(ν_{S-F}) cm^{-1}. The positive CI mass spectrum has peaks at m/e 134 ($C_4H_8NSO_2^+$, 91.3%), 86 ($C_4H_8NO^+$, 92.4%), 72 ($C_4H_8O^+$, 4.5%), 70 ($C_4H_8N^+$, 42.2%), and 67 (SOF^+, 2.58%).

(e) 3,5-Dimethylmorpholine with SOF_2. n-Hexane extraction gave a 65% yield of $C_6H_{12}NSO_2F$. The ^{19}F NMR spectrum contains a singlet at ϕ 47.3, and the ^1H NMR spectrum has ring proton signals. The infrared spectrum has bands at 2983 s, 2877 s, 1457 s, 1212 vs ($\nu_{S=O}$), and 851 m (ν_{S-F}) cm^{-1}. The positive CI mass spectrum has peaks at m/e 162 ($C_6H_{12}NSO_2^+$, 34.9%) 114 ($C_6H_{12}NO^+$, 100%), 99 ($C_5H_9NO^+$, 9%), 98 ($C_5H_8NO^+$, 90.1%), 84 ($C_4H_6NO^+$, 5%), 70 ($C_4H_6O^+$, 22%), 68 ($C_4H_6N^+$), and 67 (SOF^+, 3.27%).

(f) Thiomorpholine with SOF_2. n-Hexane extraction gave a 50% yield of $C_4H_8NS_2OF$. The ^{19}F NMR spectrum contains a singlet at ϕ 55.8, and the ^1H NMR has ring proton signals. The infrared spectrum has bands at 2962 m, 2855 m, 1450 vs, 1206 vs ($\nu_{S=O}$), and 821 w (ν_{S-F}) cm^{-1}. The positive CI mass spectrum has peaks at m/e 150 ($C_4H_8NS_2O^+$, 20.66%), 102 ($C_4H_8NS^+$, 56.15%), 88 ($C_4H_8S^+$, 9.47%), 70 ($C_4H_8N^+$, 2.74%), and 67 (SOF^+, 1.42%).

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-8100156) and the Gas Research Institute (Grant 5082-260-0654) for support of this research. Dr. G. D. Knerr obtained the nuclear magnetic resonance and mass spectra.

Registry No. SOF_2, 7783-42-8; $(C_2H_5O)_2P(O)H$, 762-04-9; $(C_2H_5O)_2P(O)F$, 358-74-7; S, 7704-34-9; Et_3NHFSO_2, 95552-60-6; $(C_4H_9O)_2P(O)H$, 1809-19-4; $(C_4H_9O)_2P(O)F$, 674-48-6; $(C_2H_5O)_3P$, 122-52-1; $(C_2H_5O)_3PF_2$, 55422-04-3; $(C_2H_5O)_3PS$, 126-68-1; $(C_2H_5O)_3PO$, 78-40-0; $(C_4H_9O)_3P$, 102-85-2; $(C_4H_9O)_3PF_2$, 91223-81-3; $(C_4H_9O)_3PS$, 78-47-7; $(C_4H_9O)_3PO$, 126-73-8; $(C_6H_5)_3P$, 603-35-0; $(C_6H_5)_3PF_2$, 845-64-7; $(C_6H_5)_3PO$, 791-28-6; $(CH_3)_3P$, 594-09-2; $(CH_3)_3PF_2$, 661-42-7; $(CH_3)_3PO$, 676-96-0; $(CH_3)_3PS$, 2404-55-9; PCl_3, 7719-12-2; PF_3, 7783-55-3; $P(OCH_2CF_3)_3$, 370-69-4; $(C_6H_5)_3CH$, 519-73-3; $(C_6H_5)_3CF$, 427-36-1; $(CH_3O)_3PO$, 512-56-1; $(CH_3)_2P(O)(OCH_3)$, 14337-77-0; $CH_3P(O)(OCH_3)_2$, 756-79-6; piperidine, 110-89-4; 1-piperidinesulfinyl fluoride, 455-33-4; 2,6-dimethylpiperidine, 504-03-0; 2,6-dimethyl-1-piperidinesulfinyl fluoride, 95533-39-4; 2,2,6,6-tetramethylpiperidine, 768-66-1; 2,2,6,6-tetramethyl-1-piperidinesulfinyl fluoride, 95533-40-7; morpholine, 110-91-8; 4-morpholinesulfinyl fluoride, 60094-26-0; 3,5-dimethylmorpholine, 123-57-9; 3,5-dimethyl-4-morpholinesulfinyl fluoride, 95533-41-8; thiomorpholine, 123-90-0; 4-thiomorpholinesulfinyl fluoride, 95533-42-9.

Contribution from Physical Chemistry 1,
Chemical Center, University of Lund, S-220 07 Lund, Sweden

Halide-Exchange Reactions of Mixed Chloro-Bromo-Iodo Trihalides. 1. Equilibria in the Chloro-Iodo System

LARS-FRIDE OLSSON

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Formation of the trihalide anions Cl_3^-, ICl_2^-, I_2Cl^-, and I_3^- from the parent halogen molecules has been studied in methanol. Equilibrium constants have been determined by spectrophotometric and potentiometric measurements at temperatures below 0 °C, with an ionic strength of 1 M ($LiCl/LiBF_4$) and under restricted illumination. Iodide has a considerably higher affinity than chloride toward halogen molecules. Reaction between iodide and halogen involves such large electron displacements that they are best described as redox reactions, whereas the reaction with chloride is a simple addition. The reaction between iodide and chlorine, $2I^- + Cl_2 \rightarrow I_2 + 2Cl^-$, is a multistep process that involves species such as the dichloroiodate(I) and, for excess chlorine, tetrachloroiodate(III) ion. Spectra of all the trihalides display large absorption maxima between 225 and 290 nm with molar absorptivities around 5×10^4 cm^{-1} M^{-1}.

Introduction

This paper reports equilibrium constants in methanol for the formation of trihalide anions from the parent halogen or interhalogen compound and the halide ion (eq 1-6) together with

$$Cl^- + Cl_2 \rightleftarrows Cl_3^- \tag{1}$$

$$I^- + Cl_2 \rightleftarrows ICl_2^- \tag{2}$$

$$Cl^- + ICl \rightleftarrows ICl_2^- \tag{3}$$

$$I^- + ICl \rightleftarrows I_2Cl^- \tag{4}$$

$$Cl^- + I_2 \rightleftarrows I_2Cl^- \tag{5}$$

$$I^- + I_2 \rightleftarrows I_3^- \tag{6}$$

constants for the halide-exchange reactions according to eq 7-9.

$$I^- + Cl_3^- \rightleftarrows ICl_2^- + Cl^- \tag{7}$$

$$I^- + ICl_2^- \rightleftarrows I_2Cl^- + Cl^- \tag{8}$$

$$I^- + I_2Cl^- \rightleftarrows I_3^- + Cl^- \tag{9}$$

The overall reaction can be written as the redox equilibrium (10).

$$3I^- + Cl_2 \rightleftarrows I^-_3 + 2Cl^- \tag{10}$$

The equilibrium constants for all the reactions are known with water as solvent.[1-3] In nonaqueous solvents (methanol in this study) only the triiodide equilibrium (eq 6) has been determined.[2,4-11] This equilibrium constant is larger by a few powers of ten in nonaqueous solvents[1,2] as compared to in water. The variation of this constant with solvent has been reported.[11] An estimate of the dichloroiodide equilibrium (eq 3) has also been reported.[12] Of the constants reported here, K_1, K_3, K_5, K_6, K_8, and K_9 have been determined spectrophotometrically. The absorption spectra of the relevant species are all known in water (cf. ref 13 and references therein) and, except for I_2Cl^-, also in methanol.[12] The spectra are very similar in these two solvents. The trihalide ions exhibit high absorption maxima in the UV spectral region,[12,14] with molar absorptivities around 5×10^4 M^{-1} cm^{-1}. Of the halide ions, only iodide has a maximum in the same region (cf. Figure 2b).

The constants according to eq 2 and 7 were determined potentiometrically. A proper combination of eq 2-5 leads to the simple redox equation (11). The electrode potentials in methanol for the redox couples Cl_2/Cl^- and I_2/I^- are known.[15]

$$2I^- + Cl_2 \rightleftarrows I_2 + 2Cl^- \tag{11}$$

The aim of this study is to give the necessary spectral and equilibrium data for a planned stopped-flow kinetic study of

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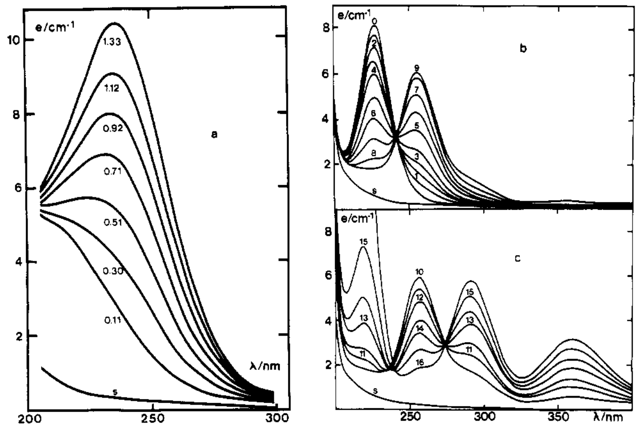

Figure 1. Spectrophotometric titrations: (a) reaction 1, $C_{Cl_2} \approx 1.9$ mM, C_{Cl}/M indicated, S = blank (i.e., solvent absorption), $t = 0.1$ °C, ionic strength 0.9–1.7 M (LiCl/LiBF$_4$); (b) reactions 8 and 9, $C_{ICl} = 1.45 \times 10^{-4}$ M, $10^4 C_{LiI}$/M = 0.00 (0), 0.119 (1), 0.237 (2), 0.355 (3), 0.472 (4), 0.704 (5), 0.935 (6), 1.16 (7), 1.45 (8), 1.73 (9); (c) reactions 8 and 9, $10^4 C_{LiI}$/M = 2.00 (10), 2.55 (11), 3.08 (12), 4.11 (13), 5.09 (14), 6.95 (15), 11.0 (16), $t = 1.0$ °C, ionic strength 1.0 M (LiCl).

possible accessible reactions. A preliminary investigation of reaction 8 has shown[13] that it is very fast at room temperature (a rate constant of about 10^7 M^{-1} s^{-1} in water at 25 °C). This is also the case in methanol, but for temperatures below 0 °C it can easily be monitored by conventional stopped-flow technique. Because it is possible to extend these measurements to, e.g. −95 °C, other very fast reactions should be accessible with this technique.

The latest reviews concerning trihalide anions are those by Downs and Adams,[16] Popov,[1] and Popov and Surles.[17] Little is known about rates and possible mechanisms[16] for halide ion exchange reactions according to eq 12. The only reaction that seems

$$XYZ^- + U^- \rightleftarrows XYU^- + Z^- \qquad (12)$$

to have been measured is of the very symmetrical type X = Y = Z = U = I (Genser: cf. ref 18), with one atom (U) isotopically labeled. In this case, the equilibrium expression (12) might be a possible stoichiometric description of the mechanism,[19] but this is impossible when not all atoms are equal. So, for instance, when Cl^- substituted by I^- according to eq 7, this one cannot mechanistically describe the process. It follows from the known structures of Cl_3^- and ICl_2^-, which are[16,17] Cl–Cl–Cl and Cl–I–Cl, respectively, that at least two steps must be involved.[20] One of these must necessarily involve oxidation, because the (central) iodide atom in ICl_2^- has a higher oxidation number than the reactant iodide ion.

Structures of the trihalide species have been comprehensively discussed.[1,16,17] They are linear (or nearly so), and the central atom has always the highest atomic number (cf. the example above).

Experimental Section

Chemicals and Solutions. Methanol (BDH, AnalaR, water content less than 0.1%, or Riedel-de-Haën AG, water content less than 0.05%), flushed with dry nitrogen, was used as solvent. Most solutions were prepared at room temperature. To minimize moisture contamination, all glassware was filled with dry nitrogen. Lithium salts were dried and stored in a desiccator placed inside a glovebag together with an electronic analytical balance. The bag was continuously flushed with dry nitrogen.[21] Anhydrous lithium iodide (EGA-Chemie, 99%) is very hygroscopic, but with the precautions described no weight increase could be observed during weighing. After weighing, the stoppered volumetric flask was transferred from the glovebag and quickly filled with methanol and nitrogen was blown over the surface. Stock solutions of lithium salts were stored in a desiccator and under restricted illumination or even wrapped in a foil (lithium iodide). A 1 M ionic strength was maintained with lithium chloride (Merck p.a.) and/or tetrafluoroborate (Ventron) as supporting electrolyte. The difference in concentrations between room temperature (about 20 °C) and the measuring temperatures (0 and −20 °C) was calculated from the known volumetric properties[22] of methanol. Some density measurements on a 1 M medium (lithium chloride and tetrafluoroborate) showed that the relative density change as a function of temperature for these media was not significantly different from that of neat methanol.

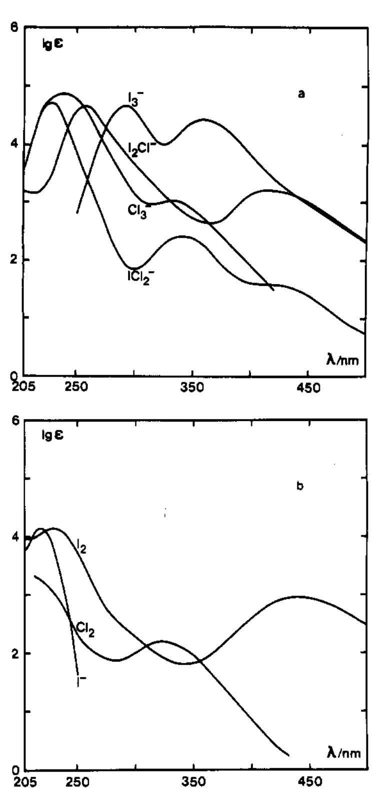

Figure 2. Spectra: (a) Cl_3^-, ICl_2^-, I_2Cl^-, and I_3^-; (b) Cl_2, I_2, and I^-. Cl^- is transparent above 205 nm.

None of the salts were recrystallized. The solutions prepared from lithium tetrafluoroborate contained immediately after dissolution a small amount of brown colloidal particles. After the mixtures were allowed to stand overnight (dark, dry), a brown precipitate was formed. This was removed by centrifugation. Chlorine was prepared by addition of about 25 mL of concentrated hydrochloric acid (Riedel-de Haën AG) to about 10 g of potassium permanganate (Merck p.a.). The gas was dried in concentrated sulfuric acid (Merck p.a.).

Stock solutions with chlorine were prepared by passing chlorine gas over the solution in exactly the same manner as described below for the potentiometric titrations (but without electrodes). The gas stream was closed when the color changed to yellow (C_{Cl_2} about 200 mM). They were analyzed spectrophotometrically for chlorine: a small volume (e.g., 0.1 mL) was transferred to 50 mL of aqueous 1 M sodium iodide. The triiodide ion produced was determined at 353 nm, where its molar absorptivity is 2.6×10^4 cm^{-1} M^{-1}. Analysis had to be performed rapidly, because the initial fast reaction according to eq 10 (in water) was followed by disturbing redox reactions that slowly increase the triiodide concentration.

Stock solutions of dichloroiodide ion were prepared by the addition of a small amount (25 mg) of iodine monochloride (Merck-Schuchardt, zur Synthese) to a weighed 100-mL volumetric flask. The flask was weighed again and filled with 1 M lithium chloride, and nitrogen was passed over the surface and the flask wrapped in a foil. Solutions of iodine monochloride are sensitive to light[12,23] to an extent that depends on the free chloride concentration. If this is sufficiently high (≥0.5 M) all light-induced reactions are reversible, but for low concentrations such

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solutions decompose. Low temperature decreases the light sensitivity. Thus, solutions with 1 M lithium chloride could be stored several days in a refrigerator without any noticeable change in the absorption spectra (cf. Figure 2a). Stock solutions of iodine (Merck doppelt sublimiert) in 1 M lithium tetrafluoroborate were prepared in a similar way. Even these solutions are sensitive to environmental influences, as revealed by the appearance of the absorption spectrum of the triiodide ion (cf. Figure 2a). Its concentration as calculated from the maxima at 290 and 360 nm was always less than 5% of the total iodine concentrations. Its influence on the calculations of the equilibria according to eq 5 and 6 was neglected. However, in order to get a spectrum of iodine in methanol free from the triiodide ion, iodine was dissolved in methanol at −20 °C and under restricted illumination. This was accomplished by means of an air-tight weighing scoop described elsewhere.[24] All concentrations displayed in the tables are those at the indicated temperatures.

Apparatus. Spectrophotometric measurements were performed on a Varian Cary 15 spectrophotometer. The closed-flow, thermostatable titration vessel described elsewhere[24] was connected to a flow-through cell (Hellma 170-QS, optical path lengths between 0.100 and 1.000 cm). It contained one of the reacting solutions. The other was added from a piston buret (Methrom AG). The spectrophotometric cell compartment was continuously flushed with dry nitrogen.

The potentiometric measurements were performed in a thermostated titration vessel of 70-mL capacity. To prevent moisture deposition it was placed in a beaker continuously flushed with dry nitrogen. The indicator electrode was made of a bright platinum wire,[8] formed as a helix of 10-mm height and 3-mm diameter. The reference was a calomel electrode[25] (Radiometer, Copenhagen, K 901) filled with methanol saturated with lithium chloride. A direct contact (via the porous plug) with the measuring solution shortens its useful life. Therefore, the lower part of the electrode was stored in a tube of ca. 1.5-mL capacity. It was sealed with an O-ring of Teflon and had a ground-glass joint at the bottom. It contained the same ionic medium as the outer solution and was completely immersed in this. A leak test showed that after 2 h of contact with a solution containing 20 mM triiodide and 70 mM of iodide ions the solution in the tube contained approximately 2×10^{-5} M of diiodochloride as found spectrophotometrically (the medium was 1.00 M lithium chloride). Thus, the liquid-junction potential was completely determined by the ionic medium used.

Temperature differences between the measuring solution and the calomel electrode were suppressed by equilibrating for more than 1 h before the titration started. Indeed, plots according to the Nernst equation (cf. Figure 3b, c) always gave fair agreement between calculated and theoretically expected ($(RT \ln 10)/nF$) slopes. This indicates that all parts of the system were rather close in temperature.

The electrodes were connected to an Orion Research Model 901A digital voltmeter via shielded leads. The reducing agent (lithium or sodium iodide) was added from a piston buret kept at room temperature, via a Teflon tube through the cover of the titration vessel. The EMF measured by three platinum electrodes vs. the same calomel electrode agreed to within 0.1 mV. There was no corresponding similarity between different calomel electrodes; they may differ by several millivolts.[26] Those used, however, always showed a Nernstian response.

Equilibrium Measurements. Both the spectrophotometric and potentiometric measurements below were performed at 0 and −20 °C. The room was kept in darkness, and during an addition the piston buret was illuminated by a pocket lamp.

Spectrophotometric Titrations. An appropriate volume (say 50 mL) of medium was pipetted into the nitrogen-flushed titration vessel. The temperature was lowered, and when a constant value was reached, a spectrum between 400 nm and solvent cut-off (200 nm for a 0.100-cm cell and 220 nm for a 1.00-cm cell) was recorded. A small volume (e.g., 1 mL) of stock solution containing the parent molecule (Cl_2, ICl, I_2) together with the appropriate ionic medium was added from a 5-mL piston buret via a Teflon tube through the cover of the titration vessel. The reacting solution containing the free halide ion in excess (Cl^-, I^-) was added from a piston buret kept at room temperature. This solution usually contained the same total concentration of the halogen as the one in the titration vessel. A spectrum was recorded 10 min after addition. The spectral changes accompanying the titration of Cl_2 by Cl^- and ICl_2^- by I^- are displayed in parts a and b Figure 1 respectively.

The titration with chlorine was slightly more complicated than indicated above. Due to the volatility of chlorine, its concentration decreased in the buret (this could be neglected in the titration vessel, because of the low temperature), and after every third addition a small portion was removed from the buret and analyzed spectrophotometrically. The decrease was linear with time (approximately 10%/h), so that notion of the time of addition made it possible to calculate that particular concentration. Prior to addition of the first portion, the concentration of chlorine in the titration vessel and buret was also determined.

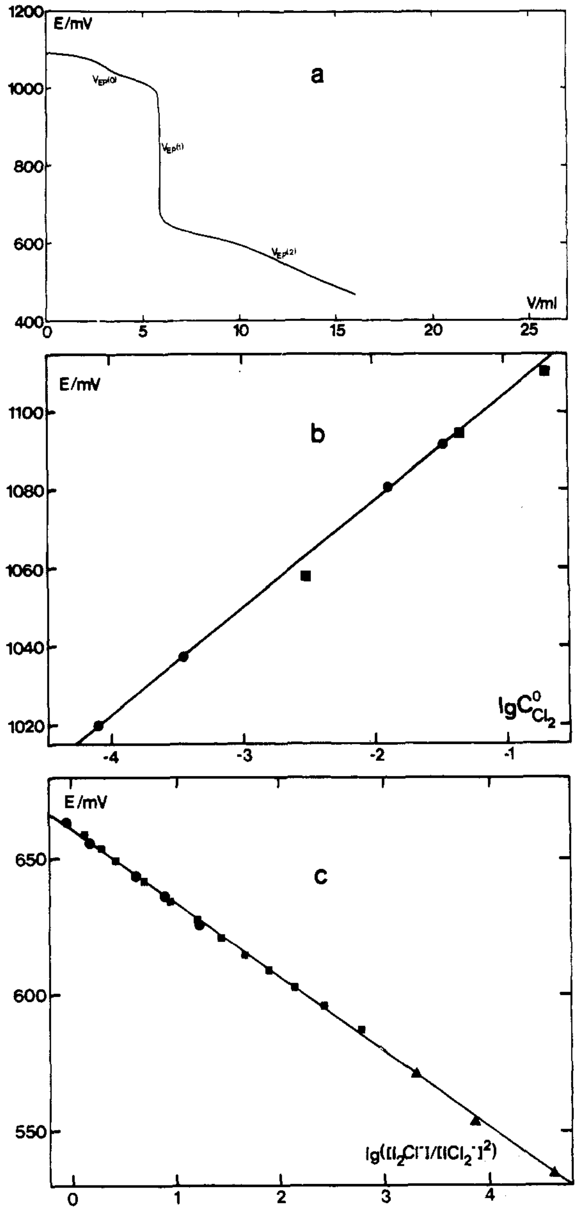

Figure 3. (a) Potentiometric titration curve. Conditions: $C^0_{Cl_2}$ = 35.5 mM (series a); t = 0 °C. (b) Plot according to eq 25 (values from Table II; t = 0 °C). $C_{Cl_2}{}^0$: determined potentiometrically (●); determined spectrophotometrically (■). (c) Plot according to eq 27 ([Cl^-] = 1.00 M, t = 0 °C). $C_{Cl_2}{}^0$/mM: 35.5 (■), 13.0 (●), 0.348 (▲).

Due to the possible reaction between chlorine and methanol, the solutions might contain methyl hypochlorite. The eventual presence of this species was checked in the following way: two solutions with C_{Cl_2} = 1.3 mM and C_{Cl} = 0.10 and 1.0 M, respectively, were acidified by addition of sulfuric acid (Merck p.a., 95%) to $C_{H_2SO_4}$ = 0.18 M. Spectra between 300 and 200 nm were recorded. No change could be detected with time, and the difference due to the two different C_{Cl} were in complete agreement with that found during the titrations (cf. Figure 1a) where $C_{H_2SO_4}$ = 0. It is therefore justified to assume that methyl hypochlorite is absent both in these solutions and in those used in the potentiometric measurements.

Potentiometric Titrations. The chlorine gas generating system and the titration vessel were flushed with nitrogen for 15 min. A tube with a drying agent and the two electrodes (including the filled salt bridge tube to the calomel electrode) were put in place, and an appropriate volume (e.g., 50 mL) of a solution containing 1 M lithium chloride was pipetted into the titration vessel. With nitrogen still passing over the surface, the

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Table I. Spectrophotometric Measurements[a]

eq no.	C_{XY}/M	equil const/M^{-1} (λ/nm)		$10^{-4}\epsilon$/cm^{-1} M^{-1}			
				225 nm	255 nm	290 nm	360 nm
1	1.9×10^{-3}	5.5 (9) $\times 10^{-2}$ (8 wavelengths, $220 \leq \lambda \leq 255$ nm cf. Figure 1a)	Cl_2	0.142 (2)	0.010 (3)		
			Cl_3^-	5.0 (7)	4.9 (7)		
3	2.01×10^{-4}	5.6 (3) $\times 10^2$ (225)	ICl	0.6 (1)			
			ICl_2^-	4.8 (2)			
5	1.76×10^{-4}	10.9 (5) (255)	I_2	1.22 (1)	0.23 (3)		
			I_2Cl^-	0.55 (1)	4.35 (7)		
6	1.75×10^{-4}	5.9 (3) $\times 10^4$ (290), 5.2 (3) $\times 10^4$ (360)	I^-	1.10 (4)	0.002	0.0000	
			I_2	1.22 (2)		0.13 (2)	0.11 (2)
			I_3^-	0.23 (5)		4.36 (2)	2.48 (2)
8	1.48×10^{-4}	3.3 (3) $\times 10^5$ (225, 255, 290) 5.4 (6) $\times 10^3$	I^-	1.19 (7)			
			ICl_2^-	5.3 (1)	0.3 (1)		
9	6.5×10^{-5}	cf. Figure 1b,c	I_2Cl^-	0.2 (1)	5.4 (2)	0.64 (8)	
			I_3^-		0.3 (1)	4.8 (2)	

[a] Equilibrium constants according to eq 1, 3, 5, 6, 8, and 9; molar absorptivities with 1 standard deviation in parentheses, total concentration (C_{XY}) according to eq 15 and 21, ionic strength 1.0 M ($LiCl9LiBF_4$) temperature 0 °C.

temperature was lowered and a slow stirring was started. The EMF was between 400 and 500 mV. The nitrogen stream was closed and chlorine gas passed over the solution. A few minutes after the first portion of the hydrochloric acid had been added to the potassium permanganate, the EMF began to rise quickly. When it had increased 550–600 mV, the chlorine gas stream was closed, and a 5-min addition of nitrogen followed. The EMF decreased a few millivolts and then became very stable within 45 min. (Because reported EMF values are based on one particular calomel electrode and therefore may not be possible to reproduce then, when an experiment is performed for the first time, it is strongly recommended to make a spectrophotometric determination of the chlorine concentration before the titration begins.) A piston buret was filled with a solution containing lithium iodide. An appropriate concentration was chosen from the known chlorine concentration in the titration vessel. The titration was then performed (cf. Figure 3a): stable EMF values were obtained within a few minutes after addition except near the equivalence point. When the titration was finished, the temperature was checked. The iodide solution was standardized against a water solution of 0.10 M silver nitrate. To 10 mL of the methanol solution of iodide was added 20 mL of distilled water. A potentiometric titration with an iodide ion selective electrode (Orion Model 94-53A) and a calomel electrode as reference was performed.

Results

1. Spectrophotometric Measurements. The main absorbing species are Cl_3^- (around 235 nm), ICl_2^-, I^-, and I_2 (225 nm), I_2Cl^- (255 nm), and I_3^- (290 and 360 nm). Absorptivity (e, cm^{-1}) data at different wavelengths, total concentrations, ionic media, and temperatures are available as supplementary material. Absorptivities are based on absorbances larger than 0.1 (corrected for background absorption). This is completely determined by the solvent absorption; there is no difference between neat methanol and 5 M lithium chloride medium. Absorbance changes when Cl^- is added to Cl_2 according to eq 1 are displayed in Figure 1a; they are typical for eq 3, 5, and 6 also.

Stoichiometry and Calculations. Two types of equilibria will be considered, eq 13 and 12. Let K_{XYZ} denote the equilibrium

$$XY + Z^- \rightleftarrows XYZ^- \tag{13}$$

constant of eq 13 (i.e., K_1, K_2, K_3, K_4, K_5, and K_6), C_{XY} the total concentration of the halogen molecule XY, and C_Z, that of the halide ion Z^- (eq 14–16). The absorptivity e is given by eq 17,

$$K_{XYZ} = [XYZ^-]/([XY][Z^-]) \tag{14}$$

$$C_{XY} = [XY] + [XYZ^-] \tag{15}$$

$$C_Z = [Z^-] + [XYZ^-] \tag{16}$$

$$e = \epsilon_Z[Z^-] + \epsilon_{XY}[XY] + \epsilon_{XYZ}[XYZ^-] \tag{17}$$

with ϵ denoting molar absorptivities. By the use of the stoichiometric relations (16) and (17), eq 18 can be written. With

$$e = \epsilon_Z C_z + \epsilon_{XY} C_{XY} + (\epsilon_{XYZ} - \epsilon_Z - \epsilon_{XY})[XYZ^-] \tag{18}$$

$[XYZ^-]$ expressed in C_{XY}, C_Z, and K_{XYZ}, eq 18 has been used in least-squares calculations for the determination of K_3, K_5, and K_6 together with the molar absorptivities at the appropriate wavelengths for ICl, ICl_2^-, I_2, I_2Cl^-, and I_3^- (cf. Table I). However, for the Cl_2/Cl_3^- equilibrium, eq 1, eq 18 is not suitable, possibly due to the very small value of K_1. In this case it is better to use the function

$$e = C_{XY}(\epsilon_{XY} + K_1\epsilon_{XYZ}C_Z)/(1 + K_1C_Z) \tag{19}$$

which is directly obtained from eq 17 ($\epsilon_{Cl} = 0$ at the wavelengths used, and $C_{Cl} \approx [Cl^-] \gg C_{Cl_2}$).

That K_1 must be small is easily verified by plots of e/C_{Cl_2} vs. C_{Cl}. These are always straight lines, which means that the denominator in eq 19 must be close to unity, and therefore $K_1 \ll 1$, because $C_{Cl} \simeq 1$ M (cf. Figure 1a). The absence of any curvature means that K_1 cannot be determined with any accuracy at one particular wavelength (it was found that $3\sigma_{K_1} \geq K_1$). However, if e data from several wavelengths are used simultaneously, a rather accurate value of K_1 is found (at the expense of the accuracy for the molar absorptivity values). The calculations were performed by the least-squares minimizing subroutine STEPIT.[27]

The calculations concerning the equilibria of eq 8 and 9 are based on the curves in Figure 1b,c.

Despite the high concentrations of Cl^- (1 M), the presence of I_2 according to eq 5 cannot be neglected ($K_5 = 11$ M^{-1}; cf. Table I), whereas ICl is totally suppressed ($K_3 = 600$ M^{-1}; cf. Table I). The following species thus contribute to the total absorption according to eq 20: ICl_2^-, I_2Cl^-, I_2, I_3^-, and I^-.

$$e = \epsilon_{ICl_2}[ICl_2^-] + \epsilon_{I_2Cl^-}[I_2Cl^-] + \epsilon_{I_2}[I_2] + \epsilon_{I_3^-}[I_3^-] + \epsilon_{I^-}[I^-] \tag{20}$$

The stoichiometry involved is given by the three equilibrium constants corresponding to eq 8, 5, and 9:

$$K_8 = [I_2Cl^-][Cl^-]/([ICl_2^-][I^-])$$

$$K_5 = [I_2Cl^-]/([I_2][Cl^-])$$

$$K_9 = [I_3^-][Cl^-]/([I_2Cl^-][I^-]) \ (=K_6/K_5)$$

and by

$$C_{ICl} = [ICl_2^-] + [I_2Cl^-] + [I_2] + [I_3^-] \tag{21}$$

$$C_I = [I^-] + [I_2Cl^-] + [I_2] + 2[I_3^-] \tag{22}$$

where C_I denotes the total concentration of *added* I^- (in the form of LiI) and C_{ICl} is the total concentration of ICl. Due to the large excess of Cl^-, $[Cl^-]$ can be put equal to the total concentration C_{Cl}.

The subroutine STEPIT[27] was used for the calculations. A fixed value was assumed for K_5 (16 M^{-1} at −20 °C and 11 M^{-1} at 0

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Table II. Emf and Total Chlorine Concentration, before Addition of Iodide Ion ($C_{\mathrm{LiCl}} = 1.00$ M)

series[a]	V/mL	$v_{\mathrm{EP}}(1)$/ mL	C^0_{I}/ mM	$C^0_{\mathrm{Cl_2}}$/ mM	$E(v = 0)$/ mV
a	40.0	5.85	243	35.5	1091.7
b		16.85	30.9	13.0	1080.4
c		0.45	30.9	0.348	1037.3
d		0.61	5.08	0.0775	1019.6
				200[b]	1111.0
				45.5[b]	1094.9
				2.9[b]	1058.0
e	50.0	6.25	220	27.5	1094.2
f	49.0	6.05	28.7	3.54	1071.8

[a] Conditions for series a-d: $t = 0$ °C; $E^0(v = 0) = 1131.3$ (4) mV (cf. Figure 3b); slope 27.2 (1) mV. Conditions for series e and f: $t = -18.7$ °C; $E^0(v = 0) = 1135.5$ mV; slope 25.2 mV. [b] Determined spectrophotometrically.

Table III. Electrode Reactions and Standard Electrode Potentials vs. Saturated Calomel Electrode[a]

electrode reactn (eq no.)	std value/mV	slope/mV
$Cl_2 + 2e^- \rightleftarrows 2Cl^-$ (24)	$E_{25}{}^\circ = 1132$ (1)	27.2 (1)
$2ICl_2^- + 2e^- \rightleftarrows I_2Cl^- + 3Cl^-$ (26)	$E_{27}{}^\circ = 661.4$ (3)	−27.4 (2)
$I_2Cl^- + 2e^- \rightleftarrows 2I^- + Cl^-$ (32)	$E_{33}{}^\circ = 351.5$ (6)	−26.6 (2)

[a] Ionic strength 1.0 M (LiCl); $t = 0$ °C; 1 standard deviation in parentheses.

°C) and also for the molar absorptivities of the following species at the indicated wavelengths (nm) in parentheses: ICl_2^- (255, 290), I_3^- (225), I^- (255, 290), I_2 (225, 255, 290). (These were taken from the preceding calculation.) When acceptable values for the remaining parameters had been found, the ϵ values for I_2 at the three wavelengths and for I_3^- at 225 nm and ICl_2^- at 255 nm were optimized. The improvement was, however, negligible. The results are displayed in Table I.

Whereas the difference between calculated and measured e values are rather small at 290 and 255 nm, it is large at 225 nm. The mean difference (calculated as $100\sum[|e_{\mathrm{exptl}} - e_{\mathrm{calcd}}|/e_{\mathrm{calcd}}]/N$, where N is the number of points at the particular wavelength), is 9.7% at 225 nm but four times smaller at the other two. One possible reason might be that the background correction (from CH_3OH) is both larger and more sensitive to any deviation at this wavelength (225 nm) (cf. Figure 1b,c). There are also more absorbing species with large molar absorptivities present.

A plot of the difference ($e_{\mathrm{exptl}} - e_{\mathrm{calcd}}$) vs. calculated log [$I^-$] values shows no trends, but those from 225 nm are considerably larger for small [I^-], where [ICl_2^-] and [I_2Cl^-] are of comparable magnitude, than at large values. Obviously this makes the spectrophotometric determination of K_8 rather uncertain. Indeed, a spectrophotometric determination of K_8 must of course be unfavorable. It is impossible to determine [I^-], because of the low value of the product $\epsilon_I[I^-]$ and also because ICl_2^- has a large absorption at the same wavelengths (225 nm) as I^-. The value of K_8 is, however, in agreement with that calculated from potentiometric measurements (vide infra).

2. Potentiometric Measurements. For the cell

$$-\ \mathrm{Hg,Hg_2Cl_2,LiCl(s)}\left|\begin{array}{cc} \mathrm{Li^+} & \mathrm{X} \\ \mathrm{Cl^-} & \mathrm{I^-} \end{array}\right|\mathrm{Pt}\ +$$

X represents Cl_2 or a reaction product between Cl_2 and I^-. A titration curve is shown in Figure 3a. The volume added at the three jumps will be denoted $v_{\mathrm{EP}}(0)$, $v_{\mathrm{EP}}(1)$, and $v_{\mathrm{EP}}(2)$. The large jump at $v_{\mathrm{EP}}(1)$ corresponds to the addition of 1 equiv of I^- to 1 equiv of Cl_2 according to eq 2 and not to the redox reaction eq 11 (cf. Table II and Figure 3b). Between $v_{\mathrm{EP}}(1)$ and $v_{\mathrm{EP}}(2)$, ICl_2^- reacts with added I^- to give I_2Cl^- (cf. eq 8) until $v = v_{\mathrm{EP}}(2)$ after which the concentration of ICl_2^- is negligible. Accordingly, $v_{\mathrm{EP}}(2) = 2v_{\mathrm{EP}}(1)$. When $v > v_{\mathrm{EP}}(2)$, the main species are I_2Cl^- (or I_2) and I_3^- (cf. eq 8). Finally, when $v > 3v_{\mathrm{EP}}(1)$, I_3^- is the only trihalide species present.

Concerning $v_{\mathrm{EP}}(0)$ and the curve for $v < v_{\mathrm{EP}}(1)$, all attempts to make a quantitative evaluation with stoichiometric relations that only involve the concentrations of Cl_2 and ICl_2^- have failed. However, if ICl_4^- also is included in the stoichiometric relations, a reasonable interpretation of the curve for $v < v_{\mathrm{EP}}(1)$ is possible. This is discussed in the Appendix.

Stoichiometry and Calculations. From $v_{\mathrm{EP}}(1)$ the total chlorine concentration ($C_{\mathrm{Cl_2}}{}^\circ$ at $v = 0$, i.e. before addition of iodine) can be calculated (cf. Table II). According to the spectrophotometrically determined value of K_1, chlorine is present mainly as Cl_2 when $C_{\mathrm{Cl}} = 1.00$ M. A plot of the emf, $E(v = 0)$, vs. log $C_{\mathrm{Cl_2}}{}^\circ$ before any addition of I^- gives straight lines (cf. Figure 3b), with slopes 27.2 ± 0.3 (0 °C) and 25.2 (−20 °C), in excellent agreement with the Nernstian relation ($(RT \ln 10)/2F$). Accordingly, the half-cell reactions can be written

$$2Hg + 2Cl^- \rightleftarrows Hg_2Cl_2 + 2e^- \qquad (23)$$

$$Cl_2 + 2e^- \rightleftarrows 2Cl^- \qquad (24)$$

with the corresponding emf E_{25} given by eq 25. (The logarithm

$$E_{25} = E_{25}{}^\circ + ((RT \ln 10)/2F) \log [Cl_2] \qquad (25)$$

of the ratio of the activity factors are included in $E_{25}{}^\circ$.) From the intercept in Table II and the known value of K_1, $E_{25}{}^\circ$ can be calculated. At 0 °C it is 1132 mV.

For $v_{\mathrm{EP}}(1) < v < v_{\mathrm{EP}}(2)$, ICl_2^- and I_2Cl^- (or I_2) exist in equilibrium according to eq 8 (or eq 5) and are the only species present in stoichiometric amounts. Their concentrations can therefore be calculated from the known concentrations ($C_{\mathrm{Cl_2}}{}^\circ$ and $C_{\mathrm{I}}{}^\circ$), volumes, and spectrophotometrically determined values of K_3 and K_5. The emf is determined by the half-cell reaction (23) together with (26). Figure 3c shows a corresponding plot. ([Cl^-]

$$2ICl_2^- + 2e^- \rightleftarrows I_2Cl^- + 3Cl^- \qquad (26)$$

$$E_{27} = E_{27}{}^\circ - ((RT \ln 10)/2F) \log ([I_2Cl^-][Cl^-]/[ICl_2^-]^2) \qquad (27)$$

is equal to 1.00 M; the slight increase due to the liberation of Cl^- according to eq 8 has been neglected.)

If the two half-cell reactions (24) and (26) are combined to give eq 28, the corresponding equilibrium constant K_{28} can be

$$Cl_2 + Cl^- + I_2Cl^- \rightleftarrows 2ICl_2^- \qquad (28)$$

Table IV. Equilibrium Constants with Estimated Maximum Uncertainties[a]

			log K_n		
reaction (eq no.)	method	K_n[b]	$t = 0$ °C	$t = -20$ °C	$t = 25$ °C[c]
$Cl^- + Cl_2 \rightleftarrows Cl_3^-$ (1)	S	K_1	−1.3 ± 0.2	−1.2 ± 0.4	−0.7 ± 0.1[9]
$I^- + Cl_2 \rightleftarrows ICl_2^-$ (2)	P	K_2	23.0 ± 0.3	25.4 ± 0.6	20.1 (calcd)
$Cl^- + ICl \rightleftarrows ICl_2^-$ (3)	S	K_3	2.75 ± 0.06	2.86 ± 0.05	2.1 ± 0.2[1]
$I^- + ICl \rightleftarrows I_2Cl^-$ (4)	$K_4 = K_8K_3$	K_4	8.4 ± 0.2	9.1 ± 0.3	8.5 ± 0.2[28]
$Cl^- + I_2 \rightleftarrows I_2Cl^-$ (5)	S	K_5	1.0 ± 0.1	1.2 ± 0.1	0.23 ± 0.03[1]
$I^- + I_2 \rightleftarrows I_3^-$ (6)	S	K_6	4.75 ± 0.05	5.20 ± 0.05	2.88 ± 0.03[4]
$I^- + Cl_3^- \rightleftarrows ICl_2^- + Cl^-$ (7)	P	K_7	24.3 ± 0.6	26.6 ± 0.9	
$I^- + ICl_2^- \rightleftarrows I_2Cl^- + Cl^-$ (8)	S, P	K_8	5.60 ± 0.15	6.20 ± 0.25	
$I^- + I_2Cl^- \rightleftarrows I_3^- + Cl^-$ (9)	S	K_9	3.75 ± 0.10	4.05 ± 0.10	

[a] S denotes spectrophotometric and P potentiometric measurements. Ionic strength is 1.0 M in methanol ($LiCl/LiBF_4$). [b] Units for K_1-K_6 are M^{-1}; K_7-K_9 are dimensionless. [c] Values in water.

calculated from eq 29. $E°$ values from Table III gives K_{28} =

$$(RT/2F) \ln K_{28} = E_{25}° - E_{27}° \qquad (29)$$

2.3 (3) × 10^{17} at 0 °C. The desired equilibrium constants K_2 and K_7 are obtained from eq 30 and 31 (cf. Table IV).

$$K_2 = K_{28}K_8 \qquad (30)$$

$$K_7 = K_2/K_1 \qquad (31)$$

Potentiometric Determination of K_8. When the added volume exceeds $v_{EP}(2)$, I_2Cl^- is the dominant species and the half-cell reaction can be written

$$I_2Cl^- + 2e^- \rightleftarrows 2I^- + Cl^- \qquad (32)$$

The cell reaction is combined from eq 23 and 32, and the emf is given by

$$E_{33} = E_{33}° - ((RT \ln 10)/2F) \log ([I^-]^2/[I_2Cl^-][Cl^-]) \qquad (33)$$

The two half-cell reactions (26) and (32) are combined to give

$$2ICl_2^- + 2I^- \rightleftarrows 2I_2Cl^- + 2Cl^- \qquad K_{34} \equiv K_8^2 \qquad (34)$$

and K_8 can be calculated from eq 35.

$$(RT/F) \ln K_8 = E_{27}° - E_{33}° \qquad (35)$$

Pairwise connected values of $E_{27}°$ and $E_{33}°$ are obtained from Table III: K_8 = 5.2 (2) × 10^5 (0 °C) and 2.5 (1.0) × 10^6 (−20 °C).

The determination of $E_{33}°$ from eq 33 consists of a calculation of $[I^-]$ and $[I_2Cl^-]$. This is rather complicated because not only I_2Cl^- but also I_3^- and I_2 are present in stoichiometric amounts, as is I^-. Several combinations of the appropriate stoichiometric relations are possible for this aim. The one presented here consists of a calculation of $[I_2]$ from the known total concentrations (C_{Cl_2}, C_I) and the relevant equilibrium constants (K_5, K_6). From the sequence of reactions (1)–(6) we conclude that

$$C_{Cl_2} = [Cl_2] + [Cl_3^-] + [ICl_2^-] + [I_2Cl^-] + [I_2] + [I_3^-] \qquad (36)$$

holds. The total concentration of I^-, C_I, is the sum of eq 21 and 22 in this case. When $v > v_{EP}(2)$, $[Cl_2]$, $[Cl_3^-]$, and $[ICl_2^-]$ are equal to zero and thus

$$C_{Cl_2} = [I_2Cl^-] + [I_2] + [I_3^-] \qquad (37)$$

$$C_I = [I^-] + 2([I_2Cl^-] + [I_2]) + 3[I_3^-] \qquad (38)$$

From

$$C_I - 2C_{Cl_2} = [I^-] + [I_3^-] \qquad (39)$$

and eq 6, $[I_3^-]$ can be eliminated and $[I^-]$ expressed as a function of $[I_2]$. This expression together with eq 5 is combined with eq 37 to give a second-degree equation in $[I_2]$ with the solution

$$[I_2] = (K_6(3C_{Cl_2} - C_I) - f)/2K_6f + [(C_{Cl_2}/K_6)f + ((K_6(3C_{Cl_2} - C_I) - f)/2K_6f)^2]^{1/2} \qquad (40)$$

where $f = 1 + K_5[Cl^-]$.

Discussion

Equilibrium Constants. The logarithmic values of the equilibrium constants in methanol and water are shown in Table IV. There is an approximate linear relationship between these sets (i.e., ln $K(CH_3OH)$ vs. ln $K(H_2O)$), which means that the free energies are (as expected) linearly related. Therefore, the reported values seem reasonable. This is further revealed if the individual constants are compared with literature values or checked for internal consistency.

The only constant reported in the literature is K_6.[2,4-11] All published values are of the same order of magnitude as the one reported here. Mostly, K_6 has been determined at 25 °C, but Mayakawa and Nakamura[10] also studied the equilibrium at various temperatures (39–12 °C). Extrapolation to 0 °C gives log K_6 = 4.32 in rather good agreement with the value in Table IV. That reported here is consistent with the values of K_5 and K_9 ($K_6 = K_5K_9$); the corresponding three reactions have been independently studied. Thus, it seems safe to assume that all three constants are reliable. The two methods from which K_8 has been calculated give consistent results. That this is so despite the large difference in the concentration of ICl, 0.15 mM and, e.g., 25 mM in the spectrophotometric and potentiometric methods, respectively, is a strong indication of the correctness of K_8.

That K_2 is, at least, of the right order of magnitude can be judged from a calculation of the equilibrium constant, K_{11}, for the redox process

$$2I^- + Cl_2 \rightleftarrows I_2 + 2Cl^- \qquad (11)$$

with $K_{11} = K_2K_8/K_5$. The values (at 0 °C) from Table IV give log K_{11} = 28.8 or $E_{12}°$ = 780 mV. The tabulated values[15] for the two half-cell reactions involved (eq 24 and its I_2/I^- analogue) give $E_{12}°$ = 770 mV in methanol, at 25 °C and 0 ionic strength. This gives log K_{11} = 26.0, which is, incidentally, the value obtained by extrapolation using the two values of log K_{11} at 0 and −20 °C. Thus, it seems fair to conclude that the value of K_{11} is well established. From the preceding discussion concerning K_8 and K_5, we can conclude that the value given for K_2 in Table IV is reasonable. K_3 was estimated by Buckles and Mills[12] to be about 300 M^{-1} at 25 °C. This is in satisfactory agreement with that extrapolated from the data at 0 and −20 °C in Table IV (450 ± 150 M^{-1}).

The constant that is most uncertain is K_1. The low value is by itself not unlikely, rather it is the high molar absorptivities ((7 ± 1) × 10^4 cm^{-1} M^{-1} at maximum) obtained in the calculation that seem less plausible. Assuming that the applied model is correct (Cl_2 and Cl_3^- are the only absorbing species and $[Cl^-] \approx C_{Cl}$), the values of $\epsilon_{Cl_3^-}$ and K_1 are strongly correlated (cf. the numerator in eq 19). If therefore the value of K_1 is increased to that given by the maximum uncertainty ($3\sigma_{K_1}$, i.e. K_1 = 0.082 M^{-1} (0 °C); cf. Table I), the molar absorptivities are lowered by a factor 1.5. The maximum between 235 to 240 nm would then have a molar absorptivity around 5 × 10^4 cm^{-1} M^{-1}, which is entirely in harmony with those of the other trihalides. However, this value is about 5 times larger than that reported by Zimmermann and Strong[3] in aqueous solution. They found a maximum at 220 nm with a molar absorptivity of about 1 × 10^4 cm^{-1} M^{-1}. It is noticeable that this maximum differs by about 18 nm from that found here, because for the other trihalides these differences, i.e. with water and methanol as solvents respectively, never exceed 7 nm. Another dissatisfying feature is that the molar absorptivities for Cl_2 also are very different. So, for instance, one can calculate ϵ_{Cl_2} at 225 nm to be 85 cm^{-1} M^{-1} in water according to the authors of ref 3 (Figure 1), whereas in this work it is 17 times larger (cf. Table I). Despite these facts, it is obvious that the curves show qualitative agreement; compare Figure 2a,b in this work with Figure 1 in ref 3.

The model with only two absorbing species can be validated by the graphical method by Coleman et al.[29] applied to the curves in Figure 1a. Further, not only can CH_3OCl be excluded, according to the earlier discussion, but also higher polychlorides, e.g. Cl_5^-, can be excluded. This follows from the potentiometric data displayed in Table II and that the Nernstian plot in Figure 3b is linear over more than 3 powers of 10 in the total chlorine concentration. To conclude, it seems safe to assume that only Cl_2 and Cl_3^- are present as absorbing species.

The large values of $\epsilon_{Cl_3^-}$ and the small value of K_1 are probably not due to ion pair formation of lithium chloride or tetrafluoroborate, which should make $[Cl^-] < C_{Cl}$. Hypothetical ion pair formation of the ionic media will of course occur in all solutions, which means that not only K_1 but all the reported equilibrium constants in Table IV may be affected. However, reported values of ion pair formation constants[30,31] exclude this to be extensive. From a conductometric determination, Kay[30] concluded that the

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ion pair formation constant K_{LiCl} must be close to 0. A comparison with other alkali chlorides,[32] and the trend in limiting ionic mobilities for the alkali cations (cf. ref 32, pages 44–47), shows this conclusion to be well founded. According to Kratochvil and Yeagar,[32] one reason to expect a low degree of ion pairing with the lithium ion is that it is strongly solvated. It is reasonable to expect that the solvent interaction energy increases when the temperature decreases, because saturated solutions of lithium chloride in methanol are in equilibrium with $\mathrm{LiCl{\cdot}3CH_3OH(s)}$ below 0.1 °C but with LiCl(s) above this temperature.[33] For this reason, and also because the dielectric constant of methanol increases when the temperature is lowered, it is unlikely that K_{LiCl} will be larger at the temperatures used in this study than at room temperature. Published temperature effects on ion pair formation constants of alkali iodides in ethanol[34] speak in favor of this conclusion.

Indeed, a discussion based on the results from the three independently studied reactions (5), (6), and (9), i.e. that $K_6 = K_5K_9$ holds rigorously at two different temperatures despite the fact that different (or changing) ionic media have been used ((5) $\mathrm{LiBF_4}$/LiCl, $C_{\mathrm{Li}} = 1.0$ M, $0 \leq C_{\mathrm{Cl}} \leq 0.21$ M; (6) 1.0 M $\mathrm{LiBF_4}$; (9) 1.0 M LiCl), also indicate a low value of K_{LiCl}. Only two possibilities can explain the experimental agreement (i.e., $K_6 = K_5K_9$): either $K_{\mathrm{LiCl}} \approx 0$, whatever the value of the corresponding constant $K_{\mathrm{LiBF_4}}$, or $K_{\mathrm{LiCl}} \approx K_{\mathrm{LiBF_4}}$ at both temperatures. Unfortunately, very little is known about the ion-pairing tendency in solutions containing the tetrafluoroborate ion. According to Kratochvil and Yeager,[32] the expected trend should be that the larger the anion, the smaller will the ionpair formation constant be, for one and the same cation (cf. ref 32; Table IV; Figure 3). Taken together, this suggests that $K_{\mathrm{LiCl}} \geq K_{\mathrm{LiBF_4}}$ and that both constants are close to zero. To conclude, the discrepancy for $\mathrm{Cl_2/Cl_3^-}$ in water and methanol cannot be explained by ion pair formation.

Reactions. Of the reactions between a halogen molecule and a halide ion (reactions 1–6), all except eq 2 (and possibly eq 4) can be regarded as simple addition reactions (cf. ref 2, page 226) because the bond in the original halogen molecule is preserved (though elongated):

$$\mathrm{X^- + Y{-}Z \rightarrow X{-}Y{-}Z^-} \qquad (41)$$

However, this is not the case in eq 2 because it involves both an extensive geometric and electronic rearrangement, the latter represented by the change in oxidation states for iodine and chlorine:

$$\overset{-\mathrm{I}}{\mathrm{I}^-} + \overset{0}{\mathrm{Cl}}{-}\overset{0}{\mathrm{Cl}} \rightarrow (\overset{-\mathrm{I}}{\mathrm{Cl}}{-}\overset{\mathrm{I}}{\mathrm{I}}{-}\overset{-\mathrm{I}}{\mathrm{Cl}})^- \qquad (42)$$

This reaction is one of several that together make up the redox reaction between iodide ion and chlorine given by the simple eq 11. As written, the change in oxidation number is only +1 (for $\mathrm{I^-}$) and −1. However, the presence of the linear dichloroiodate(I) (eq 2) and, for excess chlorine, of the square-planar tetrachloroiodate(III) (cf. Appendix) means that several electron-transfer steps are involved before the iodine(0) state is reached. The reduction I(I) → I(0) is described by reaction 4, which thus can be classified in two different ways. In this reaction the geometric change consists of a considerable change in the I–Cl bond. According to Hassel and Rømming,[35] it is expected to increase from 2.35 Å (ICl) to 2.95 Å ($\mathrm{I_2Cl^-}$; cf. the corresponding values[16] for $\mathrm{IBr/I_2Br^-}$). The latter distance is only 6% shorter than the sum of the covalent and ionic radii for iodine (1.33 Å) and chloride (1.81 Å), respectively. It is thus preferable to call reaction 4 a redox reaction. By the same arguments reaction 5 represents a simple addition reaction.

Table V. Emf for $v < v_{\mathrm{EP}}(0)$ (Left) and $v_{\mathrm{EP}}(0) < v < v_{\mathrm{EP}}(1)$ (Right) (Series a (Cf. Table II); $t = 0$ °C)

v/mL	$[\mathrm{Cl_2}]$/ mM	E_{25}/mV	v/mL	$[\mathrm{ICl_4^-}]$/ mM	$[\mathrm{ICl_2^-}]$/ mM	E_{51}/mV
0.00	33.6	1091.7	3.25	14.6	3.69	1048.2
0.20	31.2	1091.0	3.50	13.1	6.46	1041.9
0.40	28.8	1090.2	3.75	11.6	9.20	1036.7
0.60	26.3	1089.1	4.00	10.2	11.9	1032.3
0.80	25.3	1088.2	4.25	8.75	14.6	1028.1
1.00	21.6	1087.0	4.50	7.34	17.2	1024.4
1.20	19.3	1085.9	4.75	5.94	19.9	1019.9
1.50	15.8	1083.7	5.00	4.56	22.4	1015.8
1.75	12.9	1081.5	5.25	3.19	25.0	1009.8
2.00	10.1	1078.9	5.50	1.84	27.5	1002.0
2.25	7.33	1075.5				
2.50	4.57	1071.0				

$E_{25}{}^{\circ} = 1127.1$ (4) mV
slope 24.1 (2) mV

$E_{51}{}^{\circ} = 1033.6$ (2) mV
slope −26.3 (4) mV

The classification into redox and addition reactions is also connected with the magnitude of the equilibrium constants: K_2 is very large, corresponding to the largest change in oxidation state (I(−I) → I(+I)), followed by K_4 (I(I) → I(0)). K_3 and K_5 are relatively small, corresponding to no change at all, i.e. addition only, whereas K_6 is intermediate (formally corresponding to a fractional change in oxidation state). The large rearrangement of the electrons connected with redox reactions as compared to addition reactions can also be expressed in the following way: those constants that correspond to reactions between a halogen molecule and iodide are much larger than those with chloride ($K_2 \gg K_1$; $K_4 \gg K_3$; $K_6 \gg K_5$), and, conversely, the release of a chloride from a trihalide ion is much easier than for an iodide ion ($K_3^{-1} \gg K_2^{-1}$; $K_5^{-1} \gg K_4^{-1}$). I.e., with chloride the reactions can be unambiguously classified as addition reactions, whereas with iodide they are sometimes better regarded as redox reactions.

Structure. Since halogens in the same oxidation state have identical orbital symmetries and electron populations, both centrosymmetric ($D_{\infty h}$) and noncentrosymmetric ($C_{\infty v}$) isomers of the heteronuclear trihalide anions, for instance $\mathrm{ICl_2^-}$, might be expected. However, these anions "invariably adopt the form in which the halogen of highest atomic number is the central "polyvalent" atom";[16] e.g., $\mathrm{ICl_2^-}$ ($D_{\infty h}$) is the more stable isomer. This can be understood by the same argument as that used by Pauling[36] for the similarity in charge distribution between an octahedral metal complex and a charged metal sphere.

The linear $\mathrm{ICl_2^-}$ can be compared to a negatively charged, electrically conducting rod; it has its maximum electrostatic stability when the charge distribution has its highest negative value near the ends, and it is symmetrical around the midpoint.[37] This electron distribution of $\mathrm{ICl_2^-}$ is only possible in the centrosymmetric arrangement, as can be inferred from the lower electronegativity of iodine as compared to chlorine. It is then also understandable that the homonuclear species $\mathrm{Cl_3^-}$ and $\mathrm{I_3^-}$ are less stable than $\mathrm{ICl_2^-}$ ($D_{\infty h}$). Concerning $\mathrm{I_2Cl^-}$, the hypothetic structure I–Cl–I ($D_{\infty h}$) would have the negative charge concentrated to Cl and an unstable structure is expected. That the stable structure is I–I–Cl must mean that the terminal I atom is more negative than the central one.

For $\mathrm{ICl_2^-}$ ($D_{\infty h}$) it is reasonable to assign a partial positive charge to (the central) I, i.e. to classify its oxidation state as +1. Thus, in this compound, as well as in $\mathrm{ICl_4^-}$ (D_{4h}) (cf. Appendix), iodine behaves like a metal atom toward chloride. Among the transition-metal chloride complexes those of gold are identical in structure and charge and thus in the assigned oxidation state of the gold atom; they are $\mathrm{AuCl_2^-}$ ($D_{\infty h}$) and $\mathrm{AuCl_4^-}$ (D_{4h}). It is noticeable that Pauling[36] assigned nearly the same value of electronegativity to gold as to iodine. Therefore, the relative distribution of electrons in the (σ-) I–Cl bonds in $\mathrm{ICl_2^-}$ ($D_{\infty h}$)

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should be the same as for Au–Cl in $AuCl_2^-$ (note that Au has a closed (d^{10}) electron configuration, and any eventual d to p back-bonding can be neglected). Structures different from the centrosymmetric one for ICl_2^- are expected to be as unlikely as they are for $AuCl_2^-$. However, short-lived intermediates with chlorine as central atom might exist among the heteronuclear trihalide anions. That follows directly from the similarities in orbital symmetry and electron population discussed earlier.

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Appendix

The formation of ICl_4^- according to eq 43 is known from preparative polyhalogen chemistry.[2,38] The reaction may possibly

$$I^- + 2Cl_2 \rightarrow ICl_4^- \qquad (43)$$

occur in the solutions studied here, at least when C_{Cl_2} is high (cf. Table II, series a) and $C_I < {}^1/_2C_{Cl_2}$, i.e. when $v < v_{EP}(0)$ (cf. Figure 3a). Besides eq 43, eq 2 is valid and we can write (44). The

$$Cl_2 + ICl_2^- \rightleftarrows ICl_4^- \qquad (44)$$

stoichiometry is given by (45) and (46). If it is assumed that

$$C_{Cl_2} = [Cl_2] + [Cl_3^-] + [ICl_2^-] + 2[ICl_4^-] \qquad (45)$$

$$C_I = [ICl_2^-] + [ICl_4^-] \qquad (46)$$

the equilibrium according to eq 44 is displaced to the right when $v < v_{EP}(0)$, then $[ICl_2^-] \ll [ICl_4^-]$ and the relevant concentrations can simply be calculated from eq 47 and 48. When all added

$$[ICl_4^-] = C_I \qquad (47)$$

$$[Cl_2] + [Cl_3^-] = C_{Cl_2} - 2C_I \qquad (48)$$

I^- has been converted to ICl_4^-, $v = v_{EP}(0)$. As discussed earlier, $v = v_{EP}(1)$, when all I^- has been converted to ICl_2^-. It follows that (49) holds true, and the measurements displayed in Figure

$$v_{EP}(0) = {}^1/_2v_{EP}(1) \qquad (49)$$

3a show that this condition is fullfilled. The curve is based on series a, and the values in the appropriate volume region are given in Table V. It has been assumed that the emf-determining process is given by eq 25, with $[Cl_2]$ calculated from eq 48 and eq 1. The values for $E_{25}°$ (1127.1 mV) and slope (24.1 mV) are sufficiently close to those calculated earlier (1132.0 and 27.2 mV, respectively) to validate the assumptions made.

In the range $v_{EP}(0) < v < v_{EP}(1)$ it is assumed that ICl_4^- reacts with added I^- to give ICl_2^- and that the half-cell reaction is

$$ICl_4^- + 2e^- \rightarrow ICl_2^- + 2Cl^- \qquad (50)$$

This can be combined with eq 23 to give the total cell reaction. The emf, E_{51}, is given by

$$E_{51} = E_{51}° - ((RT \ln 10)/2F) \log([ICl_2^-]/[ICl_4^-]) \qquad (51)$$

The concentrations can be calculated from eq 45 and 46 with $[Cl_2] = [Cl_3^-] = 0$. The result is shown in Table V. Combining the two half-cell reactions (50) and (24) gives eq 44. The equilibrium constant K_{44} can be calculated from eq 52. Inserting the earier determined value of $E_{25}°$ (1132.0 mV) or $E_{25}°$ from Table V results in $K_{44} = 4.3\ (5) \times 10^3\ M^{-1}$. From this value we can

$$((RT \ln 10)/2F) \log K_{44} = E_{25}° - E_{51}° \qquad (52)$$

conclude that the concentration of ICl_2^- never exceeds 6×10^{-4} M when $v < v_{EP}(0)$. However, it means that eq 47 and 48 are only approximately valide. If a correction for ICl_2^- is applied to the calculated values of $[Cl_2]$ in Table V, $E_{25}°$ increases to 1129.1 mV and the slope to 25.3 mV. This is closer to the corresponding quantities in Table II than the original ones in Table V.

Registry No. Cl_3^-, 18434-33-8; I_3^-, 14900-04-0; ICl_2^-, 14522-79-3; I_2Cl^-, 17705-05-4.

Supplementary Material Available: Tables of spectrophotometric data giving total concentrations of halogen molecules and halide ions and absorptivities at several wavelengths and potentiometric data giving volumes of added reagent (I^-), emf, and calculated concentrations of the relevant species (cf. the text preceding eq 26 and 40) (15 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, Brown University, Providence, Rhode Island 02912,
and Queen Mary College, London E1 4NS, England

Effect on Redox Potentials of Hydrogen Bonding from Coordinated Imidazole in Metalloporphyrin Complexes

P. O'BRIEN*[1] and D. A. SWEIGART*[2]

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The Fe(III)/Fe(II) reduction potentials for $[Fe(porphyrin)(imidazole)_2]X$ (porphyrin = TPP, PPIXDME; imidazole = HIm, *N*-MeIm; X = Cl^-, SbF_6^-) have been measured by cyclic voltammetry in a variety of solvents. The addition of excess imidazole or 1,10-phenanthroline (phen) to $Fe(porphyrin)(HIm)_2^+$ cause a cathodic shift of ca. 60 mV in the reduction potential, and this shift is assigned to a hydrogen-bonding interaction between the coordinated imidazole N–H and free imidazole or phen. In support of this, excess phen was found to have no effect on $E_{1/2}$ for $Fe(porphyrin)(N\text{-}MeIm)_2^+$. The $E_{1/2}$ values measured relative to the ferrocene/ferrocenium couple correlate well with the solvent dielectric constant and donor number, although a simple interpretation of this correlation is not possible. Experiments were done with tetra-*n*-butylammonium perchlorate (TBAP) and tetra-*n*-butylammonium tetraphenylborate ($(TBA)BPh_4$) as the supporting electrolyte, and these show that ClO_4^- from TBAP also can hydrogen bond to coordinated imidazole. A discussion is given of these hydrogen-bonding interactions, as well as ion-pairing effects. The studies show that the redox potential changes due to hydrogen bonding from coordinated imidazole in $Fe(porphyrin)(HIm)_2^+$ is of sufficient magnitude to be considered seriously as a mechanism of redox potential regulation in heme proteins. The $E_{1/2}$ for Ru(TPP)(CO)(HIm) oxidation was found not to be influenced by phen, and it is concluded that hydrogen-bonding effects are only important when the redox change is metal centered, as with Fe(III)/Fe(II), instead of porphyrin ring centered as with Ru(TPP)(CO)(HIm) oxidation, which gives a Ru(II) cation radical.

Introduction

Variations in reactivity of the iron center in heme proteins are determined primarily by the axial ligands, the most common of which is imidazole (HIm) from a "proximal" histidine residue. Perhaps the best known example of reactivity modulation is the trigger mechanism for hemoglobin cooperativity, in which movement of the iron atom toward the porphyrin plane is restrained by virtue of the imidazole ring orientation.[3] This restraint