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Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Non-Metal Redox Kinetics: General-Acid-Assisted Reactions of Chloramine with Sulfite and Hydrogen Sulfite

Boudin S. Yiin, Dennis M. Walker, and Dale W. Margerum*

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The rate expression for chloramine oxidation of sulfite is $-d[NH_2Cl]/dt = k_{HA}[HA][SO_3^{2-}]_T[NH_2Cl]$, where HA is a general acid and $[SO_3^{2-}]_T = [SO_3^{2-}] + [SHO_3^-]$ (where $[SHO_3^-]$ is the sum of the concentrations of the isomeric forms HSO_3^- and SO_3H^-). Rate constants ($M^{-2}\ s^{-1}$, except as noted, 25.0 °C, $\mu = 0.50$) are resolved for the SO_3^{2-} reactions where HA = H_3O^+ (8×10^{10}), $H_2PO_4^-$ (1.3×10^6), SHO_3^- (3.7×10^5), $B(OH)_3$ (5.8×10^3), NH_4^+ (1.7×10^2) and H_2O ($7.7\ M^{-1}\ s^{-1}$). The k_{HA} values increase with the acid strength of HA (Brønsted $\alpha = 0.71$). In the proposed transition state, simultaneous H^+ transfer from HA to NH_2Cl and Cl^+ transfer from NH_2Cl to SO_3^{2-} occurs. The $ClSO_3^-$ thus formed hydrolyzes rapidly to give SO_4^{2-} and Cl^-. The NH_2Cl reaction with SHO_3^- also is assisted by acids, and k_{HA} values ($M^{-2}\ s^{-1}$) are resolved for H_3O^+ (3.6×10^8), CH_3COOH (2×10^5), $H_2PO_4^-$ (2×10^5), and SHO_3^- (1.3×10^6). Since the latter three acids have k_{HA} values of the same magnitude, cyclic transition states are proposed in which these acids donate a proton to NH_2Cl and accept a proton from SHO_3^- as Cl^+ transfers from nitrogen to sulfur.

Introduction

Chlorine, which is widely used as a disinfectant in potable and waste water, reacts with water to give hypochlorous and hydrochloric acids. When ammonia and organic amines are present, they react with chlorine or hypochlorous acid to form monochloramines, dichloramines, or trichloroamine,[1] and these species can cause significant environmental problems.[2] Sulfite and hydrogen sulfite ions are present in certain industrial wastes, primarily from industry where sodium sulfite is used as a pulping agent, in scrubber waste water derived largely from the burning of high-sulfur coal, and in the pyrometallurgical smelting industry.[3] Sulfur dioxide is frequently used as a dechlorination agent to reduce free chlorine residuals in waste or coolant water. There are relatively few studies of the reaction of chloramine with sulfite. In 1907 Raschig[4,5] reported the stoichiometry in eq 1. More

$$NH_2Cl + H_2SO_3 + H_2O \rightarrow NH_3 + H_2SO_4 + HCl \quad (1)$$

recently, the dechlorination of some organic chloramines with aqueous sulfite solution was shown[6] to give the corresponding amine as a product (eq 2) in a reaction similar to that reported by Raschig.

$$RHNCl + HSO_3^- + H_2O \rightarrow RNH_2 + SO_4^{2-} + Cl^- + 2H^+ \quad (2)$$

The rate of reaction of aqueous sulfite with *N*-chloroalanylalanylalanine increases as the pH of the solution decreases,[7] and the suggested reactivity is: $H_2SO_3 \gg HSO_3^- \gg SO_3^{2-}$. These reactions were studied from pH 4.9 to 9.8 in the presence of 0.02 M phosphate buffer, but the buffer dependence was not investigated.

The reaction of chloramine with iodide ion is general-acid assisted, and a Cl^+ transfer mechanism to give ICl as an intermediate species has been proposed.[8] Iodine monochloride reacts very rapidly with I^- to give I_2 and I_3^- as shown by pulsed-accelerated-flow studies.[9] In the present study, the effect of general acids on the chloroamine reaction with sulfite, is studied and a simultaneous H^+ and Cl^+ transfer mechanism is again proposed (eq 3) followed by the rapid hydrolysis of chlorosulfate (eq 4).

$$HA + NH_2Cl + SO_3^{2-} \rightarrow A^- + NH_3 + ClSO_3^- \quad (3)$$

$$ClSO_3^- + H_2O \rightarrow SO_4^{2-} + Cl^- + 2H^+ \quad (4)$$

We find that both SHO_3^- and SO_3^{2-} can act as reductants with NH_2Cl and that the reactions are general-acid assisted. It is important to note that SHO_3^- can be a redox reactant, as well as a general acid that catalyzes the reaction. Thus, rate terms are found with both first-order and second-order terms in the total concentration of sulfite and hydrogen sulfite. The multiple paths that result because of more than one reductant and various general-acid-assisted reactions are resolved by wide variations in pH and buffer concentrations.

Golding[10] proposed two isomeric forms of hydrogen sulfite: SO_3H^-, where the proton is attached to one of the oxygens, and HSO_3^-, where the proton is attached to the sulfur. Maylor et al.[11] reported evidence that HSO_3^- is present in solid compounds that show S–H stretching in their infrared spectra. Although Hayon et al.[12] found no evidence to show the isomerization of hydrogen sulfite, the existence of the two isomeric forms has been confirmed by more recent studies.[13,14] Horner and Connick[15] reported that the equilibrium concentration ratio of the two isomers, $[SO_3H^-]/[HSO_3^-]$, equals 4.9 at 25 °C in solutions of 1.0 M ionic strength. The two forms can both act as general acids. However, as reductants these two isomeric forms may act quite differently because HSO_3^- does not have an electron pair available on sulfur for the direct chlorine transfer. At high concentration in aqueous solution, hydrogen sulfite ion dimerizes[10–13] to form the species $S_2O_5^{2-}$. The equilibrium constant for eq 5 (where SHO_3^- refers

$$2SHO_3^- \rightleftarrows S_2O_5^{2-} + H_2O \quad (5)$$

to the sum of SO_3H^- and HSO_3^-)[15] equals $6.5 \times 10^{-2}\ M^{-1}$ at 25 °C and $\mu = 0.5$ M. In the present study, the total sulfite concentration is kept low in order to avoid any formation of $S_2O_5^{2-}$. At the maximum hydrogen sulfite concentration used (13.2 mM),

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the $S_2O_5^{2-}$ concentration is less than 0.1% of the hydrogen sulfite concentration.

Experimental Section

Reagents. A 5% solution of sodium hypochlorite (Mallinckrodt) was used as the source of chlorine. The concentration of stock solutions was determined by the absorbance of OCl^- at 292 nm ($\epsilon = 350\ M^{-1}\ cm^{-1}$)[16] with a Perkin-Elmer 320 spectrophotometer. Ammonium hydroxide was diluted and standardized by acidimetry using bromocresol green indicator. Acetate buffer was prepared from a stock acetic acid solution, which was standardized by titration with NaOH to the phenolphthalein end point. Other buffers were prepared from sodium salts of tetraborate and dihydrogen phosphate by weight. Ionic strength was maintained at 0.50 M with sodium perchlorate, which was prepared by the neutralization of sodium carbonate with perchloric acid. An Orion Model 601A Research digital pH meter equipped with a Corning combination electrode was used for pH measurements. The pH values were measured to within ±0.01 units and were corrected to $-\log [H^+]$ values at 25.0 °C and $\mu = 0.50$ M based on electrode calibrations by titrations of standard $HClO_4$ (0.005 M) with standard NaOH (0.10 M) solutions.

Fresh sulfite solutions were prepared by dissolving weighed amounts of sodium sulfite in water and were standardized immediately prior to use by iodometric titration.[17] Anaerobic and metal-free conditions were strictly observed during use and handling to avoid the trace-metal-catalyzed autoxidation of sulfite.[18-22]

Fresh chloramine solutions were prepared by combining solutions of hypochlorite with 5–10-fold excess ammonia thorugh a T-mixer to ensure efficient mixing. The solutions were standardized by the absorbance maximum of NH_2Cl at 243 nm ($\epsilon = 461\ M^{-1}\ cm^{-1}$).[23] The pH of both hypochlorite and ammonia solutions was adjusted to 9.0 before mixing.

Stoichiometric Measurements. The stoichiometry of the reaction was determined by spectrophotometric titration. Aliquots of sulfite (5 μL) of known titer were injected by syringe into a septum-capped 2.0-cm optical cell that contained argon-purged chloramine solution. Spectral scans were taken from 200–400 nm within 1 min of each addition. Several scans were taken of the same aliquot at 5-min intervals to determine when the reaction was complete. Concentration changes were determined by monitoring the chloramine absorbance loss at its λ_{max} (243 nm).

Kinetic Measurements. The kinetics of the acid-catalyzed reduction of NH_2Cl with sulfite were determined with a Durrum stopped-flow spectrophotometer with on-line digital data acquisition. Calculations were performed by a Hewlett-Packard 2100S minicomputer. Pseudo-first-order conditions were maintained by the use of at least a 10-fold excess of sulfite in each reaction mixture. Rate constants were determined from a least-squares linear regression plot of log $(A_\infty - A_t)$ vs time, where A_∞ represents the final absorbance and A_t is the absorbance at any time. Data were analyzed over at least 4 half-lives. The rate constants were averaged for three to five runs and had a relative error of less than 5%. All solutions were thermostated at 25.0 ± 0.1 °C.

Experimental first-order rate constants (k'_{obsd}) larger than 80 s^{-1} were corrected for mixing effects in accord with eq 6.[24] The k_m value in eq

$$k_{obsd} = k'_{obsd}/(1 - (k'_{obsd}/k_m)) \qquad (6)$$

6 is a first-order mixing rate constant that equal to 1700 s^{-1} for this instrument. The mixing correction permitted k_{obsd} values as large as 600 s^{-1} to be determined. These k_{obsd} values are used to calculate the corresponding second- and third-order rate constants.

Acetate-buffered reactions were monitored at the wavelength of maximum absorbance for chloramine. The other reactions were monitored at an absorbance shoulder (270 nm) to avoid the inteference from SO_3^{2-} absorbance. Both of the reactants were prepared in the same buffer before mixing, except for the acetate-buffered system. In the acetate-buffered study only sulfite was prepared in the buffer to avoid the slow disproportionation[1] of NH_2Cl (to $NHCl_2$ and NH_4^+) that occurs at lower pH. All measurements of pH were taken after the reactions.

Ion Chromatographic Analysis. One of the products of the redox reaction, SO_4^{2-}, was quantitatively determined by ion chromatography. A Wescan ion analyzer, Model 266, was used with a conductivity detector at 30 °C. Separation of the products was performed on a Wescan Anion/R column. The mobile phase was 4×10^{-3} M potassium hydrogen *o*-phthalate (KHP) solution adjusted to pH 4.5. A calibration curve, prepared from sodium sulfate standard solutions, used peak area measurements from a Hewlett-Packard 3390A integrator for quantitative analysis of sulfate. The retention time of the sulfate was 7.0–7.5 min and depended on the sulfate concentration (0.5–2.0 mM). The SHO_3^- ion had a retention time similar to that of SO_4^{2-} ion. To avoid interference from SHO_3^- in the quantitative measurements of sulfate, excess NH_2Cl was used to deplete the sulfite. Sulfamate ion ($SO_3NH_2^-$) was prepared from solid sulfamic acid. The retention time of sulfamate (2.5–10 mM) was 2.8–3.3 min. Chloride had a retention time similar to that for sulfamate, and the peaks usually overlapped.

Results

Stoichiometry of the Reaction. Our results give a stoichiometry of 1.03 ± 0.15 mol of sulfite/mol of chloramine in agreement with Raschig.[4] We tested the reaction with both NH_2Cl and sulfite in excess at pH 8.4. The ion chromatographic results show that SO_4^{2-} is the product as opposed to $SO_3NH_2^-$. A 98 ± 2% yield of SO_4^{2-} is observed when excess NH_2Cl (1 mM) reacts with SO_3^{2-} (0.42–0.90 mM) at pH 9. On the basis of the long lifetime[25-27] of the sulfamate ion in aqueous solution and the lack of a sulfamate peak in the ion chromatographic experiment, it cannot be an intermediate or a product of the sulfite reactions with chloramine under our conditions.

Kinetic Studies. The rate of reaction of NH_2Cl with excess sulfite in aqueous solution (with or without added buffer in solution) shows a first-order dependence upon the concentration of chloramine (eq 7). The k_{obsd} values depend upon the concen-

$$-d[NH_2Cl]/dt = k_{obsd}[NH_2Cl] \qquad (7)$$

trations of SO_3^{2-}, SHO_3^-, H^+, and buffer acids (HA). A mechanism with eight parallel reaction paths of sulfite with chloramine is proposed (eq 8–15) in order to account for observed rate de-

$$HA + NH_2Cl + SO_3^{2-} \xrightarrow{k_1} \text{products} \qquad (8)$$

$$HA + NH_2Cl + SHO_3^- \xrightarrow{k_2} \text{products} \qquad (9)$$

$$H^+ + NH_2Cl + SO_3^{2-} \xrightarrow{k_3} \text{products} \qquad (10)$$

$$H^+ + NH_2Cl + SHO_3^- \xrightarrow{k_4} \text{products} \qquad (11)$$

$$H_2O + NH_2Cl + SO_3^{2-} \xrightarrow{k_5} \text{products} \qquad (12)$$

$$H_2O + NH_2Cl + SHO_3^- \xrightarrow{k_6} \text{products} \qquad (13)$$

$$SHO_3^- + NH_2Cl + SO_3^{2-} \xrightarrow{k_7} \text{products} \qquad (14)$$

$$SHO_3^- + NH_2Cl + SHO_3^- \xrightarrow{k_8} \text{products} \qquad (15)$$

pendences. The resulting pseudo-first-order rate constant, k_{obsd}, for the reaction of excess buffer acids and sulfite with NH_2Cl is represented in eq 16, which can be rearranged to give eq 17. The

$$k_{obsd} = k_1[HA][SO_3^{2-}] + k_2[HA][SHO_3^-] + k_3[H^+][SO_3^{2-}] + k_4[H^+][SHO_3^-] + k_5[SO_3^{2-}] + k_6[SHO_3^-] + k_7[SHO_3^-][SO_3^{2-}] + k_8[SHO_3^-]^2 \qquad (16)$$

$$k_{obsd}(1 + K_H[H^+])/[SO_3^{2-}]_T = (k_1 + k_2K_H[H^+])[HA] + (k_3 + k_6K_H)[H^+] + k_4K_H[H^+]^2 + k_5 + (k_7 + k_8K_H[H^+])[SHO_3^-] \qquad (17)$$

protonation constant of SO_3^{2-}, $K_H = [SHO_3^-]/([H^+][SO_3^{2-}])$, is $4.0 \times 10^6\ M^{-1}$, and $[SO_3^{2-}]_T = [SO_3^{2-}] + [SHO_3^-]$. A log K_H

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Table I. Pseudo-First-Order Rate Constants for the Reaction of Excess Sulfite with Chloramine without Additional Buffer[a]

$-\log [H^+]$	$[SO_3^{2-}]_T$, mM	$[SHO_3^-]$, mM	k_{obsd}, s^{-1}
6.88	38.42	13.22	603 ± 5
6.88	29.15	10.03	363 ± 10
6.88	21.20	7.30	214 ± 4
6.88	9.63	3.31	86 ± 2
7.07	38.57	9.76	419 ± 16
7.07	29.15	7.38	278 ± 4
7.07	21.20	5.37	160 ± 4
7.07	9.73	2.46	60 ± 1
7.27	38.75	6.83	273 ± 7
7.27	29.15	5.13	182 ± 2
7.27	21.20	3.73	111 ± 2
7.27	9.87	1.74	42 ± 1
7.46	38.58	4.68	172 ± 3
7.46	29.15	3.54	113 ± 2
7.46	21.20	2.57	75 ± 2
7.46	9.90	1.20	27 ± 1

[a] Conditions: $\mu = 0.50$ M ($NaClO_4$), 25.0 ± 0.1 °C; $[NH_2Cl]_{init} = 5.00 \times 10^{-4}$ M.

value of 6.6 was reported[28] at $\mu = 0.50$, but the temperature was not given. However, we obtain the same value by an extrapolation against $\mu^{1/2}/(1 + \mu^{1/2})$ of values measured at lower μ and 25.0 °C.[29] These log K_H values are only 0.1 larger than that obtained by a similar correction of results in 1.0 M $NaClO_4$ at 25.0 °C.[30] The general acids (HA) from the buffers are NH_4^+, $B(OH)_3$, $H_2PO_4^-$, and CH_3COOH.

Reactions in NaOH. At high pH, with no buffers present, all the acid terms in eq 17 can be eliminated so that only the k_5 term remains (eq 18). Reactions were measured at five NaOH concentrations from 0.10 to 0.50 M with 5.00×10^{-4} M NH_2Cl and 1.0×10^{-2} M SO_3^{2-}. The k_{obsd} values did not vary with the OH^- concentration, and $k_5 = 7.7 \pm 0.2$ M^{-1} s^{-1} (25.0 °C, $\mu = 0.50$).

$$k_5 = k_{obsd}/[SO_3^{2-}]_T \qquad (18)$$

Reactions Buffered by SHO_3^- and SO_3^{2-}. Hydrogen sulfite is not only a redox reactant but is also a general acid that can assist the reaction. In order to simplify the analysis of the kinetics data, experiments were carried out without adding any other buffers, and the pH values were maintained close to the pK_a value of SO_3H^-. Under these conditions, terms with [HA] in eq 17 can be eliminated. The kinetic results and reaction conditions are listed in Table I. The values of the $k_5[SO_3^{2-}]_T/(1 + K_H[H^+])$ term in eq 17 are negligible compared to the k_{obsd} values, so the k_5 term also can be neglected. At constant $-\log [H^+]$ values of 6.88, 7.07, 7.27, and 7.46, the linear relationships between $k_{obsd}(1 + K_H[H^+])/[SO_3^{2-}]_T$ and $[SHO_3^-]$ are plotted in Figure 1. The slopes of the lines correspond to $(k_7 + k_8K_H[H^+])$ and when plotted against $[H^+]$ give a linear relationship that yields an intercept, $k_7 = 3.7\ (\pm 0.4) \times 10^5$ M^{-2} s^{-1}, and a slope, $k_8K_H = 5.2\ (\pm 0.4) \times 10^{12}$ M^{-3} s^{-1} ($k_8 = 1.3 \times 10^6$ M^{-2} s^{-1}). The values of the intercepts in Figure 1 are directly proportional to $[H^+]$, and because there is no $[H^+]^2$ dependence, the contribution of the k_4 reaction path is not significant under these conditions. The slope, $k_3 + k_6K_H$, equals $6.7\ (\pm 0.2) \times 10^{10}$ M^{-2} s^{-1}, and this path carries 41–75% of the reaction. Subsequent evaluation of k_4 shows that this term contributes less than 0.2% of the total rate under these conditions.

Reactions Buffered with Ammonia and with Borate. In the ammonia- and borate-buffered systems, the previously determined k_5, k_7, and k_8 values are used to simplify the calculation of the other rate constants. The experimental conditions and results are listed in Tables II and III. The $k_5 + (k_7 + k_8K_H[H^+])[SHO_3^-]$ term can be subtracted from the left-hand side of eq 17 to give k^{cor} values. In the ammonia-buffered system $1 + K_H[H^+] \simeq 1$, and the revised relationship given in eq 19 is plotted in Figure 2, where $[HA] = [NH_4^+]$. A pK_a value of 9.32 has been reported[31] for NH_4^+ at $\mu = 0.50$ and 25.0 °C. The data are resolved for $-\log [H^+]$ values of 9.04, 9.24, 9.43, and 9.63. The slopes from Figure 2 have a large uncertainty relative to their dependence on $[H^+]$, and their average value is taken as a k_1 value of $1.7\ (\pm 0.3) \times 10^2$ M^{-2} s^{-1}. Under these high pH conditions, the concentration of SHO_3^- is small and the k_2 term cannot be evaluated.

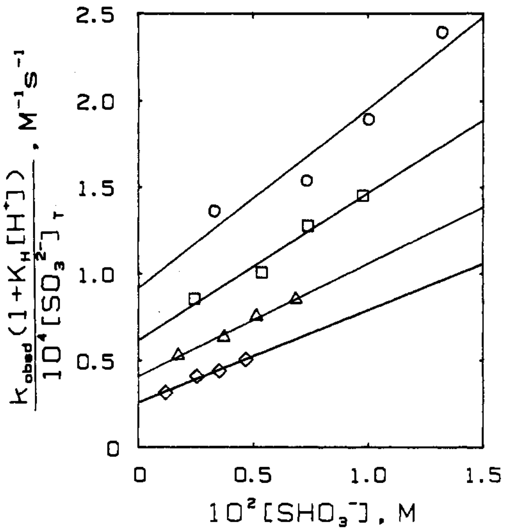

Figure 1. SHO_3^- dependence for the reaction of sulfite with NH_2Cl at different $-\log [H^+]$ values: (○) $-\log [H^+] = 6.88$; (□) $-\log [H^+] = 7.07$; (△) $-\log [H^+] = 7.27$; (◇) $-\log [H^+] = 7.46$. Slope $= k_7 + k_8K_H[H^+]$; intercept $= (k_3 + k_6K_H)[H^+]$.

Table II. Pseudo-First-Order Rate Constants for the Reaction of Excess Sulfite with Chloramine in Ammonia-Buffered Solution[a]

$-\log [H^+]$	$[NH_3]_T$, M	$[SO_3^{2-}]_T$, mM	k_{obsd}, s^{-1}
9.04	0.25	10.00	1.050 ± 0.006
9.04	0.20	9.93	0.98 ± 0.01
9.04	0.15	9.98	0.97 ± 0.01
9.04	0.10	9.97	0.843 ± 0.009
9.24	0.25	10.00	0.762 ± 0.008
9.24	0.20	9.93	0.697 ± 0.002
9.24	0.15	9.98	0.698 ± 0.008
9.24	0.10	9.97	0.58 ± 0.01
9.43	0.25	10.00	0.555 ± 0.004
9.43	0.20	9.93	0.511 ± 0.002
9.43	0.15	9.98	0.480 ± 0.003
9.43	0.10	9.97	0.46 ± 0.01
9.63	0.25	10.00	0.404 ± 0.003
9.63	0.20	9.93	0.368 ± 0.008
9.63	0.15	9.98	0.362 ± 0.002
9.63	0.10	9.97	0.332 ± 0.003

[a] Conditions: $\mu = 0.50$ M ($NaClO_4$), 25.0 ± 0.1 °C, $[NH_2Cl]_{init} = 5.00 \times 10^{-4}$ M.

$$k^{cor} = (k_1 + k_2K_H[H^+])[HA] + (k_3 + k_6K_H)[H^+] + k_4K_H[H^+]^2 \qquad (19)$$

The intercepts in Figure 2 have a linear hydrogen ion dependence (eq 20), which indicates that the k_4 term is not significant for this system. The resolved $k_3 + k_6K_H$ value equals $5.3\ (\pm 0.4) \times 10^{10}$ M^{-2} s^{-1}. It is not possible to evaluate the k_3 and k_6K_H terms separately.

$$\text{intercept} = (k_3 + k_6K_H)[H^+] \qquad (20)$$

In the borate-buffered system, the same data treatment as in the ammonia-buffered system is used. Corrected second-order rate constants are plotted against $[B(OH)_3]$ concentrations in

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Table III. Pseudo-First-Order Rate Constants for the Reaction of Excess Sulfite with Chloramine in Borate Buffer Solution[a]

$-\log [H^+]$	$[B(OH)_3]_T$, M	$[SO_3^{2-}]_T$, mM	k_{obsd}, s^{-1}
8.53	0.025	9.68	3.54 ± 0.05
8.53	0.020	10.53	3.82 ± 0.02
8.53	0.015	11.31	3.81 ± 0.03
8.53	0.010	10.83	3.56 ± 0.03
8.78	0.025	9.68	2.47 ● 0.01
8.78	0.020	10.53	2.41 ± 0.01
8.78	0.015	11.31	2.58 ± 0.05
8.78	0.010	10.83	2.21 ± 0.02
9.02	0.025	9.68	1.59 ± 0.02
9.02	0.020	10.53	1.52 ± 0.01
9.02	0.015	11.31	1.57 ± 0.01
9.02	0.010	10.83	1.28 ± 0.01
9.26	0.025	9.68	0.98 ± 0.01
9.26	0.020	10.53	0.94 ± 0.02
9.26	0.015	11.31	0.98 ± 0.01
9.26	0.010	10.83	0.82 ± 0.01
9.51	0.025	9.68	0.58 ± 0.01
9.51	0.020	10.53	0.61 ± 0.01
9.51	0.015	11.31	0.57 ± 0.01
9.51	0.010	10.83	0.50 ± 0.01

[a] Conditions: $\mu = 0.50$ M ($NaClO_4$), 25.0 ± 0.1 °C, $[NH_2Cl]_{init} = 5.00 \times 10^{-4}$ M.

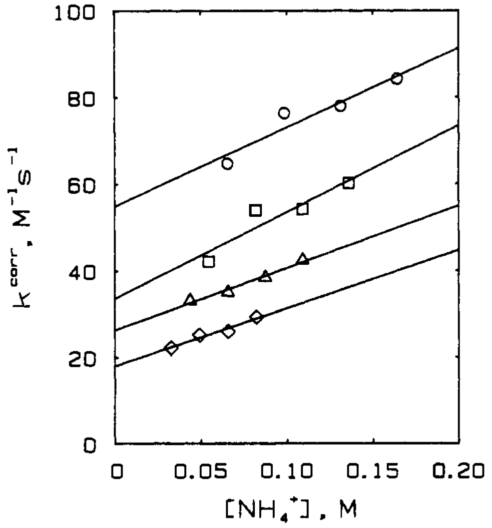

Figure 2. NH_4^+ dependence for the reaction of sulfite with NH_2Cl at different $-\log [H^+]$ values: (○) $-\log [H^+] = 9.04$; (□) $-\log [H^+] = 9.24$; (△) $-\log [H^+] = 9.43$; (◇) $-\log [H^+] = 9.63$. Slope = k_1; intercept = $(k_3 + k_6K_H)[H^+]$.

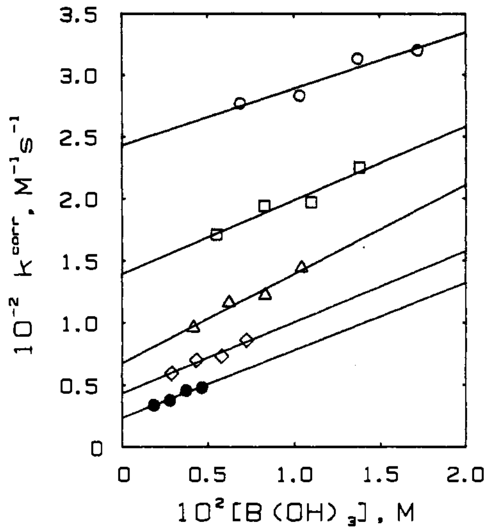

Figure 3. $B(OH)_3$ dependence for the reaction of sulfite with NH_2Cl at different $-\log [H^+]$ values: (○) $-\log [H^+] = 8.53$; (□) $-\log [H^+] = 8.78$; (△) $-\log [H^+] = 9.02$; (◇) $-\log [H^+] = 9.26$; (●) $-\log [H^+] = 9.51$. Slope = k_1; intercept = $(k_3 + k_6K_H)[H^+]$.

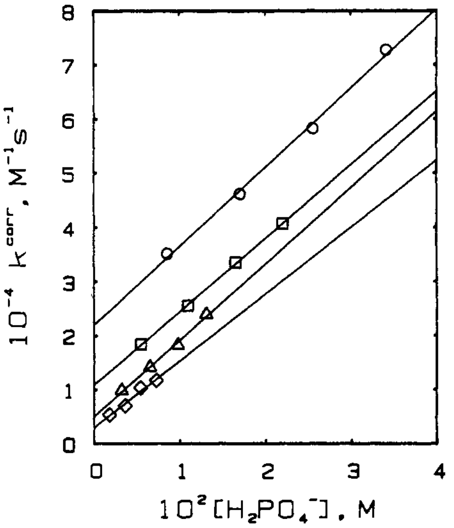

Figure 4. $H_2PO_4^-$ dependence for the reaction of sulfite with NH_2Cl at different $-\log [H^+]$ values: (○) $-\log [H^+] = 6.59$; (□) $-\log [H^+] = 6.88$; (△) $-\log [H^+] = 7.17$; (◇) = $-\log [H^+] = 7.46$. Slope = $k_1 + k_2K_H[H^+]$; intercept = $(k_3 + k_6K_H)[H^+]$.

Table IV. Pseudo-First-Order Rate Constants for the Reaction of Excess Sulfite with Chloramine in Phosphate Buffer Solution[a]

$-\log [H^+]$	$[PO_4^{3-}]_T$, M	$[SO_3^{2-}]_T$, mM	k_{obsd}, s^{-1}
6.59	0.08	9.33	373 ± 17
6.59	0.06	9.46	311 ± 14
6.59	0.04	9.23	247 ± 8
6.59	0.02	9.25	198 ± 11
6.88	0.08	9.45	274 ± 14
6.88	0.06	9.58	233 ± 8
6.88	0.04	9.40	179 ± 4
6.88	0.02	9.40	135 ± 2
7.17	0.08	9.54	191 ± 8
7.17	0.06	9.62	150 ± 3
7.17	0.04	9.52	118 ± 5
7.17	0.02	9.62	86 ± 3
7.46	0.08	9.60	105 ± 2
7.46	0.06	9.66	94 ± 3
7.46	0.04	9.60	64 ± 2
7.46	0.02	9.65	51 ± 1

[a] Conditions: $\mu = 0.50$ M ($NaClO_4$), 25.0 ± 0.1 °C, $[NH_2Cl]_{init} = 5.00 \times 10^{-4}$ M.

Figure 3 at $-\log [H^+]$ values of 8.53, 8.78, 9.02, 9.26, and 9.51. A pK_a value of 8.87 has been reported[32] for $B(OH)_3$ at $\mu = 0.50$ and 25.0 °C. The slopes in Figure 3 do not have a significant dependence on $[H^+]$. The k_2 value cannot be resolved in this buffered system because the k_1 term predominates. The k_1 value is taken as the average of these slopes ($k_1 = 5.8\ (\pm 0.9) \times 10^3\ M^{-2}\ s^{-1}$). The intercepts in Figure 3 have a linear $[H^+]$ dependence that gives a $k_3 + k_6K_H$ value of $8.4\ (\pm 0.3) \times 10^{10}\ M^{-2}\ s^{-1}$.

Reactions Buffered with Phosphate. The same method used in the above buffered systems is also used to analyze the kinetics data (in Table IV) in a phosphate-buffered system. In this system, the $k_5 + (k_7 + k_8K_H[H^+])[SHO_3^-]$ term is subtracted from the left-hand side of eq 17 to give k^{cor} values. The linear relationships between k_{cor} and $[H_2PO_4^-]$ are shown in Figure 4 for $-\log [H^+]$ values of 6.59, 6.88, 7.17, and 7.46. A pK_a value of 6.46 has been reported[33] for $H_2PO_4^-$ at $\mu = 0.50$ and 25.0 °C. The slopes in Figure 4 give linear plots against $[H^+]$ that enable both k_1 and k_2 to be resolved. $k_1 = 1.28\ (\pm 0.07) \times 10^5\ M^{-2}\ s^{-1}$, and $k_2 = 2 \times 10^5\ M^{-2}\ s^{-1}$ ($k_2K_H = 8\ (\pm 5) \times 10^{11}\ M^{-3}\ s^{-1}$). The $k_3 + k_6K_H$ term is evaluated from the intercepts in Figure 4 and equals $8.7\ (\pm 0.3) \times 10^{10}\ M^{-2}\ s^{-1}$.

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(32) Owen, B. B.; King, E. J. *J. Am. Chem. Soc.* **1943**, *65*, 1612–1620.
(33) Mesmer, R. E.; Baes, C. F. *J. Solution Chem.* **1974**, *3*, 307–321.

Table V. Pseudo-First-Order Rate Constants for the Reaction of Excess Sulfite with Chloramine in Acetate Buffer Solution[a]

$-\log [H^+]$	$[CH_3COO^-]_T$, M	$[SO_3^{2-}]_T$, mM	k_{obsd}, s^{-1}
4.45	0.150	7.01	387 ± 7
4.45	0.125	6.35	324 ± 4
4.45	0.100	5.81	285 ± 6
4.45	0.075	5.98	284 ± 2
4.55	0.150	6.99	372 ± 1
4.55	0.125	6.03	300 ± 6
4.55	0.100	5.74	277 ± 5
4.55	0.075	5.94	267 ± 9
4.68	0.150	6.91	331 ± 9
4.68	0.125	6.25	275 ± 7
4.68	0.100	5.66	240 ± 6
4.68	0.075	5.81	244 ± 3
4.78	0.150	6.86	302 ± 2
4.78	0.125	6.16	258 ± 5
4.78	0.100	5.57	229 ± 9
4.78	0.075	5.77	227 ± 8

[a] Conditions: μ = 0.50 M ($NaClO_4$), 25.0 ± 0.1 °C, $[NH_2Cl]_{init}$ = 4.25 × 10^{-4} M.

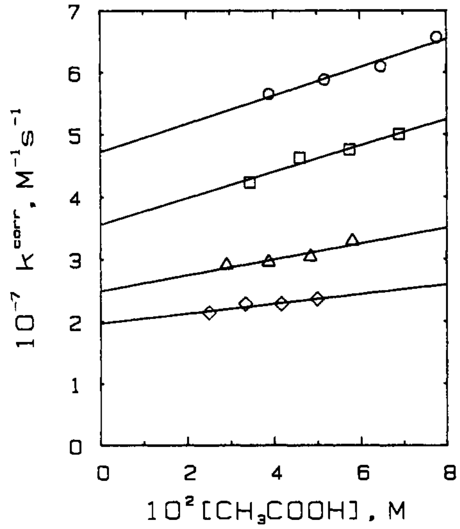

Figure 5. CH_3COOH dependence for the reaction of sulfite with NH_2Cl at different $-\log [H^+]$ values: (○) $-\log [H^+]$ = 4.45; (□) $-\log [H^+]$ = 4.55; (△) $-\log [H^+]$ = 4.68; (◇) $-\log [H^+]$ = 4.78. Slope = $k_2K_H[H^+]$; intercept = $(k_3 + k_6K_H)[H^+] + k_4K_H[H^+]^2$.

Reactions Buffered with Acetate. The conditions and results of the acetate-buffered reactions are listed in Table V. In this buffered system, the $k_5 + (k_7 + k_8K_H[H^+])[SHO_3^-]$ term in eq 17 is again subtracted from the left-hand side of eq 17, and the k^{cor} values vs $[CH_3COOH]$ are plotted (Figure 5) for $-\log [H^+]$ values of 4.45, 4.55, 4.68, and 4.78. A pK_a value of 4.48 has been reported[34] for CH_3COOH at μ = 0.50 and 25.0 °C. Once again the slopes are plotted against $[H^+]$. The least-squares line gives a negative intercept with a k_1 value of $-4\ (\pm 4) \times 10^6\ M^{-2}\ s^{-1}$. Hence, the k_1 term can be assumed to be negligible compared to the $k_2K_H[H^+]$ term. In the $-\log[H^+]$ range used for the acetate-buffered system, the SO_3^{2-} concentration is much smaller than the SHO_3^- concentration. Hence, it is difficult to determine the k_1 value under these experimental conditions. The k_2 value equals $2 \times 10^5\ M^{-2}\ s^{-1}$ ($k_2K_H = 8\ (\pm 2) \times 10^{11}\ M^{-3}\ s^{-1}$). The intercepts in Figure 5 correspond to $(k_3 + k_6K_H)[H^+] + k_4K_H[H^+]^2$, and a plot of the (intercept/$[H^+]$) vs $[H^+]$ is linear, which shows that the k_4 term is significant in this system. The resolved $k_3 + k_6K_H$ and k_4 values are 1.03 (±0.09) × 10^{11} and 2.1 × $10^8\ M^{-2}\ s^{-1}$ ($k_4K_H = 8.4\ (\pm 0.3) \times 10^{14}\ M^{-3}\ s^{-1}$), respectively.

Reactions in Dilute Acid. Below pH 3 the reactions of chloramine and hydrogen sulfite become too fast to measure by stopped-flow methods. In addition, neither reactant can be stored in acid because of SO_2 formation from sulfite and the disproportionation of chloramine to give dichloramine and ammonium ion.[1] These problems can be avoided by storing NH_2Cl in neutral solutions and mixing it with excess sulfite at pH ≈3.3, where the NH_2Cl disproportionation rate is slow compared to its reaction with sulfite and there is very little SO_2 present ($SHO_3^- + H^+ \rightleftarrows SO_2 + H_2O$; $K = 10^{1.37}\ M^{-1}$).[30] Table VI gives the reaction conditions used to study this system. The initial NH_2Cl concentration is $\sim 10^{-4}$ M and the SHO_3^- concentration is $\sim 10^{-3}$ M, so that there is only a small change in pH during the reaction. The experimental $-\log [H^+]$ value is measured after the reaction and corresponds closely to the acidity of the final fraction of the reaction that can be observed. The k_{obsd} values are corrected for small contributions by the k_8 term, and the k_3 term (an average k_3 value of $8 \times 10^{10}\ M^{-2}\ s^{-1}$ is used) in order to evaluate the k_4 term. This gives a k_4 term of 3.6 (±0.4) × $10^8\ M^{-2}\ s^{-1}$. This is larger than the value estimated from the acetate-buffered reactions, but it should be more accurate because the the k_4 path carries 85–88% of the reaction under these conditions and smaller corrections from other paths are needed to evaluate k_4.

Table VI. Pseudo-First-Order Rate Constants for the Reaction of Excess Sulfite with NH_2Cl in Dilute Acid[a]

$-\log [H^+]$	$[SO_3^{2-}]_T$, mM	k_{obsd}, s^{-1}
3.40	1.44	272 ± 17[b]
3.32	1.07	179 ± 13[c]
3.48	1.16	163 ± 9[c]
3.42	1.14	182 ± 8[c]

[a] Conditions: μ = 0.50 M ($NaClO_4$), 25.0 °C. [b] $[NH_2Cl]_{init}$ = 1.25 × 10^{-4} M. [c] $[NH_2Cl]_{init}$ = 1.08 × 10^{-4} M.

Discussion

The percent contribution of each path, in accord with the corresponding resolved rate constants, is given in Table VII for the range of conditions used. The k_5 path accounts for 100% of the reaction in NaOH, and it contributes significantly to reactions in NH_4^+ buffer (7–23%) and in $B(OH)_3$ buffer (2–17%). Its contribution is negligible for all other conditions. The contribution of the $k_4K_H[H^+]^2$ path is appreciable only in more acidic conditions with the CH_3COOH and $HClO_4$ solutions. On the other hand, the $(k_3 + k_6K_H)[H^+]$ path carriers a sizable percent of the reaction under all the conditions except in NaOH. In Table VII, we have assigned all of this path to the k_3 term rather than to the k_6K_H term, because of the low value found for k_5 (we expect $k_6 \leq k_5$), where H_2O also acts as an acid. The average k_3 value resolved from the reactions in five buffers is (8 ± 2) × $10^{10}\ M^{-2}\ s^{-1}$. The greatest source of error in the determination of the individual rate constants arises from the experimental adjustment of the pH to specified values in order to resolve the H^+ and HA terms.

As seen in Table VII, it was not possible to determine k_1 in the CH_3COOH reactions because of the combination of low SO_3^{2-} concentrations and the sizable contributions of the SHO_3^- paths (k_2, k_4, and k_8) and the H_3O^+ path (k_3). Similarly, it was not possible to determine the k_2 values in the borate and ammonia buffers where the SHO_3^- concentration is very low. Despite these difficulties, general-acid-assisted rate constants are resolved for the reactions of H_2O, NH_4^+, $B(OH)_3$, $H_2PO_4^-$, SHO_3^-, and H_3O^+ with NH_2Cl and SO_3^{2-} and for the reactions of $H_2PO_4^-$, SHO_3^-, CH_3COOH, and H_3O^+ with NH_2Cl and SHO_3^-.

Acid-Assisted Reactions of NH_2Cl with SO_3^{2-}. The summary of rate constants in Table VIII shows the clear relationship between the acidity of the general acids and the magnitude of the third-order rate constants for the reactions of NH_2Cl with SO_3^{2-}. The rate constants increase with acidity in accord with the Brønsted–Pedersen relationship[35] (eq 21), where p is the number

$$\log k_{HA}/p = \log G_A + \alpha[\log (K_a q/p)] \qquad (21)$$

of equivalent protons in the acid HA, q is the number of sites that

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(34) Deneux, M.; Meilleur, R.; Benoit, R. L. *Can. J. Chem.* **1968**, *46*, 1383–1388.

(35) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 194–201.

Table VII. Resolved Rate Constants and Percent of Reaction Carried by Each Path

path[a]	dilute $HClO_4$[b]	CH_3COOH	SHO_3^-	$H_2PO_4^-$	$B(OH)_3$	NH_4^+	NaOH[c]
k_1, M^{-2} s^{-1}	NA[d]	ND[e]	NA	1.3×10^6	5.8×10^3	1.7×10^2	NA
% of reacn	NA	0	NA	26–76	12–45	16–34	NA
k_2, M^{-2} s^{-1}	NA	2×10^5	NA	2×10^5	ND	ND	NA
% of reacn	NA	13–28	NA	1–6	0	0	NA
k_3, M^{-2} s^{-1}	8×10^{10}[f]	1.0×10^{11}	6.7×10^{10}	8.7×10^{10}	8.4×10^{10}	5.3×10^{10}	ND
% of reacn	11–13	47–65	41–75	24–53	43–75	21–52	0
k_4, M^{-2} s^{-1}	3.6×10^8	2.1×10^8	ND	ND	ND	ND	ND
% of reacn	85–88	8–16	<0.2	<0.2	0	0	0
k_5, M^{-1} s^{-1}	C[g]	C	C	C	C	C	7.7
% of reacn	0[g]	0	<0.3	<0.2	2–17	7–23	100
k_7, M^{-2} s^{-1}	C	C	3.7×10^5	C	C	C	ND
% of reacn	0	0	9–35	2–7	7–14	9–14	0
k_8, M^{-2} s^{-1}	C	C	1.3×10^6	C	C	C	ND
% of reacn	0.8–1.0	15–20	7–42	2–15	<0.6	<0.2	0

[a] From eq 8–15. Third-order rate constants except for k_5, which is a second-order constant. The k_3 values are based on the assumption $k_3 \gg k_6K_H$. [b] $-\log [H^+] = 3.3–3.5$. [c] $[NaOH] = 0.1–0.5$ M. [d] NA = not applicable. [e] ND = not determined. [f] The k_3 value is taken as the average of the rate constants determined with buffers. [g] C = Calculation contributions from values determined the in NaOH or SHO_3^- systems; a zero value for % of reacn is less than 0.1%.

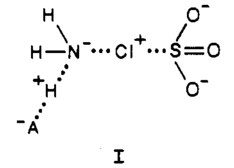
Table VIII. Third-Order Rate Constants as a Function of the Acidity of General Acids

HA	p/q	$\log K_a$	k_{HA}, M^{-2} s^{-1}
		$HA + NH_2Cl + SO_3^{2-}$	
H_2O	2/3	−15.46[a]	1.4×10^{-1}[h]
NH_4^+	4/1	−9.32[b]	1.7×10^2
$B(OH)_3$	1/4	−8.87[c]	5.8×10^3
SHO_3^-	1/3	−6.6[d]	3.7×10^5
$H_2PO_4^-$	2/3	−6.46[e]	1.3×10^6
H_3O^+	3/2	+1.74[f]	8×10^{10}
		$HA + NH_2Cl + SHO_3^-$	
SHO_3^-	1/3	−6.6[d]	1.3×10^6 (1.1×10^6)[i]
$H_2PO_4^-$	2/3	−6.46[e]	2×10^5 (1.7×10^5)[i]
CH_3COOH	1/2	−4.48[g]	2×10^5 (1.7×10^5)[i]
H_3O^+	3/2	+1.74[f]	3.6×10^8 (3.0×10^5)[i]

[a] Based on $pK_w = 13.72$ ($\mu = 0.50$, 25.0 °C) and 55.5 M H_2O. [b] Reference 31. [c] Reference 32. [d] Reference 33. [e] References 28–30. [f] Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, New York, 1973; p 200. [g] Reference 34. [h] $k_7/55.5$. [i] Values corrected for the fraction of SO_3H^- relative to $HSO_3^- + SO_3H^-$.

can accept a proton in the conjugated base, A^-, and G_A is a proportionality constant. The Brønsted plot in Figure 6 gives a linear relationship with a slope of 0.71 (±0.05) that corresponds to the α value. The fact that the H_3O^+ value (k_3) falls on the Brønsted plot supports the postulate that $k_3 \gg k_6K_H$.

The proposed mechanism in eq 3 consists of a proton transfer to NH_2Cl as Cl^+ transfers to the sulfur of SO_3^{2-}. The initial product of the reaction is chlorosulfate, which is reported[36,37] to hydrolyze rapidly in water (eq 4). The proposed transition state for eq 3 is shown in structure I, where there is an expanded number of electron pairs around chlorine due to nucleophile attack by SO_3^{2-}. The fact that the reactions are general-acid assisted means that (except for H_3O^+) there cannot be a fast preequilibrium proton transfer from HA to NH_2Cl to give NH_3Cl^+ and A^- followed by a rate-determining reaction of NH_3Cl^+. If a preequilibrium existed, then the rates would depend only upon the H_3O^+ concentration (specific-acid catalyzed) and not on the HA concentrations. The magnitude of the α value reflects the degree of proton transfer (α can vary from 0 to 1 for 0 to 100% transfer) in the transition state.



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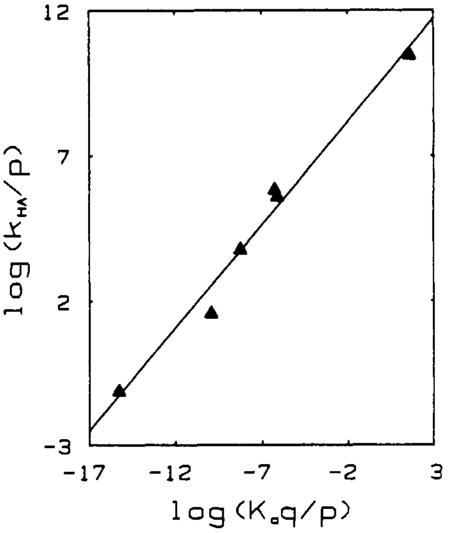
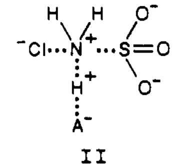


Figure 6. Brønsted–Pedersen plot for the general-acid-assited reaction of SO_3^{2-} with NH_2Cl. Conditions: $\mu = 0.50$ M ($NaClO_4$), 25.0 ± 0.1 °C, $\alpha = 0.71$.

An alternate mechanism in which SO_3^{2-} reacts at the nitrogen (structure II) can be ruled out because the first product of this reaction would be the sulfamate ion, $NH_2SO_3^-$. Sulfamate hydrolyzes very slowly to give NH_3 and SO_4^{2-}, and therefore $NH_2SO_3^-$ would be detected as a reaction product if it formed. However, it is not detected. Hence, the nucleophilic attack by SO_3^{2-} must occur at chlorine and not at nitrogen. The role of the general acid is to provide a better leaving group (NH_3 rather than NH_2^-) and to make it easier for Cl^+ to react with SO_3^{2-}.



II

A parallel reaction is found[8] in the general-acid-assisted reaction of NH_2Cl with I^-, which has an α value of 0.65 and a rate constant for the reaction with H_3O^+ equal to 2.4×10^{10} M^{-2} s^{-1}. The proposed transition state has I^- instead of SO_3^{2-} in structure I. Sulfite is a stronger nucleophile than iodide, so the α value is slightly larger (0.71 compared to 0.65) as is the k_H rate constant (8×10^{10} M^{-2} s^{-1}).

Acid-Assisted Reactions of NH_2Cl with SHO_3^-. The reaction of chloramine with hydrogen sulfite is also catalyzed by general

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(37) Ciruna, J. A.; Robinson, E. A. *Can. J. Chem.* **1968**, *46*, 1715–1718.

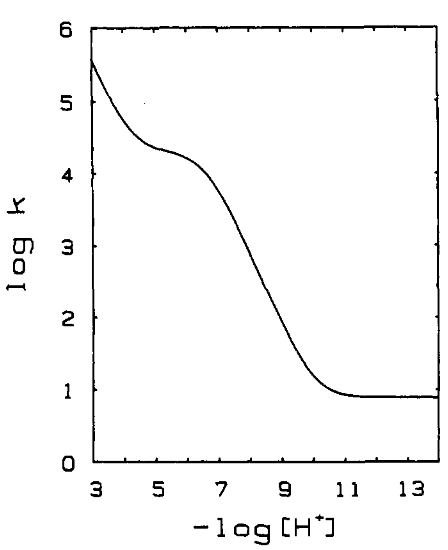
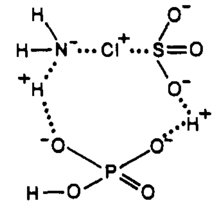


Figure 7. Acid dependence of the logarithm of the second-order rate constant for the reaction of NH_2Cl with total sulfite. The curve is calculated from eq 23.

acids, but CH_3COOH is no more effective than $H_2PO_4^-$ or SHO_3^-. As seen in Table VIII, these three acids have third-order rate constants of the same magnitude, and the strongest acid (CH_3COOH) actually gives the smallest value (2×10^5 M^{-2} s^{-1}). A concerted mechanism is suggested, such as that outlined by Jencks[38] for a bifunctional catalyst that contains both acidic and basic groups. Structure III shows the proposed transition state for $H_2PO_4^-$, in which there is a concerted transfer of protons from $H_2PO_4^-$ to the chloramine nitrogen and from SO_3H^- to a phosphate oxygen as Cl^+ transfers from N to S. Thus, $H_2PO_4^-$ acts as both an acid and as a base to facilitate the rate of chlorine transfer to SO_3H^-. A similar concerted mechanism is proposed for acetic acid and for SHO_3^- when it acts as a general acid. The weaker acids can accept a proton more readily from the nucleophile (SO_3H^-) and this makes them better proton donors to the chloramine nitrogen. The SO_3^{2-} ion is a stronger nucleophile than SO_3H^-, as is shown by their relative rate constants with H_3O^+ (8×10^{10} M^{-2} s^{-1} vs 3.6×10^8 M^{-2} s^{-1}). The concerted mechanism accounts for the fact that the general-acid-assisted rate constants (with $H_2PO_4^-$ and SHO_3^-) are the same order of magnitude with SO_3H^- and SO_3^{2-} as the nucleophile.



III

Jencks[38] points out that ammonium ion cannot act as a bifunctional catalyst, because it has no basic site. Similarly, $B(OH)_3$ does not have a suitable basic site because the conjugate base, $B(OH)_4^-$, requires a change of coordination number around boron. Furthermore, these reactions were studied at pH values where the SHO_3^- concentration is very small, so the k_2 paths are not seen for either NH_4^+ or $B(OH)_3$.

Isomeric Forms of Hydrogen Sulfite. The ratio $[SO_3H^-]/[HSO_3^-]$ is reported[15] to be 4.9. The measured K_H value for sulfite ion reflects the average protonation at both oxygen and sulfur. Hence, the presence of two forms will have little effect on the general-acid role of hydrogen sulfite. However, the sulfur atom in HSO_3^- cannot be an active nucleophile, while it can be an active nucleophilic site in SO_3H^-. Table VIII includes third-order rate constants that are corrected for the ratio $[SO_3H^-]/[SHO_3^-]$. This assumes that the equilibration between HSO_3^- and SO_3H^- is rapid compared to the reactions with NH_2Cl.

Dependence of the Second-Order Rate Constant on Hydrogen Ion Concentration. The rate expression in eq 22 has a second-order

$$\text{rate} = k[NH_2Cl][SO_3^{2-}]_T \qquad (22)$$

rate constant, k, that varies with acidity according to eq 23 if all

$$k = \frac{k_5 + (k_3 + k_6K_H)[H^+] + k_4K_H[H^+]^2}{1 + K_H[H^+]} \qquad (23)$$

buffer contributions are kept negligibly small. Figure 7 plots log k (based on values of $k_5 = 7.7$ M^{-1} s^{-1}, $(k_3 + k_6K_H) = 8 \times 10^{10}$ M^{-2} s^{-1}, $k_4 = 3.6 \times 10^8$ M^{-2} s^{-1}, and $K_H = 4.0 \times 10^6$ M^{-1}) against $-\log [H^+]$ values from 3 to 14. The large increase in rate constant from pH 10 to pH 6 is due to the H_3O^+-assisted reaction of NH_2Cl with SO_3^{2-} as opposed to the previously suggested[7] greater reactivity of hydrogen sulfite. The plateau around pH 6 is due to offsetting effects of increased H^+ concentration and formation of SHO_3^-, which has a lower nucleophilic reactivity than SO_3^{2-}. Below pH 5 the rate increases again due to the k_4 path (i.e. $H^+ + NH_2Cl + SO_3H^-$), where higher $[H^+]$ overcomes the lower reactivity of SO_3H^-. We have not been able to study the reaction below pH 3, where NH_3Cl^+ ($pK_a = 1.5$)[1] and SO_2 will form. The equilibrium constant for $[H^+][SO_3H^-]/([H_2SO_3] + [SO_2])$ is 4.3×10^{-2} M,[30] and earlier studies[39] gave a ratio of $[SO_2]/[H_2SO_3] \approx 20$. The reactivity of NH_3Cl^+ should be large, because it has been shown to be more reactive than HOCl in the chlorination of amino acids.[40] The reactivity of SO_2 is uncertain, but it should be a very poor nucleophile. Hence, the k value can be expected to reach a maximum in the vicinity of pH 1.5–1.8.

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