Equilibrium, Kinetic, and UV-Spectral Characteristics of Aqueous Bromine Chloride, Bromine, and Chlorine Species

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Bromine chloride in the presence of chloride ion forms the dichlorobromate(I) ion, $BrCl_2^-$, where $K_1 = [BrCl_2^-]/([BrCl(aq)][Cl^-]) = 6.0\ M^{-1}$. Equilibrium constants (all at 25.0 °C, $\mu = 1.00$ M) are also determined for $K_2 = [Br_2Cl^-]/([BrCl(aq)][Br^-]) = 1.8 \times 10^4\ M^{-1}$, for $K_3 = [Br_2Cl^-]/([Br_2(aq)][Cl^-]) = 1.3\ M^{-1}$ and for $K_4 = [Br_3^-]/[Br_2(aq)][Br^-] = 16.1\ M^{-1}$. UV absorption bands are resolved for $BrCl_2^-$ at 232 nm (ϵ 32 700 $M^{-1}\ cm^{-1}$) and 343 nm (ϵ 312 $M^{-1}\ cm^{-1}$), for Br_2Cl^- at 245 nm (ϵ 24 900 $M^{-1}\ cm^{-1}$) and 381 nm (ϵ 288 $M^{-1}\ cm^{-1}$), and for Br_3^- at 266 nm (ϵ 40 900 $M^{-1}\ cm^{-1}$). The UV spectral properties of $Cl_2(aq)$, Cl_3^-, $Br_2(aq)$, and Br^- are examined and compared. The reaction between $Cl_2(aq)$ and Br^- to form $BrCl_2^-$ occurs at the diffusion-controlled limit; the rate constant, $(7.7 \pm 1.3) \times 10^9\ M^{-1}\ s^{-1}$, is measured by the pulsed-accelerated-flow method. The rapid formation of $BrCl_2^-$ can be used as an analytical method for trace bromide ion, where as little as 10^{-5} mol % Br^- can be detected in aqueous solutions of HCl or chloride salts.

Introduction

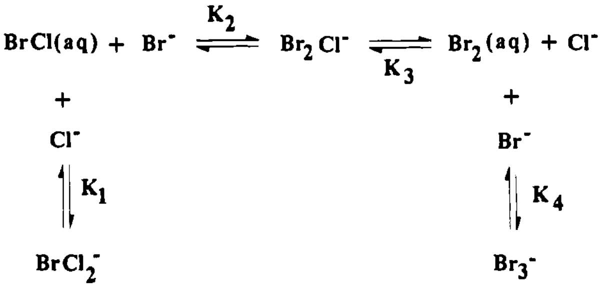
Bromine chloride (BrCl) was first prepared in 1826 by Balard,[1] although its existence was not confirmed until 1929 when Gillam and Morton[2] showed that the absorption spectrum of a Br_2/Cl_2 mixture is very different than the sum of the individual components. In 1952, Popov and Mannion[3] studied the reaction in eq 1 and determined a value for the disproportionation equilibrium constant, $K_D = 0.145$ in CCl_4. In 1958, a series of papers by Schulek, Burger, and Pungor[4–9] described the preparation of aqueous BrCl by eq 2. They determined that

$$2BrCl \overset{K_D}{\rightleftharpoons} Br_2 + Cl_2 \qquad (1)$$

$$KBrO_3 + 2KBr + 6HCl \rightarrow 3BrCl(aq) + 3KCl + 3H_2O \qquad (2)$$

the reaction takes place in two steps: first, the formation of Br_2 and second, further oxidation by BrO_3^- to give BrCl. They also stated that, in acid, BrCl(aq) reacts with bromide ion to yield molecular bromine. These authors[6] concluded that in aqueous solution with chloride ion present, BrCl(aq) exists primarily as $BrCl_6^{5-}$. In 1968, Gutman, Lewin, and Perlmutter-Hayman[10] studied BrCl in aqueous solutions and also found that it exists as a complex ion of the form $BrCl_x^{1-x}$. However, they rejected the suggestion that the actual formula is $BrCl_6^{5-}$ and preferred to consider the composition as uncertain. In 1966 Bell and Pring[11] used redox potentials to determine stability constants for species that were assumed to be $BrCl_2^-$ and Br_2Cl^-. They also assumed negligible concentrations of BrCl(aq) under their conditions. The stability constants were based on the equilibrium constants determined for the hydrolysis of BrCl[12] and for the hydrolysis of Br_2.[13] In the present work we confirm that $BrCl_2^-$ is the correct stoichiometry for $BrCl_x^{1-x}$ rather than species with more than two chloride ions. We determine equilibrium constants (25.0 °C, $\mu = 1.0$ M) for the reactions in Scheme 1, where K_1, K_2, K_3, and K_4 are all stability constants (M^{-1}). The K_1 value was previously unknown and the product of $K_1K_3/K_2 = [BrCl_2^-][Br^-]/([Br_2][Cl^-]^2)$ is a factor of 14 smaller than reported by Bell and Pring.[11] We also determine the UV spectral properties of BrCl(aq), $BrCl_2^-$, Br_2Cl^-, $Br_2(aq)$, and Br_3^-. Tribromide ion is a well known species, but literature values for its peak molar absorptivity range from 25,000 $M^{-1}\ cm^{-1}$ at 266 nm[14] to 39,000 $M^{-1}\ cm^{-1}$ at 270 nm.[15] We believe that bromine volatility has been a source of error, so we generate Br_2/Br_3^- in situ and determine reliable molar absorptivity values for Br_3^- based on K_4 values determined at the same ionic strength and 25.0 °C. In previous

Scheme 1



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work[15-17] there has also been serious disagreement about the molar absorptivities of Cl_2 and Cl_3^- at 200 to 240 nm, and we show that this is due in part to trace Br^- contamination.

Bromine chloride is used in large quantities for wastewater disinfection[18,19] as an alternative to the use of chlorine. Its chemical stability and reactions in water are important industrially. Our equilibrium constants permit the species distribution of BrCl(aq), HOBr, Cl_2 and Br_2 to be calculated.

Margerum and co-workers[20-22] have studied the equilibrium and kinetics of other interhalogen compounds in aqueous solution. In the presence of excess chloride ion,[21] iodine chloride exists primarily as ICl_2^-; in the presence of excess bromide ion,[22] iodine bromide exists primarily as IBr_2^-. Both ICl and IBr hydrolyze rapidly and both react with I^- rapidly. The present work shows that BrCl also hydrolyzes rapidly and reacts with Br^- rapidly.

Experimental Section

Reagents. Aqueous solutions of bromine chloride were prepared by dissolving stoichiometric amounts of sodium bromide and sodium bromate (eq 2) in 1 M HCl, in accord with the method outlined by Schulek, Burger, and Pungor.[4-9] Concentrations of HCl were kept high during the preparation and storage of BrCl(aq) in order to prevent the formation of Br_2. These solutions were standardized by iodometry and stored to prevent the loss of the volatile BrCl. The HCl solutions were prepared from 37% HCl diluted with filtered deionized/distilled water and were standardized with NaOH, which had in turn been standardized against potassium hydrogen phthalate with phenolphthalein indicator.

Stock solutions of aqueous chlorine were prepared by bubbling Matheson high purity gas, prewashed in H_2SO_4, either directly into distilled, deionized water, or into ~0.2 M "carbonate-free" NaOH, and diluted with an additional volume of NaOH. This latter hypochlorite solution was assayed at 292 nm, $\epsilon_{OCl} = 350\ M^{-1}cm^{-1}$, and stored at ~5 °C in Nalgene bottles (aged by previous exposure to hypochlorite) for a period of weeks without significant loss of A_{292}. Raphael[15] explicitly recommends passing source Cl_2 gas through a −30 °C cold trap to remove Br_2 and BrCl prior to dissolution. We found that this treatment had no effect on the spectra of the solutions obtained with high purity $Cl_2(g)$. Chlorine solutions were prepared by dilution of stock OCl^- in NaOH with excess HCl and transferred with glass syringes and Kel-F tubing to stoppered glassware with minimal head spaces and used immediately. Checks for loss by volatility were performed by repetitive scans.

Spectrophotometric Measurements. UV/vis measurements were made with a Perkin-Elmer Lambda-9 UV/vis/NIR spectrophotometer interfaced to a Zenith 386/20 computer. All scans were performed at 25.0 ± 0.2 °C. Spectral data from 200 to 500 nm were examined for $BrCl_2^-$, BrCl, Br_2Cl^-, Br_2, Br_3^-, Cl_2, and Cl_3^-. Spectra from 170–500 nm were also obtained for Br_3^-, Br_2, Br^-, Cl^- and $HClO_4$. In the far UV region the instrument slit width was set at 5 nm, whereas 2 nm is the default setting used for other wavelengths.

Pulsed-Accelerated-Flow Measurements. Reactions of Cl_3^-/Cl_2(aq) with Br^- were monitored with a pulsed-accelerated-flow spectrophotometer (PAF),[23,24] Model IVA. The Model IVA PAF instrument is an updated version of an instrument described previously,[24] where several features used in PAF Model IV[25,26] are incorporated. The Model IVA PAF instrument consists of three hardware assemblies and three controllers. The three hardware assemblies are: (1) a DC servo motor syringe driver assembly that includes a zero-backlash ball bearing loaded screw (Model PR-1105-12F-O-D-D-W, Warner Electric Brake & Clutch CO.; Beloit, WI), a MAX 400 servo amplifier (Electro-Craft Corp., Hopkinton, MN) and a motor (Model E 728-39-003, Electro-Craft Corp.) with a tachometer that provides velocity feedback and an optical encoder with 1000 line resolution that provides positional feedback; (2) a hydraulic flow assembly which includes driving and receiving syringes, and a twin-path mixing/observation cell made of black Kel-F following the previous design for a PVC cell;[24] and (3) a spectrophotometer assembly which includes lamp power supplies and housing, a double monochrometer with a 200–850 nm wavelength range and low stray light (Model DH-10, Instruments SA, Inc., Edison, NJ), transfer optics, and a photodiode detector (HUV-400B, EG&G electro Optics, Salem, MA), and custom made filters.

The first controller is a PRO-400 velocity controller (Electro-Craft Corp.). The PRO-400 develops a velocity command signal (VCS) from preprogrammed velocity profile statements. The VCS is then amplified by the MAX-400 to drive the motor to follow the programmed velocity profile. The second controller is a LAB MASTER interface card with a 12-bit A/D converter (Scientific Solution, Inc., Solon, OH), which is installed directly into the computer data bus. It is used to control data acquisition and to synchronize the data acquisition and the motion of the motor. The third control system is a Zenith Computer model Z-151. We have developed a program in C language for data acquisition and communication to the PRO-400 which controls the DC servo motor system.

The PAF spectrometer employs integrating observation in the twin-path mixing/observation cell during continuous flow of short duration (a 0.22 s pulse). The reactions are observed along the direction of flow from their point of mixing to their exit from the observation tube. The flow was decelerated during the pulse to give a linear velocity ramp, and 250 measurements of the transmittance were taken as the flow velocity changed from 12.0 to 3.0 m s^{-1}. Solution reservoirs, drive syringes, and the mixing cell were thermostated at 25.0 ± 0.1 °C. A second-order unequal concentration apparent rate constant, k_{12app}, was obtained by iteration on the R value at different velocities from the absorbance data in eq 3.[23,24] M_{exptl} represents the fraction not reacted

$$M_{exptl} = \frac{A_v - A_A(1-q) - A_p}{A_A + \frac{1}{q}(A_B - A_p)} = \frac{1-q}{R}\ln\left(\frac{1-qe^{-R}}{1-q}\right) \qquad (3)$$

$$R = \frac{bK_{12app}C_A(1-q)}{v} \qquad (4)$$

in the observation path, A_v is the absorbance at an individual velocity (v), b is the cell length (1.025 cm), A_A is the absorbance of reactant A, A_B is the absorbance of reactant B, A_p is the absorbance of the products only, C_A is the initial concentration of reactant A, C_B is the initial concentration of reactant B, and q is the concentration ratio ($q = C_B/C_A$; $C_A > C_B$). The k_{12app} value was a function of the velocity, v, of the solution in the observation cell as in eq 5,[23-24] where k_{m12} is a mixing

$$\frac{1}{k_{12app}} = \frac{1}{k_{m12}v} + \frac{1}{k_{12}} \qquad (5)$$

constant, and k_{12} is the second-order rate constant. The k_{12} value can be obtained from the intercept of a double-reciprocal plot of $1/k_{12app}$ vs $1/v$.

Solutions used for the PAF experiments were filtered, degassed, and equilibrated at 25.0 ± 0.1 °C before experimental runs. The reaction

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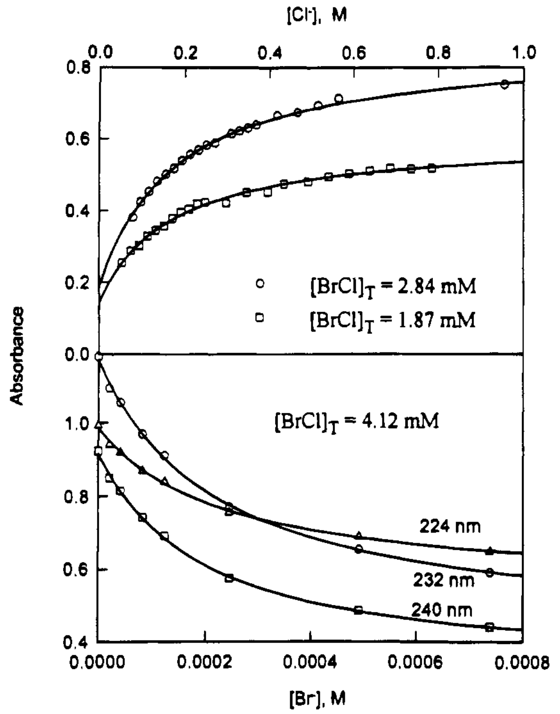

Figure 1. Absorbance data (1 cm cell) for the evaluation of K_1. (top) Absorbance at 343 nm for $[BrCl]_T$ as a function of $[Cl^-]$. Curves are fit to eq 7 for $BrCl_2^-$ formation; $K_1 = 6.0 \pm 0.3$ M^{-1}. (bottom) Absorbance at 224, 232, and 240 nm for $[BrCl]_T$ as a function of $[Br^-]$. Curves are fit to eq 16; $K_1 = 6.1 \pm 0.3$ M^{-1}.

was monitored at 232 nm for the formation of $BrCl_2^-$. Six PAF runs were averaged to obtain the experimental rate constant and its standard deviation.

Results and Discussion

Equilibrium Constant for $BrCl_2^-$ Formation. We found no evidence for bromine chloride species with Cl/Br ratios greater than 2. The equilibrium constant, K_1, for the reaction given in eq 6 was determined spectrophotometrically at 25.0

$$BrCl(aq) + Cl^- \rightleftharpoons BrCl_2^- \qquad (6)$$

°C, $\mu = 1.0$ M. A known quantity of bromine chloride in hydrochloric acid solution was diluted into 1.00 M perchloric acid, placed into a quartz cell, and its absorbance at 343 nm (the reported maximum for BrCl(aq)[6]) was measured. Small aliquots (0.0100 mL) of 1.00 M HCl were added to this solution, and the absorbance was determined after each addition. A nonlinear curve-fitting program with a Marquardt–Levenberg algorithm (Sigma Plot)[27] was used to fit the absorbance dependence on chloride ion concentration. The $[Cl^-]$ comes from the original HCl in the stock solution of BrCl and the HCl added in small aliquots. The relationship between the observed absorbance (after correction for dilution, 1.00 cm cell) and the concentrations of the absorbing species is given in eq 7 where $[BrCl]_T = [BrCl(aq)] + [BrCl_2^-]$ and ϵ = molar

$$A_{343} = \frac{(\epsilon_{BrCl} + K_1[Cl^-]\epsilon_{BrCl_2^-})[BrCl]_T}{K_1[Cl^-] + 1} \qquad (7)$$

absorptivity (M^{-1} cm^{-1}) of the respective species. A K_1 value of (6.0 ± 0.3) M^{-1} is determined from spectrophotometric measurements. Figure 1 (top) shows the absorbance at 343 nm vs $[Cl^-]$ data as fitted to eq 7 for two concentrations of $[BrCl]_T$. The resulting molar absorptivity values at 343 nm are 70 ± 6 M^{-1} cm^{-1} for BrCl(aq) and 312 ± 8 M^{-1} cm^{-1} for $BrCl_2^-$. The molar absorptivity for $BrCl_2^-$ is in good agreement with the value of 310 M^{-1} cm^{-1} obtained by Gabes and Stufkens[28] in a study of alkali metal salts of the interhalogen anions. Figure 2 is the spectrum of $[BrCl]_T$ in 1.072 M HCl, where the $BrCl_2^-$/BrCl(aq) ratio is 6.4 and the molar absorptivity of $BrCl_2^-$ is much greater than that of BrCl(aq). The intense absorption band for $BrCl_2^-$ at 232 nm (ϵ 32,700 M^{-1} cm^{-1}) is used in our study of the reactions in Scheme 1, in trace Br^- determinations, and in the kinetics of the reaction between Cl_2(aq) and Br^-.

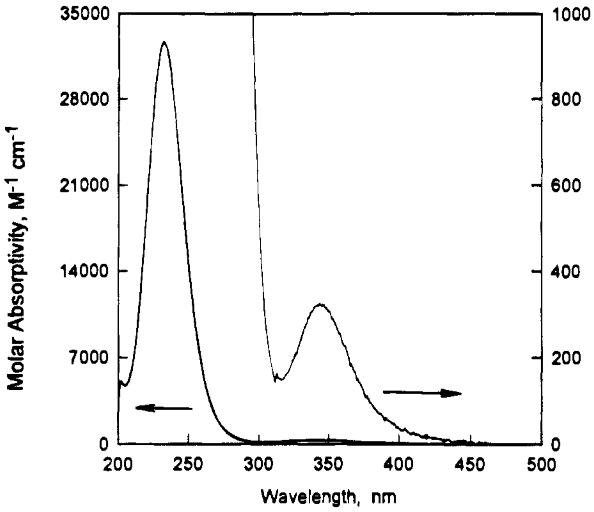

Figure 2. Spectrum of $BrCl_2^-$ with λ_{max} at 343 and 232 nm.

Table 1. Bromide Ion Content of Analytical Reagent Grade Chemicals Determined by the $BrCl_2^-$ Method[a]

compound	source	reagent grade specifications,[b] wt % Br^- (mol % Br^-)	mol % Br^- found
HCl	Mallinckrodt	0.005 (6×10^{-3})	$<10^{-5}$
HCl	J. T. Baker	0.005 (6×10^{-3})	0.0080
NaOH	J. T. Baker		$<10^{-5}$ [c]
$CaCl_2$	J. T. Baker		0.00075[d]
NH_4Cl	J. T. Baker		0.0015
LiCl	J. T. Baker		0.0080
NaCl	J. T. Baker	0.01 (7×10^{-3})	0.011
KCl	Mallinckrodt	~0.01 (9×10^{-3})	>0.14

[a] 0.9 M solutions in 0.1 M Mallinckrodt HCl reacted with 10^{-4} M Cl_2. [b] Reference 29. [c] Neutralized with Mallinckrodt HCl. [d] 0.45 M solution in 0.1 M Mallinckrodt HCl; percent Br per Cl.

Trace Br^- Determination. A Beer's law calibration for $BrCl_2^-$ at 232 nm (1.0 cm cell) was established based on the reaction of Cl_2 (1.07×10^{-4} M) in 0.98 M HCl (negligible Br^- content) with NaBr added to give a range of (1.9 to 7.6) x 10^{-5} M Br^-. A linear plot was obtained from 0.33 to 2.58 absorbance units for $BrCl_2^-$/BrCl and an intercept of 0.332 ± 0.007 that corresponds to the absorbance of Cl_3^-/Cl_2. The bromide content of HCl, NaOH and various analytical reagent grade chloride salts were determined spectrophotometrically from the absorbance of $BrCl_2^-$ after the addition of chorine (Table 1). In some cases the Br^- content of these compounds met ACS reagent chemicals specifications,[29] but we found that the source of the HCl was important for our studies when low Br^- content was important. Our method is extremely sensitive and can determine Br^- at ± 10^{-5} mol %.

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Table 2. Determination of $K_{Cl_3^-}$ at 25 °C

method	$K_{Cl_3^-}$, M^{-1}	ref
spectrophotometry	0.19 ± 0.02	16
solubility, Cl_2 in MCl, HCl	0.18–0.21	30
solubility, Cl_2 in HCl	0.16[a]	31
	av 0.18 ± 0.02	

[a] Extrapolated from 40–90 °C.

UV Molar Absorptivities of Cl_2(aq) and Cl_3^-: the Cl_3^- Stability Constant. Estimates[15–17] of the absorptivities of Cl_2(aq) and Cl_3^- near their common maximum at 325 nm are in general agreement, but values for absorptivities of these species in the far UV region, 210–230 nm, differ widely. Thus, at 233 nm Cl_3^- is reported[17] to have $\epsilon = 18\,500$ M^{-1} cm^{-1}, while at 230 nm a value of 350 M^{-1} cm^{-1} is reported[15] and at 220 nm a value of 10 000 M^{-1} cm^{-1} is reported.[16]

To resolve these discrepancies, the absorbance of Cl_2(aq) solutions, in the range of 0.17 to 1.1 mM, were measured from 210–355 nm in 0.53 and 1.06 M HCl (Br^--free). The effective absorptivities, ϵ^*, based on total $[Cl_2]_i$ were calculated from the slopes of Beer's law plots where the intercepts coincided with the corresponding blanks for HCl.

To interpret these effective absorptivities, ϵ^*, in terms of molar absorptivities, ϵ_{Cl_2} and $\epsilon_{Cl_3^-}$, eqs 8 and 9, reliable estimates

$$\epsilon^* = \frac{\epsilon_{Cl_2} + K_{Cl_3^-}[Cl^-]\epsilon_{Cl_3^-}}{1 + K_{Cl_3^-}[Cl^-]} \tag{8}$$

$$K_{Cl_3^-} = \frac{[Cl_3^-]}{[Cl_2][Cl^-]} \tag{9}$$

of $K_{Cl_3^-}$ at 25 °C are required. The three estimates[16,30,31] of $K_{Cl_3^-}$ in the literature are based on a variety of measurements as shown in Table 2. The value attributed to Hine and Inuta[31] was extrapolated with the use of the van't Hoff expression, eq 10, from data collected over 40–90 °C; their value at 30 °C

$$\frac{d \ln K}{d\frac{1}{T}} = -\frac{\Delta H}{R} \tag{10}$$

was obviously discrepant and omitted from this calculation.

With measured ϵ^* at two $[Cl^-]$ and $K_{Cl_3^-} = 0.18 \pm 0.02$, values of ϵ_{Cl_2} and $\epsilon_{Cl_3^-}$ were obtained by rearranging eq 8 and solving eq 11 for two $[Cl^-]$ simultaneously at each wavelength.

$$\epsilon^*(1 + K_{Cl_3^-}[Cl^-]) = \epsilon_{Cl_2} + K_{Cl_3^-}[Cl^-]\epsilon_{Cl_3^-} \tag{11}$$

Values obtained are listed in Table 3 together with estimated uncertainties. The ϵ_{Cl_2} and $\epsilon_{Cl_3^-}$ values in the range of 300–350 nm fall within the range previously reported for Cl_2/Cl_3^-; however, in the range 210–235 nm our values correspond much closer to those of Zimmerman and Strong[16] than those of either Soulard *et al.*[17] or Raphael.[15] The anomalous value of Soulard *et al.*[17] $\epsilon_{233} = 18\,500$ M^{-1} cm^{-1}, we attribute to an adventitious Br^- impurity, which generated $BrCl_2^-$ in Cl_2/Cl_3^- media. We are unable to account for Raphael's anomalously low absorptivities in this wavelength range.

Table 3. Molar Absorptivities for Aqueous Chlorine and Trichloride Ion[a]

λ, nm	ϵ_{Cl_2}	$10^{-2}\epsilon_{Cl_3^-}$
210	290(30)	92(2)
215	145(25)	100(2)
220	57(24)[b]	104(2)[b]
225	9(23)	101(2)
230	~0[c]	94(2)[c]
235	~0	82(1)[d]
275	9(2)	5.0(0.2)
285	20(1)	2.1(0.1)
295	35(1)	1.4(0.1)
305	52(2)	1.5(0.1)
315	66(2)	1.8(0.1)
325	70(2)	1.8(0.2)
335	64(2)	1.7(0.2)
345	52(1)	1.3(0.1)
355	37(1)	1.0(0.1)

[a] Values are calculated based on $K_{Cl_3^-} = 0.18$ M^{-1}. [b] Reference 16 gave $\epsilon_{Cl_2} = 210$ M^{-1} cm^{-1} and $\epsilon_{Cl_3^-} = 10\,000$ M^{-1} cm^{-1} at 220 nm. [c] Reference 15 gave $\epsilon_{Cl_2} = 14$ M^{-1} cm^{-1} and $\epsilon_{Cl_3^-} = 350$ M^{-1} cm^{-1} at 230 nm. [d] Reference 17 gave $\epsilon_{Cl_3^-} = 18\,500$ M^{-1} cm^{-1} at 233 nm.

Table 4. Kinetics of $BrCl_2^-$ Formation from the Reaction of Aqueous Chlorine with Bromide Ion[a]

$[Cl_2]_T$, M[b]	$[Br^-]_i$, M	$10^{-9}k_r$, M^{-1} s^{-1}
2.5×10^{-6}	5.0×10^{-6}	6.9 ± 1.2
6.1×10^{-6}	7.5×10^{-6}	6.5 ± 1.0
7.5×10^{-6}	1.0×10^{-5}	6.0 ± 1.2

av = $(6.5 \pm 1.1) \times 10^9$ M^{-1} s^{-1} for $[Cl_2]_T$
$k_{12} = (7.7 \pm 1.3) \times 10^9$ M^{-1} s^{-1} for Cl_2(aq)

[a] Conditions: 1.00 M HCl, 25.0 °C, PAF IVA, second-order unequal concentrations, six runs at each set of conditions. [b] $[Cl_2]_T = [Cl_2(aq)]_i + [Cl_3^-]_i$.

$$Cl_2(aq) + Br^- \xrightarrow{k_{12}} BrCl_2^- \tag{12}$$

Kinetics of $BrCl_2^-$ Formation from Br^- and Cl_2. The PAF method was used to study the reaction in eq 12 in 1.0 M HCl at 232 nm. Second-order unequal concentration conditions were used as given in Table 4. The observed second-order rate constant for 18 runs was $(6.5 \pm 1.1) \times 10^9$ M^{-1} s^{-1}. After correction for the fraction of Cl_3^- present that is considered to be less reactive than Cl_2(aq), the k_{12} value is $(7.7 \pm 1.3) \times 10^9$ M^{-1} s^{-1} which is at the diffusion limit.

Molar Absorptivity and Equilibrium Constant for Br_3^-. In order to avoid problems with volatility in transfers of liquid or aqueous bromine, we choose to generate bromine and tribromide ion *in situ* within a spectrophotometric cell by the reaction of bromate ion with bromide ion in acid solution (eqs 13 and 14). This procedure has the advantage of using a

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2(aq) + 3H_2O \tag{13}$$

$$Br_2(aq) + Br^- \overset{K_4}{\rightleftharpoons} Br_3^- \tag{14}$$

primary standard ($KBrO_3$) to give accurate concentrations of $[Br_2]_T = ([Br_2] + [Br_3^-])$. The reaction with excess NaBr (0.045 to 0.113 M) in 0.366 M $HClO_4$ (with $NaClO_4$ to give μ = 1.00 M) is complete in a few minutes. The rate constant for the loss of BrO_3^- is known[32] and equals $3.3[Br^-][H^+]^2$ (s^{-1}). Equation 14 is a very rapid equilibrium. Spectral measurements with absorbance values at 266 nm (A_{266}) are taken after 5–10 min in a 1.00 cm cell. The experimental data were fit by a Marquardt–Levenberg nonlinear curve fitting algorithm to eq 15 and gave $\epsilon_{Br_3^-} = 40\,900 \pm 400$ M^{-1} cm^{-1}, $K_4 = 16.1 \pm 0.3$ M^{-1}. (Correction due to the absorbance of Br_2(aq) is negligible.) Because our molar absorptivity value was 5% higher than the previous largest value,[15] we also measured $\epsilon_{Br_3^-}$ by the same

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(30) Sherrill, M. S.; Izard, E. F. *J. Am. Chem. Soc.* **1931**, *53*, 1667–1675.
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$$A_{266} = \frac{(\epsilon_{\mathrm{Br_3^-}})K_4[\mathrm{Br^-}][\mathrm{Br_2}]_\mathrm{T}}{1 + K_4[\mathrm{Br^-}]} \qquad (15)$$

technique in solutions where the ionic strength was 0.54 M and the K_4 value at this μ value is known[33] to be 16.8 M^{-1}. Once again we find that $\epsilon_{\mathrm{Br_3^-}}{}^{266} = 40\,900 \pm 400\ M^{-1}\ cm^{-1}$, so we regard this as a valid value for the molar absorptivity for Br_3^- at its absorption maximum.

Spectrophotometric data from 220 nm to 500 nm are used in studies of the equilibria in Scheme 1, so molar absorptivities are needed for Br^-, $Br_2(aq)$, and Br_3^- over this spectral region. A $Br_2(aq)$ solution in 1.0 M $HClO_4$ was prepared from Br_2 vapor to avoid undesirable reactions when liquid bromine initially comes in contact with water.[34] We confirmed experimentally the molar absorptivity value of 175 M^{-1} cm^{-1} reported[17] for $Br_2(aq)$ at 390 nm. (Once again, precautions to avoid loss of volatile Br_2 are important.) Strong absorption bands for Br^- at 197.6, 185.5 and 175.1 nm have been reported previously,[13] but we did not find reports for the similar absorption bands for $Br_2(aq)$ that we resolved and give in Table 5. The spectrum for Br_3^- (corrected for contributions in the experimental data from $Br_2(aq)$ and Br^-) is fit to four Gaussian bands as given in Table 5. The Br_3^- spectrum has three overlapping bands at 261, 273, and 282 nm that cause the observed maximum at 266 nm and a fourth much less intense band at 362 nm.

Spectrophotometric Studies of Br^- Reactions with $BrCl_2^-$. Solutions with $[BrCl]_T = 3.55 \times 10^{-5}$ M or 4.12×10^{-5} M in 1.072 M HCl were reacted with variable Br^- concentrations from 2.0×10^{-5} M to 0.208 M. Digitized spectral data at 2 nm intervals from 220–300 nm were obtained for 22 different Br^- concentrations (Figure 3). The observed absorbance (1.00 cm cell) at each wavelength, A_λ, as a function of $[Br^-]$ is given in eq 16, where ϵ_1 to ϵ_6 are the molar absorptivities of BrCl(aq),

$$A_\lambda = \left[[\mathrm{BrCl_2^-}]_\mathrm{T}\Big/\left(1 + \frac{1}{K_1[\mathrm{Cl^-}]} + \frac{K_2[\mathrm{Br^-}]}{K_1[\mathrm{Cl^-}]} + \frac{K_2[\mathrm{Br^-}]}{K_1K_3[\mathrm{Cl^-}]^2} + \frac{K_2K_4[\mathrm{Br^-}]^2}{K_1K_3[\mathrm{Cl^-}]^2}\right)\right]\left[\epsilon_2 + \frac{\epsilon_1}{K_1[\mathrm{Cl^-}]} + \frac{\epsilon_3K_2[\mathrm{Br^-}]}{K_1[\mathrm{Cl^-}]} + \frac{\epsilon_4K_2[\mathrm{Br^-}]}{K_1K_3[\mathrm{Cl^-}]^2} + \frac{\epsilon_5K_2K_4[\mathrm{Br^-}]^2}{K_1K_3[\mathrm{Cl^-}]^2}\right] + \epsilon_6[\mathrm{Br^-}] \qquad (16)$$

$BrCl_2^-$, Br_2Cl^-, $Br_2(aq)$, Br_3^-, and Br^-, respectively. Known values for K_1 and K_4 and for $(\epsilon_2 + \epsilon_1/K_1[Cl^-])$, ϵ_4, ϵ_5, ϵ_6 at each wavelength are used. The A_λ values as a function of $[Br^-]$ were fitted by eq 16 using the Marquardt–Levenberg algorithm to solve K_2, K_3, and ϵ_3 values. Data obtained at low Br^- concentrations show the disappearance of $BrCl_2^-$ and the appearance of Br_2Cl^-. Therefore, these data are best for the initial evaluation of K_2 and ϵ_3. On the other hand, data obtained at higher Br^- concentrations show the characteristic Br_3^- spectra and are most sensitive to values of K_3 and ϵ_3. The nonlinear iteration starts by optimizing K_2 and ϵ_3 values with data obtained at lower Br^- concentrations from 220 to 280 nm. Initially, the K_3 value was assumed to be 1.14 M^{-1}.[11] Data between 250 to 260 nm were not used for the evaluation, because the absorbance change is small near the isosbestic point. The newly resolved K_2 value was then used to iterate K_3 and ϵ_3 values from 260 to 300 nm with data at higher Br^- concentrations. The resulting K_3 value, in turn, was used to reiterate K_2 and ϵ_3 values. This process continued until the average K_2 and K_3 values converged. The results are $K_2 = (1.8 \pm 0.2) \times 10^4$ M^{-1} and $K_3 = 1.3 \pm 0.3$ M^{-1}.

Table 5. Spectral Bands within the $Br_2(aq)$, Br^-, and Br_3^- Absorbance Peaks[a]

	λ, nm	$10^{-4}\epsilon$, M^{-1} cm^{-1}	fwhm,[b] nm
		Br^- [c]	
band 1	175.1	0.5	
band 2	185.5	1.35	
band 3	197.6	1.3	
		$Br_2(aq)$[d]	
band 1	184.5 ± 0.1	0.33 ± 0.05	15 ± 4
band 2	190.8 ± 0.9	0.38 ± 0.07	18 ± 1
band 3	198.1 ± 1.4	0.46 ± 0.04	30 ± 1
		Br_3^- [e]	
band 1	261.4 ± 0.8	1.55 ± 1.4	23 ± 1
band 2	272.7 ± 0.4	1.60 ± 1.5	29 ± 2
band 3	281.9 ± 0.8	1.62 ± 1.6	60 ± 5
band 4	362 ± 4	0.0853 ± 0.0002	100 ± 10

[a] Gaussian fits are used for absorption bands with nonlinear iteration by the Marquardt–Levenberg algorithm, step size 0.001, tolerance = 10^{-7}. [b] Full width at half maximum height. [c] Reference 5. [d] Data for Br_2 is from: $[Br_2]_T = 8.4 \times 10^{-5}$ M in 1.0 M $HClO_4$. [e] $[Br_3^-]_T = 1.6 \times 10^{-5}$ M in 1.6 M Br^-.

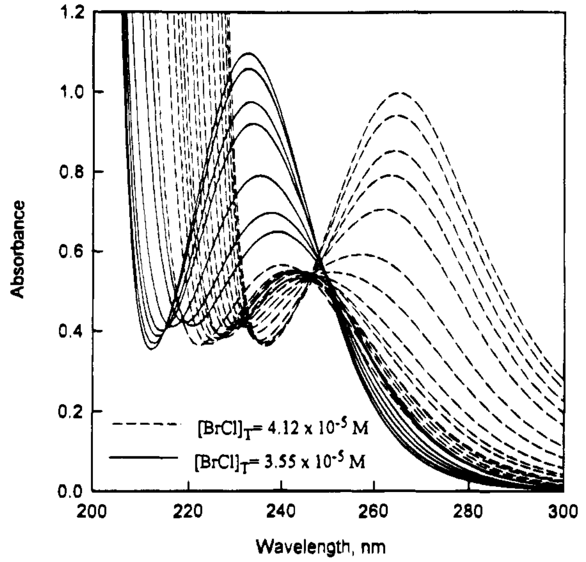

Figure 3. Spectral changes (1.00 cm cell) for solutions of $BrCl_2^-$ in 1.072 M HCl with variable added Br^- concentrations. Solid curves for 3.55×10^{-5} M $[BrCl]_T$ show a decrease in absorbance at 232 nm as the $[Br^-]_{added}$ increases from 0 to 7.38×10^{-4} M. Dashed curves for 4.12×10^{-5} M $[BrCl]_T$ show an increase in absorbance at 266 nm as the $[Br^-]_{added}$ increases from 1.03×10^{-3} to 0.208 M.

Spectral data at 224, 232, and 240 nm in Figure 1 (bottom) for eight different Br^- concentrations less than 8×10^{-4} M were also used to evaluate K_1 as well as K_2 and ϵ_3. The resulting K_1 value was 6.1 ± 0.3 M^{-1} which is in excellent agreement with the spectrophotometric data at 343 nm where the Cl^- concentration was varied.

Figure 3 shows the spectra of 3.55×10^{-5} M $BrCl_2^-$ in 1.072 M HCl with variation of $[Br^-]$ from 0 to 7.38×10^{-4} M (solid curves) and 4.12×10^{-5} M $BrCl_2^-$ with variation of $[Br^-]$ from 1.03×10^{-3} to 0.208 M (dashed curves). In the absence of Br^-, the solution contains 87% $BrCl_2^-$ and 13% BrCl ($K_1 = 6.0$ M^{-1}). Since the BrCl(aq) absorption is much less than $BrCl_2^-$, the initial spectrum with no Br^- added is primarily due to the $BrCl_2^-$. The peak height decreases rapidly and shifts to longer wavelength as the Br^- concentration increases due to the disappearance of $BrCl_2^-$ and the formation of Br_2Cl^- and

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(34) Liebhafsky, H. A. *J. Am. Chem. Soc.* **1934**, *56*, 1500–1505.

Table 6. Formation Equilibrium Constants[a]

equilib	const, M^{-1}
$K_{Cl_3} = [Cl_3^-]/([Cl_2(aq)][Cl^-])$	0.18 ± 0.02
$K_1 = [BrCl_2^-]/([BrCl(aq)][Cl^-])$	6.0 ± 0.3
$K_2 = [Br_2Cl^-]/([BrCl(aq)][Br^-])$	$(1.8 \pm 0.2) \times 10^4$
$K_3 = [Br_2Cl^-]/([Br_2(aq)][Cl^-])$	1.3 ± 0.3
$K_4 = [Br_3^-]/([Br_2(aq)][Br^-])$	16.1 ± 0.3

[a] Conditions: 25.0 °C, $\mu = 1.0$ M.

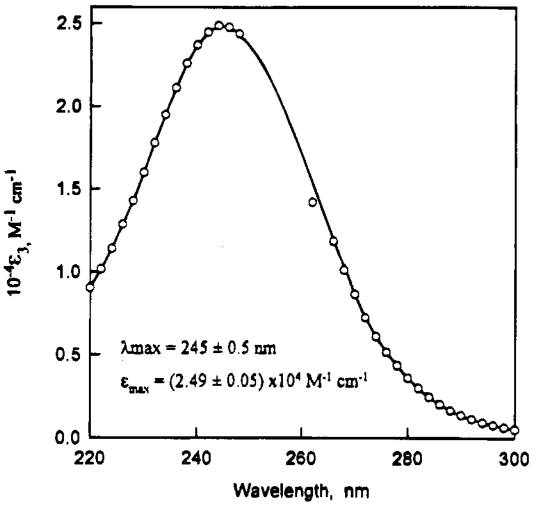

Figure 4. Br_2Cl^- spectrum from 220 to 300 nm as evaluated from eq 16.

Br_2. The absorbance at 266 nm increases with Br^- concentration due to the formation of Br_3^-. The spectral data in Figure 3 were used to fit eq 16 to obtain the K_2 and K_3 values and the molar absorptivities of Br_2Cl^- (ϵ_3) at different wavelengths.

Our value of 1.3 M^{-1} for K_3 is not greatly different than the value of 1.14 M^{-1} reported by Bell and Pring[11] and is in good agreement with a value of 1.4 M^{-1} determined by distribution methods much earlier.[35] On the other hand, Bell and Pring evaluated the equilibrium constant for $[BrCl_2^-][Br^-]/([Br_2][Cl^-]^2)$ as 7.2×10^{-3} M^{-1}, while a we find a value of only 5.0×10^{-4} M^{-1} for this product of K_1K_3/K_2. The reason for this factor of 14 disagreement is not clear, but their potentiometric method depended in part upon the response of a glass electrode in very acidic solutions, a measurement that is often unreliable. Our K_1 value of 6.0 M^{-1}, obtained from direct spectrophotometric measurements, is much smaller than their indirectly estimated value of ~720 M^{-1}. The equilibrium constants evaluated in the present work are summarized in Table 6.

Spectrum of Br_2Cl^- and Comparison of Trihalide Spectra. The iterative evaluation of eq 16 gives ϵ_3 for Br_2Cl^- at wavelengths from 220 to 300 nm as shown in Figure 4. This intense absorption peak with a λ_{max} at 245 nm (ϵ 24,900 M^{-1} cm^{-1}) has not been reported previously. It falls between the UV absorption bands for $BrCl_2^-$ at 232 nm and for Br_3^- at 266 nm. Another absorption band for Br_2Cl^- is found at 381 nm (288 M^{-1} cm^{-1}). Figure 5 shows the resolution of the Br_2Cl^- spectrum from 300 to 500 nm in a mixture of $BrCl_2^-$, $Br_2(aq)$, Br_2Cl^- and Br_3^-. Table 7 summarizes the spectral characteristics of all the halogen species studied in this work. The spectral bands for the trihalide species (Cl_3^-, $BrCl_2^-$, Br_2Cl^-, Br_3^-) shift systematically from 220 nm to 266 nm with increased number of bromine atoms. This is shown in Figure 6 in terms of the energy of the bands. The spectral transition for Cl_3^- has been described[16] in terms of the generation of a (Cl^----Cl^+---Cl^-) excited state species.

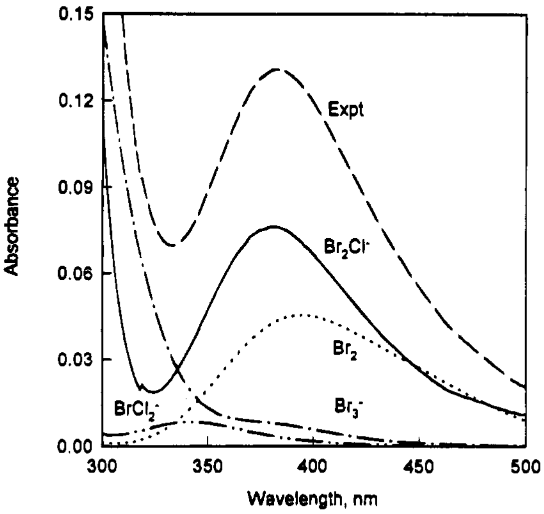

Figure 5. Resolved spectra (300–500 nm) for a mixture of Br_2Cl^-, $Br_2(aq)$, Br_3^-, and $BrCl_2^-$.

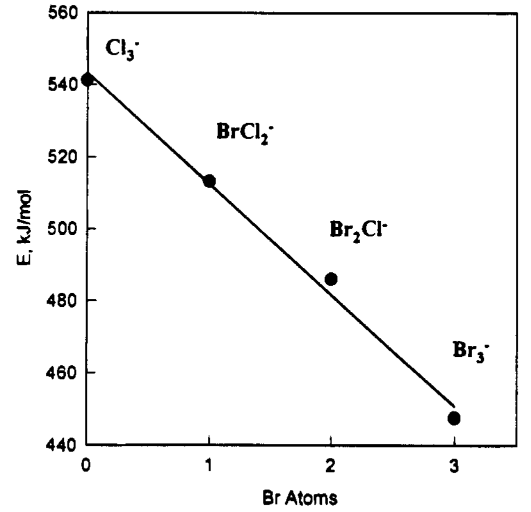

Figure 6. Correlation of energies of UV spectral bands for Cl_3^-, $BrCl_2^-$, Br_2Cl^- and Br_3^- with the number of Br atoms.

Table 7. Spectral Characteristics of Aqueous Halogen Species Obtained in This Study

species	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
$BrCl_2^-$	343	312 ± 9
	232	$32\,700 \pm 400$
BrCl(aq)	343	70 ± 6
	<240	>166
Br_2Cl^-	381	288 ± 50
	245	$24\,900 \pm 500$
$Br_2(aq)$	390	175 ± 5
	186	8240 ± 400
Br_3^-	362 (sh)	850 ± 10
	266	$40\,900 \pm 400$
$Cl_2(aq)$	325	70 ± 2
	<210	>290
Cl_3^-	325	180 ± 20
	220	$10\,400 \pm 200$
Br^-	186	$12\,100 \pm 600$

Dissociation Equilibria. The extent of dissociation of aqueous bromine chloride (eq 17) can be calculated from the

$$2BrCl(aq) \overset{K_D}{\rightleftharpoons} Br_2(aq) + Cl_2(aq) \qquad (17)$$

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(35) Ray, P.; Sarkar, P. V. *J. Chem. Soc.* **1922**, 1453.

electrode potentials[36] of Br_2(aq) and Cl_2(aq) and from our K_2 and K_3 constants. The K_D value equals 5.0×10^{-3}, so that pure BrCl(aq) will be only 7% dissociated in water. The K_D value is 29 times smaller in water than in CCl_4,[3] which indicates preferred aqueous solvation of the polar BrCl molecule compared to Br_2 and Cl_2. In 1.0 M HCl the value for the equilibrium constant ($K_D' = [Br_2]_T[Cl_2]_T/[BrCl]_T^2$) that takes into account Br_2Cl^-, Cl_3^-, and $BrCl_2^-$, is 2.98×10^{-4} so that only 1.7% of the $[BrCl]_T$ solution will be dissociated. The contribution of these species to the spectral and equilibrium observations is small enough to be neglected.

Bell and Pring[11] discussed the disproportionation reaction of Br_2Cl^- and suggested that the reaction in eq 18 takes place to

$$2Br_2Cl^- \overset{K_5}{\rightleftharpoons} Br_3^- + BrCl_2^- \qquad (18)$$

a considerable extent. The value of $K_5 = K_1K_4/K_2K_3 = 3.58 \times 10^{-3}$. This indicates that Br_2Cl^- will be only 6.0% dissociated into Br_3^- and $BrCl_2^-$ rather than exhibiting a large degree of disproportionation. This reaction is not a problem in our data treatment, because $BrCl_2^-$ and Br_3^- equilibration with Br_2Cl^- is taken into consideration. Our constant for K_5 confirms the difficulty of attempting to isolate pure Br_2Cl^- in solution.

Hydrolysis of Bromine Chloride. As the acidity and chloride ion concentrations are lowered, BrCl(aq) will hydrolyze to HOBr (eq 19). The corresponding hydrolysis constant for

$$BrCl(aq) + H_2O \overset{K_6}{\rightleftharpoons} HOBr + H^+ + Cl^- \qquad (19)$$

Br_2(aq) at 25.0 °C and 1.0 M ionic strength is 1.3×10^{-9} M^2.[37] Combination of this constant with K_2 and K_3 permits calculation of the hydrolysis constant for BrCl(aq), $K_6 = 1.8 \times 10^{-5}$ M^2. The corresponding hydrolysis constant for $BrCl_2^-$ is given in eq 20. In 1 M [Cl^-], $BrCl_2^-$ will be 50% hydrolyzed at p[H^+]

$$K_7 = \frac{[HOBr][H^+][Cl^-]^2}{[BrCl_2^-]} = 3.0 \times 10^{-6}\ M^3 \qquad (20)$$

5.5, whereas in 0.01 M [Cl^-], 50% hydrolysis of BrCl(aq) will occur at p[H^+] 2.7.

The hydrolysis of BrCl(aq) is very rapid in comparison to Br_2(aq), $k_{H_2O}^{Br_2} = 37$ s^{-1} ($\mu = 0.5$ M),[37] or Cl_2(aq), $k_{H_2O}^{Cl_2} = 22.3$ s^{-1}.[38] In earlier work by Margerum et al.,[21,22] the kinetics of hydrolysis of ICl(aq) and IBr(aq) were measured by PAF methods. The first-order hydrolysis rate constants are 2.4×10^6 s^{-1} for ICl(aq) and 8×10^5 s^{-1} for IBr(aq). In these studies Cl^- and Br^- suppressed the hydrolysis rate due to the formation of ICl_2^- and IBr_2^-, respectively. The stability constant for $[ICl_2^-]/([ICl(aq)][Cl^-])$ is 77 M^{-1}, and the stability constant for $[IBr_2^-]/([IBr(aq)][Br^-])$ is 286 M^{-1}. Hence, high concentrations of [Cl^-] or [Br^-] could be used to bring the observed hydrolysis rate constants within range of the PAF method (*i.e.* k_{obsd} values less than 200 000 s^{-1}). The value of the formation constant (K_1) for $BrCl_2^-$ is one to two orders of magnitude smaller, and it is therefore more difficult to use high Cl^- concentration to suppress the hydrolysis rate of BrCl(aq). Our attempts to measure its hydrolysis rate constant by the PAF method were not successful, but the lack of a signal suggests that $k_{H_2O}^{BrCl}$ is greater than 6×10^5 s^{-1}. The experiment is complicated by the need to add base and/or buffer solutions in the PAF mixing reaction to neutralize acidic solutions of $BrCl_2^-$, while avoiding reactions of OH^- or buffer with BrCl(aq). As a consequence it is probably safer to state that $k_{H_2O}^{BrCl}$ is greater than 10^5 s^{-1}.

Rapid Equilibration of $BrCl_2^-$ and Br^-. We also attempted without success to measure the kinetics of the Br^- reaction with BrCl(aq) by the PAF method. The rate constants for ICl(aq) + I^- and for IBr(aq) + I^- are 5.1×10^8 M^{-1} s^{-1} and 2.0×10^9 M^{-1} s^{-1}, respectively. These constants were measured by PAF methods[21,22] with suppression of the rates in excess Cl^- and in excess Br^- because ICl_2^- and IBr_2^- do not react directly with I^-. The small value for K_1 makes it difficult to use $BrCl_2^-$ in a similar manner to suppress the rate of the reaction of BrCl(aq) with Br^-. As a result we can only conclude that k_{Br}^{BrCl} is greater than 10^8 M^{-1} s^{-1}. All of the reactions in Scheme 1 equilibrate very rapidly.

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