of electrons involved in a given diffusion-controlled electron-transfer step.

The calculated values of formation constants from eq 11 are summarized in Table IV, which also lists literature values for py binding to neutral and oxidized (TPP)Co under similar experimental conditions. One might expect to observe higher py binding constants to the charged TMpyP complex due to the macrocycle's electron-withdrawing properties.[8,13] However, this is not the case in DMF or Me$_2$SO and suggests that the solvated ligands (DMF or Me$_2$SO) that are displaced by py are more tightly bound to the TMpyP cobalt complexes then to the TPP cobalt derivatives. A binding of py to the doubly reduced [(TPP)Co]$^{2-}$ is not observed, but formation constants of 58 M^{-1} and 151 M^{-1} were calculated for the binding of py to doubly reduced [(TMpyP)Co]$^{2+}$ in Me$_2$SO and DMF, respectively.

Summary. The mechanism for oxidation or reduction of [(TMpyP)Co]$^{4+}$ in DMF, Me$_2$SO, or py involves three or five electron-transfer steps, all of which occur in a potential range of +0.4 to -1.20 V. Unlike [(TMpyP)M]$^{4+}$ complexes where M = Cu(II), Zn(II), and VO, [(TMpyP)Co]$^{4+}$ undergoes an oxidative process and this step involves the removal of one electron from Co(II) to generate the solvated [(TMpyP)Co^{III}(S)$_2$]$^{5+}$ species. No porphyrin ring oxidation is observed up to potentials of +1.0 V, and this behavior is consistent with that of [(TMpyP)Cu]$^{4+}$, [(TMpyP)VO]$^{4+}$, or [(TMpyP)Zn]$^{4+}$ under similar experimental conditions.

The reduction of [(TMpyP)Co]$^{4+}$ in DMF, Me$_2$SO, or py involves a total of six electrons, all of which are added to the complex at potentials between -0.4 and -1.2 V vs SCE. Electrochemical and spectral data indicate that the first one-electron reduction involves electron addition to the Co(II) center while the second one-electron reduction involves an electron addition to the porphyrin π-ring system. An intramolecular electron transfer occurs after electroreduction of [(TMpyP)Co^I]$^{3+}$ in py solutions, and this reaction leads to [(TMpyP)Co^{II}(py)]$^{2+}$, which

was characterized by ESR spectroscopy. Two consecutive reversible two-electron reductions are observed in the potential range of -0.90 to -1.10 V, and these reactions are due to an electroreduction of the four *N*-methylpyridiniumyl groups.

The very facile porphyrin ring reduction of [(TMpyP)Co]$^{4+}$ (process II) is similar to the facile ring reductions of other [(TMpyP)M]$^{4+}$ complexes which are shifted by up to 1200 mV with respect to the (TPP)M derivatives under the same experimental conditions. However, much smaller shifts occur for the metal-centered reductions. These shifts range between 200 and 250 mV for the Co^{II}/Co^{III} reaction and between 320 and 350 mV for the Co^{II}/Co^I reaction in the three investigated solvents. The difference in $E_{1/2}$ shifts between the first and the second reduction suggests that the effect of the four *N*-methylpyridiniumyl substituents is to lower the energy levels of the porphyrin e$_g$ orbitals as well as the metal d$_{z^2}$ orbitals to a lesser extent.

Studies of other ionic [(TMpyP)M]$^{5+}$ and metal–carbon-bonded [(TMpyP)M(R)]$^{4+}$ derivatives are now underway to see if similar substituent effects will be observed for complexes with different metals and with different types of metal–ligand binding.

Non-Metal Redox Kinetics: Hypochlorite and Hypochlorous Acid Reactions with Cyanide

Cynthia M. Gerritsen and Dale W. Margerum*

The rate expression for OCl$^-$ oxidation of CN$^-$ is $-d[OCl^-]/dt = (k_1 + k_2/[OH^-])[CN^-][OCl^-]$, where k_1 is 310 M^{-1} s^{-1} and k_2 is 583 s^{-1} (25.0 °C, μ = 1.00 M). The observed inverse [OH$^-$] dependence is due to the great reactivity of HOCl, which is 3.9 × 10^6 times more reactive than OCl$^-$ with CN$^-$. The proposed mechanism with HOCl is

$$OCl^- + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HOCl + OH^-$$

$$HOCl + CN^- \overset{k_4}{\longrightarrow} CNCl + OH^-$$

$$CNCl + 2OH^- \rightarrow OCN^- + Cl^- + H_2O$$
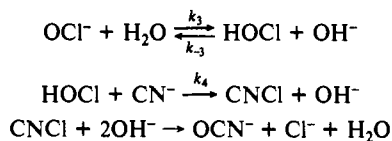
where k_4 is 1.22 × 10^9 M^{-1} s^{-1}, on the basis of pK_a = 7.47 for HOCl at μ = 1.00 M, 25.0 °C. At high CN$^-$ concentration the HOCl reaction becomes so fast that proton-transfer reactions from H$_2$O to OCl$^-$ and from HCN to OCl$^-$

$$OCl^- + HCN \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} HOCl + CN^-$$
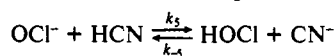
contribute to the rate, where the values for k_3 and k_{-3} are 9 × 10^3 s^{-1} and 1.9 × 10^{10} M^{-1} s^{-1} and the values for k_5 and k_{-5} are 2.2 × 10^7 M^{-1} s^{-1} and 6.6 × 10^8 M^{-1} s^{-1}. Rate constants for Cl$^+$ transfer from HOCl to nucleophiles decrease in value by 10 orders of magnitude with CN$^- \geq$ SO$_3^{2-} >$ I$^- \gg$ Br$^- \gg$ Cl$^-$, in accord with the decrease of anion nucleophilicity.

Introduction

The addition of chlorine or hypochlorite to waste water has long been an established process for the destruction of cyanide.[1-7] Price

et al.[8] reported instantaneous formation of CNCl from HOCl and CN$^-$ at pH 8. Eden et al.[9] studied the reaction at pH 11 and found

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very rapid formation of cyanogen chloride (eq 1). The initial

$$CN^- + OCl^- + H_2O \rightarrow CNCl + 2OH^- \qquad (1)$$
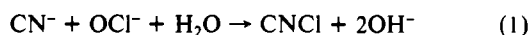
reaction gives complete conversion of CN^- to $CNCl$. Cyanogen chloride is volatile and extremely toxic. Its formation is a safety hazard in the chlorination process.[9]

Cyanogen chloride hydrolyzes in base to give cyanate and chloride ions (eq 2). Price et al. measured the rate of appearance

$$CNCl + 2OH^- \rightarrow OCN^- + Cl^- + H_2O \qquad (2)$$
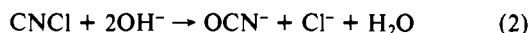
of Cl^- and the rate of loss of $CNCl$ (based on its reaction with reagent A, whose identity could not be disclosed).[8] The lack of UV–vis spectral bands for $CNCl$ has led to the development of several colorimetric procedures for its determination by the use of benzidine–pyridine[10,11] or 1,4-diaminobenzene–pyridine reagents.[12] The kinetics of hydrolysis of $CNCl$ is base-assisted and has been studied in carbonate,[8,13,14] phosphate,[8] and borax[9] buffers. Bailey and Bishop[13] resolved contributions from the individual species (eq 3), where $k_a = 2.58 \times 10^{-6}$ s^{-1}, $k_b = 4.53$ M^{-1} s^{-1}, and $k_c = 3.3 \times 10^{-2}$ M^{-1} s^{-1} at 26.5 °C.

$$\frac{-d[CNCl]}{dt} = (k_a + k_b[OH^-] + k_c[CO_3^{2-}])[CNCl] \qquad (3)$$

There is general agreement that the rate of formation of $CNCl$ (eq 1) is very fast, but there has been only one attempt to measure the rate constant. Mapstone and Thorn[15] followed the disappearance of hypochlorite at 209 nm in the presence of excess cyanide. They reported the rate expression in eq 4, with a k_1' value

$$\frac{-d[OCl^-]}{dt} = k_1'[CN^-][OCl^-] \qquad (4)$$

equal to 0.23 M^{-1} s^{-1} (20.0 °C, pH 10.5). They suggested that the initial reaction gave equal amounts of cyanate and cyanogen chloride. No evidence was presented to support this conclusion, which disagrees with the work of Eden et al.[9] and others.[8] Our kinetic studies indicate that their observed rate constant is in error by a factor of 10^7 at pH 10.5. It appears that they measured some artifact, such as the mixing rate constant of their apparatus. We use stopped-flow and pulsed-accelerated-flow[16,17] techniques to measure the reaction kinetics.

The rate of reaction of $HOCl$ has been recently studied with iodide,[18] bromide,[19] and sulfite.[20] In all three cases a Cl^+-transfer mechanism has been proposed to give ICl, $BrCl$, and $ClSO_3^-$, respectively. In the case of SO_3^{2-} the rapid formation of $ClSO_3^-$ (eq 5) was shown to be accompanied by release of OH^-. The

$$HOCl + SO_3^{2-} \rightarrow ClSO_3^- + OH^- \qquad (5)$$

$$ClSO_3^- + H_2O \rightarrow Cl^- + SO_4^{2-} + 2H^+ \qquad (6)$$
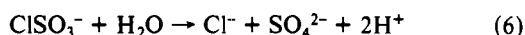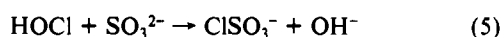
subsequent rapid hydrolysis of $ClSO_3^-$ (eq 6) was measured with

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an indicator to monitor the release of acid.[21] A similar Cl^+-transfer reaction occurs with CN^- to give $CNCl$ and OH^-; however, the hydrolysis of $CNCl$ is much slower than is the case for ICl^{22} or $ClSO_3^-$.

In the present work we show that both OCl^- and $HOCl$ react with CN^- and that $HOCl$ is nearly 4×10^6 times more reactive than OCl^-. The very large Cl^+-transfer rate constant for the $HOCl + CN^-$ reaction agrees with the relative nucleophilicity of CN^- compared to Cl^-, Br^-, I^-, and SO_3^{2-}.

Experimental Section

Reagents. Solutions of sodium hydroxide, perchloric acid, and sodium cyanide were prepared by dilution of the analytical reagent into distilled deionized water. The NaOH solution was protected from CO_2 contamination, and its concentration was determined by titration against potassium hydrogen phthalate. The $HClO_4$ solution was standardized by titration with the NaOH. The concentration of NaCN was determined by potentiometric titration with a standardized silver nitrate solution. An Orion 94-06A cyanide-selective electrode and an Orion 90-02 double-junction reference electrode were used to determine the end point of the titration. Solutions of sodium perchlorate were prepared from recrystallized $NaClO_4$ and were standardized gravimetrically.

The hypochlorite stock solution was prepared by bubbling research purity chlorine gas (Matheson) through a 0.5 M NaOH solution. The hypochlorite solution was used within 1 week. The amount of OCl^- produced was determined spectrophotometrically at 292 nm ($\epsilon_{292} = 350$ M^{-1} cm^{-1})[23] with a Perkin-Elmer Model 320 spectrophotometer.

Measurements of pH were made by means of an Orion Model 610A research digital pH meter equipped with a Corning combination electrode. The values were corrected to p[H$^+$] at 25.0 °C by a strong acid ($HClO_4$) versus strong base (NaOH) titration at constant ionic strength ($\mu = 1.00$ M $NaClO_4$). Data for both pH and absolute voltage were collected for each addition of base. Voltage readings were analyzed by the method of Gran[24] to determine the actual concentration of H$^+$ at each titration point.

HOCl pK_a Determination. The acid dissociation constant of $HOCl$ was not known at 1.00 M ionic strength. A calibrated electrode was used to measure the change in p[H$^+$] as $HClO_4$ was added to a basic OCl^- solution. All solutions had an ionic strength of 1.00 M, and the temperature was maintained at 25.0 °C. A Gran plot was used to determine the strong base end point. The ratio of $HOCl$ to OCl^- concentrations was calculated from the amount of $HClO_4$ added with a microburet, the initial concentration of OCl^-, the strong base end point, and the change in volume. The data were analyzed by use of eq 7 over the p[H$^+$] range

$$pK_a = p[H^+] + \log \frac{[HOCl]}{[OCl^-]} \qquad (7)$$

8–7 with at least 20 points taken in each of the two titrations. A pK_a value of 7.47 ± 0.01 was found for $\mu = 1.00$ M, 25.0 °C. The pK_a value at $\mu = 0.50$ M is 7.50,[20] so ionic strength changes in this range have little effect on the pK_a.

Stopped-Flow Measurements. Kinetic data for the reaction of cyanide with hypochlorite (25.0 °C, $\mu = 1.00$ or 0.10 M) were obtained with a Durrum stopped-flow (1.88-cm cell path) spectrophotometer interfaced to a Zenith 151 PC with a MetraByte DASH-16 A/D interface card. The reaction was monitored by the disappearance of OCl^- at 292 nm until the initial absorbance decreased by at least a factor of 4. Second-order unequal conditions were used with CN^- in 1.5–6-fold excess. Nonlinear regression analysis of the data provided values for initial absorbance (A_0), final absorbance (A_∞), and the second-order rate constant (k_{obsd}) as defined by eq 8. The reported values and their corresponding

$$\ln\left[1 + \frac{C_2 - C_1}{C_1} \frac{A_0 - A_\infty}{A_t - A_\infty}\right] = \ln\frac{C_2}{C_1} + (C_2 - C_1)k_{obsd}t \qquad (8)$$

standard deviations are the average of at least five runs. Excellent agreement with the second-order kinetic model confirms the dependence of the reaction on [CN$^-$] and [OCl$^-$] given by eq 9.

$$\frac{-d[OCl^-]}{dt} = k_{obsd}[CN^-][OCl^-] \qquad (9)$$

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Table I. Second-Order Rate Constants from Stopped-Flow Measurements of CN^- Reaction with OCl^- in NaOH Medium[a]

$[OCl^-]_i = 5.53 \times 10^{-4}$ M, $[OH^-]_{av} = 9.53 \times 10^{-3}$ M, $\mu = 0.1$ M

$10^3[CN^-]$, M	$10^{-4}k_{obsd}$, $M^{-1} s^{-1}$	$10^3[CN^-]$, M	$10^{-4}k_{obsd}$, $M^{-1} s^{-1}$
1.14	6.3 ± 0.1	2.84	6.2 ± 0.1
1.70	6.2 ± 0.1	3.41	6.1 ± 0.1
2.27	6.2 ± 0.1		

$[OCl^-]_i = 9.0 \times 10^{-4}$ M, $[CN^-]_i = 1.4 \times 10^{-3}$ M, $\mu = 1.00$ M

$[OH^-]_{av}$, M	$10^{-4}k_{obsd}$, $M^{-1} s^{-1}$	$[OH^-]_{av}$, M	$10^{-4}k_{obsd}$, $M^{-1} s^{-1}$
0.0517	1.16 ± 0.02	0.553	0.138 ± 0.001
0.152	0.41 ± 0.01	0.904	0.095 ± 0.001
0.306	0.224 ± 0.002		

[a] Conditions: 25.0 °C, $\lambda = 292$ nm.

Pulsed-Accelerated-Flow Measurements. The kinetics of the reaction between hypochlorite and excess cyanide (25.0 °C, $\mu = 1.00$ M) were followed by the pulsed-accelerated-flow (PAF) method.[16,17] PAF model IV,[25] which was used in the UV spectral region, can easily measure first-order rate constants as large as 200 000 s^{-1}.[20] Pseudo-first-order conditions were used with CN^- in at least a 78-fold excess over OCl^-. Velocity-dependent absorbance changes were observed at 292 nm as OCl^- reacted with CN^- in the twin-path mixing/observation cell of PAF-IV. In this study, the flow was decelerated during the pulse to give a linear velocity ramp, and 250 measurements were taken as the flow velocity in the observation tube changed from 12.5 to 3.0 m s^{-1}. Apparent first-order rate constants are calculated from eq 10, where M_{exptl} represents the

$$M_{exptl} = \frac{A_v - A_\infty}{A_0 - A_\infty} = \frac{1 - e^{-Y}}{Y} \qquad Y = \frac{k_{app}b}{v} \qquad (10)$$

degree of reaction in the observation path. In eq 10, A_0 is the initial absorbance of the reactants, A_∞ is the final absorbance of the products, A_v is the instantaneous absorbance at each velocity sampled, k_{app} is the apparent rate constant (s^{-1}), b is the cell path in meters, and v is the flow velocity in the observation tube (m s^{-1}). When k_{app} is large (>5000 s^{-1}), then $e^{-Y} \ll 1$ and there is a linear relationship between M_{exptl} and v. The apparent rate constant is related to the reaction rate constant, k'_{obsd} (s^{-1}), and a mixing rate constant that depends upon the velocity (eq 11).

$$\frac{1}{k_{app}} = \frac{1}{k_m v} + \frac{1}{k'_{obsd}} \qquad (11)$$

$$M_{exptl} = \frac{A_v - A_\infty}{A_0 - A_\infty} = \frac{1}{bk_m} + \frac{v}{bk'_{obsd}} \qquad (12)$$

Substitution of eq 11 into eq 10 simplifies to give to eq 12 when $e^{-Y} \ll 1$. A plot of M_{exptl} versus v has a slope of $1/(bk'_{obsd})$ and an intercept of $1/(bk_m)$ for first-order reactions. Most of the k'_{obsd} values were measured in this manner for the PAF studies. However, in one study k_{app} is less than 5000 s^{-1} so an iterative method is used to solve for k_{app} from eq 10. The double reciprocal relationship (eq 11) is then used to evaluate k'_{obsd}. At least four PAF runs were measured for each set of conditions, and average k'_{obsd} values are reported with their standard deviations.

Results and Discussion

Stopped-Flow Reactions. Table I gives the observed second-order rate constants (eq 9) measured under unequal concentration conditions ($[CN^-]_i$ (i = initial) is in 2–6-fold excess of $[OCl^-]_i$, which is 5.53×10^{-4} M) at the same concentration of OH^-. The reaction is followed by the rate of loss of OCl^-, which is much faster than the rate of loss of CNCl under these conditions. As eq 1 indicates, OH^- is released during the reaction. Hence, the final $[OH^-]$ is $[OH^-]_i + 2[OCl^-]_i$. For the first five sets of conditions in Table I the hydroxide ion concentration increases about 10% during the reaction and the $[OH^-]_{av}$ value of 9.53×10^{-3} M corresponds to the conversion of half of the OCl^- to CNCl. The rate of hydrolysis of CNCl is negligible compared to its rate of formation. A constant k_{obsd} value of $(6.2 \pm 0.1) \times 10^4$ M^{-1} s^{-1} is found for these conditions ($[OH^-]_{av} = 9.53 \times 10^{-3}$ M, 25.0 °C, $\mu = 0.10$ M) in agreement with the proposed first-order dependence in $[CN^-]$ and in $[OCl^-]$.
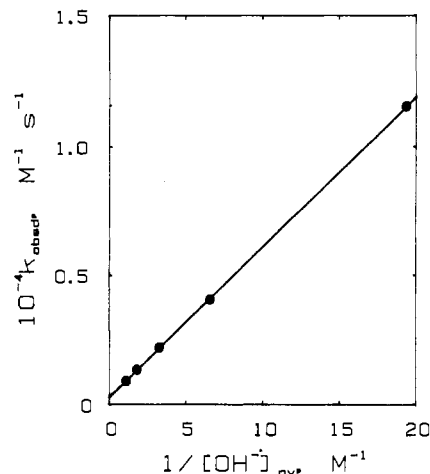

Figure 1. Dependence of the second-order rate constant for the reaction of OCl^- with CN^- on the reciprocal of the OH^- concentration (eq 13).
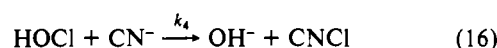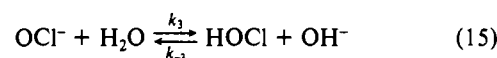
Table I also shows the effect on k_{obsd} of variation in the hydroxide ion concentration from 0.05 to 0.90 M (at a constant $\mu = 1.00$ M) when $[CN^-]_i/[OCl^-]_i$ is 1.5. (In 0.05 M OH^- only a 3% increase in $[OH^-]$ occurs during the formation of CNCl. In 0.90 M OH^- the increase is only 0.2%.) The k_{obsd} values are almost proportional to $1/[OH^-]$, but as shown in Figure 1 there is a small intercept that corresponds to a hydroxide-independent term as given by eq 13. The rate constants calculated by linear

$$k_{obsd} = k_1 + k_2/[OH^-] \qquad (13)$$

regression analysis are $k_1 = 310 \pm 20$ M^{-1} s^{-1} and $k_2 = 583 \pm 2$ s^{-1} (25.0 °C, $\mu = 1.00$ M). There are two reaction paths, and the hydroxide-independent reaction corresponds to eq 14, where

$$OCl^- + CN^- \xrightarrow{k_1} \text{products} \qquad (14)$$
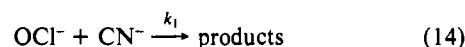
the products could be CNCl or OCN^-. The second path is attributed to the formation of HOCl (eq 15) and the reaction of

$$OCl^- + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HOCl + OH^- \qquad (15)$$

$$HOCl + CN^- \xrightarrow{k_4} OH^- + CNCl \qquad (16)$$

HOCl with CN^- (eq 16). An alternative rate expression between HCN and OCl^- may appear to be kinetically indistinguishable from the proposed reaction between CN^- and HOCl, but this alternative can be ruled out for two reasons. First, a reaction between H—C≡N and OCl^- does not provide a reasonable pathway for the formation of the carbon–chlorine bond in Cl—C≡N. The situation is similar to classic kinetics studies for the formation of urea from either NH_3 and HCNO or NH_4^+ and CNO^-. The kinetic results cannot distinguish between these reaction pairs, but stereochemical analysis of the way in which the reaction proceeds indicates that NH_3 and HCNO are far more likely reactants.[26] The second reason is that the typical proton ambiguity does not exist for this system, where the reaction is studied at high cyanide concentrations. This is because proton-transfer rate constants can limit the overall rate, as will be discussed.

The steady-state approximation for HOCl in eqs 15 and 16 gives the overall rate expression in eq 17. This corresponds to the

$$\frac{-d[OCl^-]}{dt} = \left(k_1 + \frac{k_3 k_4}{k_{-3}[OH^-] + k_4[CN^-]} \right)[CN^-][OCl^-] \qquad (17)$$

observed dependence when $k_{-3}[OH^-] \gg k_4[CN^-]$. The lowest OH^- concentration is about 60 times the initial CN^- concentration. Hence, the inequality will be valid if the value for k_{-3} is equal

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Table II. Dependence of Pseudo-First-Order Rate Constants Measured by the Pulsed-Accelerated-Flow Method for the Reaction of Hypochlorite with Excess Cyanide[a]

[CN⁻]$_T$, M	$10^{-4}k'_{obsd}$, s⁻¹	[CN⁻]$_T$, M	$10^{-4}k'_{obsd}$, s⁻¹
0.0672	0.387 ± 0.004	0.202	1.0 ± 0.1
0.101	0.562 ± 0.003	0.269	1.12 ± 0.03
0.168	0.80 ± 0.02	0.336	1.33 ± 0.04

[a]Conditions: 25.0 °C, μ = 1.00 M, [OCl⁻]$_i$ = 8.56 × 10⁻⁴ M, [OH⁻]$_i$ = 5.95 × 10⁻³ M, λ = 292 nm.

to or larger than the value for k_4. Proton-transfer reactions from weak acids to OH⁻ are extremely fast with rate constants that range from 10^9 to 5×10^{10} M⁻¹ s⁻¹.[27] Therefore, k_{-3}[OH⁻] should be much larger than k_4[CN⁻], and it follows that $k_2 = k_3k_4/k_{-3}$. The ratio of k_3/k_{-3} equals K_w/K_a, where pK_w is 13.79[28] and pK_a is 7.47 at 25.0 °C, μ = 1.00 M. The resulting value of k_4 is (1.22 ± 0.03) × 10⁹ M⁻¹ s⁻¹. This Cl⁺-transfer rate constant is extremely large and is comparable to some H⁺-transfer rate constants.

Pulsed-Accelerated-Flow Reactions. High concentrations of CN⁻ (0.07–0.34 M) and a lower OH⁻ concentration (6.0 × 10⁻³ M) greatly accelerate the rate of reaction with OCl⁻. The observed first-order rate constants (Table II) vary from 3870 to 13 300 s⁻¹. These conditions were selected in order to evaluate the k_3 and k_{-3} proton-transfer rate constants. However, the concentration of HCN becomes appreciable at such high cyanide levels and this acid provides another proton-transfer path (eq 18). The rate

$$OCl^- + HCN \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} HOCl + CN^- \qquad (18)$$

$$\frac{-d[OCl^-]}{dt} = \frac{k_4(k_3 + k_5[HCN])[OCl^-][CN^-]}{k_{-3}[OH^-] + (k_{-5} + k_4)[CN^-]} \qquad (19)$$

expression in eq 19 is derived for the PAF conditions by application of the steady-state approximation for HOCl. Contributions from the k_1[CN⁻] term can be neglected in eq 19 because of the much larger terms due to the HOCl reactivity. The value for K_3 = k_3/k_{-3} = 4.79 × 10⁻⁷ M is calculated from K_w/K_a^{HCN}. The value for $K_5 = k_5/k_{-5}$ = 0.0331 is calculated from K_a^{HCN}/K_a^{HOCl}, on the basis of pK_a^{HCN} = 8.95, 25.0 °C, μ = 1.00 M.[29] Hydrolysis of the added CN⁻ (eq 20) will contribute to the concentration of

$$CN^- + H_2O \rightleftharpoons HCN + OH^- \qquad (20)$$

OH⁻ present in the solutions. Equation 21 permits the value of

$$[HCN]^2 + \left(\frac{K_w}{K_a^{HCN}} + [OH^-]_i\right)[HCN] - \frac{K_w}{K_a^{HCN}}[CN^-]_T = 0 \qquad (21)$$

$$k'_{obsd} = \frac{k_4(k_3 + k_5[HCN])[CN^-]}{k_3/K_3([OH^-]_i + [HCN]) + (k_5/K_5 + k_4)[CN^-]} \qquad (22)$$

[HCN] to be calculated and leads to eq 22, where [OH⁻] = [OH⁻]$_i$ + [HCN]. There are only two unknowns in eq 22 (k_5 and k_3), and a simplex optimization procedure[30,31] is used to fit the six sets of PAF data given in Table II. Curve a in Figure 2 shows a fit of k'_{obsd} from eq 22 against [CN⁻]$_T$ for these data on the basis of k_3 = (9 ± 2) × 10³ s⁻¹ and k_5 = (2.2 ± 0.3) × 10⁷ M⁻¹ s⁻¹. It follows that k_{-3} = (1.9 ± 0.4) × 10¹⁰ M⁻¹ s⁻¹ and k_{-5} = (6.6 ± 0.9) × 10⁸ M⁻¹ s⁻¹. Curve b in Figure 2 shows the predicted behavior if eq 13 were valid (where $k'_{obsd} = k_{obsd}$[CN⁻]) and if proton-transfer limitations did not enter into the mechanism. Curve c in Figure 2 shows the predicted behavior if eq 17 were valid and the proton transfer to OCl⁻ came only from H₂O (eq 15). The actual behavior in curve a is the result of combined H⁺-transfer and Cl⁺-transfer paths that are the same order of
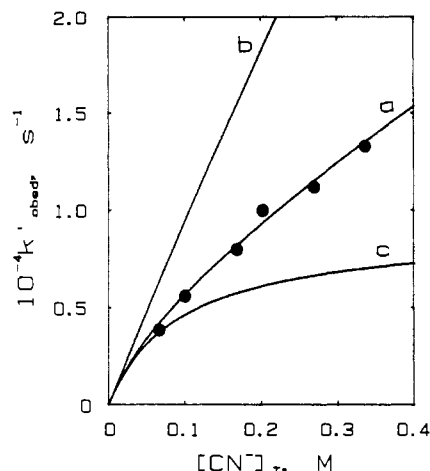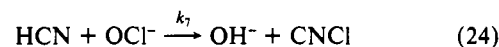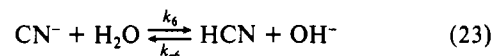

Figure 2. Proton-transfer effects for the reaction of OCl⁻ with excess CN⁻: (a) fit of the observed first-order rate constant to eq 22 where k_4 = 1.22 × 10⁹ M⁻¹ s⁻¹, k_3 = 9 × 10³ s⁻¹, and k_5 = 2.2 × 10⁷ M⁻¹ s⁻¹; (b) predicted k'_{obsd} if proton-transfer limitations did not occur; (c) predicted k'_{obsd} if the proton transfer to OCl⁻ came only from H₂O (k_3).

magnitude. The value of 1.9 × 10¹⁰ M⁻¹ s⁻¹ for k_{-3} is larger than a previous estimate of this rate constant in 0.5 M ionic strength,[20] but it is in good agreement with other rate constants (M⁻¹ s⁻¹) for OH⁻ with weak acids (1.0 × 10¹⁰ for adenine, 2.5 × 10¹⁰ for H(imidazole)⁺, 6 × 10⁹ for HCO₃⁻, 3.7 × 10⁹ for HCN).[27] The value of 6.6 × 10⁸ M⁻¹ s⁻¹ for k_{-5} also agrees with values of $\simeq 10^9$ M⁻¹ s⁻¹ for reactions of weak acids and weak bases when the ΔpK_a value is 1.5.[27]

Proton Ambiguity? We can now examine the postulate that the reactants might be HCN and OCl⁻ rather than CN⁻ and HOCl. The mechanism would be given by eqs 23 and 24 and the rate expression by eq 25. The value of k_{-6} is known[27] to be 3.7

$$CN^- + H_2O \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} HCN + OH^- \qquad (23)$$

$$HCN + OCl^- \overset{k_7}{\longrightarrow} OH^- + CNCl \qquad (24)$$

$$\frac{-d[OCl^-]}{dt} = \frac{k_6k_7[CN^-][OCl^-]}{k_{-6}[OH^-] + k_7[OCl^-]} \qquad (25)$$

× 10⁹ M⁻¹ s⁻¹, and the value of k_7 would have to be 1.22 × 10⁹ × (K_a^{HCN}/K_a^{HOCl}) = 4.04 × 10⁷ M⁻¹ s⁻¹. It is easily shown that k_{-6}[OH⁻] ≫ k_7[OCl⁻] under all the conditions used and therefore the rate expression in eq 26 results. If eq 26 were valid, a linear

$$\frac{-d[OCl^-]}{dt} = \frac{k_6k_7[CN^-][OCl^-]}{k_{-6}[OH^-]} \qquad (26)$$

dependence in cyanide concentration would have been found as in line b of Figure 2. Instead, the data follow curve a because of proton-transfer limitations in the formation of HOCl and its reaction with CN⁻, as discussed above. It can be seen that the measurement of large rate constants by the pulsed-accelerated-flow technique removes the question of proton ambiguity.[26]

Reaction Products. There is ample evidence[8,9,32,33] to show that the reaction of HOCl and CN⁻ gives CNCl even when the reactions are carried out at high pH.[9,33] It is not known whether the k_1 reaction path also gives CNCl initially via Cl⁺ transfer to CN⁻ with H₂O assistance (eq 27) or if the k_1 path is a direct

$$H_2O + OCl^- + CN^- \rightarrow 2OH^- + CNCl \qquad (27)$$
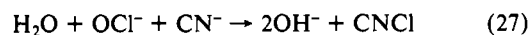
oxygen atom transfer (eq 28) to give cyanate ion. The k_1 path

$$OCl^- + CN^- \rightarrow Cl^- + OCN^- \qquad (28)$$
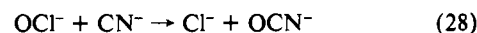
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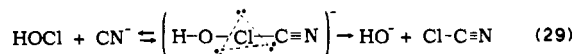
Table III. Comparison of Second-Order Rate Constants for the Reactions of HOCl and OCl⁻ with Nucleophilic Anions

| nucleophiles (X)	n^a	HOCl + X k_{HOCl}, $M^{-1} s^{-1}$	OCl⁻ + X k_{OCl}, $M^{-1} s^{-1}$	k_{HOCl}/k_{OCl}	ref
CN⁻	5.1	1.22×10^9	310	3.9×10^6	b
SO$_3^{2-}$	5.1	7.6×10^8	2.3×10^4	3.3×10^4	20
I⁻	5.04	1.4×10^8	<30	$>4 \times 10^6$	18
Br⁻	3.89	1.55×10^3	0.9×10^{-3}	1.7×10^6	19
Cl⁻	3.04	≤0.16			36, 38

^{a} Reference 40. ^{b} This work.

constitutes only 35% of the reaction in 1 M OH⁻. In 5 M OH⁻ the k_1 path should constitute 73% of the reaction, but it is not possible to analyze for the products in such high base, because the hydrolysis of CNCl (eq 3) is too fast. (If 0.1 M CN⁻ were used in 5 M OH⁻, the half-life of the k_1 path would be 22 ms, while the half-life for the decay of CNCl would be 30 ms.) In the absence of a direct spectrophotometric or other rapid analytical method for CNCl or for OCN⁻, it is very difficult to determine whether the k_1 path corresponds to eq 27 or to eq 28. We can conclude, however, that direct oxygen transfer is a minor path below pH 14.

Cl⁺-Transfer Reactions of HOCl. We propose that cyanide ion reacts with hypochlorous acid by nucleophilic attack at chlorine (eq 29). This is accompanied or followed by Cl–O bond cleavage
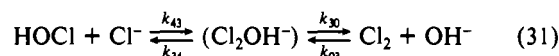
$$\text{HOCl} + \text{CN}^- \rightleftharpoons \left[\text{H-O} \overset{\cdots}{\underset{\cdots}{\longrightarrow}} \text{Cl} \overset{\cdots}{\longrightarrow} \text{C} \equiv \text{N} \right]^- \rightarrow \text{HO}^- + \text{Cl-C} \equiv \text{N} \quad (29)$$

and loss of hydroxide ion. Valence shell electron pair repulsion theory[34,35] predicts a linear arrangement of O–Cl–C bonds for the intermediate (or transition state) in eq 29, where there are 10 valence electrons around the chlorine atom. The rapidity of the reaction is attributed to the ease of valence shell expansion of chlorine, the strong nucleophilicity of CN⁻, and the suitability of OH⁻ as a leaving group. The net result is a Cl⁺ transfer from HOCl to CN⁻ to form CNCl. Similar mechanisms have been proposed for sulfite,[20] iodide,[18] bromide,[19] and chloride[36] reactions with hypochlorous acid. Several of these nucleophiles appear to form adducts with HOCl that are pre-transition-state reaction intermediates. Thus, a stability constant of 220 M^{-1} was determined[37] for the reaction HOCl + I⁻ ⇌ HOClI⁻. Kinetic evidence indicated that HOClSO$_3^{2-}$ was also a reactive intermediate.[20] Eigen and Kustin[36] proposed Cl$_2$OH⁻ as an intermediate in the base hydrolysis of chlorine.

Table III compares the values of rate constants for the reaction of HOCl with five nucleophilic anions. Cyanide ion is about 10^{10} times faster to react with HOCl than is chloride ion. The rate constant for the latter reaction is estimated from previous studies.[36,38] The equilibrium constant for eq 30 is 1.6×10^{-11}, on the

$$\text{HOCl} + \text{Cl}^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{Cl}_2 + \text{OH}^- \quad (30)$$
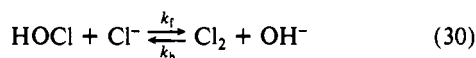
basis of the equilibrium constant of 980 M^{-2} for ($[\text{Cl}_2][\text{H}_2\text{O}]/[\text{HOCl}][\text{Cl}^-][\text{H}^+]$) measured at 25.0 °C, $\mu = 0.5$, and p$K_w = 13.79$ (25.0 °C, $\mu = 1.00$ M). Eigen and Kustin[36] propose the mechanism in eq 31, where $k_{03} \simeq 10^{10}$ $M^{-1} s^{-1}$ and Cl$_2$OH⁻ is a

$$\text{HOCl} + \text{Cl}^- \underset{k_{34}}{\overset{k_{43}}{\rightleftharpoons}} (\text{Cl}_2\text{OH}^-) \underset{k_{03}}{\overset{k_{30}}{\rightleftharpoons}} \text{Cl}_2 + \text{OH}^- \quad (31)$$

steady-state intermediate. Therefore, $k_b = k_{03}k_{34}/(k_{34} + k_{30}) =$

Figure 3. Swain–Scott plot of log k (for the reaction of HOCl with Cl⁻, Br⁻, I⁻, SO$_3^{2-}$, and CN⁻) versus the nucleophilicity (n) of the anions. The slope is 4.7 ± 0.1.

$k_{03}/(1 + k_{30}/k_{34})$, and thus $k_b \leq 10^{10}$ $M^{-1} s^{-1}$. Since $k_f = (1.6 \times 10^{-11})k_b$, it follows that $k_f \leq 0.16$. This is the estimated value used in Table III.

The Swain–Scott relationship (eq 32)[39,40] correlates rate con-

$$\log (k/k_0) = sn \quad (32)$$

stants with the nucleophilicity (n) of anions and the sensitivity (s) of the reaction site. The relationship was derived for nucleophilic attack at carbon, where the typical values for s are 1.0 ± 0.5. Table III gives values of n, and Figure 3 is a plot of log k against n for the reactions of X + HOCl. The slope corresponds to an s value of 4.7 ± 0.1, in good agreement with an initial correlation[20] of only the Br⁻, I⁻, and SO$_3^{2-}$ data. It is remarkable that this simple relationship, which is based on nucleophilic substitution reactions at carbon, should hold over a range of 10^{10} in rate constants for reactions with HOCl. It is apparent that nucleophilic reactions at chlorine (in HOCl) are far more sensitive to the nucleophilic strength of the anions than are reactions at carbon. The reactions at chlorine are also much faster than at carbon. This can be attributed in part to the much easier expansion of the number of valence electrons around chlorine.

HOCl versus OCl⁻ Rate Constants with Nucleophiles. The rate expressions for SO$_3^{2-}$, Br⁻, and CN⁻ all have a contribution from their reactions with OCl⁻ as well as the reactions with HOCl (eq 33, where X is the nucleophile). A reexamination of the original

$$\text{rate} = (k_{HOCl}[\text{HOCl}] + k_{OCl}[\text{OCl}^-])[\text{X}] \quad (33)$$

data[41] for the reactions of I⁻ with OCl⁻ as a function of [OH⁻] indicates that if a OCl⁻ path exists, its rate constant must be less than 30 $M^{-1} s^{-1}$. As shown in Table III, the ratio of k_{HOCl}/k_{OCl} is greater than 10^6 for X = CN⁻, I⁻, or Br⁻, while the ratio is only 3.3×10^4 for SO$_3^{2-}$. Thus, the SO$_3^{2-}$ reaction is actually independent of the hydroxide ion concentration above 0.05 M [OH⁻]. The rates of reaction of CN⁻, I⁻, and Br⁻ are suppressed by an increase in base concentration even above 1 M [OH⁻]. The reason for the smaller k_{HOCl}/k_{OCl} ratio with SO$_3^{2-}$ is not clear. Nor is it known if the OCl⁻ reaction with any of these nucleophiles occurs by an oxygen-atom-transfer path as given in eq 28 or if a H$_2$O-assisted proton-transfer/Cl⁺-transfer path occurs as given in eq 27. Nucleophilic attack at oxygen would be expected to be much less favorable than attack at chlorine, so this could account for the large k_{HOCl}/k_{OCl} ratios. (The effect of charge repulsion for the OCl⁻ path will not be great, because all the reactions are studied at very high ionic strength.) On the other hand the OCl⁻ ion is undoubtedly hydrogen bonded through the oxygen atom

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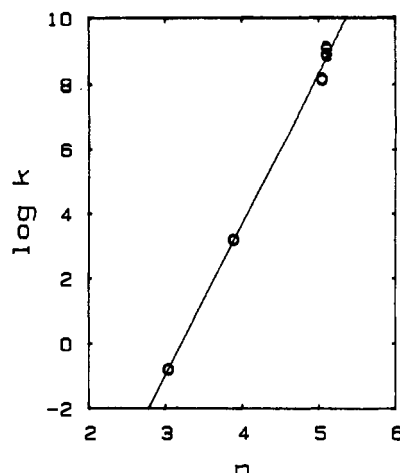
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to water. The reaction of nucleophiles (X) with (H–O–H--O–Cl)⁻ at chlorine to give OH⁻ + (H–O–Cl–X)⁻ is an attractive alternative to the reaction at oxygen, and the rate constants would be expected to be much less than the direct reaction with HOCl. At present we are not able to distinguish between these two paths for OCl⁻, but we believe there is overwhelming evidence for a Cl⁺-transfer path for the HOCl reactions.

Conclusions

Contrary to a previous report,[15] the reactions between CN⁻ and OCl⁻/HOCl are extremely rapid. The Cl⁺-transfer reaction of HOCl with CN⁻ to give ClCN and OH⁻ ($k_4 = 1.22 \times 10^9$ M⁻¹ s⁻¹) is even faster than H⁺ transfer for the same reactants to give OCl⁻ and HCN ($k_{-5} = 6.6 \times 10^8$ M⁻¹ s⁻¹). A typical concern about kinetic ambiguity[26,42] (or proton ambiguity) for the choice of either HOCl + CN⁻ or OCl⁻ + HCN as reactants is resolved in this case because only the HOCl path has the observed proton-transfer limitations. Hence, the usual statement that the two pathways are kinetically indistinguishable is no longer valid. The

HCN pathway can also be ruled out mechanistically, because HOCl is needed to give CNCl as the product.

For many years non-metal redox reactions of OCl⁻/HOCl with a variety of reducing agents[43–47] have been thought to proceed by oxygen-atom-transfer mechanisms. The present work and other recent studies[18–21,37] show a strong preference for Cl⁺-transfer mechanisms for the reactions of HOCl with a series of nucleophiles. An excellent correlation is found between the nucleophilicity of anions and log k values for their rate constants with HOCl. Attack at chlorine is extremely sensitive to nucleophilic strength.

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Redox Behavior of Nitro Substituents of Cage Complexes[1]

Peter A. Lay*,† and Alan M. Sargeson*,‡

The redox behavior of nitro groups bonded in the apical (1,8) positions of sar (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane) cage complexes is very diverse. Nitroso, hydroxylamine, amine, and nitro radical anions result as primary products from such reductions, depending on the type of reductant, pH, solvent, and the amount of reductant supplied. Secondary products also vary greatly according to the above parameters. The ultimate reduction products with Zn/HCl as the reductant contain amine substituents, whereas reductions with Sn²⁺/HCl or S₂O₄²⁻, or electrochemical reductions at a Hg-pool electrode, yield hydroxylamine-substituted cage complexes as the ultimate products. The behavior mirrors that normally associated with tertiary nitro groups in organic chemistry and allows the syntheses of a large variety of useful substituted cage complexes. The kinetic data on the reduction of nitro-substituted cage complexes by dithionite[11] have been reinterpreted in light of our studies in this area. No evidence has been found for nitro groups mediating the rate of electron transfer to the Co(III) center.

Introduction

The reduction of nitro substituents to amine substituents is a precursor to the synthesis of a large variety of cage complexes.[1–10] In addition to the reduction of the nitro groups to amines, hydroxylamine, nitroso, nitro radical ion derivatives, and their secondary reaction products were synthesized or implicated in the products.[1,6] An exclusive reduction of the nitro groups of [Co(NO₂)₂–sar)]³⁺ to the hydroxylamine derivative by the dithionite ion has also been reported.[11]

Further, it has been reported, on the basis of kinetic results with dithionite reductions,[11] that the nitro substituents of cage complexes mediate the rate of electron transfer to Co(III). In this paper, our earlier work on the reduction of the nitro groups is described in detail. This chemistry shows some parallels to reductions of tertiary nitro groups in organic chemistry and addresses the possibility of electron transfer being mediated by the nitro substituents.[12–18]

Experimental Section

Absorption spectra and molar absorptivities (ϵ, M⁻¹ cm⁻¹) were recorded by using Cary 14 and 118C spectrophotometers. ¹H NMR spectra were recorded with a JEOL 100-MHz Minimar spectrometer using sodium 3-(trimethylsilyl)propanesulfonate (NaTPS) or tetramethylsilane (TMS) as internal standards or with a Varian HA 100 spectrometer using TMS as a standard. Decoupled spectra were obtained from the Varian instrument. ¹H-decoupled ¹³C NMR spectra were

obtained by using a JNM-FX 60 Fourier transform spectrometer with 1,4-dioxane as an internal standard. All chemical shifts (δ) are expressed

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