xrightarrow{k_3 \text{ (with } H_2O)} OH \cdot + OH^- + 2O_2 \qquad (13)$$

$$HCN \rightleftarrows H^+ + CN^- \qquad pK_a = 9.3 \qquad (14)$$

$$HCN + OH \cdot \xrightarrow{k_{p1} \text{ (with } O_2)} HCNO + HO_2 \cdot \qquad (15)$$

$$CN^- + OH \cdot \xrightarrow{k_{p2} \text{ (with } O_2)} CNO^- + HO_2 \cdot \qquad (16)$$

$$HCNO \rightleftarrows H^+ + CNO^- \qquad pK_a = 3.9 \qquad (17)$$

$$S_i + OH \cdot \xrightarrow{k_i} products \qquad (18)$$

$$CN^- + OH \cdot \xrightarrow{k_{CN}} CN \cdot + OH^- \qquad (19)$$

$$CN \cdot + CN \cdot \xrightarrow{k_4} (CN)_2 \qquad (20)$$

$$(CN)_2 + 2OH^- \xrightarrow{k_5} CNO^- + CN^- + H_2O \qquad (21)$$
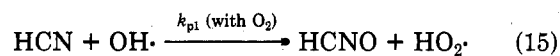
The first reaction represents the direct reaction of molecular ozone with cyanide ion. The chain reaction is initiated by the reaction of ozone with hydroxide ion (reaction 11). According to Staehelin and Hoigne (11), this reaction might lead to the formation of 2 mol of radical $O_2^- \cdot$ above pH 4.8 (see reaction 12) with a rate constant of 70 M^{-1} s^{-1}. Ozone is further consumed by reacting with $O_2^- \cdot$ in water with a rate constant of 10^9 M^{-1} s^{-1} (12), forming OH $\cdot$ (reaction 13). The OH $\cdot$ radical react rather nonselectively with solutes. These reactions might lead to the formation of reactive radicals that promote the chain reaction by reacting further with ozone, or the radicals might be scavenged, leading to the termination of the chain reaction (9, 19). The rate constants of OH $\cdot$ with solutes relevant to this study are listed in Table I. According to the observations in this study, cyanide promotes the chain reaction. Reaction 15 and 16 represent the promotion reactions, as suggested by Hoigne et al. (19). Phosphate and carbonate ions and TBA inhibit the chain reaction by the termination step represented by reaction 18. Reaction 19, which is another termination reaction, might compete with reaction 16 in the oxidation of cyanide to cyanate, leading to the formation of the intermediate cyanogen, $(CN)_2$, as proposed by Deltombe and Pourbaix (24). Cyanogen was identified as a reaction intermediate by Gurol and Holden (14). Reaction 19 is also consistent with

Table I. Reaction Rate Constants for Hydroxyl Radicals in Water

solute	k ($\times 10^{-6}$ M^{-1} s^{-1})	ref
HPO$_4^{2-}$	5	20
PO$_4^{3-}$	<10	20
HCO$_3^-$	15	21
CO$_3^{2-}$	420	21
TBA	470	9
CN$^-$	2800	22
O$_3$	3000	23

the observations that the contribution of the indirect reaction to the overall disappearance rate of ozone is reduced at high concentrations of cyanide (Figure 5).

On the basis of the reaction scheme proposed above, the rate of disappearance of ozone can be described as

$$-d[O_3]/dt = k_1[O_3][CN^-] + k_2[O_3][OH^-] + k_3[O_3][O_2^-\cdot] \quad (22)$$

Assumption of steady state for radicals $O_2^-\cdot$ and OH· results in the following equations, respectively:

$$d[O_2^-\cdot]/dt = 2k_2[O_3][OH^-] + k_{p1}[HCN][OH\cdot] + k_{p2}[CN^-][OH\cdot] - k_3[O_3][O_2^-\cdot] = 0 \quad (23)$$

$$d[OH\cdot]/dt = k_3[O_3][O_2^-\cdot] - k_{p1}[HCN][OH\cdot] - k_{p2}[CN^-][OH\cdot] - \sum k_i[S_i][OH\cdot] - k_{CN}[CN^-][OH\cdot] = 0 \quad (24)$$

From eq 23 and 24, the steady-state concentration of $O_2^-\cdot$ is derived as

$$[O_2^-\cdot] = (2k_2[OH^-]/k_3) \times$$
$$[1 + (k_{p1}[HCN] + k_{p2}[CN^-])/(k_{CN}[CN^-] + \sum k_i[S_i])] \quad (25)$$

Substitution of eq 25 in 22 yields

$$-\frac{d[O_3]/dt}{[O_3]} = k_1[CN^-] + 3k_2[OH^-] + \frac{2k_2[OH^-](k_{p1}[HCN] + k_{p2}[CN^-])}{k_{CN}[CN^-] + \sum k_i[S_i]} \quad (26)$$

Equation 26 is the overall rate expression for the disappearance of ozone according to the proposed scheme. It is first order with respect to ozone and mixed order with respect to cyanide, as observed experimentally. The first term on the right side of the equation represents the rate of direct ozone reaction with cyanide ion. The second term, which is 3 times the rate of hydroxide ion initiated ozone decomposition, is negligible in the presence of cyanide, according to our experimental observations. The last term is contributed to the overall rate by the free radical reactions. At high pH where HCN is negligible, and for high concentrations of scavengers (TBA, carbonate, etc.) or cyanide ion, the last term cancels, and eq 26 converges to the following:

$$-\{1/[O_3]\}d[O_3]/dt = k_1[CN^-] \quad (27)$$

Equations 26 and 27 are in agreement with the observations made at high pH values (pH > pK_a) that the observed rate constant is reduced in magnitude and the fractional order gets closer to 1.0 in the presence of radical scavengers (see Figure 5).

At neutral and acidic pH where cyanide ion concentration is low (pK_a = 9.3), such that $k_{CN}[CN^-] < \sum k_i[S_i]$ and $k_{p1}[HCN] > k_{p2}[CN^-]$, eq 26 is reduced to

$$-\{1/[O_3]\}d[O_3]/dt = \{(k_1K_a/[H^+]) + 2k_2k_{p1}[OH^-]/\sum k_i[S_i]\}[HCN] \quad (28)$$
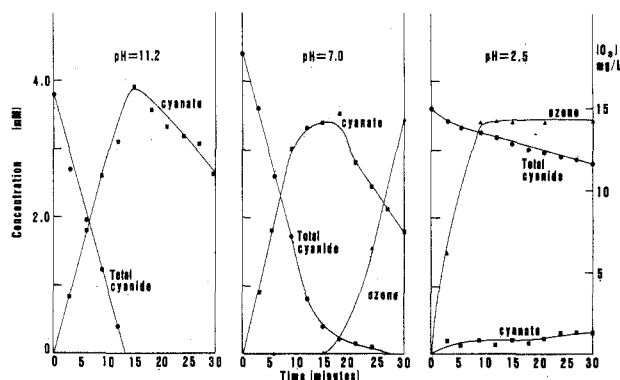

Figure 6. Profiles of total cyanide, cyanate, and ozone residual in the bubble column for pH 11.2, 7.0, and 2.5.

Equation 28 describes a first-order rate expression with respect to cyanide even in the absence of excess amounts of radical scavengers, which is consistent with the observations at pH 7.0 (see Figure 4). Furthermore, this equation can be used to explain why at pH 7.0 and in the absence of radical scavengers such as TBA and carbonate the observed rate is greater than the rate accountable by the direct reaction of cyanide ion at that pH value (the first term on the right side of eq 28). In the presence of high concentrations of radical scavengers, eq 28 is expected to reduce to eq 27.

According to the proposed reaction scheme (reactions 10–21), in the absence of significant amounts of substances other than cyanide, the stoichiometric ratio for the consumption of ozone per mole of cyanide is predicted to be 1.3–1.5, depending upon the relative rates of the promotion vs. the scavenging reactions of OH· with cyanide (reactions 15 and 16 vs. 18). This is in agreement with the average experimental ratio of 1.2 ± 0.2.

Assuming that the use of excess amounts of TBA can reduce eq 26 to eq 27, a second-order rate constant, k_1, of 2600 ± 700 M^{-1} s^{-1} is calculated from the intercepts of the lines 2 and 3 in Figure 5. It should be noted that lines 1 and 2 in Figure 2 also converge with lines 2 and 3 in Figure 5 for approximately 1 M cyanide concentration, suggesting that cyanide ion itself can scavenge the OH· radical if present at very high concentrations (eq 19). Under such conditions, and when pH > pK_a, eq 26 is reduced to

$$-\{1/[O_3]\}d[O_3]/dt = k_1[CN^-] + 2k_2k_{p2}[OH^-]/k_{CN} \quad (29)$$

and the contribution of the second term in eq 29 to the overall rate becomes negligible, if it is assumed that k_{p2} and k_{CN} are in the same order of magnitude, and k_2 is 70 M^{-1} s^{-1} (11). Equation 29 could not be tested experimentally, since the maximum observable rate by the stopped-flow spectrophotometer corresponded approximately to 0.25 M cyanide ion.

Bubble-Column Experiments. The observed concentrations of total cyanide, cyanate, and ozone residual are shown in Figure 6 as a function of time of ozonation in the bubble column for the pH values of 11.2, 7.0, and 2.5.

At pH 11.2, the removal rate of cyanide is mass transfer limited because of its very high oxidation rate with ozone, as indicated by the zero-order behavior of the cyanide profile. Cyanate appears in the solution at a rate which is equal to the rate of removal of cyanide. After cyanide is oxidized completely, cyanate starts to react with ozone at a much slower rate. During the course of the experiment at this pH, ozone does not appear in solution because of its rapid consumption by the oxidation and the decomposition reactions.

The removal rate of cyanide at pH 7.0 is equal to the rate at pH 11.2 and is mass transfer limited for the first 12 min of ozonation under the experimental conditions of this study. However, after the total cyanide concentration is reduced to about 0.8 mM, the oxidation reaction becomes the rate-limiting step. Ozone appears in solution as soon as the system becomes reaction rate limited and accumulates until reaching a plateau at about 14 mg/L. Cyanate is produced at an equal rate the cyanate is oxidized; however, oxidation of cyanate starts while cyanide still exists in solution.

At pH 2.5, volatilization of HCN contributes more to the removal of cyanide than its oxidation by ozone, as demonstrated by independent experimentations with pure oxygen. Nevertheless, oxidation of cyanide produces equal moles of cyanate. Due to slow oxidation and decomposition of ozone at this pH, ozone appears in solution instantaneously and stabilizes at a saturation value of about 14 mg/L.

Ozone concentration in the effluent gas was measured continuously for mass-balance calculations which resulted in a stoichiometric ratio of 1.2 ± 0.2 for ozone consumption/mol of cyanide for the pH values of 11.2 and 7.0. The results obtained with the bubble column, batch reactor, and the stopped-flow spectrophotometer confirm each other and imply an overall economic advantage for the high-pH oxidation process.

Summary and Conclusions

The kinetics and the mechanism of the ozonation reaction of free cyanide species were investigated in aqueous solution in the pH range 2.5–12.0. According to the kinetic results obtained with a stopped-flow spectrophotometer, the reaction is first order with respect to ozone, and the rate increases with increasing pH. The rate shows a varying dependence on cyanide concentration for different pH values.

Upon oxidation of each mole of cyanide, 1.2 ± 0.2 mol of ozone is consumed, and 1 mol of cyanate is produced as the reaction product.

Molecular ozone reacts primarily with cyanide ion. However, free radical reactions contribute significantly to the overall rate of removal of ozone. According to a reaction scheme proposed in this study, the decomposition of ozone that is initiated by hydroxide ion serves as the initiation step in a chain reaction, although the rate of this reaction is negligible compared to the overall removal rate of ozone. Cyanide ion and hydrogen cyanide promote the chain reaction. On the basis of the experimental results obtained in the presence of high concentrations of a radical-scavenging compound (TBA), a rate constant of 2600 $\pm$ 700 M^{-1} s^{-1} is predicted for the molecular reaction of ozone with cyanide ion.

Ozonation of cyanide-bearing wastewaters at high pH is expected to be mass transfer limited under the operating conditions of most experimental or full-scale contactors. The kinetic regime for the process at neutral pH should depend upon the mass-transfer characteristics of the ozone contactors.

Registry No. CN⁻, 57-12-5.

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