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Kinetics of Hydrolysis of Iodine Monochloride Measured by the Pulsed-Accelerated-Flow Method

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Abstract: First-order rate constants from 75 000 to 150 000 s^{-1} are measured by the pulsed-accelerated-flow technique for the rate of loss of ICl_2^- in neutral and basic solutions. The rate varies inversely with the Cl^- concentration because ICl(aq) is the reactive form. The hydrolysis of ICl(aq) to give HOI and Cl^- is extremely rapid ($k_{H_2O} = 2.4 \times 10^6$ s^{-1} at 25.0 °C, $\mu = 0.50$). Hydroxide ion accelerates the rate of hydrolysis. The second-order rate constant for the reaction of OH^- with ICl(aq) is very large ($k_{OH} = 4.5 \times 10^9$ M^{-1} s^{-1}). Reactions of ICl(aq) with $H_2PO_4^-/HPO_4^{2-}$ and with HCO_3^-/CO_3^{2-} buffers are also very rapid and are first order in the total buffer concentration, with resulting second-order rate constants, $(1.3 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, that do not depend on the basicity of the buffer or the ratio of buffer species. Two ICl(aq) species are proposed to be in rapid equilibria: H_2OICl (82%) and ICl (18%). Kinetic data indicate that ICl (the less hydrated species) is so reactive that it is unselective and reacts with $H_2PO_4^-$, HPO_4^{2-}, HCO_3^-, CO_3^{2-}, and OH^- at the diffusion limit (7×10^9 M^{-1} s^{-1}). The more hydrated species, H_2OICl, also reacts rapidly with OH^- (3.9×10^9 M^{-1} s^{-1}) by proton transfer to form H_2O and $HOICl^-$, which rapidly loses Cl^- to give HOI. Spectrophotometric measurements of the equilibrium constants at 25.0 °C give $([ICl(aq)][Cl^-])/[ICl_2^-] = 0.013$ M ($\mu = 1.0$ and 0.5) and $([HOI][Cl^-]^2[H^+])/[ICl_2^-] = 1.06 \times 10^{-6}$ M^3 ($\mu = 0.5$).

Kinetics of the hydrolysis of Cl_2, Br_2, and I_2 have been determined by relaxation techniques[1] and for Cl_2 by stopped-flow[2] and continuous-flow[3] methods. However, the kinetics of hydrolysis of interhalogens, such as ICl, have not been examined. This had been due to the lack of a method suitable to the study of reactions that are too fast to measure by stopped-flow methods and cannot be maintained under equilibrium conditions as necessary to apply relaxation methods. The development of the pulsed-accelerated-flow (PAF) method[4-6] permits very fast reactions ($t_{1/2} \geq 2$ μs) to be studied. This makes it possible for the first time to study the kinetics and mechanism of iodine monochloride hydrolysis. The PAF method uses integrating observation of the reaction mixture under continuous-flow conditions for short time periods (pulse) during which the flow is accelerated.[4,5] The reactants are observed as they mix in order to eliminate the dead time (time between mixing and observation) that is typically 3–5 ms for stopped-flow instruments.[7] Variation of the flow velocity in the PAF instrument enables the physical mixing process and the chemical reaction process that occur in the observation tube to be resolved from each other so that the rate constant of the actual chemical reaction can be calculated.[4,5] The PAF method has been applied in studies of a number of very fast non-metal redox reactions.[8-10]

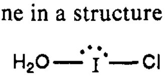
Iodine monochloride is proposed as an intermediate in oxidation reactions of iodide by chloramines,[11] nitrogen trichloride,[9] and hypochlorous acid.[9,11] All these reactions involve the transfer of a Cl^+ ion to I^-. Iodine monochloride also is proposed as a key intermediate[12] in the chlorite–iodide oscillating reaction system.[13,14] It has long been known that iodine monochloride is labile and that it hydrolyzes extensively in aqueous solutions.[15] In a study of the autocatalytic reaction between I_2 and ClO_2^-, an estimated value of 100 s^{-1} is given as the rate constant for ICl hydrolysis.[14] We shall see that this estimate is too small by a factor of 2.4×10^4. Nevertheless, the hydrolysis path was not observed in the study of the ICl_2^- reaction with I^- in 0.1–1.0 M Cl^- concentration for either 0.10 or 1.0 M H^+ concentrations.[8] It is therefore of interest to measure how rapidly iodine monochloride hydrolyzes and to determine the reaction mechanism for this process.

The final products of the hydrolysis of ICl in acid are iodate and iodine (eq 1a) and in base are iodate and iodide (eq 1b).

$$5ICl(aq) + 3H_2O \rightleftarrows IO_3^- + 2I_2 + 5Cl^- + 6H^+ \quad K_{1a} \qquad (1a)$$

$$3ICl(aq) + 6OH^- \rightleftarrows IO_3^- + 2I^- + 3Cl^- + 3H_2O \quad K_{1b} \qquad (1b)$$

Iodine monochloride in water is written as ICl(aq) to indicate that it includes both ICl and H_2OICl. The latter species (I) will have two electron-pair bonds and three nonbonding electron pairs around iodine in a structure similar to ICl_2^- (II). It is apparent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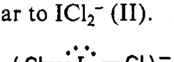
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that the overall reactions in eq 1a,b involve multiple steps because the products are derived from disproportionation as well as hydrolysis reactions. The initial product of ICl hydrolysis is HOI (eq 2). The disproportionation of HOI in acid gives IO_3^- and I_2.[16-18] Kinetic studies have shown that the disproportionation of HOI is both slow and complex.[17]

$$ICl(aq) + H_2O \rightleftarrows HOI + Cl^- + H^+ \qquad K_2 \qquad (2)$$

Iodine monochloride readily forms dichloroiodate(I) (eq 3), ICl_2^-, which is very stable in solutions where the HCl concentration is 0.5 M or greater.[19] We will show that the value of the

$$ICl_2^- \rightleftarrows ICl(aq) + Cl^- \qquad K_3 \qquad (3)$$

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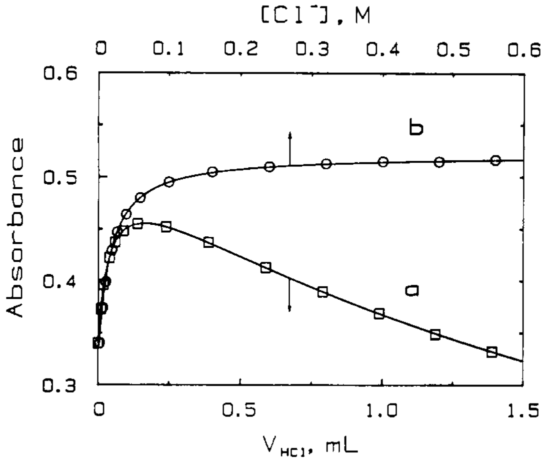

Figure 1. (a) Absorbance change in the spectrophotometric titration of ICl/ICl_2^- with 1.00 M HCl (V_{HCl}). Conditions: 2.50 mL of 1.90×10^{-3} M $[ICl_2^-]_{init}$ in 1.00 M $HClO_4$ at 25.0 °C, 1.00-cm cell, 343 nm. (b) Absorbance versus the iteratively calculated chloride concentration.

equilibrium constant K_3 is 0.013 M, which differs significantly from the long-established value of 0.006 M.[15] The UV spectrum of ICl_2^- has characteristic absorption bands at 224 nm (ϵ = 47 000 $M^{-1}\,cm^{-1}$)[19] and 343 nm, where ϵ ($M^{-1}\,cm^{-1}$) values of 243[19] and 275[20] have been reported. Our results indicate that the latter value is correct. Equations 2 and 3 can be combined to give the equilibrium in terms of ICl_2^- and HOI (eq 4). We have measured

$$ICl_2^- + H_2O \rightleftarrows HOI + 2Cl^- + H^+ \qquad K_4 \qquad (4)$$

this equilibrium constant and find a K_4 value of 1.06×10^{-6} M^3. A K_2 value of 8.2×10^{-5} M^2 can be calculated from our values of K_3 and K_4. These equilibrium constants are obtained by more direct measurements than those previously reported.[15]

The hydrolysis of ICl can be suppressed by Cl^- due to the formation of ICl_2^-, but the hydrolysis is nevertheless far too rapid to be measured by stopped-flow spectrophotometry. The PAF method extends accessible first-order rate constants by a factor of 10^3 beyond the limit of stopped-flow methods. This makes it possible to measure the rate of reaction of iodine monochloride with water, with hydroxide ion, and with phosphate and carbonate buffers.

Experimental Section

A 0.060 M stock solution of ICl_2^- was prepared[8,21] by addition of standardized[22] NaI solution to a solution of primary standard-grade $NaIO_3$ in HCl. Two moles of NaI was added for each mole of $NaIO_3$ (eq 5). A brown precipitate of I_2 formed initially but redissolved with

$$2I^- + IO_3^- + 6H^+ + 6Cl^- \rightarrow 3ICl_2^- + 3H_2O \qquad (5)$$

stirring after 30 min. The final concentrations of H^+ and Cl^- are 0.20 and 1.0 M, respectively, and under these conditions the ICl_2^- stock solution is very stable. The ICl_2^- solutions used in the hydrolysis experiments were made by dilution of the stock solution with the reaction medium immediately prior to the experiments.

Solutions of $HClO_4$ and HCl were standardized against NaOH, which had been standardized with primary standard potassium hydrogen phthalate. Solutions used in the PAF kinetic experiments were filtered through 0.22-μm Triton-free Millipore type HA filter and were degassed by aspiration for at least 10 min. An Orion 601A pH meter with a combination electrode was used to measure the pH of solutions after the reactions were complete. These readings were corrected to $-\log [H^+]$ values on the basis of electrode calibration by titration of standardized $HClO_4$ with standardized NaOH at μ = 0.50 ($NaClO_4$) and 25.0 °C.

A Perkin-Elmer Model 320 spectrophotometer was used to acquire UV–vis spectra and to obtain spectrophotometric titration data. The titration was carried out by adding HCl to a dilute acidic ICl_2^- solution.

Table I. Stopped-Flow Determination of K_4 Based on the Immediate Absorbance Decrease on Mixing ICl_2^- with Buffers[a]

$[Cl^-]$, M	$p[H^+]$	A_e(343 nm)	$[Cl^-]$, M	$p[H^+]$	A_e(343 nm)
0.3	3.56[b]	0.218	0.4	5.51[c]	0.109
0.3	4.12[b]	0.199	0.4	6.05[c]	0.074
0.3	4.64[b]	0.167	0.4	6.54[c]	0.061
0.3	5.06[b]	0.128	0.5	3.99[b]	0.215
0.3	5.61[c]	0.087	0.5	4.97[b]	0.172
0.3	6.08[c]	0.067	0.5	5.29[b]	0.146
0.4	3.59[b]	0.221	0.5	5.98[c]	0.084
0.4	4.17[b]	0.204	0.5	6.44[c]	0.068
0.4	4.66[b]	0.179	0.5	6.85[c]	0.060
0.4	5.08[b]	0.146			

[a] 25.0 °C, μ = 0.50, $[ICl_2^-]_0 = 4.3 \times 10^{-4}$ M, A_0 = 0.223, 1.89-cm cell. [b] $[OAc^-]_T$ = 0.05 M. [c] $[PO_4]_T$ = 0.05 M.

A stoppered 1-cm spectral cell (4-mL capacity) was loaded with 2.50 mL of a 1.9×10^{-3} M ICl_2^- solution in 1.0 M $HClO_4$. The absorbance at 343 nm was measured as small increments of 1.0 M HCl were added to give a final volume of 3.89 mL. The absorbance during the titration increased initially as more ICl_2^- formed and then decreased due to dilution (Figure 1a).

A Durrum stopped-flow spectrometer interfaced[23] to a Hewlett-Packard 2100S minicomputer was used to determine the total change of absorbance of ICl_2^- after it was mixed with phosphate buffer. The rate of loss of ICl_2^- is too fast to be measured by this method, but the equilibrium in eq 4 can be established within 5–20 ms without significant disproportionation of HOI.

A pulsed-accelerated-flow spectrometer was used to obtain kinetic data for the reaction of ICl_2^- with dilute NaOH solutions, with phosphate buffer, and with carbonate buffer. This instrument employs integrating observation with continuous flow[4] over a short time period to conserve reagents (only 5–6 mL is needed per push). Key features of the PAF spectrometer include a twin-path mixing/observation cell[5] and a programmed-flow velocity. The two reactant solutions enter the observation cell via 10 jets, which intersect in the middle of the observation tube, and the reacting mixture then flows parallel to the direction of observation.[5] The velocity of the solution in the observation tube is programmed to change from 3.0 m s^{-1} at the beginning of the push to 12.5 m s^{-1} at the end of the push in the acceleration mode or from 12.5 to 3.0 m s^{-1} in the deceleration mode. Turbulent flow that is necessary for mixing the solutions exists at these velocities, and the mixing rate constant is proportional to the velocity. The change of the velocity permits resolution of the physical mixing process and the chemical reaction process. Calibration reactions have been used to verify the resolved rate constants.[4,5] The Model IV PAF instrument used in this work has a double-grating monochromator with a wavelength range of 200–850 nm and minimal stray light. The instrumental features have been summarized in a previous application.[10] Details of the construction, computer interfacing, and measurement of rate constants as large as 350 000 s^{-1} will be provided elsewhere.[6] In the present work first-order rate constants are measured in the range 75 000–150 000 s^{-1} by the PAF method.

All PAF experiments were carried out under pseudo-first-order conditions at 25.0 °C and μ = 0.50 ($NaClO_4$). Reactions were monitored at 230 nm in order to take advantage of the high molar absorptivity of ICl_2^- (ϵ_{230} = 42 000 $M^{-1}\,cm^{-1}$) compared to the much lower absorptivities of HOI and OI^- at this wavelength. A typical initial absorbance (A_0) was 1.22 ($[ICl_2^-] = 1.4 \times 10^{-5}$ M, 2.05-cm cell), and typical A_∞ values were 0.11. The observed first-order rate constant, k_r, is the result of a linear regression of the M_{exptl}[5,10] values versus the flow velocity in the observation tube. $M_{exptl} = (A_v - A_\infty)/(A_0 - A_\infty)$, where A_v is the instantaneous absorbance for each of 250 points taken over a velocity range of 12–7 m s^{-1}. These high velocities are needed to give linear plots of M_{exptl} against v because of the magnitude of the rate constants in this study. The rate constants are corrected in accordance with the calibration of the PAF instrument for large k_r values (>100 000 s^{-1}).[6] The reported k_r values and standard deviations are obtained from at least seven trials for each set of conditions. The average relative standard deviation is ±9%.

Results and Discussion

Equilibrium Constant for the Hydrolysis of ICl_2^-. A stopped-flow instrument was used to study the extent of hydrolysis of ICl_2^- to give HOI (eq 4) in the $p[H^+]$ range from 3.56 to 6.91, with $[Cl^-]$ = 0.30–0.50 M. The loss of ICl_2^- was monitored at 343 nm. The

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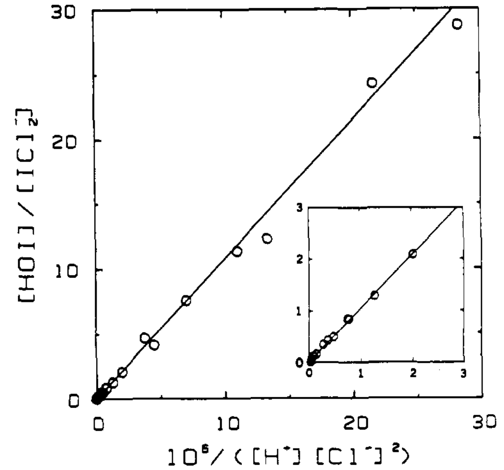

Figure 2. Plot of eq 7 with slope = K_4 = (1.06 ± 0.03) × 10^{-6} M^3 at 25.0 °C, $\mu = 0.50$, based on the molar absorptivities given in Table II. The inset shows the validity of the fit at lower HOI concentrations.

initial absorbance change takes place within the dead time of the instrument (<4 ms). The stopped-flow spectrometer was used so that the subsequent disproportionation of HOI did not interfere. The data (Table I) show that at a given $[Cl^-]$ the loss of ICl_2^- increases as $p[H^+]$ increases as expected from eq 4. The equilibrium constant K_4 is defined by eq 6. The ratio of [HOI] to

$$K_4 = \frac{[Cl^-]^2[H^+][HOI]}{[ICl_2^-]} \tag{6}$$

$[ICl_2^-]$ can be obtained from the original absorbance of the ICl_2^- solution ($A_0 = b\epsilon_{ICl_2}[ICl_2^-]_0$) and the equilibrium absorbance ($A_e = b(\epsilon_{ICl_2}[ICl_2^-]_e + \epsilon_{HOI}[HOI]_e)$). A plot of the ratio against $1/([H^+][Cl^-]^2)$ should give a straight line with slope of K_4. In eq 7, the molar absorptivity value for ICl_2^- is 275 M^{-1} cm^{-1} but

$$\frac{[HOI]}{[ICl_2^-]} = \frac{A_0 - A_e}{A_e - A_0(\epsilon_{HOI}/\epsilon_{ICl_2})} = \frac{K_4}{[H^+][Cl^-]^2} \tag{7}$$

the ϵ value for HOI at 343 nm has not been reported. However, ϵ values for HOI and OI^- at other UV wavelengths are available. For HOI, the known value is $\epsilon_{278}^{max} = 200$,[24] and for OI^-, $\epsilon_{365} = 58$[24] and $\epsilon_{363} = 60$.[18] We tested a range of the ϵ values from 60 to 70 M^{-1} cm^{-1} for HOI at 343 nm in order to give a linear fit for eq 7. The results of the weighted linear regression show that the best fit (Figure 2) is achieved when the ϵ value for HOI at 343 nm is 67 M^{-1} cm^{-1}. The slope from the regression treatment gives a new value of K_4 equal to (1.06 ± 0.03) × 10^{-6} M^3 (25.0 °C, $\mu = 0.50$). This is the first direct measurement of this equilibrium constant, as previous measurements had interference from the disproportionation of HOI. Our experimental value for K_4 is larger than the previously estimated value (~6 × 10^{-7} M^3).[15]

Equilibrium Constant for ICl_2^-/ICl. The equilibrium constant for the hydrolysis of ICl_2^- indicates that the concentration of HOI is only 1% of the initial ICl_2^- concentration in 1.0 M H^+ and 0.010 M Cl^-. However, ICl_2^- will partially dissociate into ICl(aq) and Cl^- under these conditions, and another species, H_2OI^+, also must be considered. Bell and Gelles[25] found that the hydrated iodine cation is in equilibrium with HOI in highly acidic solutions (eq 8). The equilibrium constant, K_5, is 35 M^{-1}. Since the formation

$$HOI + H^+ \rightleftarrows H_2OI^+ \qquad K_5 \tag{8}$$

of H_2OI^+ is favorable in high acid, it needs to be considered in the calculation of the equilibrium constant for ICl_2^-/ICl. Therefore, three equilibria (eq 3, 4, and 8) must be considered in the calculation of the concentration of each species. The concentration of HOI can be neglected since it is only 2.8% of the H_2OI^+ concentration in 1.0 M acid. The concentrations of ICl_2^-, ICl(aq), and H_2OI^+ can be derived as shown by eq 9–11, where $[ICl_2^-]_{init} = [ICl_2^-] + [ICl(aq)] + [H_2OI^+]$, $K_2K_3 = K_4 = 1.06 \times 10^{-6}$ M, and $K_5 = 35$ M^{-1}.

$$[ICl_2^-] = \frac{[ICl_2^-]_{init}[Cl^-]^2}{K_4K_5 + K_3[Cl^-] + [Cl^-]^2} \tag{9}$$

$$[ICl(aq)] = \frac{[ICl_2^-]_{init}K_3[Cl^-]}{K_4K_5 + K_3[Cl^-] + [Cl^-]^2} \tag{10}$$

$$[H_2OI^+] = \frac{[ICl_2^-]_{init}K_4K_5}{K_4K_5 + K_3[Cl^-] + [Cl^-]^2} \tag{11}$$

A spectrophotometric titration with HCl was used to measure the K_3 equilibrium constant. A 1.9 × 10^{-3} M ICl_2^- solution ($[Cl^-]$ = 0.0020 M) in 1.0 M $HClO_4$ was titrated with 1.0 M HCl so that the $[H^+]$ concentration remained constant while the $[Cl^-]$ concentration increased. The titration data are shown in Figure 1a. The increase of absorbance at the first half of the titration indicates the progressive formation of ICl_2^- with added Cl^-. The subsequent decrease of the absorbance is due to the dilution caused by adding more HCl. The increase of absorbance due to ICl_2^- formation as the $[Cl^-]$ increases has been observed previously,[19] although another report[20] claimed that no absorbance change was observed under the same conditions.

Assuming that all three species (ICl_2^-, ICl(aq), and H_2OI^+) absorb at 343 nm, a relationship between the absorbance (A_{obsd}) and $[Cl^-]$ can be derived (eq 12 and 13), where the cell path is 1.0 cm. In eq 13, K_3, ϵ_{ICl_2}, ϵ_{ICl}, and ϵ_{H_2OI} are the parameters to

$$A_{obsd} = [ICl_2^-]\epsilon_{ICl_2} + [ICl(aq)]\epsilon_{ICl} + [H_2OI^+]\epsilon_{H_2OI} \tag{12}$$

$$A_{obsd} = \left[\frac{[ICl_2^-]_{init}}{K_4K_5 + K_3[Cl^-] + [Cl^-]^2}\right] \times ([Cl^-]^2\epsilon_{ICl_2} + K_3[Cl^-]\epsilon_{ICl} + K_4K_5\epsilon_{H_2OI}) \tag{13}$$

be calculated, $[Cl^-]$ and A_{obsd} are the independent and dependent variables, and K_4 (1.06 × 10^{-6} M^3) and K_5 (35 M^{-1}) are known values. The parameters can be resolved when eq 13 is fitted to the titration data by use of a nonlinear regression curve-fitting procedure, which employs a Marquardt algorithm[26] to change the initially estimated values of the parameters iteratively until the minimum on the χ^2 surface is found. The fitting, however, needs a value for the total chloride concentration, $[Cl^-]$, in the solution, which comes from three sources: One source is the original Cl^- in the solution to be titrated, the second source is from the HCl added during the titration, and the third source is from the dissociation of ICl_2^-. To calculate the Cl^- contribution, $[Cl^-]_d$, from the dissociation of ICl_2^- a quadratic equation (eq 14) must be

$$[Cl^-]_d = [-([Cl^-] + K_3) + [([Cl^-] + K_3)^2 + 4K_3[ICl_2^-]_{init}]^{1/2}]/2 \tag{14}$$

solved. This requires knowledge of K_3, which in turn, is not known until the $[Cl^-]$ can be calculated. This circular logic situation is resolved iteratively. The fitting function (eq 13) is expanded to include a nested iterative process that calculates $[Cl^-]_d$ from eq 14 by using an assumed K_3 value. The $[Cl^-]_d$ value is then added to the other sources of chloride ion to give $[Cl^-]$, and a new $[Cl^-]_d$ value is calculated. This process continues until $[Cl^-]$ does not change. The total Cl^- concentration, $[Cl^-]$, is then substituted into the fitting function (eq 13) to produce a new set of parameters including K_3. In the second iteration the new K_3 value is used to calculate $[Cl^-]$ again in the process just described. The curve-fitting procedure eventually converges upon a set of parameters that best fit the data. The line through the data points in Figure 1a is the result of this fit in terms of the absorbance versus the volume of HCl added. Figure 1b is the plot of absorbance against the calculated $[Cl^-]$. The fitted parameters are K_3 = 0.013 ± 0.001 M (25.0 °C, $\mu = 1.0$) with molar absorptivity

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Table II. Equilibrium Constants and Molar Absorptivities of Iodine(I) Species in Aqueous Solutions[a]

Equilibration Constants

$K_3 = ([ICl(aq)][Cl^-])/[ICl_2^-] = (1.3 \pm 0.1) \times 10^{-2}$ M
$K_4 = ([HOI][Cl^-]^2[H^+])/[ICl_2^-] = (1.06 \pm 0.03) \times 10^{-6}$ M^3
$K_2 = ([HOI][Cl^-][H^+])/[ICl(aq)] = 8.2 \times 10^{-5}$ M^2[b]
$K_5 = [H_2OI^+]/([HOI][H^+]) = 35$ M^{-1}[c]
$[H_2OICl]/[ICl] = 4.5$[d]

Molar Absorptivities (M^{-1} cm^{-1})

species	343 nm	230 nm
ICl_2^-	274 ± 3	$(4.2 \pm 0.5) \times 10^4$
ICl(aq)	176 ± 8	
HOI	67 ± 2[e]	$(4 \pm 1) \times 10^3$
H_2OI^+	149 ± 7	

[a] Conditions: 25.0 °C, $\mu = 0.50$, [ICl(aq)] = [ICl] + [H_2OICl]. [b] Calculated from K_3 and K_4. [c] Reference 25. [d] Ratio is estimated from kinetic behavior of ICl(aq) with bases, where [ICl(aq)] = [H_2OICl] + [ICl]. [e] The uncertainty is estimated from the best fit of the data in Figure 2.

values at 343 nm for $\epsilon_{ICl_2} = 274 \pm 3$, $\epsilon_{ICl} = 176 \pm 8$, and $\epsilon_{H_2OI} = 149 \pm 7$. All values are averages from four experiments. The value of K_3 is the same, within experimental error, at $\mu = 0.50$ as it is at $\mu = 1.0$. The ϵ value found for ICl_2^- agrees within experimental error with the earlier report[20] of 275 M^{-1} cm^{-1}.

The results show that ICl(aq) absorbs significantly at 343 nm with $\epsilon = 176$ M^{-1} cm^{-1}. This value is comparable to the ϵ values given[27] for ICl in polar organic solvents: 181 at 343 nm in C_2H_5OH, 189 at 344 nm in CH_3OH, and 188 at 346 nm in $(CH_3)_3COH$. The absorption band is due to a $\pi^* \rightarrow \sigma^*$ transition.[28] The molar absorptivity value for H_2OI^+ (149 M^{-1} cm^{-1} at 343 nm) is larger than that of HOI (67 M^{-1} cm^{-1} at 343 nm).

The equilibrium constant, K_3, differs by slightly more than a factor of 2 from the value of 0.0060 M that was reported previously.[15] The previous method was less accurate because it involved more indirect measurements of different constants or concentrations, such as the distribution coefficients for ICl between aqueous and CCl_4 solutions, and because the H_2OI^+ contribution was neglected. Our determination of the overall equilibrium constant K_4 for the hydrolysis of ICl_2^- to HOI also disagrees with the value estimated by Faull.[15] Thermodynamic data for ICl_2^-, ICl, and IOH and values of electrode potentials[29] all appear to be based on Faull's values.[15] We recommend use of the revised values for the equilibrium constants that are given in Table II.

Chloride Ion Suppression of the Rate of Hydrolysis of Iodine Monochloride. The reaction in eq 4 is too fast for the stopped-flow time scale, but it can be measured by the pulsed-accelerated-flow method. A wavelength of 230 nm was selected to observe the reaction in order to take advantage of the large absorbance decrease as ICl_2^- is converted to HOI (Table II). Pseudo-first-order rate constants (k_r) decrease from 150 000 to 77 000 s^{-1} as the chloride ion concentration increases from 0.25 to 0.50 M (Figure 3). The $[ICl_2^-]_{init}$ is 3.0×10^{-5} M, and the hydrolysis of ICl_2^- occurs in dilute phosphate buffer at p[H^+] = 6.50. The results are consistent with a rapid preequilibrium between ICl(aq) and ICl_2^- followed by a rate-determining hydrolysis reaction (eq 15). The curved line in Figure 3 is a fit to eq 16 where k' is 3.1×10^6 s^{-1} and K_3 is 0.013 M.

$$ICl_2^- \overset{K_3}{\rightleftharpoons} ICl(aq) + Cl^-$$

$$ICl(aq) \xrightarrow{k'} IOH + Cl^- + H^+ \tag{15}$$

$$k_r = k'K_3/(K_3 + [Cl^-]) \tag{16}$$

Hydroxide Ion Effect. The rate of hydrolysis of ICl_2^- increases greatly with increase in hydroxide ion concentration. The reaction is so rapid that [Cl^-] is adjusted to 0.50 M, and even with [OH^-] concentrations of only 0.27–0.51 mM the k_r values increase from 93 000 to 120 000 s^{-1} (Table III). A linear regression of the k_r values as a function of hydroxide ion concentration is shown in Figure 4a, where the intercept is $(6.2 \pm 0.2) \times 10^4$ s^{-1} and the slope is $(1.1 \pm 0.1) \times 10^8$ M^{-1} s^{-1}. A chloride-independent rate constant for the hydroxide path can be calculated from the product of the slope × (K_3 + [Cl^-])/K_3. This gives a value of $(4.5 \pm 0.4) \times 10^9$ M^{-1} s^{-1} for the reaction of ICl(aq) with OH^-.

Because ICl is a strong Lewis acid,[30] it is very easy for it to accept lone-pair (or π) electrons from electron-donating solvents. Charge-transfer molecular complexes have been reported[31] to form

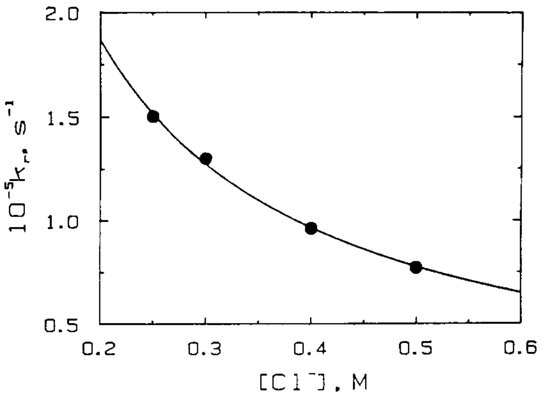

Figure 3. Rate constants from PAF measurements of the hydrolysis of ICl_2^- as a function of chloride ion concentration. Conditions: 25.0 °C, 0.50 μm, $[ICl_2^-]_{init} = 3.0 \times 10^{-5}$ M, $[PO_4]_T = 0.6 \times 10^{-3}$ M, p[H^+] = 6.50, 230 nm.

Table III. Effect of Hydroxide Ion and Buffers on the First-Order Rate Constant for the Hydrolysis of ICl_2^- Measured by the PAF Method[a]

p[H^+]	10^3[B], M	$10^{-5}k_r$, s^{-1}
	B = OH^-	
	0.27	0.93 ± 0.07
	0.41	1.1 ± 0.1
	0.51	1.2 ± 0.1
	B = $H_2PO_4^-$ + HPO_4^{2-}	
6.11	1.00	0.91 ± 0.08
6.20	1.25	1.0 ± 0.1
6.14	1.50	1.0 ± 0.1
6.14	2.00	1.2 ± 0.1
6.48	0.60	0.77 ± 0.07
6.49	1.20	1.0 ± 0.1
6.50	1.80	1.2 ± 0.1
6.50	2.40	1.3 ± 0.1
6.50	3.00	1.5 ± 0.2
7.11	0.50	0.75 ± 0.06
7.11	0.75	0.82 ± 0.06
7.10	1.00	0.89 ± 0.07
7.11	1.50	1.1 ± 0.1
7.12	2.00	1.2 ± 0.1
7.09	3.00	1.5 ± 0.2
	B = HCO_3^- + CO_3^{2-}	
9.19	0.75	0.94 ± 0.08
9.19	1.00	1.0 ± 0.1
9.18	1.25	1.1 ± 0.1
9.18	1.50	1.2 ± 0.1
9.17	2.00	1.4 ± 0.2
9.68	0.90	1.04 ± 0.09
9.69	1.20	1.1 ± 0.1
9.68	1.50	1.3 ± 0.1

[a] [Cl^-] = 0.50 M, 25.0 °C, $\mu = 0.5$, $[ICl_2^-]_{init} = 1.1 \times 10^{-5}$ M for reactions with OH^- and 3.0×10^{-5} M for reactions in buffers. pK_a($H_2PO_4^-$) = 6.46 (Mesmer, R. E.; Baes, C. F. *J. Solution Chem.* **1974**, *3*, 307–321) and pK_a(HCO_3^-) = 9.70 (Odier, M.; Plichon, V. *Anal. Chim. Acta* **1971**, *55*, 209–220; ref 10).

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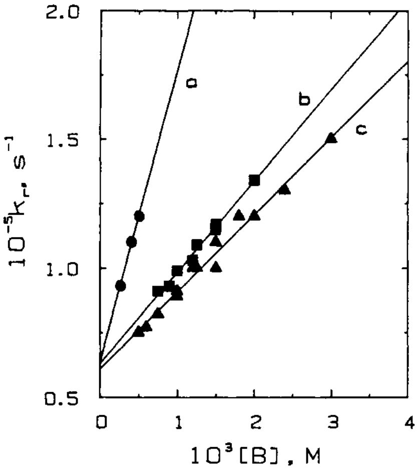
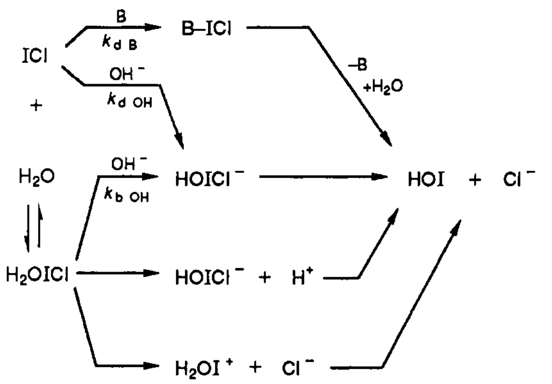


Figure 4. Rate constants from PAF measurements of the hydrolysis of ICl_2^- as a function of base concentrations. $[Cl^-] = 0.50$ M, 230 nm. Key: (a) $[B] = [OH^-]$, $[ICl_2^-]_{init} = 1.1 \times 10^{-5}$ M; (b) $[B] = [CO_3]_T$, $p[H^+] = 9.2–9.7$; (c) $[B] = [PO_4]_T$, $p[H^+] = 6.1–7.1$. $[ICl_2^-]_{init} = 3.0 \times 10^{-5}$ M for (b) and (c).

Scheme I. Pathways for the Hydrolysis of ICl with H_2O, OH^-, and Buffers (B)



between electron-donating solvents and ICl. It is inevitable that some ICl would be specifically hydrated by water to form H_2OICl, as the coordination sphere of the iodine in ICl is unsaturated and the oxygen atom of the water molecule can donate its lone-pair electrons to form a complex. The H_2OICl complex will be in equilibrium with ICl molecules that maintain an octet of valence electrons around iodine. We will refer to the latter species as unhydrated ICl or more accurately as a less hydrated form because it will have dipole–dipole interactions with water. The possible presence of both ICl and H_2OICl in water indicates that OH^- could react with ICl(aq) by a direct nucleophilic attack of OH^- on ICl or by deprotonation of H_2OICl. Both reactions give the same product, $HOICl^-$, which can dissociate to form HOI as shown in Scheme I.

The rate constant for the hydroxide path, k_{OH}, is the sum of the two paths defined in eq 17 where [ICl(aq)] denotes the sum of the [ICl] and $[H_2OICl]$ concentrations, and $k_{d\,OH}$ and $k_{b\,OH}$ are the rate constants for the path of direct attack and base catalysis, respectively.

$$k_{OH} = k_{d\,OH}\frac{[ICl]}{[ICl(aq)]} + k_{b\,OH}\frac{[H_2OICl]}{[ICl(aq)]} \qquad (17)$$

The intercept in the linear plot (Figure 4a) indicates the existence of a base-independent or water path in the hydrolysis of ICl(aq). The rate constant for the water path is the product of the intercept and $(K_3 + [Cl^-])/K_3$. This gives a value of $k_{H_2O} = 2.4 \times 10^6$ s^{-1} for the hydrolysis of ICl(aq). The water path of the ICl hydrolysis would proceed via the H_2OICl species, which could either deprotonate to form $HOICl^-$ or ionize to form H_2OI^+ as shown in Scheme I. Although H_2OI^+ is a stable species only in high acid,[32,33] it cannot be ruled out as an intermediate. Both $HOICl^-$ and H_2OI^+ would proceed rapidly to form HOI, by loss of Cl^- and H^+, respectively. We cannot distinguish between these two paths, but an $HOICl^-$ intermediate seems more likely.

ICl(aq) Hydrolysis with Buffers. The kinetics of the hydrolysis of ICl(aq) were studied with variation of buffer concentrations. Pseudo-first-order conditions, where [buffer] $\gg$ $[ICl_2^-]_{init}$, were maintained for all reactions. The reactions are so fast that low concentrations of buffer ($<3 \times 10^{-3}$ M) must be used because buffers accelerate the rate.

In phosphate buffer, the observed rate constants for the hydrolysis of ICl_2^- increase from 75 000 to 150 000 s^{-1} as the buffer concentration increases from 0.50 to 3.00 mM (Table III). The increase is proportional to the total concentration of phosphate, $[PO_4]_T$, rather than to the concentration of the more basic form of the buffer, $[HPO_4^{2-}]$. Figure 4c is a plot of the observed rate constants in 0.50 M $[Cl^-]$ measured at different $p[H^+]$ values versus the total concentration of phosphate. A linear regression of the data for the phosphate study gives an intercept of $(6.1 \pm 0.2) \times 10^4$ s^{-1} and a slope of $(3.0 \pm 0.2) \times 10^7$ M^{-1} s^{-1}. A chloride-independent rate constant for the phosphate path of the hydrolysis of ICl(aq) can be calculated by use of eq 18. This

$$k_{PO_4} = \text{slope} \times (K_3 + [Cl^-])/K_3 \qquad (18)$$

gives a k_{PO_4} value of $(1.2 \pm 0.1) \times 10^9$ M^{-1} s^{-1}. The intercept again means that a water path exists, and its value agrees very well with that obtained from the study of the OH^- dependence.

The observed rate constants for the hydrolysis of ICl_2^- in carbonate buffer also increase from 94 000 to 140 000 s^{-1} with an increase of total carbonate concentration from 0.75 to 2.00 mM (Table III). Again, the rate constant is proportional to the total concentration of buffer, $[CO_3]_T$, rather than to the concentration of the more basic form of carbonate, $[CO_3^{2-}]$. Calculations show that in carbonate buffer the contribution of OH^- to the observed rate constant cannot be ignored and therefore must be taken into account. At $p[H^+] = 9.20$ and 9.70 with $pK_w = 13.74$ ($\mu = 0.5$),[34] the contributions of OH^- to the observed rate constants are 3×10^3 and 1.1×10^4 s^{-1}, respectively. These values are subtracted from each of the corresponding observed rate constants for the carbonate path to give the rate constants plotted in Figure 4b. The slope of the plot for $[CO_3]_T$ is $(3.5 \pm 0.2) \times 10^7$ M^{-1} s^{-1}, and the intercept is $(6.3 \pm 0.2) \times 10^4$ s^{-1}. This gives a chloride-independent rate constant for the carbonate path equal to $(1.4 \pm 0.1) \times 10^9$ M^{-1} s^{-1}. The intercept of the plot (Figure 4b) indicates that the water path also exists in the hydrolysis of ICl(aq) in carbonate buffer, and the value is very close to the intercepts for the phosphate and hydroxide studies. These results confirm that the base-independent ICl hydrolysis (i.e., the water path) has an average rate constant of $(6.2 \pm 0.2) \times 10^4$ s^{-1} in 0.50 M $[Cl^-]$. A chloride-independent rate constant for the water path, k_{H_2O}, is 2.4×10^6 s^{-1}.

Mechanism. As is the case for the OH^- path, there are two possible reaction pathways for the reaction of ICl(aq) with buffers. The buffers (B) could react as bases to deprotonate the hydrated H_2OICl and give $HOICl^-$, or they could react directly with the unhydrated ICl to form molecular complexes, B–ICl. The first pathway, in which the buffers act as proton-transfer agents, can be eliminated because $H_2PO_4^-$, HPO_4^{2-}, HCO_3^-, and CO_3^{2-} all have the same rate constant (av = 1.3×10^9 M^{-1} s^{-1}) with ICl(aq). Proton-transfer rate constants would depend on the basicity of the buffer species, and this is not the case. The indiscriminate reactivity of these species is explained by the second mechanism, where the reaction of the unhydrated form of ICl with all the buffer species occurs at diffusion-controlled rate constants (7 ×

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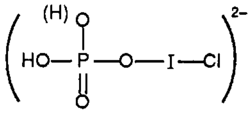
Table IV. Rate Constants for the Reactions of ICl(aq)[a]

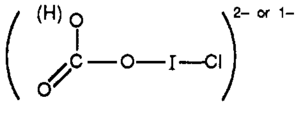
reaction	rate const	value[b]
$ICl(aq) + H_2O$	k_{H_2O}	$(2.4 \pm 0.2) \times 10^6\ s^{-1}$
$ICl(aq) + OH^-$	k_{OH}	$(4.5 \pm 0.4) \times 10^9\ M^{-1}\ s^{-1}$
$ICl(aq) + [PO_4]_T$	k_{PO_4}	$(1.2 \pm 0.1) \times 10^9\ M^{-1}\ s^{-1}$
$ICl(aq) + [CO_3]_T$	k_{CO_3}	$(1.4 \pm 0.1) \times 10^9\ M^{-1}\ s^{-1}$
$ICl(aq) + I^-$	k_2 (in ref 8)	$(5.1 \pm 0.4) \times 10^8\ M^{-1}\ s^{-1}$
$H_2OICl + OH^-$	$k_{b\,OH}$	$\sim 4 \times 10^9\ M^{-1}\ s^{-1}$
$ICl + OH^-$	$k_{b\,OH}$	$\sim 7 \times 10^9\ M^{-1}\ s^{-1}$
$ICl + B^c$	$k_{d\,B}$	$\sim 7 \times 10^9\ M^{-1}\ s^{-1}$

[a] $[ICl(aq)] = [ICl] + [H_2OICl]$. [b] 25.0 °C, $\mu = 0.50$. [c] $B = CO_3^{2-}$, HCO_3^-, HPO_4^{2-}, $H_2PO_4^-$.

$10^9\ M^{-1}\ s^{-1}$) to form B–ICl (III and IV). The breakup of the B–ICl species to form HOI could involve loss of Cl^- and subsequent P–O or C–O bond cleavage. Our studies only monitor the loss of ICl_2^-, so the subsequent reactions need not be fast.



III



IV

It is well-known that iodine monochloride, as a strong electron acceptor, forms 1:1 charge-transfer molecular complexes with electron-pair donors.[31] These electron donors include benzene and its derivatives,[35] amine,[36] pyridine,[37,38] and oxygen-containing organic solvents.[27] Numerous kinetic studies have been carried out for the reactions of ICl with alcohols,[39,40] aniline and substituted anilines,[32,33,41,42] alkenes,[43–45] and phenol and substituted phenols.[46,47] All these studies show that a 1:1 molecular complex is formed in the first step of the reaction. Some of the molecular complexes proceed to form iodination products, such as ROI in alcohols where the O–I bond is confirmed by infrared spectroscopy.[39] Similar reactions could occur in the hydrolysis of ICl with phosphate and carbonate buffers, where molecular complexes between ICl and phosphate or carbonate are formed.

We propose that ICl(aq) exists as two forms in rapid equilibrium, ICl and H_2OICl, and that the direct attack of B on ICl is diffusion controlled. Because the average k_B value is $1.3 \times 10^9\ M^{-1}\ s^{-1}$ and the diffusion-controlled rate constant is $7 \times 10^9\ M^{-1}\ s^{-1}$, the concentration of unhydrated ICl in solution is estimated to be 18% of the total ICl(aq) concentration. This value gives the observed second-order rate constant of $1.3 \times 10^9\ M^{-1}\ s^{-1}$. The mechanism explains the nonselective attack by $HPO_4^{2-}/H_2PO_4^-$ and by CO_3^{2-}/HCO_3^-, because all species react with the less hydrated ICl at diffusion-controlled rates.

The free energy of hydration for the reaction of ICl(g) to give ICl(aq) is -9.26 kJ mol^{-1}, while the corresponding $\Delta G°$ change for I_2 is -2.94 kJ mol^{-1}.[29] If the difference between these hydration energies (-6.34 kJ mol^{-1}) was entirely due to the specific formation of H_2OICl, the equilibrium constant for $[H_2OICl]/[ICl]$ would be 13. Our experimental value of 4.6 for this equilibrium constant is reasonable because dipole–dipole interactions between ICl and H_2O will also make some contribution to its free energy of hydration.

In the case where hydroxide is the only base, the reaction must proceed by both direct attack on unhydrated ICl and deprotonation of H_2OICl because the rate constant is larger than the k_B values. So OH^- must accelerate the reaction by a proton-transfer reaction with H_2OICl to form $HOICl^-$. The rate constants $k_{d\,OH}$, for direct attack, and $k_{b\,OH}$, for base catalysis, are defined in eq 17 and shown in Scheme I. The $k_{d\,OH}$ value should be $7 \times 10^9\ M^{-1}\ s^{-1}$ for the diffusion-controlled direct reaction of OH^- with ICl. The rate constant for the base-catalyzed path, $k_{b\,OH} = 3.9 \times 10^9\ M^{-1}\ s^{-1}$, can be calculated by use of eq 17 with $k_{OH} = 4.5 \times 10^9\ M^{-1}\ s^{-1}$, $[ICl]/[ICl(aq)] = 0.18$, and $[H_2OICl]/[ICl(aq)] = 0.82$. The resolved rate constants are summarized in Table IV. Actually, $k_{b\,OH}$ is not very sensitive to changes in the ratio of $[ICl]/[ICl(aq)]$. The corresponding proton-transfer reactions between H_2OICl and CO_3^{2-} or HPO_4^{2-} should be much slower because they are much weaker bases than OH^-. Hence, the buffers react preferentially with ICl.

The hydrolysis of ICl(aq) ($k_{H_2O} = 2.4 \times 10^6\ s^{-1}$) is many orders of magnitude faster than that of Cl_2 ($29\ s^{-1}$) and I_2 ($3\ s^{-1}$).[1] The huge difference is related to the polarity of the ICl molecule. Unlike Cl_2 and I_2, ICl has a large dipole moment (1.3 D).[30] It is, therefore, more susceptible to attack by water and other donors. It has been noted[1] that in the hydrolysis of Cl_2, Br_2, and I_2 the tendency to form a ternary complex such as X_2OH^- increases in the order $Cl_2 < Br_2 < I_2$. The degree of polarizability of the halogen atoms and the relative ease of valence shell expansion play important roles in the acceptance of an electron-donating group to saturate the coordination sphere. Since I_2 and Cl_2 are nonpolar species, while ICl is a highly polarized species, the formation of H_2OICl as a major species in aqueous solution is reasonable and also reflects the tendency of iodine to expand its valence shell. The reactivity of H_2OICl is not surprising, because it can readily lose a proton to form $HOICl^-$ or might lose Cl^- to form H_2OI^+, and both these species will rapidly give HOI.

Kinetics of ICl(aq) and I⁻. A previous PAF study[8] showed that ICl_2^- and I^- react via ICl(aq) (eq 3 and 19–21) where k_2 is the rate-determining step and the formation of I_3^- was observed. Our

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

$$ICl(aq) + I^- \xrightarrow{k_2} I_2Cl^- \tag{19}$$

$$I_2Cl^- \rightleftarrows I_2 + Cl^- \tag{20}$$

$$I_2 + I^- \rightleftarrows I_3^- \tag{21}$$

new value for K_3 changes the k_2 value from 1.1×10^9 to $5.1 \times 10^8\ M^{-1}\ s^{-1}$, as reported in Table IV. In terms of our ratio of ICl/H_2OICl, we would have expected a value of $1.3 \times 10^9\ M^{-1}\ s^{-1}$ for k_2, based on a diffusion-controlled rate constant between ICl and I^-. The reason for this discrepancy is not clear, but the ICl_2^-/I^- study was carried out at higher ionic strength, $\mu = 1.0$. This ionic strength difference does not affect the K_3 value but might influence the k_2 rate constant or change the ratio of ICl/H_2OICl.

Since we now know that the hydrolysis rate of ICl(aq) is extremely fast, we need to consider why this path was not seen in the study with I^-.[8] There are several reasons: First, the equilibrium in eq 4 in 1 M $[H^+]$ concentrations gives only 1% HOI at the lowest Cl^- concentration used (0.1 M) and in 0.1 M $[H^+]$ only 10% HOI when $[Cl^-]$ is 0.1 M. Second, the rate constant for the reaction between HOI and I^- (eq 22) is only 3.2×10^5

$$HOI + I^- \rightleftarrows I_2OH^- \tag{22}$$

$M^{-1}\ s^{-1}$ and the pathway between H_2OI^+ and I^- does not contribute.[48] (This suggests that H_2OI^+ should be written as $H_2OIOH_2^+$ in order to account for its lower reactivity.) Thus, even if 10% of the ICl_2^- formed HOI, the rate of production of I_3^- via HOI would be negligible compared to the formation via

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ICl(aq) and I^-. Hence, the absence of a hydrolysis path in the previous study[8] is verified.

Conclusion

The hydrolysis of iodine monochloride in water is 5–6 orders of magnitude faster than that of Cl_2 and I_2. The difference is attributed to the dipole moment and polarizability of ICl and to the ease of valence shell expansion of iodine. This leads to the formation of ICl molecular complexes with H_2O, OH^-, and buffers. We propose that both ICl and H_2OICl exist in aqueous solution and that the reaction with ICl to form molecular complexes is diffusion controlled. Hydroxide ion has a dual role in the hydrolysis of ICl(aq). It can directly attack ICl to give $HOICl^-$, and it can deprotonate H_2OICl to give $HOICl^-$. The $HOICl^-$ intermediate rapidly loses Cl^- to give HOI.

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Organo-f-Element Thermochemistry. Absolute Metal–Ligand Bond Disruption Enthalpies in Bis(pentamethylcyclopentadienyl)samarium Hydrocarbyl, Hydride, Dialkylamide, Alkoxide, Halide, Thiolate, and Phosphide Complexes. Implications for Organolanthanide Bonding and Reactivity

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Abstract: Absolute samarium–ligand bond disruption enthalpies in the series $Cp'_2Sm{-}R/X$ ($Cp' = \eta^5\text{-}(CH_3)_5C_5$) have been measured by iodinolytic and alcoholytic isoperibol titration calorimetry of $Cp'_2Sm/(Cp'_2Sm{-}I)_n$, $(Cp'_2Sm{-}O^tBu)_2/Cp'_2Sm{-}R/X$ ensembles in toluene. Derived $D(Cp'_2Sm{-}R/X)$ values in toluene solution are as follows (kcal/mol, R/X): 47.0 (1.5), $CH(SiMe_3)_2$; 45.0 (1.5), $\eta^3\text{-}C_3H_5$; 93.2, CCPh; 54.2 (3.0), H; 48.2 (1.8), NMe_2; 82.4 (3.5), O^tBu; 81.3 (1.0), $OCH(^tBu)_2$; 97.1 (3.0), Cl; 83.6 (1.5), Br; 69.4 (2.4), I; 73.4 (2.4), S^nPr; 32.6 (2.0), PEt_2. $D(Cp'_2Sm{-}THF)$ and $D(Cp'_2Sm(THF){-}THF)$ values were also determined in toluene and are 7.3 (0.4) and 4.9 (1.0) kcal/mol, respectively, while $D(Cp'_2Sm(THF){-}I)$ was found to be 72.7 (2.9) kcal/mol. The observed D(Sm–halogen) parameters are close to the D_1 values of the corresponding samarium trihalides. Important trends in $D(Cp'_2Sm{-}R/X)$ include a relatively small value of $D(Sm{-}H) - D(Sm{-}alkyl)$, a large value of $D(Sm{-}I) - D(Sm{-}alkyl)$, and generally strong bonds to group 15 and group 16 ligands. A variety of Sm-centered ligand transposition and oxidative addition/reductive elimination processes are analyzed in light of the present data. The formation of strong Sm–heteroelement bonds makes an important contribution to the driving force. Hydrocarbon functionalization via dinuclear Sm(II) → Sm(III) oxidative addition processes is only expected to be exothermic in special cases.

Recent developments in organometallic thermochemistry have demonstrated the considerable insight into bonding and reaction chemistry that metal–ligand bond disruption enthalpy (eq 1 for

$$D(L_nM{-}R) = \Delta H_f^\circ(L_nM) + \Delta H_f^\circ(R^\bullet) - \Delta H_f^\circ(L_nM{-}R) \quad (1)$$

$$L_n = \text{ancillary ligands}$$

$$L_nM{-}R \rightarrow L_nM + R^\bullet \quad (2)$$

the adiabatic, homolytic process of eq 2) information can provide.[1,2] In the solution phase, *relative* metal–ligand bond enthalpies have been obtained by equilibration or various calorimetric techniques[1,2] and have shed considerable light on bonding patterns and the driving forces for important reactions. *Absolute* metal–ligand bond enthalpies provide, in addition, an absolute quantitation of the energetics of eq 2 and a means of comparing bond enthalpies for different M and L_nM centers. Relative metal–ligand enthalpies can be placed on an approximately absolute scale by judicious choice of a reference ("anchor") point, such as the corresponding $D_1(MX_n)$ datum for an L_nMR/L_nMX series.[3,4] However, this approximation assumes aspects of transferability that may not always be general and certainly warrants further scrutiny. Direct measurements of absolute metal–ligand bond enthalpies have included kinetic,[2c,h,5] photoacoustic,[2j,6] laser pyrolytic,[7] two-electron

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