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Atom-Transfer Redox Kinetics: General-Acid-Assisted Oxidation of Iodide by Chloramines and Hypochlorite

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The rate of oxidation of iodide equals k_{HA}[HA][chlorine species][I^-], where HA is a general acid and the reactivity order for the chlorine species is $OCl^- >> NH_2Cl >> NHCl_2$. In the proposed rate-determining step chlorine (Cl^+) transfer to iodide ion is simultaneous with proton transfer to nitrogen or oxygen. This is followed by rapid reactions of ICl with I^- to give I_3^- and Cl^-. The relative reactivity depends on the acid strength of HA and correlates with the basicity of the proton acceptor site of the chlorine species. The Brønsted α values (0.75 for OCl^-, 0.65 for NH_2Cl, and 0.48 for $NHCl_2$) indicate the relative degree of proton and Cl^+ transfer in the transition state. In the case of H_3O^+ and OCl^- a preequilibration with HOCl must occur before the I^- reaction, but prior proton transfer to the chlorine species cannot occur when there is a general-acid dependence. The third-order rate constants ($M^{-2}\ s^{-1}$ at 25.0 °C, $\mu = 0.50$) for H_3O^+ and I^- are 4.4×10^{15} (OCl^-), 2.4×10^{10} (NH_2Cl), and 9.3×10^5 ($NHCl_2$). The initial reaction of NCl_3 with iodide to give I_3^- is too fast to measure by stopped-flow techniques; $HNCl_2$ is formed and its reaction with I^- is observed.

Introduction

Iodometric methods are widely used for the determination of active chlorine species.[1,2] In some cases "free chlorine" (i.e. Cl_2, HOCl, or OCl^-) is distinguished from residual chlorine (such as chloramine or dichloroamine species) by adjustment of pH, iodide ion concentrations, and the time allowed for the reaction.[2–4] The quantitative conversion of iodide to iodine or triiodide ion by hypochlorous acid (eq 1) is well-established. However, corresponding proof of the stoichiometry for the reaction of various chloramines with iodide is needed. These reactions have often been assumed to be quantitative, and we verify that this is indeed the case for NH_2Cl,[5] for several other monochloramines (eq 2), and for several dichloramines (eq 3). We find that reaction 3

$$HOCl + 3I^- + H^+ \rightarrow I_3^- + Cl^- + H_2O \qquad (1)$$

$$RNHCl + 3I^- + H^+ \rightarrow I_3^- + RNH_2 + Cl^- \qquad (2)$$

$$RNCl_2 + 6I^- + 2H^+ \rightarrow 2I_3^- + RNH_2 + 2Cl^- \qquad (3)$$

for $NHCl_2$ is quantitative, although an earlier report indicated that this was not the case.[6] However, the reaction of trichloroamine with iodide ion is not quantitative, in agreement with an earlier report.[7]

In the present study we show the rate expression for the reaction of mono- and dichloroamines is given by eq 4, where k_{HA}[HA] refers to the summation of rate constants times the concentration of each of the general-acid species present in solution. With

$$-d[\text{chlorine species}]/dt = k_{HA}[HA][\text{chlorine species}][I^-] \qquad (4)$$

H_3O^+, the reactivity of NH_2Cl is many orders of magnitude greater (a factor of 2.6×10^4) than the reactivity of $NHCl_2$. These reactions are postulated to proceed by chlorine atom transfer (actually Cl^+ transfer) to iodide ion to form ICl, which reacts very rapidly with excess iodide ion[8] to give I_3^-. The fact that the reactions are general-acid-dependent is significant in regard to the intimate mechanism.

Table I. Absorption Spectral Characteristics

species	λ_{max}, nm	ϵ, $M^{-1}\ cm^{-1}$	ref
OCl^-	292	350	*a*
HOCl	228	120	*a*
NH_2Cl	243	461	*b*
$NHCl_2$	294	272	*b*
CH_3NHCl	253	363	*b*
	253	372	*c*
N-Cl(gly)	256	350	*c*
N-ClAib$_2$	248	370	*b*
N-Cl(glygly)	254	332	*a*
N,N-Cl$_2$Aib$_2$	307	306	*b*
I_3^-	353	26400	*d*
I_2	460	746	*d*
IO^-	372	60	*e*
I^-	225	12600	*d*

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In previous studies[9,10] the conversion of hypochlorite to hypoiodite (eq 5) was shown to be fast and to have the rate expression in eq 6 over a limited range of hydroxide ion concentration. We

$$OCl^- + I^- \rightarrow OI^- + Cl^- \qquad (5)$$

$$-d[OCl^-]/dt = k[OCl^-][I^-]/[OH^-] \qquad (6)$$

have extended the pH range and have shown that the reaction rate is accelerated by general acids. The reaction was postulated to proceed either by oxygen atom transfer or by chlorine atom transfer, and oxygen transfer from HOCl via OH^+ was selected as the preferred mechanism.[9,10] Nevertheless, the parallel behavior of the hypochlorite reactions and the chloramine reactions leads us to propose that an analogous chlorine atom transfer occurs with ICl as an intermediate.

Experimental Section

Reagents. A 5% solution of sodium hypochlorite was used as the source of chlorine. Stock solutions were standardized by iodometric titrations[11] and were monitored by the absorbance of OCl^- at 292 nm (Table I). Sodium iodide was standardized by oxidation to iodate, followed by iodometric titration. Stock NaI solutions were purged with argon to minimize reaction with oxygen[12] and stored in the dark. Sodium thiosulfate solutions were standardized against potassium iodate (re-

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crystallized from water and dried) after the addition of excess iodide and acid. Ammonia solutions were prepared by dilution of reagent grade ammonium hydroxide and were titrated with standardized acid. Methylamine hydrochloride (Baker) was purified by sublimation.[13] Solutions were standardized by the addition of excess NaOH, boiled to remove methylamine, and back-titrated with standard acid. Glycine (MCB), glycylglycine (Sigma), and Aib_2 (the dipeptide of α-aminoisobutyric acid) were pure solids (based on elemental and chromatographic analysis). Aib_2 was prepared[14] in this laboratory by A. Hamburg.

All monochloramine solutions were prepared fresh daily in metal-free glassware by mixing NaOCl solution with the amine, amino acid, or dipeptide solution at pH 8–10. This was accomplished by rapid flow through a double twin-jet tangential mixer to avoid local excesses of reagents. Monochloramines were prepared with a 10–100% excess of ammonia or methylamine and a 5–10-fold excess of amino acid or peptide relative to the hypochlorite concentration.

Dichloroamine was prepared by the disproportionation of chloramine (eq 7) at pH 3.5–4.[15,16] Slow addition of acid was used, and the reaction

$$2NH_2Cl + H^+ \rightleftarrows NHCl_2 + NH_4^+ \qquad (7)$$

was allowed to proceed for about 5 h. Caution was taken not to go below pH 3 in order to minimize trichloramine formation. Dichloromethylamine was formed by mixing chloromethylamine with 6×10^{-3} M $HClO_4$. Precautions were taken to avoid losses of $NHCl_2$ and of CH_3NCl_2 because of their volatility. The *N*,*N*-dichloro derivative of Aib_2 was formed by mixing *N*-Cl-Aib_2 with 0.1 M $HClO_4$ and allowing the reaction to stand in the dark for 12 h.

Trichloroamine for the kinetics studies was prepared either by mixing dichloramine solution with 0.2 M $HClO_4$ or by mixing NH_3 solution with a 3-fold excess of HOCl at pH 3–4. The amount of NCl_3 formed was always less than the initial NH_3 concentration due to N_2 formation.[15] After standing overnight, the NCl_3 solutions were relatively stable in dilute acid (pH 3–4) when protected from volatilization.

Sodium perchlorate, prepared from Na_2CO_3 and $HClO_4$, was used to maintain the ionic strength of the reactions. Distilled deionized water and reagent grade buffers, acids, and bases were used.

Methods. Solution pH values were measured with a Corning Model 476051 combination glass electrode and an Orion Model 601 pH meter. All pH values were corrected to give hydrogen ion concentrations ($-\log [H^+] = pH + 0.15$ at $\mu = 0.50$ ($NaClO_4$) and 25.0 °C) based upon the electrode response in titrations with standard solutions of NaOH and $HClO_4$. Gran plots[17] were used in the calibration of the electrodes.

Iodometric titrations with sodium thiosulfate were performed immediately after acidification in the presence of iodide.

Spectrophotometric measurements were made with a Perkin-Elmer Model 320 interfaced to a Perkin-Elmer 3600 data station or with Cary Models 14, 16, and 17. The spectral characteristics of various species are given in Table I.

Most of the kinetic studies were performed under pseudo-first-order conditions with iodide in large excess and with buffer control of hydrogen ion concentrations. In neutral or acidic solutions the reactions were monitored by the formation of I_3^- at 353 nm ($\epsilon = 26\,400$ M^{-1} cm^{-1}). The rapid equilibrium with I_2 and I^- ($K = 748$ M^{-1})[18] was taken into account. The reaction of OCl^- with I^- was studied in NaOH solutions, and the disappearance of OCl^- was followed at 292 nm ($\epsilon = 350$ M^{-1} cm^{-1}). Absorbance vs. time data were obtained with a Durrum stopped-flow spectrophotometer interfaced to a Hewlett-Packard computer (HP 2108 or 2100). Rate constants (k_{obsd}, s^{-1}) were determined from a least-squares linear regression analysis of ln $(A_t - A_\infty)$ vs. time from data collected over at least 4 half-lives. Five or more runs were performed under each set of conditions, and most results give better than a 1% standard deviation of the rate constants. Nearly all the k_{obsd} values had less than a 3% standard deviation. The reproducibility of the third-order rate constants depends primarily on the care taken with the calculation of the hydrogen ion or general-acid concentrations.

The reactions of NCl_3 with I^- were too fast to measure by stopped-flow techniques and were tested by the pulsed-accelerated-flow method.[8,19,20]

Table II. Stoichiometry of the Iodide Reaction

chloramine species	I_2 yield[a] per Cl, %
NH_2Cl	99.6 ± 0.8
	100.2 ± 1.6[b]
	98.1 ± 0.8[c]
chloromethylamine	99.2 ± 0.5
N-chloroglycine	99.9 ± 0.2
N-ClAib$_2$	100.1 ± 0.2
$NHCl_2$	99.0 ± 0.6[d]
	100.8 ± 1.0
	97.2 ± 2.5[e]
dichloromethylamine	104.0 ± 3.0
N,*N*-Cl$_2$Aib$_2$	98.7 ± 0.8

[a] Titrimetric. [b] $\mu = 0.1$ M ($NaClO_4$). [c] $\mu = 1.0$ M ($NaClO_4$). [d] With and without acetate buffer. [e] Spectrophotometric: I_3^-.

Results and Discussion

Stoichiometry of the Iodide Reactions. Monochloramines. The iodine yields from reactions of the *N*-chloro derivatives of ammonia, methylamine, glycine, and Aib_2 with iodide ion were determined by iodometric titrations. The results in Table II show that the reactions are essentially quantitative when compared to the yield from the hypochlorite solution used to prepare the *N*-chloro compounds in solution. Previous studies showed that *N*-chloroglycine undergoes a slow fragmentation redox reaction,[21] but this was negligible under the conditions used. The *N*-chloro derivative of Aib_2 was used rather than *N*-chloroglycylglycine because the latter compound undergoes rapid redox decomposition.

***N*,*N*-Dichloramines.** The volatility and decomposition of dichloramine creates problems in its determination.[22] Our concern is whether or not the reaction of $NHCl_2$ with I^- gives 2 equiv of I_2. Precautions were taken to minimize loss of dichloramine due to volatility by the use of stoppered containers with minimal head space. A key to reducing the rate of decomposition of dichloramine is to have some ammonium ion present in the solution.[15] Thus, the $NHCl_2$ solutions had both NH_2Cl and NH_4^+ present, but negligible amounts of NCl_3. The initial active chlorine concentration was determined by absorbance measurements at 277 nm, which is an isosbestic for mono- and dichloramine ($\epsilon_{NH_2Cl} = \epsilon_{NHCl_2} = 87.5$ M^{-1} cm^{-1}). The individual concentrations were calculated from simultaneous measurements at 243 nm ($\epsilon_{NH_2Cl} = 461$ M^{-1} cm^{-1}, $\epsilon_{NHCl_2} = 245$ M^{-1} cm^{-1}) and at 294 nm ($\epsilon_{NH_2Cl} = 13.1$ M^{-1} cm^{-1}, $\epsilon_{NHCl_2} = 272$ M^{-1} cm^{-1}). The pH of the solutions was varied from pH 4 to 6, and the total chlorine concentration was varied from 0.1 to 10 mM. In half of the cases an acetate buffer was used, whereas the other solutions were not buffered.

The iodide solutions were adjusted to pH 1–4 with appropriate buffers prior to the addition of dichloramine. The rate of acid decomposition of dichloramine is slow compared to the rate of oxidation of iodide under all these conditions. Titrimetric and spectral methods were used to determine the total iodine ($I_2 + I_3^-$) produced. In the titrimetric method the iodine was determined with thiosulfate, while in the spectral method the absorbance of triiodide was measured at 353 nm ($\epsilon = 26\,400$ M^{-1} cm^{-1}) after appropriate dilution in 0.1 M iodide solutions. The results summarized in Table II indicate that the stoichiometry in eq 3 is correct within experimental error. Variations of the buffer and pH of the reaction with iodide did not affect the results.

Trichloramine. There are several complications in attempts to measure the stoichiometry of the reaction of trichloramine with iodide. First, the preparation of trichloramine, whether by the addition of hypochlorous acid to ammonia or by the acidification of dichloramine, gives appreciable loss of active chlorine due to the formation of dinitrogen.[15] Second, the reaction of trichloramine with iodide does not appear to have a simple stoichiometry. Third, trichloramine is very volatile (the vapor pressure is 150

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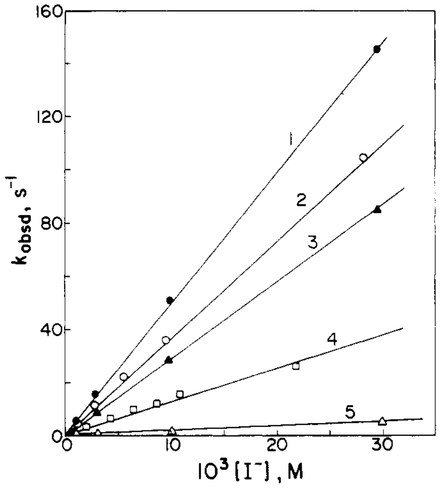

Figure 1. Iodide dependence of monochloramine rate constants (25.0 °C, $\mu = 0.5$): (1) CH_3NHCl, $-\log [H^+] = 6.89$; (2) NH_2Cl, $-\log [H^+] = 6.93$; (3) *N*-Cl(gly), $-\log [H^+] = 6.89$; (4) *N*-Cl(glygly), $-\log [H^+] = 6.11$; (5) *N*-ClAib$_2$, $-\log [H^+) = 7.21$.

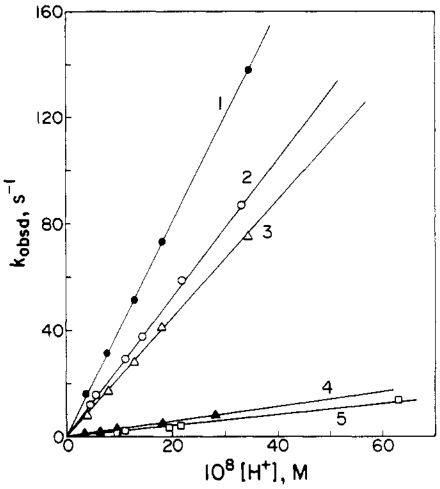

Figure 2. Hydrogen ion dependence of monochloramine rate constants (25.0 °C, $\mu = 0.5$): (1) CH_3NHCl, $[I^-] = 9.82 \times 10^{-3}$ M; (2) NH_2Cl, $[I^-] = 9.40 \times 10^{-3}$ M; (3) *N*-Cl(gly), $[I^-] = 9.82 \times 10^{-3}$ M; (4) *N*-ClAib$_2$, $[I^-] = 10.1 \times 10^{-3}$ M; (5) *N*-Cl(glygly), $[I^-] = 8.70 \times 10^{-3}$ M.

mmHg at room temperature[23]) and is easily lost from aqueous solution. Although NCl_3 forms characteristic absorption bands at 220 and 336 nm, there is substantial disagreement in regard to its molar absorptivity values because of the above factors. In short, NCl_3 is easily formed and is relatively stable in acidic solution, but since neither its formation nor its iodide reactions are quantitative, it is difficult to assign an exact stoichiometry for the individual steps. We determined the yield of iodine before and after hypochlorous acid was converted to nitrogen trichloride under three sets of conditions: (1) Dichloramine (formed from 2:1 NH_3–1.25×10^{-3} M HOCl mixtures) was reacted with 1 M $HClO_4$ for 1–2 h. The resulting NCl_3 was added to acetate-buffered iodide solutions and was titrated immediately. This gave a 67 (±2)% yield of iodine. (2) Dichloramine (formed from 1:1 NH_3–1.25×10^{-3} M HOCl mixtures) was treated similarly with 1 M $HClO_4$ to give NCl_3, which was reacted with iodide to give a 60 (±3)% yield of iodine. (3) Trichloramine solutions prepared at pH 4 (acetate buffer) by mixing 1:3 NH_3–3×10^{-3} M HOCl mixtures gave a 52 (±2)% overall yield of iodine. In the above three sets the apparent yield of I_2 from NCl_3 was 83%, 81%, and 80%, respectively. However, this yield is based on estimated values of NCl_3 molar absorptivities at 336 nm and at 278 nm (apparent isosbestic points for NCl_3 and $NHCl_2$) and must be used with caution. It appears that the yield of NCl_3 decreases with a lower excess of NH_4^+ and with higher pH. This is consistent with earlier work.[15]

Kinetics and Mechanisms. Chloramines. The rate dependence for the reaction of chloramine in a buffered solution with excess iodide is first order in chloramine (eq 8). The observed rate

$$-d[NH_2Cl]/dt = k_{obsd}[NH_2Cl] \qquad (8)$$

constants are directly proportional to the iodide ion concentration (Figure 1) and to the hydrogen ion concentration (Figure 2). The k_{obsd} values are not affected by variations in the ammonium ion concentrations at low levels, but the k_{obsd} values do increase with buffer concentration when the hydrogen ion and iodide ion concentrations are constant (Table III). This behavior is consistent with the observation of other buffer-catalyzed reactions.[24-27] The combined effects are expressed by eq 9, where HA is the acid form

$$k_{obsd} = (k_H[H^+] + k_{HA}[HA])[I^-] \qquad (9)$$

of the buffer. The expression in terms of the total buffer concentration and the acid dissociation constant of the buffer is given by eq 10. Values for k_{HA} and k_H are resolved for a series of acids

$$\frac{k_{obsd}}{[H^+][I^-]} = k_H + \frac{k_{HA}[\text{buffer}]_T}{K_a + [H^+]} \qquad (10)$$

and increase with the acid strength of HA: $H_2PO_4^- < H_2edta^{2-} < Hsucc^- < CH_3COOH < H_3O^+$ (H_4edta = ethylenediaminetetraacetic acid, H_2succ = succinic acid; Table IV).

Table III. Conditions Used and Range of First-Order Rate Constants Measured To Resolve the General-Acid-Assisted Rate Constants[a,b]

buffer (total concn, M)	$-\log [H^+]$	$10^3[I^-]$, M	k_{obsd}, s^{-1}
Chloramine ($[NH_2Cl]_i = (1.0–1.2) \times 10^{-5}$ M with 10% Excess NH_3)			
phosphate (0.010–0.20)	6.15–7.36	0.94–30.5	3.7–120
edta (0.010–0.050)	6.11–6.14	0.74	15–23
acetate (0.025–0.20)	5.65	0.43	21–29
succinate (0.010–0.100)	5.37	0.74	108–133
Chloromethylamine (1.50×10^{-5} M)			
phosphate (0.010)	6.46–7.41	0.98–29.5	5.20–145
N-Chloroglycine (1.50×10^{-5} M)			
phosphate (0.010)	6.46–7.42	0.98–29.5	2.82–85.0
N-ClAib$_2$ (1.50×10^{-5} M)			
phosphate (0.010)	6.55–7.45	1.00–100	0.170–17.4
N-Chloroglycylglycine (1.00×10^{-5} M)			
phosphate (0.010–0.125)	5.68–7.31	2.18–21.75	0.74–30.5
acetate (0.025–0.125)	5.00–5.02	0.87	18.9–21.6
Dichloramine ($(0.60–1.25) \times 10^{-5}$ M)			
phosphate (0.025–0.175)	6.14	40.00	0.089–0.247
phosphate (0.025–0.150)	2.65	4.30	9.1–16.9
acetate (0.005–0.213)	3.95–5.12	0.94–94.0	0.040–12.2
chloroacetate (0.010–0.100)	3.18–3.25	0.74	0.497–0.57
Dichloromethylamine (7.5×10^{-6} M)			
acetate (0.005)	3.62–4.41	0.986–29.6	0.141–13.6
N,N-Cl$_2$Aib$_2$ (7.5×10^{-6} M)			
acetate (0.005)	3.03–4.30	1.00–100	0.0711–7.20
Hypochlorite ($[OCl^-]_i = (1.0–2.5) \times 10^{-4}$ M)			
[NaOH] (0.0024–0.250)		0.87–21.70	1.33–154
phosphate (0.005–0.075)	11.04–11.23	1.74–4.35	99–177
carbonate (0.010–0.075)	10.46–10.92	0.87	94.3–173

[a] Conditions: 25.0 °C; $\mu = 0.50$ M ($NaClO_4$). [b] Individual rate constants are available in the supplementary material. First-order rate constants larger than 100 s^{-1} were corrected for mixing effects (Dickson, P. N.; Margerum, D. W. *Anal. Chem.*, in press.

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Table IV. General-Acid-Assisted Rate Constants for the Reaction of Iodide with Chloramines and Hypochlorite[a]

		third-order rate const, $M^{-2}\ s^{-1}$			
HA	pK_a[b]	NH_2Cl	*N*-Cl(glygly)	$NHCl_2$	OCl^-
H_3O^+	-1.74[c]	$(2.40 \pm 0.05) \times 10^{10}$	$(1.97 \pm 0.07) \times 10^9$	$(9.3 \pm 0.6) \times 10^5$	$(4.4 \pm 0.3) \times 10^{15}$
H_3PO_4	1.75[d,e]			$(1.02 \pm 0.08) \times 10^5$	
$ClCH_2COOH$	2.60[f]			$(7.8 \pm 2.1) \times 10^3$	
CH_3COOH	4.64[g]	$(1.3 \pm 0.1) \times 10^6$	$(1.8 \pm 0.3) \times 10^5$	$(2.60 \pm 0.07) \times 10^2$	
$Hsucc^-$	5.1[h]	$(1.2 \pm 0.4) \times 10^6$			
H_2edta^{2-}	6.07[i]	$(5.6 \pm 0.8) \times 10^5$			
$H_2PO_4^-$	6.8[d]	$(5.4 \pm 0.4) \times 10^4$	$(1.2 \pm 0.2) \times 10^4$	34.0 ± 0.7	
HCO_3^-	9.8[j]				$(9.4 \pm 0.8) \times 10^6$
HPO_4^{2-}	11.30[d]				$(9.3 \pm 0.7) \times 10^5$
H_2O	15.52[k]			10^{-2}	

[a] Conditions: 25.0 °C; $\mu = 0.5$ M ($NaClO_4$). [b] Literature values are corrected for ionic strength effects. [c] Reference 33, p 200. [d] Sillen, L. G.; Martell, A. E. 2nd ed., *Spec. Publ.—Chem. Soc.* **1964**, *No. 17*, 180. [e] Elliot, J. S.; Sharp, R. F.; Lewis, L. *J. Phys. Chem.* **1958**, *62*, 686–689. [f] Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1982; Vol. 5, p 287. [g] Feldman, I.; Koval, L. *Inorg. Chem.* **1963**, *2*, 145–150. [h] Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1982; Vol. 5, p 313. [i] Carr, J. D.; Swartzfager, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 3569–3572. [j] MacInnes, D. A.; Belcher, D. J. *J. Am. Chem. Soc.* **1935**, *57*, 1683–1685. [k] Lagerstrom, G. *Acta Chem. Scand.* **1959**, *13*, 722–736. Value calculated by dividing by 55.5 for water molarity.

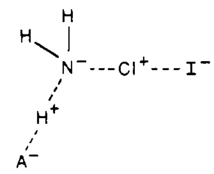
The proposed rate-determining reaction in eq 11 is followed by extremely fast reactions (eq 12[8] and 13[28]).

$$HA + NH_2Cl + I^- \xrightarrow{k} A^- + NH_3 + ICl \qquad (11)$$

$$ICl + I^- \rightarrow I_2 + Cl^- \qquad (12)$$

$$I_2 + I^- \rightleftarrows I_3^- \qquad (13)$$

Acid is consumed in reaction 11, so we have termed this a general-acid-assisted rate. Otherwise, the reactions have all the characteristics of general-acid-catalyzed rate processes. It is important to realize that in these processes the proton from HA cannot be transferred to NH_2Cl in a preequilibration step, because the rates would then degenerate to specific-acid catalysis (i.e. where the rates are dependent only on the H_3O^+ concentration and not on the HA concentration). This means that the transition state must contain HA as well as NH_2Cl and I^-. Thus, structure I is proposed. In this transition state the nitrogen accepts a proton



I

as it transfers Cl^+ to I^-. There are five electron pairs around the chlorine atom in the transition state. This valence shell expansion of chlorine is not at all unusual and is found in stable species such as Cl_3^-. Valence shell electron pair repulsion theory[29] predicts a linear N–Cl–I arrangement.

The formation of the transition state need not occur by a three-body collision. Instead, AH could approach a weakly associated $(H_2NClI)^-$ species or I^- could approach a hydrogen-bonded $(AHNH_2Cl)$ species. However, as stated before, the general-acid-assisted process cannot have a complete proton transfer to give NH_3Cl^+ before the reaction with I^-. This restriction does not apply to the H_3O^+ reaction, of course. The third-order rate constant for H_3O^+ and I^- with NH_2Cl (from the intercept of buffer dependencies) is 2.4×10^{10} $M^{-2}\ s^{-1}$. The K_a value for NH_3Cl^+ is 0.036, so that the second-order rate constant for the reaction of NH_3Cl^+ with I^- would have to be 8.6×10^8 $M^{-1}\ s^{-1}$. This value is well below the expected diffusion-limiting rate constant ($\sim 10^{10}$ $M^{-1}\ s^{-1}$ for these oppositely charged species).

Similar studies of the dependence of iodide ion concentrations, hydrogen ion concentrations, and buffer concentrations were carried out for the reactions of *N*-chloroglycylglycine (*N*-Cl(glygly)). The third-order rate constant for H_3O^+, I^-, and *N*-Cl(glygly) is 1.97×10^9 $M^{-2}\ s^{-1}$, a factor of 12 less than the corresponding rate constant for chloramine. The reactions are also general-acid-assisted in the presence of CH_3COOH and $H_2PO_4^-$.

Table V. Third-Order Rate Constants for the Reaction of Monochloramines with Iodide and Hydrogen Ion as a Function of Protonation Constants

	log K_H		
species	amine	chloramine[a]	$10^{-10}k_H$, $M^{-2}\ s^{-1}$
CH_3NHCl	10.80	1.55	4.04
NH_2Cl	9.43	1.45	2.40
N-Cl(gly)	9.65		2.26
N-ClAib$_2$	8.26		0.285
N-Cl(glygly)	8.11	-0.67	0.197

[a] Reference 37.

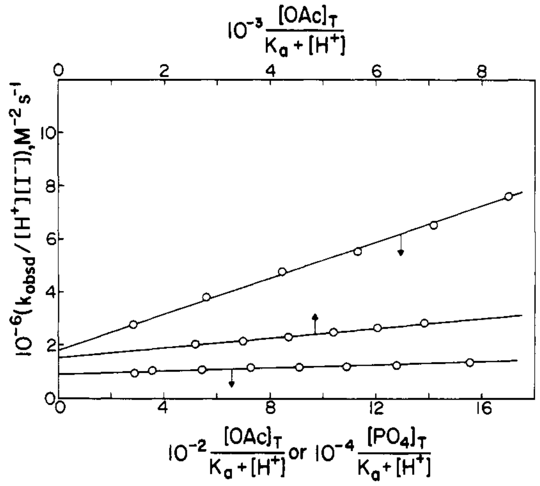


Figure 3. Resolution of buffer dependence in the reaction of iodide with dichloramine (eq 10; 25.0 °C, μ = 0.5).

The reactions of chloromethylamine, *N*-chloroglycine, and *N*-ClAib$_2$ were also studied as a function of hydrogen ion and iodide concentrations, but without variation of the buffer concentrations. The third-order rate constants for these chloramines with I^- and H_3O^+ were calculated after correction for a small buffer contribution (based on the parallel behavior of NH_2Cl and *N*-Cl(glygly)). The third-order rate constants decrease as the basicity of the chloramines decreases (Table V).

Dichloramines. The rate of iodide reaction with dichloramines is much slower than with monochloramines. Hence, with excess iodide the presence of NH_2Cl in the sample preparation does not interfere with the $NHCl_2$ kinetics. An absorbance jump occurs before the observed reaction. Data from the conditions in Table

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(28) Turner, D. H.; Flynn, G. W.; Sutin, N.; Beitz, J. V. *J. Am. Chem. Soc.* **1972**, *94*, 1554–1559.

(29) Gillespie, R. J. *J. Chem. Educ.* **1970**, *47*, 18–23.

Table VI. Effect of Ionic Strength on the Reaction of Dichloramine with Iodide[a]

μ, M[b]	k_{obsd}, s^{-1}	$10^{-5}k$, $M^{-2}\ s^{-1}$	μ, M[b]	k_{obsd}, s^{-1}	$10^{-5}k$, $M^{-2}\ s^{-1}$
0.0057	7.80 ± 0.16	13.6	0.0531	6.43 ± 0.01	11.2
0.0178	7.23 ± 0.04	12.6	0.0649	6.41 ± 0.02	11.0
0.0354	6.60 ± 0.07	11.5	0.124	5.97 ± 0.03	10.4

[a] Conditions: $[NHCl_2] = 1.0 \times 10^{-5}$ M; $[I^-] = 4.4 \times 10^{-3}$ M; $[H^+] = 1.3 \times 10^{-3}$ M; 25.0 °C. [b] Adjusted with $NaClO_4$.

Table VII. Temperature Dependence for the Reaction of Dichloramine with Iodide[a]

T, °C	k_{obsd}, s^{-1}	T, °C	k_{obsd}, s^{-1}
12.0	3.81 ± 0.08	35.4	7.20 ± 0.09
19.5	4.11 ± 0.11	46.2	8.76 ± 0.12
25.0	5.50 ± 0.05	50.0	9.3 ± 0.3
29.4	6.01 ± 0.06	55.0	10.6 ± 0.2

[a] Conditions: $[NHCl_2] = (0.5-1.5) \times 10^{-5}$ M; $[H^+] = 1.3 \times 10^{-3}$ M; $[I^-] = 4.40 \times 10^{-3}$ M; $\mu = 0.5$.

III show the same rate dependence given in eq 4. However, a plot of the buffer dependence in Figure 3 does not give the constant intercept that would be expected from eq 10. This is because water also acts as a general acid; thus, the rate expression is given by eq 14. An iterative procedure was used to resolve the values for k_{H_2O}, k_{HA}, and k_H that are given in Table IV.

$$\text{rate} = (k_H[H^+] + k_{HA}[HA] + k_{H_2O}[H_2O])[I^-][NHCl_2] \quad (14)$$

The reactions of dichloromethylamine and N,N-Cl_2Aib_2 were studied with various iodide and hydrogen ion concentrations (Table III). The third-order rate constants are 1.1×10^6 $M^{-2}\ s^{-1}$ for CH_3NCl_2 and 2.6×10^5 $M^{-2}\ s^{-1}$ for N,N-Cl_2Aib_2, which are similar to the value for dichloramine and decrease as the basicity of the amine decreases.

The effect of ionic strength on the dichloramine reaction with iodide was studied at constant acid concentration without added buffer (Table VI). The rate decreased as the sodium perchlorate concentration (used to adjust μ) increased in accord with the relationship expected (eq 15) when the reaction order is greater than 2,[30] where A is 0.509 for water at 25.0 °C and $\Delta Z^2 = (Z_{\ddagger}^2 - Z_P^2 - Z_Q^2 - Z_R^2) = -2$ for $P = H^+$, $Q = NHCl_2$, and $R = I^-$. An estimate of B was obtained by assuming that $(\Delta Z^2)A$ was -1.02. The best fit of the data with $B = 0.74$ then gave $(\Delta Z^2)A = -1.05$ (±0.03) and $\log k° = 6.204$ (±0.006). Thus, the ionic strength dependence is consistent with the proposed mechanism.

$$\log k = \log k° + (\Delta Z^2)A\frac{\mu^{1/2}}{1 + \mu^{1/2}} + B\mu \quad (15)$$

The temperature dependence of the dichloramine reaction at constant hydrogen ion and iodide ion concentrations was determined from 12.0 to 55.0 °C in 0.50 M $NaClO_4$ (Table VII). The activation parameters for the third-order rate constants are $\Delta H^{\ddagger} = 3.8 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18.3 \pm 0.5$ cal $K^{-1}\ mol^{-1}$. It is interesting that the $\Delta S^{\ddagger}$ value is negative despite the fact that charge neutralization occurs in the rate-determining step. The negative value is consistent with the proposed highly structured transition state in which three species are brought together.

Trichloramine. A rapid absorbance jump followed by a slower reaction was observed when trichloramine was mixed with excess iodide from pH 3 to pH 5. The magnitude of the absorbance jump corresponded to less than 1 equiv of I_3^- per estimated equivalent of NCl_3. The slower reaction gave rate constants identical with those of $NHCl_2$ although the UV spectra showed no evidence of $NHCl_2$ in the initial NCl_3 solution. Thus, the reaction in eq 16

$$NCl_3 + H^+ + 3I^- \rightarrow NHCl_2 + I_3^- + Cl^- \quad (16)$$

has taken place very rapidly, but as pointed out previously the stoichiometry is not exact. Tests were performed from pH 3 to pH 11 by monitoring NCl_3 loss at 336 nm as well as I^- and NCl_3 loss at 225 nm and OI^- formation at 372 nm (for higher pH conditions). In all cases the reaction is too fast for the stopped-flow technique. Work in progress[8] that uses pulsed-accelerated-flow spectroscopy shows that the NCl_3 and I^- reaction is about 2 orders of magnitude too fast for stopped-flow methods.

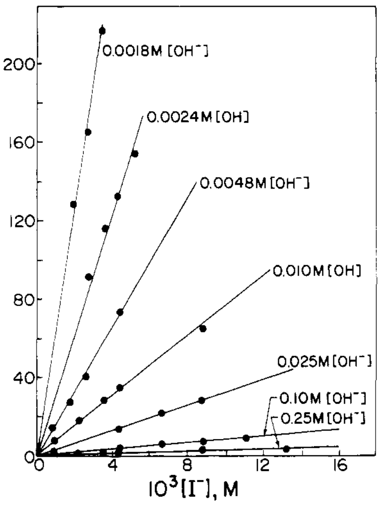

Figure 4. Iodide and hydroxide ion dependence of the hypochlorite rate constants (25.0 °C, μ 0.5).

Table VIII. Temperature Dependence for the Reaction of Hypochlorite with Iodide[a]

T, °C	k_{obsd}, s^{-1}	T, °C	k_{obsd}, s^{-1}
12.0	1.76 ± 0.03	40.0	10.4 ± 0.2
19.5	2.29 ± 0.06	46.0	15.3 ± 0.3
25.0	3.57 ± 0.08	50.0	18.2 ± 0.8
36.0	6.5 ± 0.3		

[a] Conditions: $[OCl^-] = 2.5 \times 10^{-4}$ M; $[OH^-] = 0.10$ M; $[I^-] = 4.35 \times 10^{-3}$ M; $\mu = 0.5$.

Hypochlorite. Chia and Connick[9] studied the reaction of hypochlorite with iodide (eq 5) under second-order conditions in 0.25–1.0 M hydroxide ion concentrations. They followed the reaction at 400.6 nm by use of a syringe injection technique with a mixing time of about 1 s. They established the rate expression in eq 6 and reported a k value of 60 ± 5 s^{-1} at 25 °C and $\mu = 1.0$. Lister and Rosenblum[10] studied the same reaction in 0.14–0.45 M NaOH with a continuous-flow mixer mounted on a trolley that moved the observation tube through the light path of a spectrophotometer. Their mixing was better, and they found a larger rate constant ($k = 91$ (±3) s^{-1} at 25.0 °C and $\mu = 1.0$). They also studied the reaction at 17.7 and 34.3 °C and reported an activation energy of 11.9 kcal mol^{-1}.

We studied the reaction from 0.0024 to 0.25 M $[OH^-]$ at $\mu = 0.50$ ($NaOH + NaClO_4$) with a wide range of iodide ion concentrations (Figure 4 and Table III). Stopped-flow methods were used to monitor the loss of OCl^- at 290 nm. The results fit the same rate law (eq 6). For 29 different sets of conditions, $k = k_{obsd}[OH^-]/[I^-] = 80$ (±5) s^{-1} (25.0 °C, $\mu = 0.5$). When the difference in ionic strength is considered, this is in reasonable agreement with Lister's value.[10] We also studied the temperature dependence of the reaction from 12.0 to 50.0 °C (Table VIII) and found activation parameters of $\Delta H^{\ddagger} = 11.3$ (±0.6) kcal mol^{-1} and $\Delta S^{\ddagger} = -17$ (±1) cal $K^{-1}\ mol^{-1}$. This is in excellent agreement with Lister's E_a value ($\Delta H^{\ddagger} = E_a - 0.6$).

The rate expression can be written in terms of $k_H[H^+][OCl^-][I^-]$, where $k_H = k/K_W = 4.4 \times 10^{15}$ $M^{-2}\ s^{-1}$ (by use of the pK_W value of 13.74 at 25.0 °C and $\mu = 0.5$). The magnitude of k_H is too great for a three-body interaction unless there is a strong association ($>10^5$ M^{-1}) between two of the species. The only logical pair for strong association is H^+ and OCl^- to give HOCl ($K_{HOCl} = 3.1 \times 10^7$ M^{-1}). (Any association of OCl^- and I^- to give $OClI^{2-}$ would be expected to be no larger than the value[31]

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[30] Pethybridge, A. D.; Prue, J. E. *Prog. Inorg. Chem.* **1972**, *17*, 327–390.

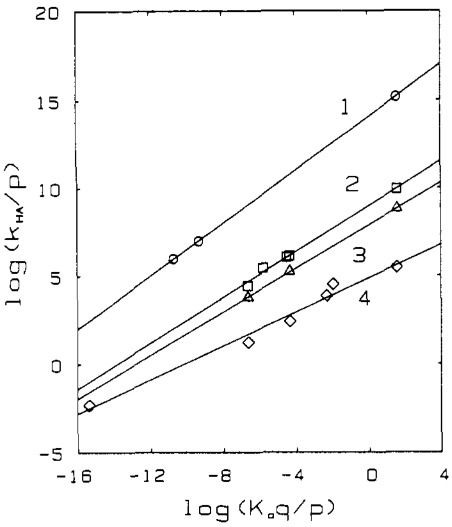


Figure 5. Brønsted–Pedersen plots for general-acid-assisted iodide reactions: (1) OCl^-, $\alpha = 0.75$; (2) NH_2Cl, $\alpha = 0.65$; (3) N-Cl(glygly), $\alpha = 0.62$; (4) $NHCl_2$, $\alpha = 0.48$.

of 0.045 M^{-1} for $OI^- + I^- \rightleftharpoons OI_2^{2-}$.) In this case a complete proton transfer to give HOCl is expected, and the proposed mechanism (eq 17–19) has a k_2 value of 1.4×10^8 M^{-1} s^{-1} at 25.0 °C, μ =

$$H_2O + OCl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + OH^- \quad \text{fast} \qquad (17)$$

$$HOCl + I^- \xrightarrow{k_2} OH^- + ICl \quad \text{rds} \qquad (18)$$

$$ICl + 2OH^- \xrightarrow{k_3} OI^- + Cl^- + H_2O \quad \text{fast} \qquad (19)$$

0.5. The heat of hydrolysis of OCl^- is 11.0 kcal mol^{-1}, which gives a very small $\Delta H_2^{\ddagger}$ value of 0.3 kcal mol^{-1}. This is in accord with the large k_2 rate constant.

At lower hydroxide ion concentrations the nature of the product changes because of the rapid equilibria in eq 20–22.[32] The

$$HOI \rightleftharpoons H^+ + OI^- \quad K = 2.3 \times 10^{-11} \qquad (20)$$

$$OI^- + I^- + H_2O \rightleftharpoons I_2OH^- + OH^- \quad K = 0.13 \qquad (21)$$

$$HOI + I^- + H^+ \rightleftharpoons I_2 + H_2O \quad K = 2.3 \times 10^{12} \qquad (22)$$

concentration of HOI and I_2OH^- can be appreciable. Although the concentration of I_3^- is always small under the conditions used, it has a strong absorbance. As a result the magnitude and even direction of the absorbance signal at 290 nm sometimes changed at lower hydroxide and higher iodide concentrations, but excellent first-order plots were observed in all cases.

The rate of reaction 5 is catalyzed by hydrogen carbonate and by hydrogen phosphate. The effects are not large but are significant. This catalysis cannot be attributed to prior proton-transfer steps with the buffer acids and hypochlorite to give hypochlorous acid, because once again this would degenerate into specific-acid catalysis. The observed rate dependence is given by eq 23. The values of k_{HA} are 9.4 (±0.8) × 10^6 M^{-2} s^{-1} for HCO_3^- and 9.3 (±0.7) × 10^5 M^{-2} s^{-1} for HPO_4^{2-}.

$$\text{rate} = (k_H[H^+] + k_{HA}[HA])[OCl^-][I^-] \qquad (23)$$

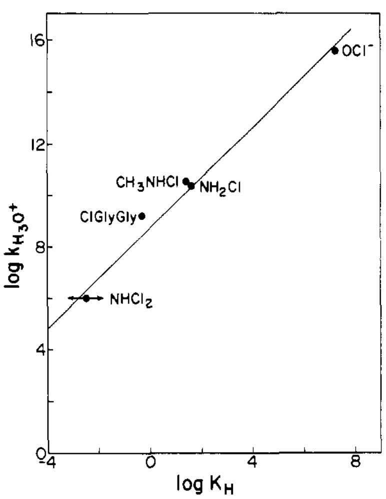
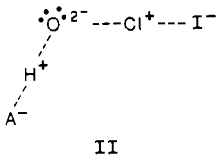


Figure 6. Dependence of the third-order rate constant for H_3O^+ and I^- on the protonation constants of the chlorine species.

Brønsted Relationship. The rates of the iodide reactions with OCl^-, NH_2Cl, N-Cl(glygly), and $NHCl_2$ depend on the strength of the general acids that are present in solution. They follow the Brønsted relationship[33] in eq 24, where p is the number of

$$\frac{k_{HA}}{p} = G_A\left(\frac{K_a q}{p}\right)^{\alpha} \qquad (24)$$

equivalent acidic protons in HA and q is the number of equivalent basic sites in A^-. Figure 5 shows the Brønsted–Pedersen plot for all these systems. The α values increase with the basicity of the protonation site and are 0.48 for $NHCl_2$, 0.62 for N-Cl(glygly), 0.65 for NH_2Cl, and 0.75 for OCl^-. The larger the α value, the greater the degree of H^+ and Cl^+ transfer in the transition state (structure I or its equivalent for monochloramines and dichloramines). Structure II shows the proposed transition state for the hypochlorite reaction, where H^+ transfer reduces the charge buildup at oxygen as Cl^+ bonds to I^-. Although a proton preequilibration is needed for the $k_H[H^+][OCl^-][I^-]$ rate term, the transition state $(HOClI^-)^{\ddagger}$ closely resembles that proposed for HCO_3^- and HPO_4^{2-} (i.e. HA in II). Hence, the k_H value falls on the same Brønsted line as the rate constants for these acids.



II

The relative reactivity of $OCl^- >> NH_2Cl >> NHCl_2$ parallels the base strength of these species rather than the O–Cl or N–Cl bond strengths. The bond dissociation energy (kcal mol^{-1}) of OCl^- is 64.3,[34] while the estimated value for NH_2Cl is 43.[35] A comparison of N–Cl force constants (mdyn $Å^{-1}$) shows that the bond strength decreases slightly in the order NH_2Cl (3.06) > $NHCl_2$ (2.75) > NCl_3 (2.72).[36] Figure 6 shows the correlation between the third-order rate constants for H_3O^+, I^-, and various chlorine species as a function of the protonation constant of the species. (A log K_H value of −2.5 is estimated for $NHCl_2$ on the basis of the correlation of HOCl rate constants with the base strengths of amines and chloramines.[37])

However, the correlation with basicity does not hold for NCl_3, which is an extremely weak base and hence might be expected to react slowly. Instead, NCl_3 reacts very rapidly with I^- and does not appear to involve simultaneous proton transfer.[8] The N–Cl bond energy is calculated to be 45 kcal mol^{-1},[38] which is close to the estimated value of the bond in NH_2Cl. The greater reactivity

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(31) Chia, Y. T. U.S. Atomic Energy Commission Report UCRL-8311, 1958.

(32) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355–1361.

(33) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; p 198.

(34) Darwent, B. *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1970**, *NSRDS-NBS 31*.

(35) Livett, M. K.; Nagy-Felsobuki, E.; Peel, J. B.; Willett, G. D. *Inorg. Chem.* **1978**, *17*, 1608–1612.

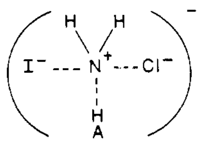
(36) Jander, J.; Engelhardt, U. In *Developments in Inorganic Nitrogen Chemistry*; Colburn, C. B., Ed.; Elsevier: Amsterdam, 1973; Vol. II, pp 70–228.

(37) Margerum, D. W.; Gray, E. T., Jr.; Huffman, R. P. In *Organometals and Organometalloids, Occurrence and Fate in the Environment*; ACS Symposium Series 82; Brinckman, F. E., Bellama, J. M., Eds.; American Chemical Society: Washington, DC, 1978, pp 278–291.

(38) Huggins, M. L. *J. Am. Chem. Soc.* **1953**, *75*, 4123–4126.

may be due to a stronger interaction of NCl_3 as a Lewis acid with I^- as a Lewis base.

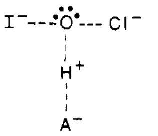
Comparison of Mechanisms. We propose that iodide ion attacks the chlorine (structure I) rather than the nitrogen. The latter would give an S_N2 type transition state such as structure III. First,



III

it is much easier to expand the coordination number of chlorine than that of nitrogen. This is reflected in the rapid reactions found in this work compared to relatively slow corresponding S_N2 reactions of $CH_3Cl + I^-$, where the rate constant is only 2.0×10^{-5} $M^{-1}\ s^{-1}$ at 25 °C in water.[39] Thus, the ratio of rate constants for the reactions of NH_3Cl^+ with I^- compared to CH_3Cl with I^- is 4.3×10^{13}. The difference is that I^- can attack the chlorine atom in NH_3Cl^+ with NH_3 as a favorable leaving group, whereas this cannot occur with CH_3Cl because CH_3^+ is a very poor leaving group. Second, in a nitrogen-centered mechanism, such as structure III, it is not clear why acids should necessarily accelerate the reaction. Although protonation would make the I^- attack more favorable, it would also make the Cl^- leaving step less favorable. Third, if NH_2I and Cl^- were the initial products of the reaction, then I^- would have to attack at the iodine in NH_2I to give I_2. Hence, in any case a halide attack on a bound halogen atom must take place, and it is logical to initiate the iodide reaction at chlorine.

Analogous arguments apply to the reaction of I^- with OCl^-, where we prefer the transition state in II to that in IV. We cannot



IV

rule out the OH^+-transfer mechanism from Cl^- to I^-, but we suggest that this is less likely than Cl^+ transfer to I^-. Hydroxide ion is a reasonable leaving group. Furthermore, this is one of the general pathways proposed for the reversible hydrolysis of halogens[32] (eq 25, 26), where X_2OH^- is proposed as an intermediate.

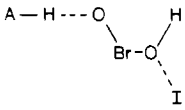
$$\mathrm{XOH + X^- \rightleftarrows X_2OH^- \rightleftarrows X_2 + OH^-} \tag{25}$$

$$\mathrm{XOH + X^- \rightleftarrows X_2OH^- + H^+ \rightleftarrows X_2 + H_2O} \tag{26}$$

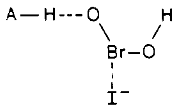
Ferranti and Indelli[27] observed both specific- and general-acid-assisted reactions between bromite and iodide with the rate expression in eq 27. They found a Brønsted α value of 0.19 for

$$\text{rate} = k_1[H^+][BrO_2^-][I^-] + k_2[H^+][BrO_2^-][I^-][HA] \tag{27}$$

k_2 and suggested simultaneous attack of I^- and HA on OBrOH with a transition state V that leads to O–Br bond cleavage and



V



VI

O–I bond formation. An alternate transition state with I^- attack on Br(III) is given in VI with O–Br bond cleavage and Br–I bond formation. Barton and Wright[24] reported a rate expression for iodide reactions with bromate with a $[H^+]^2[B^-]$ term (eq 28),

$$\text{rate} = k_0[H^+]^2[BrO_3^-][I^-] + k_b[B^-][H^+]^2[BrO_3^-][I^-] \tag{28}$$

where B^- is a carboxylate ion. This term cannot be distinguished from a term with $[H^+][HB]$, and that seems more likely to us. If treated as a general-acid-assisted rate, their data give an α value of 0.22. Similar rate expressions are found for the iodide reaction with iodate.[25] Barton and Wright outline possible mechanisms with I^- attack on Br(V) and on I(V) or with I^- attack on oxygen. They also suggest direct base interaction with Br(V) and with I(V) in both mechanisms. We suggest that general-acid interaction with the bromate and iodate oxygens is more likely. In either case the low α value is indicative of a weakly basic site that influences but does not dominate the reactivity with iodide ion.

Conclusions

Mixtures of hypochlorite, monochloramines, and dichloramines can be distinguished from one another on the basis of the very large differences in their rates of reaction with iodide. In the application of analytical methods for these species it is important to realize that the rates will depend on buffer concentrations as well as pH and iodide ion concentrations. When trichloramine is present, its very fast reaction with iodide cannot be easily distinguished from that of hypochlorous acid. The trichloramine reaction with iodide does not appear to be quantitative. Furthermore, the reaction will generate dichloramine, which will cause erroneously high estimates of the initial dichloramine concentration in a sample.

The general-acid-assisted character of the iodide reactions with hypochlorite, monochloramines, and dichloramines show that proton transfer takes place as the molecules move through the transition state. The relative rates depend on the basicity of the chlorine species and the acidity of the general acid rather than on the strength of the O–Cl or N–Cl bond. We propose that the reactions occur by Cl^+ transfer to I^- with simultaneous H^+ transfer to the adjacent nitrogen or oxygen. The greater the Brønsted α value, the greater the degree of H^+ and Cl^+ transfer in the transition state for a given acid strength.

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Supplementary Material Available: Listings of pseudo-first-order rate constants for the reaction of iodide with chloramines, dichloramines, and hypochlorite as a function of buffer, iodide, and hydrogen ion concentrations (9 pages). Ordering information is given on any current masthead page.

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(39) Bathgate, R. H.; Moelwyn-Hughes, E. A. *J. Chem. Soc.* **1959**, 2642–2648.