Supplementary Material Available: First- and second-order rate constants, k_1 and k_2, respectively, for solvent S exchange on BeS_4^{2+} in CD_3NO_2 as diluent, at variable pressure (Table SI), relaxation rates, $1/T_2^b$, of the bound-water ^{17}O NMR signal of $[Be(H_2O)_4]^{2+}$ in ^{17}O-enriched water as a function of temperature (Table SII) and pressure (Table SIII), and elementary analyses of the nonaqueous solvates (Table SIV) (3 pages). Ordering information is given on any current masthead page.

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Non-Metal Redox Kinetics: Reactions of Sulfite with Dichloramines and Trichloramine

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Pulsed-accelerated-flow (PAF) and stopped-flow techniques are used to study the kinetics of $HNCl_2$ and CH_3NCl_2 reactions with sulfite. Pseudo-first-order rate constants with excess sulfite at p[H$^+$] 3.7–6.4 are measured from 35–45 000 s^{-1} (25.0 °C, μ = 0.50). Acid suppresses the rate because SO_3H^- is much less reactive than SO_3^{2-}. The rate expression is $-d[RNCl_2]/dt = k_1[RNCl_2][SO_3^{2-}]$, where k_1 (M^{-1} s^{-1}) is 5.8×10^6 for $HNCl_2$ and 2.4×10^7 for CH_3NCl_2. The initial nitrogen product is RNHCl, which reacts further with sulfite. Trichloramine reactions with sulfite are measured by the PAF method under second-order conditions with unequal concentrations (25.0 °C, μ = 0.50) from p[H$^+$] 3.8 to 4.6. The rate expression is $-d[NCl_3]/dt = (k_1[SO_3^{2-}] + k_2[SO_3H^-])[NCl_3]$, where k_1 is 4.5×10^9 M^{-1} s^{-1} and k_2 is 1.4×10^7 M^{-1} s^{-1}. The initial nitrogen product is $HNCl_2$, which reacts further with sulfite. A Cl^+-transfer mechanism is proposed for all the reactions with sulfite to give $ClSO_3^-$ as an initial product that hydrolyzes to give Cl^- and SO_4^{2-}. The relative reactivities of active chlorine species with SO_3^{2-} are $NCl_3 \gg HNCl_2 \gg NH_2Cl \ll OCl^-$, where the NCl_3 and $HNCl_2$ reactions are suppressed by acid whereas the NH_2Cl and OCl^- reactions are acid assisted.

Introduction

Sulfite, hydrogen sulfite, and sulfur dioxide are well-known as dechlorinating agents that remove or reduce the chlorine residuals (OCl^-, HOCl, NH_2Cl, $HNCl_2$, NCl_3) in coolant water and waste water.[1] All these chlorine species react relatively rapidly with sulfite, but there are great differences in the magnitude of the rate constants and in their rate expressions. The second-order rate constant for the reaction of OCl^- with SO_3^{2-} is 2.3×10^4 M^{-1} s^{-1} (25.0 °C, μ = 0.50),[2] while the corresponding value for NH_2Cl with SO_3^{2-} is only 7.7 M^{-1} s^{-1}.[3] These rate constants are appropriate for reactions at high pH; however, the observed rate constants for the hypochlorite reaction increase greatly below pH 12. The reactivity of HOCl (pK_a = 7.50, μ = 0.50) with SO_3^{2-} is 3.3×10^4 times greater than that of OCl^- ($k_{HOCl} = 7.6 \times 10^8$ M^{-1} s^{-1}).[2] Similarly, the rate of the chloramine reaction with SO_3^{2-} increases greatly below pH 10 and the reaction is general-acid assisted by NH_4^+, $B(OH)_3$, $H_2PO_4^-$, H_3O^+, and other acids (HA).[3] The Brønsted α value is 0.71, and the third-order rate constant for $H_3O^+ + NH_2Cl + SO_3^{2-}$ is 8×10^{10} M^{-2} s^{-1}. The corresponding third-order rate constant for $H_3O^+ + OCl^- + SO_3^{2-}$ is 2.4×10^{16} M^{-2} s^{-1}. Thus, the relative reactivity is $OCl^- \gg NH_2Cl$ and both reactions with SO_3^{2-} are strongly acid assisted. These are Cl^+-transfer reactions, where chlorosulfate is the initial product (eqs 1 and 2). The hydrolysis of $ClSO_3^-$ (eq 3) is also rapid, and the k_h value at 25.0 °C is 270 s^{-1}.[4]

$$HOCl + SO_3^{2-} \rightarrow ClSO_3^- + OH^- \quad (1)$$

$$HA + NH_2Cl + SO_3^{2-} \rightarrow A^- + NH_3 + ClSO_3^- \quad (2)$$

$$ClSO_3^- + H_2O \xrightarrow{k_h} SO_4^{2-} + Cl^- + 2H^+ \quad (3)$$

Rate constants have also been resolved for the general-acid-assisted reactions of chloramine with hydrogen sulfite (eq 4).[3] The

$$HA + NH_2Cl + SO_3H^- \rightarrow A^- + NH_3 + ClSO_3^- + H^+ \quad (4)$$

rate constant for $H_3O^+ + NH_2Cl$ with SO_3^{2-} is larger than the corresponding rate constant with SO_3H^- by a factor of 220. This reflects the stronger nucleophilicity of SO_3^{2-} compared to SO_3H^-. However, the overall effect of increased acid concentration is to increase the reaction rate. The observed second-order rate constant for NH_2Cl with total sulfite ($[SO_3^{2-}]_T = [SO_3^{2-}] + [SO_3H^-]$) increases by nearly 5 orders of magnitude from pH 10 to pH 3.[3]

Many years ago Dowell and Bray[5] showed that sulfite quantitatively reduces NCl_3 to ammonia and chloride (eq 5), while

$$3Na_2SO_3 + NCl_3 + 3H_2O \rightarrow 3Na_2SO_4 + 2HCl + NH_4Cl \quad (5)$$

other reducing agents cause some evolution of N_2. Our work demonstrates the stepwise nature of this reaction and the intermediate formation of $HNCl_2$, NH_2Cl, and $ClSO_3^-$.

In the present study we examine the kinetics of reactions of two dichloramines ($HNCl_2$ and CH_3NCl_2) and of trichloramine (NCl_3) with sulfite. The reactions are very rapid and require stopped-flow or pulsed-accelerated-flow (PAF)[6-8] techniques. We find that acid suppresses the reaction rates because of the much greater reactivity of SO_3^{2-} compared to SO_3H^- and because the reactions are not acid catalyzed. The sequence of reactions that occur for NCl_3 with SO_3^{2-} is given in eqs 6 and 7. This is followed

$$NCl_3 + SO_3^{2-} + H_2O \rightarrow HNCl_2 + ClSO_3^- + OH^- \quad (6)$$

$$HNCl_2 + SO_3^{2-} + H_2O \rightarrow NH_2Cl + ClSO_3^- + OH^- \quad (7)$$

by the reactions in eqs 2–4. The measurement of rate constants for the NCl_3 reaction is a difficult challenge. It requires use of the PAF technique in the UV region where only NCl_3 absorbs and low concentrations are needed with second-order unequal conditions. Nevertheless, we are able to resolve the second-order rate constants for the reactions of SO_3^{2-} and SO_3H^- with NCl_3.

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Table I. Ultraviolet Absorption Spectral Characteristics[a]

species	λ, nm	ε, M^{-1} cm^{-1}	species	λ, nm	ε, M^{-1} cm^{-1}
OCl^-	292 (max)	350[b]	NH_2Cl	310	≃0
NCl_3	336 (max)	195[c]	CH_3NCl_2	253	235
	360	130		303 (max)	275[e]
$HNCl_2$	243	245		320	200
	294 (max)	272[d]	CH_3NHCl	253 (max)	363[d]
	310	200		303	≃25
	336	≃30		320	≃6
	360	≃3	SO_3^{2-}	253	≃40
NH_2Cl	243 (max)	461[d]		≥280	≃0
	294	≃20	SO_3H^-	≥250	≃0

[a] This work except where noted. [b] Reference 11. [c] References 20 and 21. [d] Reference 9. [e] Reference 17.

A comparison of the reactivity of SO_3^{2-} as a nucleophile with four Cl^+-donating electrophiles (NCl_3, $HNCl_2$, NH_2Cl, OCl^-) is now possible. We are also able to contrast the reactivity of I^- as a nucleophile with the same electrophiles.[9,10]

Experimental Section

Reagents. A 5% solution of sodium hypochlorite (Mallinckrodt) was used as the source of active chlorine. The concentration of stock OCl^- solutions was determined spectrophotometrically at 292 nm ($\epsilon = 350\ M^{-1}\ cm^{-1}$).[11] Stock solutions of methylamine (CH_3NH_2) and NH_3 were standardized acidimetrically by using bromocresol green as the indicator. Acetate buffer was prepared from acetic acid and sodium acetate solutions. Phosphate buffer was prepared from Na_2HPO_4 and NaH_2PO_4. Fresh sulfite solutions were prepared by dissolving weighed amounts of sodium sulfite in aqueous buffer solutions and were standardized by iodometric titration. Anaerobic and metal-free conditions were strictly observed during use to avoid the trace-metal-catalyzed autoxidation of sulfite.[12-16] Ionic strength was maintained at 0.50 with recrystallized sodium perchlorate.

Preparation of Chloramines. Monochloramine solutions were prepared by mixing OCl^- and NH_3 solutions through a T-mixer at pH 9–10, and NH_3 was about 50% in excess in the final solution. Dichloramine solutions were prepared by dropwise addition of 0.1 M perchloric acid to the NH_2Cl solutions until the final pH was 3.5–4.0. The reaction mixture was allowed to stand 4 h to complete the formation of $HNCl_2$. The solutions were placed in a stoppered flask with no headspace to avoid volatilization of $HNCl_2$. Solutions prepared in this way were stable for 1 day. It is important to keep the pH above 3 during the preparation, because if any NCl_3 forms it reacts with $HNCl_2$ and the solutions are not stable. The $HNCl_2$ solutions were standardized spectrophotometrically at 294 nm ($\epsilon = 272\ M^{-1}\ cm^{-1}$).[9] Methylchloramine solutions were prepared by mixing OCl^- with a 1-2-fold excess of CH_3NH_2 through a T-mixer, and CH_3NCl_2 solutions were obtained by the dropwise addition of perchloric acid to the CH_3NHCl solutions in a procedure similar to the preparation of $HNCl_2$. The CH_3NCl_2 solutions were stored without headspace and were standardized spectrophotometrically at 303 nm ($\epsilon = 275\ M^{-1}\ cm^{-1}$).[17] Trichloramine ($NCl_3$) solutions were prepared from 3:1 equiv of HOCl and NH_3 with both solutions initially at pH 3–4. The NH_3 and HOCl solutions were mixed through a T-mixer, and the resulting NCl_3 solutions were kept overnight in the dark to allow all side reactions to go to completion. The amount of NCl_3 formed was always less than the initial NH_3 concentration due to the formation of N_2.[18] The acidic NCl_3 solution is relatively stable; however, the vapor pressure of NCl_3 is 150 mmHg at room temperature,[19] so the NCl_3 solutions were also stored in stoppered flasks with no headspace.

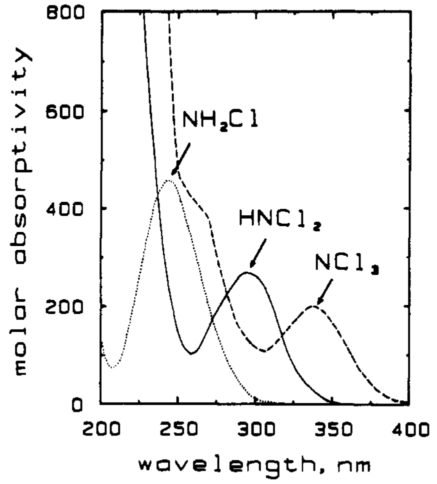

Figure 1. Spectral characteristics of chloramine species: (···) NH_2Cl; (—) $HNCl_2$; (- - -) NCl_3.

UV Spectral Characteristics of Chloramine Species. A Perkin-Elmer Model 320 spectrophotometer with PE 3600 data station was used. Figure 1 shows the absorption spectra of NCl_3, $HNCl_2$, and NH_2Cl, and Table I gives the molar absorptivities at various wavelengths of these and other species used in this study. The distinct UV absorption bands of the different *N*-chloro species permit a selection of wavelengths to monitor each species. This is of particular importance in the PAF method, where the absorbance change must be associated with a single reaction. The disappearance of NCl_3 is monitored at 360 nm rather than its absorption maximum (336 nm) in order to avoid interference from the slower rate of loss of $HNCl_2$. Similarly, the PAF studies of $HNCl_2$ and CH_3NCl_2 with sulfite in phosphate buffer are carried out at 310 and 320 nm (rather than at the absorption maxima of 294 and 303 nm) in order to avoid interference from the subsequent reactions of NH_2Cl and CH_3NHCl.

The kinetics of the NCl_3 and sulfite reactions are studied under second-order conditions, where it is important to know the initial concentration of each reactant. The NCl_3 concentration is determined spectrophotometrically at 336 nm on the basis of a molar absorptivity value of 195 $M^{-1}\ cm^{-1}$ that was measured from the stoichiometric reaction with sulfite.[20,21]

p[H⁺] Measurements. An Orion Model 601A research digital pH meter equipped with a Corning combination electrode was used. The pH measurements were corrected to p[H^+] values at 25.0 °C and $\mu = 0.50$ on the basis of electrode calibration by titration of standard $HClO_4$ with standard NaOH solution.

Stopped-Flow Spectrophotometer. Kinetic data for the reactions of SO_3^{2-} with $HNCl_2$ and CH_3NCl_2 in acetate buffer (25.0 °C, $\mu = 0.50$) 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 $HNCl_2$ reaction was monitored at 294 nm, and the CH_3NCl_2 reaction was monitored at 303 and 320 nm. Pseudo-first-order conditions were maintained with a 10-fold or greater excess of total sulfite. The observed first-order rate constants (k'_{obsd}, s^{-1}) for the reactions were determined from a least-squares linear regression plot of ln ($A_t - A_\infty$) vs time (eq 8), where A_∞ represents the final absorbance

$$\ln \frac{A_t - A_\infty}{A_0 - A_\infty} = -k'_{obsd}t \tag{8}$$

and A_t is the absorbance at any time. All the experimental k'_{obsd} values were corrected for mixing effects (eq 9)[22] to give the k_{obsd} values, where

$$k_{obsd} = k'_{obsd}/(1 - k'_{obsd}/k_{mix}) \tag{9}$$

$k_{mix} = 1700\ s^{-1}$ for this Durrum stopped-flow spectrophotometer. The average k_{obsd} value from three to five runs is reported with its standard deviation.

Pulsed-Accelerated-Flow Spectrophotometer.[6,7] PAF model IV[8] was used to obtain kinetic data for the reactions of sulfite with $HNCl_2$ in phosphate-buffered reactions and with CH_3NCl_2 in phosphate and acetate buffer (high sulfite concentrations). All the NCl_3 reactions with

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sulfite were measured by the PAF method. In these studies the flow was decelerated during the pulse to give a linear velocity profile, and 250 measurements of transmittance were taken as the flow velocity in the observation tube changed from 12.5 to 3.0 m/s. The transmittance measurements were converted to the absorbance values. For pseudo-first-order reactions with excess sulfite (with the $HNCl_2$ and CH_3NCl_2 reactions), the analysis is based on eq 10 for integrated observation of continuous flow.[7,23,24] M_{exptl} is the defined absorbance ratio, A_v is the absorbance of the reactant mixture at a given instantaneous velocity, A_∞ is the absorbance at infinite time, A_0 is the absorbance at time zero, k_{app} is the apparent rate constant (s^{-1}), b is the path length of the observation tube (0.01025 m), and v is the solution velocity in the observation tube (m/s) at the time A_v is measured. Equation 10 is valid when k_{app} is greater than 4000 s^{-1} and less than 100000 s^{-1}.[7] The apparent rate constant, k_{app}, is related to the first-order rate constant, k_{obsd}, and the mixing rate constant, k_{mix} (s^{-1}), as given in eq 11.[6-8] The mixing rate constant depends on the velocity (eq 12), where k_m (m^{-1}) is a proportionality constant and v varies from 12.5 to 3.0 m/s. Substitution of eqs 11 and 12 into eq 10 yields eq 13. Plots of M_{exptl} vs v are linear with a slope of $1/(bk_{obsd})$ and an intercept of $1/(bk_m)$ for first-order reactions.

$$M_{exptl} = \frac{A_v - A_\infty}{A_0 - A_\infty} = \frac{v}{bk_{app}} \tag{10}$$

$$\frac{1}{k_{app}} = \frac{1}{k_{mix}} + \frac{1}{k_{obsd}} \tag{11}$$

$$k_{mix} = k_m v \tag{12}$$

$$M_{exptl} = \frac{A_v - A_\infty}{A_0 - A_\infty} = \frac{1}{bk_m} + \frac{v}{bk_{obsd}} \tag{13}$$

For the irreversible reaction of sulfite with NCl_3 under second-order conditions, the mathematical model used in the analysis of the PAF data is given in eqs 14 and 15.[23-24] A_a and A_b are the initial absorbances of the reactants, $q = C_b/C_a$, and C_a and C_b are the initial concentrations of the reactants (M). The apparent second-order rate constant, k_{12app}, is iterated to fit into eqs 14 and 15. Equation 16 shows that k_{12app} is related to the second-order rate constant, k_{12} (M^{-1} s^{-1}). The mixing rate constant, k_{12mix} (M^{-1} s^{-1}), is proportional to the velocity (v), $k_{12mix} = k_{12m}v$, where k_{12m} is a proportionality constant (M^{-1} m^{-1}). Substitution of this relationship into eq 16 yields eq 17.[7] In this work, the reaction of sulfite with NCl_3 was studied under second-order experimental conditions. The second-order rate constants, k_{12}, were obtained from the double-reciprocal plots of $1/k_{12app}$ vs $1/v$. Three runs were measured for each set of conditions, and the average k_{obsd} values are reported with their standard deviations. The k_{obsd} values for the dichloramine reactions are from 4200 to 45000 s^{-1} and the k_{12} values for the NCl_3 reactions are in the range of (1.9-5.8) × 10^7 M^{-1} s^{-1}.

$$M_{exptl} = \frac{A_v - A_a(1-q) - A_\infty}{A_a + (1/q)(A_b - A_\infty)} = ((1-q)/R)\ \ln\ [(1 - qe^{-R})/(1-q)] \tag{14}$$

$$R = \frac{k_{12app}C_a(1-q)b}{v} \tag{15}$$

$$\frac{1}{k_{12app}} = \frac{1}{k_{12mix}} + \frac{1}{k_{12}} \tag{16}$$

$$\frac{1}{k_{12app}} = \frac{1}{k_{12m}}\frac{1}{v} + \frac{1}{k_{12}} \tag{17}$$

Results

Reactions of Dichloramines. The reactions of excess sulfite with CH_3NCl_2 in acetate buffer give first-order plots from stopped-flow data that correspond to the rate expression in eq 18. The k_{obsd} values are directly proportional to $[SO_3^{2-}]_T$, are independent of buffer concentration, and increase with an increase in p[H^+] from 3.72 to 4.39 (Table II). A reaction mechanism consistent with this behavior is given in eqs 19 and 20, where SO_3^{2-} is the only reactive sulfite species even though SO_3H^- is the predominant species at this acidity. In eq 21 the K_H value[25,26] is measured at 25.0 °C, μ = 0.50, and SO_3H^- refers to the sum of the two isomeric forms of $O_2SO{-}H^-$ and $H{-}SO_3^-$, where the proton is on an oxygen and on the sulfur, respectively.[27-32] The hydrogen ion and sulfite

$$\frac{-d[CH_3NCl_2]}{dt} = k_{obsd}[CH_3NCl_2] \tag{18}$$

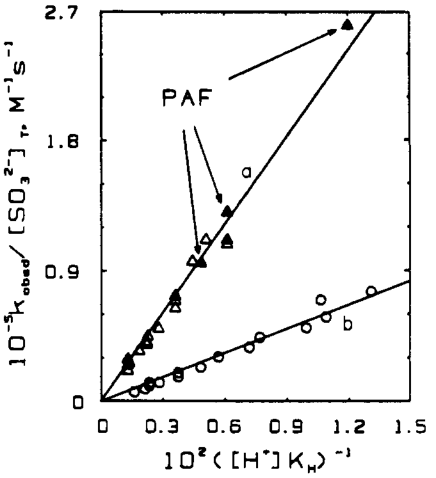

Figure 2. Resolution of k_1 values from stopped-flow data (acetate buffer): (a) CH_3NCl_2 with SO_3^{2-} (△); (b) $HNCl_2$ with SO_3^{2-} (○). PAF data (▲) for the CH_3NCl_2 reaction are indicated.

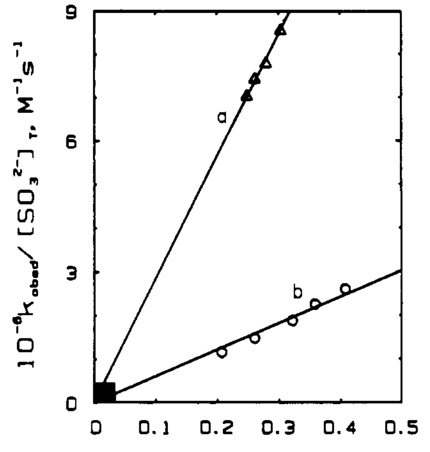

Figure 3. Resolution of k_1 values from PAF data (phosphate buffer): (a) CH_3NCl_2 with SO_3^{2-} (△); (b) $HNCl_2$ with SO_3^{2-} (○). The solid square indicates the region for the data in Figure 2.

$$SO_3^{2-} + H^+ \xrightleftharpoons{fast} SO_3H^- \tag{19}$$

$$CH_3NCl_2 + SO_3^{2-} + H_2O \xrightarrow{k_1} CH_3NHCl + ClSO_3^- + OH^- \tag{20}$$

$$K_H = \frac{[SO_3H^-]}{[SO_3^{2-}][H^+]} = 4.0 \times 10^6\ M^{-1} \tag{21}$$

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Table II. Pseudo-First-Order Rate Constants for the Reactions of Excess Sulfite with Dichloramines in Aqueous Solution[a]

buffer (tot. concn, M)	p[H$^+$]	$[SO_3^{2-}]_T$, mM	k_{obsd}, s^{-1}
Methyldichloramine ($[CH_3NCl_2]$ = (2.50–4.24) × 10^{-4} M)			
acetate (0.10)[b]	3.72	2.53	62 ± 2
	3.95	2.53	103 ± 3
	4.16	2.53	163 ± 4
	4.39	2.53	274 ± 13
	3.72	10.07	290 ± 9
	3.74	5.05	134 ± 3
	3.96	5.05	225 ± 11
acetate (0.15)[c]	3.87	3.49	121 ± 4
	4.05	3.49	174 ± 5
	4.16	3.49	241 ± 14
	4.25	3.49	335 ± 25
	4.31	3.49	386 ± 16
acetate (0.20)[b]	3.72	3.50	73 ± 1
	3.95	3.50	136 ± 6
	4.16	3.50	253 ± 13
	4.39	3.50	388 ± 20
acetate (0.10)[b]	4.29	44.18	4.2 (±0.1) × 10^3
	4.39	44.18	5.8 (±0.1) × 10^3
	4.68	44.18	1.14 (±0.01) × 10^4
phosphate (0.10)[c]	6.12	5.27	3.7 (±0.2) × 10^4
	6.15	4.85	3.6 (±0.2) × 10^4
	6.19	5.27	4.1 (±0.2) × 10^4
	6.24	5.27	4.5 (±0.2) × 10^4
Dichloramine ($[HNCl_2]$ = (4.25–5.92) × 10^{-4} M)			
acetate (0.10)[d]	3.98	7.28	94 ± 1
	4.18	7.28	144 ± 1
	4.36	7.28	223 ± 2
	4.49	7.28	321 ± 3
	4.63	7.28	509 ± 32
acetate (0.20)[d]	3.82	5.00	33.3 ± 0.5
	3.94	5.00	43.3 ± 0.6
	3.98	5.00	55 ± 1
	4.06	5.00	67 ± 1
	4.18	5.00	87 ± 1
	4.29	5.00	118 ± 2
	4.46	5.00	186 ± 4
	4.60	5.00	253 ± 4
	4.64	5.00	290 ± 9
	4.72	5.00	379 ± 22
phosphate (0.10)[e]	6.02	7.09	0.82 (±0.02) × 10^4
	6.15	7.09	1.05 (±0.01) × 10^4
	6.28	7.09	1.33 (±0.04) × 10^4
	6.35	7.09	1.60 (±0.06) × 10^4
	6.44	7.09	1.85 (±0.05) × 10^4

[a] Conditions: μ = 0.50, 25.0 °C; k_{obsd} values ≤509 s^{-1} were measured by the stopped-flow methods; all other k_{obsd} values were measured by the PAF technique. [b] λ_{obsd} = 303 nm. [c] λ_{obsd} = 320 nm. [d] λ_{obsd} = 294 nm. [e] λ_{obsd} = 310 nm.

Table III. Kinetic Data for the Reaction of Sulfite with NCl_3 under Second-Order Conditions[a]

p[H$^+$]	$10^4[SO_3^{2-}]_T$, M	$10^4[NCl_3]$, M	$10^{-7}k_{12}$, M^{-1} s^{-1}
$[acetate]_T$ = 0.10 M			
3.80	4.18	4.08	2.4 ± 0.1
3.96	5.75	4.03	1.9 ± 0.1
4.03	4.18	4.08	2.2 ± 0.1
4.18	4.18	4.08	2.4 ± 0.1
4.23	5.75	4.03	2.8 ± 0.1
4.24	3.16	3.18	3.1 ± 0.3
4.30	3.16	3.18	3.9 ± 0.3
4.31	4.18	4.08	2.9 ± 0.1
4.44	4.18	4.08	3.3 ± 0.1
4.46	3.16	3.18	4.2 ± 0.4
4.46	5.75	4.03	5.2 ± 0.2
4.53	4.18	4.08	5.4 ± 0.1
$[acetate]_T$ = 0.20 M			
3.92	2.65	2.46	2.7 ± 0.2
3.96	2.65	2.46	3.1 ± 0.1
4.06	4.13	3.33	2.6 ± 0.1
4.07	2.65	2.46	3.2 ± 0.1
4.16	4.13	3.33	3.1 ± 0.1
4.24	2.65	2.46	3.5 ± 0.1
4.29	4.13	3.33	4.1 ± 0.4
4.34	2.65	2.46	4.0 ± 0.1
4.39	4.13	3.33	5.8 ± 0.7
4.48	2.65	2.46	4.5 ± 0.2
4.56	2.65	2.46	5.8 ± 0.2

[a] Conditions: μ = 0.50, 25.0 °C; λ_{obsd} = 360 nm.

dependence for the pseudo-first-order rate constant is given in eq 22, where $[SO_3^{2-}]_T = [SO_3^{2-}] + [SO_3H^-]$. At p[H$^+$] 3.7–4.7,

$$k_{obsd} = \frac{k_1[SO_3^{2-}]_T}{1 + [H^+]K_H} \tag{22}$$

$$\frac{k_{obsd}}{[SO_3^{2-}]_T} = \frac{k_1}{[H^+]K_H} \tag{23}$$

$[H^+]K_H \gg 1$, and the dependence given in eq 23 is plotted in Figure 2a. Reactions with acetate buffer at p[H$^+$] 4.29–4.68 and with 1 order of magnitude higher $[SO_3^{2-}]_T$ are measured by the PAF method (Table II). The data points fall on the same line as the stopped-flow data in Figure 2a. This shows that there is no saturation effect even with 44 mM $[SO_3^{2-}]_T$ and rate constants up to 11 400 s^{-1}. The k_1 value is 2.02 (±0.04) × 10^7 M^{-1} s^{-1}, and the intercept is not statistically different from zero.

Figure 3a is plot of eq 22 from PAF data measured with excess $[SO_3^{2-}]_T$ in phosphate buffer from p[H$^+$] 6.12–6.24, where the k_{obsd} values vary from 36 000 to 45 000 s^{-1}. The measured k_1 value is 2.8 (±0.1) × 10^7 M^{-1} s^{-1} for CH_3NCl_2, and the intercept is again negligible. Since the p[H$^+$] measurements as well as the k_{obsd} measurements contribute to the errors in the k_1 determination, the average value from slopes in Figures 2a and 3a is used. This gives k_1 = 2.4 (±0.5) × 10^7 M^{-1} s^{-1}.

The reaction of excess sulfite with dichloramine (Table II) is similar to the behavior of methyldichloramine. Figure 2b gives a k_1 value of 5.5 (±0.1) × 10^6 M^{-1} s^{-1}, and Figure 3b gives a value of 6.1 (±0.2) × 10^6 M^{-1} s^{-1}. The average value over the entire p[H$^+$] range 3.82–6.44 is 5.8 (±0.4) × 10^6 M^{-1} s^{-1}. The $HNCl_2$ rate constant is a factor of 4.1 times smaller than the CH_3NCl_2 rate constant.

Figures 2 and 3 show excellent agreement for the k_1 rate constants resolved by stopped-flow and by PAF measurements despite the large difference in magnitude of the k_{obsd} values.

Reactions of Trichloramine. The NCl_3 reaction with sulfite is extremely fast and cannot be measured by stopped-flow methods. A wavelength of 360 nm is selected for PAF measurements in order to observe the loss of NCl_3 with no interference from absorbance changes due to subsequent reactions of $HNCl_2$ and NH_2Cl (Figure 1). Since the molar absorptivity of NCl_3 is only 130 M^{-1} cm^{-1} at 360 nm, the concentration of NCl_3 must be 0.4 mM in order to have 0.1 absorbance change (2.05-cm cell path) for the reaction. Pseudo-first-order conditions with excess sulfite (>4 mM) give rates that are too fast even for the PAF method. However, it is possible to observe the reaction under second-order conditions with initial NCl_3 concentrations of 0.24–0.41 mM, initial $[SO_3^{2-}]_T$ of 0.26–0.58 mM, and p[H$^+$] 3.80–4.56 (Table III). The p[H$^+$] range is selected to avoid SO_2 formation, to stay within the buffer capacity, and to keep the p[H$^+$] low enough to measure the second-order rate constant with good signal-to-noise. The absorbance vs velocity data are analyzed on the basis of eqs 14–17, where the k_{12} value is defined by eq 17 and eq 24. Table

$$-\frac{d[NCl_3]}{dt} = k_{12}[SO_3^{2-}]_T[NCl_3] \tag{24}$$

III shows that the k_{12} values are independent of the acetate buffer concentration but increase with an increase in p[H$^+$]. The proposed mechanism is given in eqs 25 and 26, where SO_3^{2-} and

$$SO_3^{2-} + NCl_3 + H_2O \xrightarrow{k_1} ClSO_3^- + HNCl_2 + OH^- \tag{25}$$

$$SO_3H^- + NCl_3 \xrightarrow{k_2} ClSO_3^- + HNCl_2 \tag{26}$$

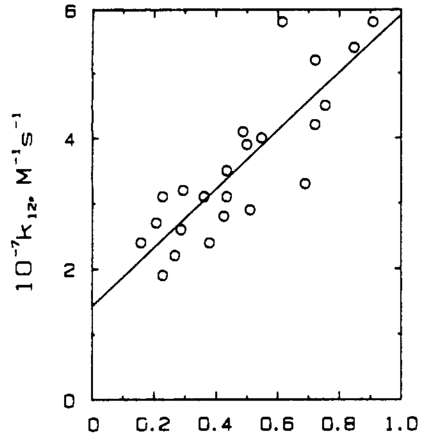


Figure 4. Resolution of rate constants for the reactions of NCl_3 with SO_3^{2-} and SO_3H^- in acetate buffer from PAF data obtained under second-order unequal concentration conditions: $k_1 = 4.5\ (\pm 0.6) \times 10^9$ M^{-1} s^{-1} (slope); $k_2 = 1.4\ (\pm 0.3) \times 10^7$ M^{-1} s^{-1} (intercept).

SO_3H^- react by parallel paths. This gives the rate expression in eq 27. Since $[H^+]K_H \gg 1$, the relationship between experimental

$$-\frac{d[NCl_3]}{dt} = (k_1[SO_3^{2-}] + k_2[SO_3H^-])[NCl_3] \qquad (27)$$

$$k_{12} = \frac{k_1}{[H^+]K_H} + k_2 \qquad (28)$$

k_{12} values and the $[H^+]$ concentration is given by eq 28. Figure 4 shows the linear relationship between k_{12} and $1/([H^+]K_H)$ and gives a k_1 value of $4.5\ (\pm 0.6) \times 10^9$ M^{-1} s^{-1} from the slope and a k_2 value of $1.4\ (\pm 0.3) \times 10^7$ M^{-1} s^{-1} from the intercept. (The k_2 value refers to the average rate constant from the two isomeric forms of hydrogen sulfite, which are present in a 4.9 ratio for $[O_2SO\text{-}H^-]/[H\text{-}SO_3^-]$.[32] Since we expect only the O_2SOH^- form to be reactive, the corrected rate constant for this species is $(1.4 \times 10^7) \times (5.9/4.9) = 1.7 \times 10^7$ M^{-1} s^{-1}.) The k_1 value is close to the diffusion-limited rate constant of 7×10^9 M^{-1} s^{-1} in water at 25.0 °C.[33] High acetate buffer concentrations keep the proton-transfer reactions in eq 29 rapid in comparison to the observed rate so that proton-transfer steps do not limit the reaction. In addition there is no evidence of general-acid catalysis.

$$SO_3H^- + CH_3COO^- \rightleftarrows SO_3^{2-} + CH_3COOH \qquad (29)$$

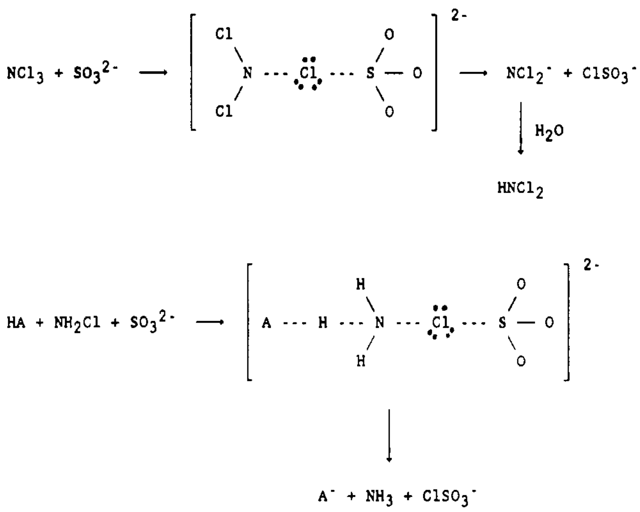
Subsequent Reactions. Methylchloramine is proposed as the initial product in the reaction between SO_3^{2-} and CH_3NCl_2 (eq 20). Table IV gives conditions where the reaction between CH_3NCl_2 and excess sulfite is complete within the stopped-flow deadtime (4.2 ms),[22] and the subsequent reaction of CH_3NHCl with sulfite is monitored at 253 nm (λ_{max} of CH_3NHCl). The k_{obsd} values found are similar to the values predicted for the reaction of NH_2Cl and sulfite in 0.10 M phosphate buffer at $p[H^+]$ 6.0–6.8.[3] This shows that CH_3NCl_2 is initially converted to CH_3NHCl as proposed.

Table IV. Pseudo-First-Order Rate Constants for the Subsequent Reactions of Excess Sulfite with Methyldichloramine and Trichloramine[a]

buffer (tot. concn, M)	$p[H^+]$	$[SO_3^{2-}]_T$, mM	k_{obsd}, s^{-1}	k_{calc}, s^{-1}
$[CH_3NCl_2]_i = 3.20 \times 10^{-4}$ M; CH_3NHCl Reaction Observed[b]				
phosphate (0.10)	5.97	3.84	210 ± 11	
	6.28	3.84	232 ± 5	
	6.57	3.84	224 ± 5	
	6.77	3.84	205 ± 11	
$[NCl_3]_i = 2.00 \times 10^{-4}$ M; $HNCl_2$ Reaction Observed[c]				
acetate (0.20)	3.88	2.15	17.8 ± 0.2	19
	4.10	2.15	30 ± 1	32
acetate (0.10)	4.46	3.54	122 ± 3	132
	4.58	3.54	180 ± 4	174

[a] $\mu = 0.50$, 25.0 °C; $[SO_3^{2-}]_T$ is the initial total sulfite concentration. The k_{calc} values (s^{-1}) are based on the rate constant of 5.8×10^6 M^{-1} s^{-1} for the reaction of SO_3^{2-} and $HNCl_2$. In the calculation, $[SO_3^{2-}]_T$ was corrected for 2-equiv consumption in the reactions with NCl_3 and NH_2Cl. [b] $\lambda_{obsd} = 253$ nm. [c] $\lambda_{obsd} = 294$ nm.

Scheme I



Solutions of NCl_3 and excess sulfite are mixed in the stopped-flow instrument at $p[H^+]$ 3.88–4.58, and an absorbance decay is observed at 294 nm (λ_{max} of $HNCl_2$). Under these conditions all the NCl_3 is lost within the deadtime of the instrument and the rate of loss of $HNCl_2$ is observed. The subsequent reaction of NH_2Cl does not interfere because its molar absorptivity is only 7% of that of $HNCl_2$ at 294 nm. The experimental k_{obsd} values are in good agreement with values calculated from $k_1 = 5.8 \times 10^6$ M^{-1} s^{-1} for the SO_3^{2-} reaction with $HNCl_2$. Hence, the first product of the NCl_3 reaction with sulfite is $HNCl_2$, as proposed in eqs 25 and 26. Thus, there are three sequential reactions with sulfite in which $NCl_3 \rightarrow HNCl_2 \rightarrow NH_2Cl \rightarrow NH_3$. We propose a Cl^+ transfer for each step to give $ClSO_3^-$, which hydrolyzes to Cl^- and SO_4^{2-}.[3]

Discussion

Scheme I contrasts the proposed pathways for nucleophilic attack by sulfite on NCl_3 and NH_2Cl. In both cases chlorine expands its valence shell prior to the transfer of Cl^+ to sulfur. The NCl_3 reaction path does not require a proton and is not acid assisted. The release of a NCl_2^- group is shown, although water could transfer a proton to give $HNCl_2$ and OH^- prior to the complete loss of NCl_2^- (i.e. there is a large degree of Cl^+ transfer to SO_3^{2-} with NCl_2^- separation prior to any H^+ transfer). On the other hand, the NH_2Cl path is strongly acid assisted by H_3O^+ and buffer acids (HA). The proton transfer that takes place as the Cl^+ is transferred to sulfur permits NH_3 to be released. The difference in the behavior of NCl_3 and NH_2Cl correlates with the lack of basicity of NCl_3 compared to the modest basic properties of NH_2Cl (i.e. the pK_a of NH_3Cl^+ is 1.5[34]). Similar behavior was found in the reactions of NCl_3 and NH_2Cl with I^-.[9,10]

In the reaction between NCl_3 and I^- kinetic evidence is found[10] for a NCl_3I^- intermediate with a stability constant of 6×10^3 M^{-1} for $[NCl_3I^-]/([NCl_3][I^-])$. This species dissociates to give NCl_2^- and ICl with a first-order rate constant of 1.5×10^4 s^{-1}. We do not have evidence that requires the corresponding $NCl_3SO_3^{2-}$ species be an intermediate rather than just a transition state because saturation kinetics are not observed for the SO_3^{2-} reaction.

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Table V. Resolved Rate Constants for the Reactions of Chlorine Species with Sulfite and Iodide[a]

reacn	k, $M^{-1}\ s^{-1}$	ref
$OCl^- + SO_3^{2-}$	$2.3\ (\pm 0.4) \times 10^4$	2
$HOCl + SO_3^{2-}$	7.6×10^8	2
$NH_2Cl + SO_3^{2-}$	$7.7\ (\pm 0.2)$	3
$HNCl_2 + SO_3^{2-}$	$5.8\ (\pm 0.2) \times 10^6$	this work
$CH_3NCl_2 + SO_3^{2-}$	$2.4\ (\pm 0.1) \times 10^7$	this work
$NCl_3 + SO_3^{2-}$	$4.5\ (\pm 0.6) \times 10^9$	this work
$NCl_3 + SO_3H^-$	$1.4\ (\pm 0.3) \times 10^7$	this work
$HOCl + I^-$	1.4×10^8	10[b]
$HNCl_2 + I^-$	0.56	9
$NCl_3 + I^-$	9×10^7	10[b]

reacn	k, $M^{-2}\ s^{-1}$	ref
$H_3O^+ + OCl^- + SO_3^{2-}$	2.4×10^{16}	2
$H_3O^+ + NH_2Cl + SO_3^{2-}$	8.0×10^{10}	3
$H_3O^+ + NH_2Cl + SO_3H^-$	3.6×10^8	3
$H_3O^+ + OCl^- + I^-$	$4.4\ (\pm 0.3) \times 10^{15}$	9
$H_3O^+ + NH_2Cl + I^-$	$2.40\ (\pm 0.05) \times 10^{10}$	9
$H_3O^+ + HNCl_2 + I^-$	$9.3\ (\pm 0.6) \times 10^5$	9

[a] $\mu = 0.50$, 25.0 °C. [b] $\mu = 0.10$, 25.0 °C.

In our studies of SO_3^{2-} with NCl_3, the SO_3^{2-} concentration is much lower than the I^- concentration used in studies of the I^- and NCl_3 reaction.[10] If there were a saturation kinetic effect for the SO_3^{2-} concentrations used in this study, the stability constant of $NCl_3SO_3^{2-}$ would have to be at least 2 orders of magnitude larger than that of NCl_3I^-. Since we do not observe this effect, the stability constant must be less than 6×10^5 M^{-1}. Furthermore, in the sulfite reaction the loss of NCl_3 is observed, while in the iodide reaction the formation of I_3^- is observed. It is even possible that the rapid loss of NCl_3 could be due to the formation of appreciable amounts of $NCl_3SO_3^{2-}$, provided that this species does not absorb at 360 nm. However, we know from the subsequent reaction studies that $HNCl_2$ is formed rapidly from the NCl_3 reaction with sulfite. Hence, if $NCl_3SO_3^{2-}$ were an intermediate, it would break up rapidly.

The reaction of excess OH^- with NCl_3 provides kinetic evidence of a NCl_3OH^- intermediate.[35] In the reaction of HOCl with SO_3^{2-} a $HOClSO_3^{2-}$ intermediate is proposed with chlorine bridged between sulfur and oxygen.[2] Hence, a $NCl_3SO_3^{2-}$ intermediate with chlorine bridged between nitrogen and sulfur is quite possible.

The ratio of k_1/k_2 for the SO_3^{2-} and SO_3H^- reactions with NCl_3 is 320. Since SO_3H^- is a weaker nucleophile than SO_3^{2-}, its smaller reactivity is to be expected. However, the k_1 value of 4.5×10^9 $M^{-1}\ s^{-1}$ for NCl_3 and SO_3^{2-} is close to the diffusion-limited rate constant. We do not know if the high ionic strength (0.50) has any effect on the actual diffusion limit, but two other reactions with SO_3^{2-} have similar values (eqs 30 and 31).[2,35] Hence, the

$$HOCl + SO_3^{2-} \xrightarrow{5 \times 10^9\ M^{-1}\ s^{-1}} HOClSO_3^{2-} \qquad (30)$$

$$I_2 + SO_3^{2-} \xrightarrow{3.2 \times 10^9\ M^{-1}\ s^{-1}} I^- + ISO_3^- \qquad (31)$$

ratio of k_1/k_2 might be even larger for NCl_3 if it were not for the diffusion limit. We do not see any contribution for SO_3H^- in the sulfite reactions with $HNCl_2$ or CH_3NCl_2. Therefore, the corresponding ratio of k_1/k_2 must be larger than 3000 for the reactions of SO_3^{2-} compared to SO_3H^- with the dichloramines.

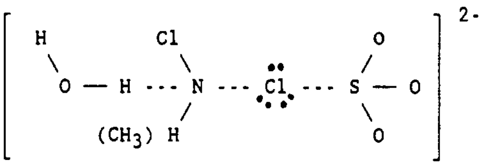
The absence of acid assistance and of SO_3H^- reactivity for the dichloramine reactions suggests a transition state that is similar to that for NCl_3 in Scheme I. The behavior of $HNCl_2$ with SO_3^{2-} is completely different from the kinetic behavior of the $HNCl_2$ reaction with I^-. The latter reaction is general-acid assisted and is much slower than the acid-assisted reactions of $NH_2Cl + I^-$.[9] As shown from the values in Table V, the third-order rate constant for $HNCl_2 + H^+ + I^-$ is 2.6×10^4 times smaller than the rate constant for $NH_2Cl + H^+ + I^-$. In contrast the SO_3^{2-} reaction with $HNCl_2$ is not acid assisted, but it is much faster than the NH_2Cl reaction with SO_3^{2-}. The second-order rate constant for $HNCl_2 + SO_3^{2-}$ is 7.5×10^5 times larger than that for $NH_2Cl + SO_3^{2-}$. With $HNCl_2$ the k_{obsd} values decrease as the pH decreases, because SO_3H^- is not reactive. On the other hand, with NH_2Cl the k_{obsd} values increase as the pH decreases, because acids assist the SO_3H^- and the SO_3^{2-} reaction paths. Chart I summarizes the relative reactivity of four active chlorine electrophiles with I^- and with SO_3^{2-}. Above pH 5 the observed rate constants with $[SO_3^{2-}]_T$ are larger for $HNCl_2$ than for NH_2Cl, whereas below pH 4 the reverse is true. We also studied the CH_3NCl_2 reaction with SO_3^{2-} to confirm the acid dependence that we found with the less stable $HNCl_2$.

Chart I

nucleophile	relative reactivity of electrophile	
	acid assisted	not acid assisted
I^-	$OCl^- \gg NH_2Cl \gg HNCl_2$	$\ll NCl_3$
SO_3^{2-}	$OCl^- \gg NH_2Cl$	$\ll HNCl_2 \ll NCl_3$

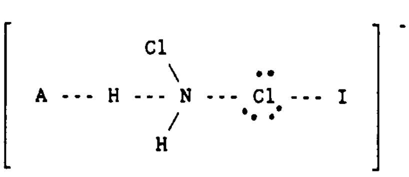
Table V gives rate constants for the reactions of SO_3^{2-}, SO_3H^-, and I^- with the active chlorine species. The ratio of the SO_3^{2-} to I^- rate constants is 5.5 for the H^+-assisted reactions with OCl^- and is 3.3 for the H^+-assisted reactions with NH_2Cl. However, the ratio of the SO_3^{2-} to I^- rate constants is 1.0×10^7 for the second-order reactions with $HNCl_2$ (i.e. not acid assisted except for H_2O). For NCl_3 the ratio of SO_3^{2-} to I^- rate constants is only 50. This implies the SO_3^{2-} reaction with NCl_3 may be a diffusion-limited process.

We propose a transition state for the dichloramine reaction with sulfite (structure I) that has a large degree of Cl^+ transfer to SO_3^{2-} with relatively little proton transfer from water to nitrogen. The fact that CH_3NCl_2, with a more basic nitrogen site than $HNCl_2$, is 4 times faster to react with SO_3^{2-} suggests some degree of solvent participation. However, the lack of general-acid assistance by acetic acid indicates that such proton transfer does not have a big effect on the height of the transition-state energy barrier for structure I.



I

The proposed transition state for the reaction of $HNCl_2$ with I^- (structure II) has a much larger degree of proton transfer from general acids to the nitrogen in order to permit Cl^+ transfer to I^-. Since water is a very weak acid, the rate constant for the $HOH-HNCl_2-I^-$ path is 10^7 times smaller than for the $HOH-HNCl_2-SO_3^{2-}$ path, where proton transfer is much less important. The N–Cl bond becomes weaker for the NH_2Cl, $HNCl_2$, NCl_3 sequence, where the force constants (mdyn $Å^{-1}$) are 3.06, 2.75, and 2.72, respectively.[37] The basicity of the nitrogen also greatly



II

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diminishes in this sequence. The weaker the N–Cl bond and the stronger the nucleophile that reacts at chlorine, the less the need for proton transfer to nitrogen in order to have Cl^+ transfer to the nucleophile. Sulfite is a stronger nucleophile than iodide, as is reflected in its Brønsted base strength and in its much more positive reduction potential (eqs 32 and 33). Sulfite also would

$$SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^- \qquad E^\circ = 0.936\ V \qquad (32)$$

$$I^- + 2OH^- \rightarrow OI^- + H_2O + 2e^- \qquad E^\circ = -0.472\ V \qquad (33)$$

be expected to have a stronger attraction than iodide for a hard acid species such as Cl^+.[38] For the sequence in Chart I with other nucleophiles we can predict that the weaker the nucleophile, the more acid assistance will be needed, and conversely the stronger the nucleophilic attraction to Cl^+, the less acid assistance will be needed.

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Pressure Effect on the Kinetics of the Hexaaquairon(II/III) Self-Exchange Reaction in Aqueous Perchloric Acid

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The effect of pressure on the rates of the $Fe(H_2O)_6^{3+/2+}$ and the $Fe(H_2O)_5OH^{2+}/Fe(H_2O)_6^{2+}$ exchange reactions in homogeneous aqueous perchlorate solution can be represented by mean volumes of activation of −11.1 ± 0.4 and +0.8 ± 0.9 $cm^3\ mol^{-1}$, respectively, over the range 0–140 MPa at 2 °C and ionic strength 0.5 mol L^{-1}. These results can be accounted for essentially quantitatively on the basis of the Marcus–Hush theory, with minor modifications to accommodate the pressure dependences of the Fe–Fe separation and presumed anion–cation pairing, on the basis of an adiabatic outer-sphere mechanism for the $Fe(H_2O)_6^{3+/2+}$ exchange and a hydroxide-bridged inner-sphere mechanism for the $Fe(H_2O)_5OH^{2+}/Fe(H_2O)_6^{2+}$ reaction. For the $Fe(H_2O)_6^{3+/2+}$ self-exchange, the question of possible ligand interpenetration in the precursor complex is not unequivocally resolved, but neither aqua-bridged inner-sphere nor markedly nonadiabatic outer-sphere mechanisms are consistent with these measurements.

Silverman and Dodson[5] presented a definitive experimental study of the rate of the hexaaquairon(III/II) self-exchange reaction in homogeneous acidic aqueous solution as long as 1952, but since 1980, the kinetics and mechanism of this reaction have become the subject of extensive theoretical investigations and controversy.[6-18]

In noncomplexing (e.g., perchlorate) media, the reaction occurs by two parallel pathways, one involving $Fe(H_2O)_6^{3+}$ as the oxidant

$$Fe(H_2O)_6^{3+} + {}^*Fe(H_2O)_6^{2+} \overset{k_1}{\rightleftharpoons} Fe(H_2O)_6^{2+} + {}^*Fe(H_2O)_6^{3+} \qquad (1)$$

and the other its conjugate base $Fe(H_2O)_5OH^{2+}$[5,9]

$$Fe(H_2O)_6^{3+} \overset{K_a}{\rightleftharpoons} Fe(H_2O)_5OH^{2+} + H^+ \qquad (2)$$

$$Fe(H_2O)_5OH^{2+} + {}^*Fe(H_2O)_6^{2+} \overset{k_2}{\rightleftharpoons} {}^*Fe(H_2O)_5OH^{2+} + Fe(H_2O)_6^{2+} \qquad (3)$$

The latter path, like those occurring in the presence of complexing anions such as chloride[5] or sulfate,[19] may be expected to be of the inner-sphere (ligand-bridged) type. The mechanism of pathway 1, however, is less readily assigned. An outer-sphere mechanism is usually assumed, but $Fe(H_2O)_6^{3+}$[20,21] and especially $Fe(H_2O)_6^{2+}$[22] are substitutionally labile on the time scale of electron transfer, and an inner-sphere mechanism, presumably involving a bridging aqua ligand, has been proposed by Hupp and Weaver[15] and Bernhard et al.[18] to account for what has been perceived as the anomalously rapid self-exchange of hexaaquairon(II) and -(III) in homogeneous solution. In particular, Hupp and Weaver's electrochemical estimation of the $Fe(H_2O)_6^{3+/2+}$ self-exchange rate[15] gave a result at least 4 orders of magnitude slower than the rate determined directly for homogeneous solution by Silverman and Dodson[5] but in agreement with the self-exchange rate calculated by the Marcus cross-relation from the rates of redox reactions of $Fe(H_2O)_6^{3+}$ or $Fe(H_2O)_6^{2+}$ with other reagents.

Sutin and co-workers,[9] however, have redetermined the homogeneous $Fe^{III/II}(aq)$ exchange rate, and their results are in good agreement with those of Silverman and Dodson[5] and with the

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