Kinetics of Reversible Chlorine Hydrolysis: Temperature Dependence and General-Acid/Base-Assisted Mechanisms

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Rate constants of the forward reaction for the reversible hydrolysis of $Cl_2(aq)$ at $\mu = 0.50$ M increase from 1.9 s^{-1} at 0.0 °C to 30.5 s^{-1} at 30.0 °C. The activation parameters at 15.0 °C are $\Delta H^{\ddagger} = 63 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -8 \pm 4$ J mol^{-1} K^{-1} for the forward reaction and $\Delta H^{\ddagger} = 27 \pm 1$ kJ mol^{-1} and $\Delta S^{\ddagger} = -71 \pm 9$ J mol^{-1} K^{-1} for the reverse reaction. The $\Delta H^{\ominus}$ values at $\mu = 0.50$ M decrease markedly with increase in temperature ($\Delta C_p = -537 \pm 7$ J mol^{-1} deg^{-1}), and therefore the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are not constant over a range of temperatures. The equilibrium constant, $K = ([HOCl][H^+][Cl^-])/[Cl_2(aq)]$, equals 1.04×10^{-3} M^2 at 25.0 °C, $\mu = 0.50$ M. The K value depends on the ionic strength as well as the temperature. In the reversible hydrolysis reaction, general bases (A^-) assist the hydrolysis rate (the Brønsted β value is 0.58 ± 0.06) and general acids (HA) assist the reverse reaction (the Brønsted α value is 0.40 ± 0.05): $Cl_2 + H_2O + A^- \rightleftarrows HOCl + Cl^- + HA$ (k_2/k_{-2}).

Introduction

The kinetics of Cl_2 hydrolysis is of importance in water chlorination treatment and in many reactions for both organic and inorganic constituents in water. Lifshitz and Perlmutter-Hayman[1] determined the forward rate constant in eq 1 by use

$$Cl_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + Cl^- + H^+ \qquad (1)$$

of a continuous-flow instrument that utilized the heat of reaction to monitor the hydrolysis rate. Eigen and Kustin[2] determined the forward and reverse rate constants by a temperature-jump relaxation method. Margerum, Gray, and Huffman[3] determined the forward and reverse rate constants by a stopped-flow method (concentration jump relaxation). The rate constants from the different techniques appear to be in poor agreement (Table 1), but the three studies were at different temperatures and ionic strengths. Activation parameters for Cl_2 hydrolysis have not been reported.

Connick and Chia,[4,5] Lewis and Randall,[6] and Morris[7] gave the temperature dependence of the equilibrium constant for Cl_2 hydrolysis. Connick and Chia measured $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values (defined as the thermodynamic parameters that are not extrapolated to infinite dilution) and found a rapid change of $\Delta H^{\ominus}$ with temperature due to the large negative value of the partial molal heat capacity, ΔC_p, for Cl_2 hydrolysis. They also found that $\Delta S^{\ominus}$ varied from +38.62 J mol^{-1} K^{-1} at 0 °C to −20.64 J mol^{-1} K^{-1} at 45 °C.

Lifshitz and Perlmutter-Hayman determined the forward rate constant, k_2, for Cl_2 hydrolysis in the presence of acetate, chloroacetate, and formate buffers (eq 2).[8,9] They were unable to determine the effect of sulfate and phosphate buffers, because these reactions were too fast. Their results showed evidence of base-assisted Cl_2 hydrolysis, and they proposed a two-step mechanism (eqs 3 and 4), where the reaction in eq 3 is the rate-determining step and the reaction in eq 4 is very rapid. The $HOCl_2^-$ ion was postulated by Anbar and co-workers[10] as an intermediate in the isotopic exchange of chlorine between HOCl and Cl^- in basic solutions. Lifshitz and Perlmutter-Hayman's studies[8,9] of the reactions in eqs 1 and 2 were not performed under reversible conditions, so they did not determine the reverse rate constants k_{-1} and k_{-2}.

Table 1. Summary of Rate Constants for Cl_2 Hydrolysis from the Literature

temp, °C	μ, M	k_1, s^{-1}	$10^{-4}k_{-1}$, M^{-2} s^{-1}	ref
9.5	~0.01	5.60		1
20.0	0.10	15.0	1.82	2
25.0	0.50	28.6	2.81	3

$$Cl_2 + A^- + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HOCl + Cl^- + HA \qquad (2)$$

$$Cl_2 + H_2O + A^- \rightarrow HOCl_2^- + HA \qquad (3)$$

$$HOCl_2^- \rightleftarrows HOCl + Cl^- \qquad (4)$$

In the present study, we use a stopped-flow method with spectrophotometric observation. Faster reactions can be studied with better quality data than was possible with the technique used by Lifshitz and Perlmutter-Hayman. We determine the temperature dependence and the ionic strength (μ) dependence for the kinetics of Cl_2 hydrolysis. Activation parameters for the forward and reverse reactions are obtained, and the thermodynamic quantities of the overall reaction are evaluated. We find a general-base-assisted Cl_2 hydrolysis and a general-acid-assisted reverse reaction. A comparison of the acid-assisted mechanism for reactions of HOCl with Cl^-, Br^-, and I^- is now possible.

Experimental Section

Reagents. Solutions of sodium chloride, sodium perchlorate, hydrochloric acid, and perchloric acid were prepared by dilution of the analytical reagents into distilled deionized water. The sodium hydroxide solution

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was made by dilution of a saturated sodium hydroxide solution into boiled CO_2-free distilled deionized water, and its concentration was determined by titration against primary standard potassium hydrogen phthalate. The concentrations of HCl and $HClO_4$ were determined by titration with standardized NaOH.

Sodium hypochlorite stock solutions were prepared by bubbling Cl_2 gas (research purity, Matheson) through 0.60 M NaOH solution. The concentration of NaOCl was determined spectrophotometrically at 292 nm (ϵ = 350 M^{-1} cm^{-1})[11] with a Perkin-Elmer Lambda 9 spectrophotometer, and the NaOCl solution was used within 1 week of its preparation.

Hypochlorite ion solutions used for kinetic measurements were freshly prepared from the stock NaOCl solution by adjusting the solution to pH 8.5 with $HClO_4$; an Orion Model 720 pH meter equipped with a Sargent-Welch glass electrode was used.

Buffer solutions were prepared by adding different amounts of $HClO_4$/H_2SO_4 or $HClO_4$/H_3PO_4 solutions to maintain [H^+] at 0.101 M. The buffer-catalyzed reactions were studied at 15.0 °C. The K_a value for HSO_4^- used to calculate the solution composition was 5.37×10^{-2} M (μ = 0.50 M, 15.0 °C).[12] The K_a for H_3PO_4 at μ = 0.50 M and 15.0 °C was calculated from constants measured[12] at different temperatures and ionic strengths as follows. First, the K_a values at different temperatures and at zero ionic strength are used to calculate the K_a at 15.0 °C according to the van't Hoff equation from a plot of ln K_a vs $1/T$. The K_a value obtained from the plot is 8.18×10^{-3} at 15.0 °C (μ = 0.0 M). The ionic strength effect was then evaluated by a modified Debye–Hückel equation (eq 5), which predicts the effect of ionic strength up to 1 M.[13] In eq 5,

$$\log f_{\pm} = \log\left(\frac{K_a}{K_a^{\circ}}\right) = \frac{-A|Z_1Z_2|\mu^{1/2}}{1 + Ba\mu^{1/2}} + b\mu \qquad (5)$$

$f_{\pm}$ is the mean rational activity coefficient of H^+ and $H_2PO_4^-$, and K_a and K_a° are dissociation constants of the acid at a specified ionic strength and at zero ionic strength, respectively. A and B are constants for a given solvent and temperature; for water A = 0.5092, B = 0.3286×10^8 at 25.0 °C, and A = 0.5002, B = 0.3267×10^8 at 15.0 °C.[14] The a and b terms are parameters for a given species, whose values are independent of temperature. K_a values at different ionic strengths and at 25.0 °C were used to obtain optimal a and b values by fitting the data to eq 5. The resulting a and b values are -2.81×10^{-9} and 0.103, respectively. The calculated K_a value for H_3PO_4 is 1.74×10^{-2} M (μ = 0.50 M, 15.0 °C). The ionic strengths of all solutions were controlled at 0.50 M with $NaClO_4$.

Stopped-Flow Measurements. Kinetic data for Cl_2 hydrolysis at different temperatures and in buffer solutions at 15.0 ± 0.1 °C were obtained with a Hi-Tech Model SF-3L stopped-flow spectrophotometer equipped with a specially designed ball-type mixing-observation cell with a 1.60-cm light path[15] and interfaced to a Zenith 151 PC with a MetraByte DASH-16 A/D converter card. The dead time for this apparatus is 2.7 ms. The reaction was monitored by the formation of Cl_2 at 325 nm (ϵ = 69.7 M^{-1} cm^{-1}).[16] Reversible pseudo-first-order conditions were maintained with a 10-fold or greater excess of total Cl^- and H^+ concentrations for Cl_2 hydrolysis in water and with excess buffer concentrations as well for the buffer-catalyzed Cl_2 hydrolysis. The observed reversible pseudo-first-order rate constants (k_{obsd}, s^{-1}) were determined from a least-squares linear regression plot of $\ln(A_t - A_\infty)$ vs time (eq 6),

$$\ln\left[\frac{A_t - A_\infty}{A_0 - A_\infty}\right] = -k_{obsd}t \qquad (6)$$

where A_0 and A_∞ represent the initial and final absorbance, and A_t is the absorbance at time t. The average k_{obsd} from three to five runs is reported. The typical standard deviation for the experimental data is ± 3%.

Results and Discussion

Chlorine Hydrolysis. The hydrolysis reaction (eq 1) has the rate expression given in eq 7, where $[Cl_2]_\infty$ is the equilibrium concentration and k_{obsd} is given by eq 8 (see Appendix). Figure

$$-\frac{d[Cl_2]}{dt} = (k_1 + k_{-1}[H^+][Cl^-])([Cl_2] - [Cl_2]_\infty) \qquad (7)$$

$$k_{obsd} = k_1 + k_{-1}[H^+][Cl^-] \qquad (8)$$

1 shows plots of k_{obsd} vs ([H^+][Cl^-]) at temperatures from 0.0 to 30.0 °C. The H^+ concentrations range from 0.0125 to 0.0625 M, and [Cl^-] is maintained at 0.0425 M. The k_1 and k_{-1} values are listed in Table 2.

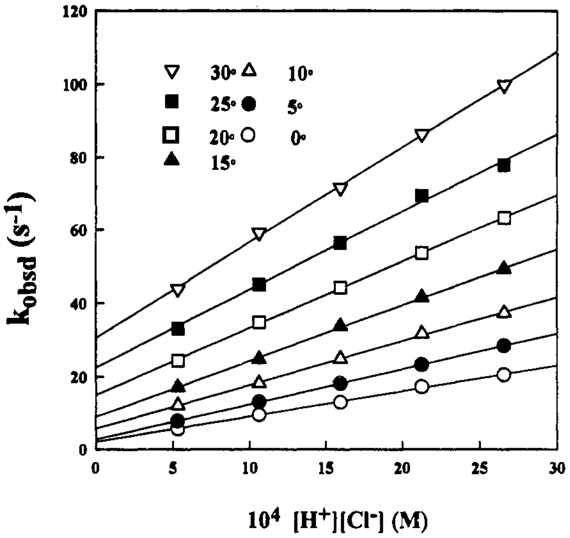

Figure 1. Plot of k_{obsd} vs [H^+][Cl^-] for the reversible Cl_2 hydrolysis reaction. The solid lines are the least-squares fits of eq 8. The experimental conditions are given in Table 2.

Table 2. Rate Constants for the Forward and Reverse Reactions of Chlorine Hydrolysis at Different Temperatures[a]

temp, °C	k_1, s^{-1}	$10^{-3}k_{-1}$, M^{-2} s^{-1}
0.0	1.9 ± 0.1	7.1 ± 0.3
5.0	2.7 ± 0.1	9.7 ± 0.5
10.0	5.7 ± 0.2	12.0 ± 0.4
15.0	9.1 ± 0.3	15.2 ± 0.6
20.0	15.0 ± 0.4	18.2 ± 0.7
25.0	22.3 ± 0.6	21.4 ± 0.8
30.0	30.5 ± 0.9	26.2 ± 0.9

[a] Conditions: [Cl^-] = 0.0425 M; $[Cl_2]_T$ = 1.25×10^{-3} M; [H^+] = $(1.25–6.25) \times 10^{-2}$ M; μ = 0.50 M.

Thermodynamic Results. Table 3 summarizes the kinetic and thermodynamic parameters that we obtained in this study. The activation enthalpy, ΔH^{*}, and the activation entropy, ΔS^{*}, of the forward and reverse reactions are obtained from the Eyring equation[17] (eq 9)

$$k = \frac{RT}{Nh}\exp\left(\frac{\Delta S^{*}}{R}\right)\exp\left(-\frac{\Delta H^{*}}{RT}\right) \qquad (9)$$

by using the data in Table 2. Parts a and b of Figure 2 show that Eyring plots for the forward and reverse reactions are slightly curved. The effective ΔH^{*} and ΔS^{*} values at 15.0 °C are 63 ± 2 kJ mol^{-1} and −8 ± 4 J mol^{-1} K^{-1}, respectively, for the forward reaction, and are 27 ± 1 kJ mol^{-1} and −71 ± 9 J mol^{-1} K^{-1}, respectively, for the reverse reaction. The large negative ΔS^{*} value for the reverse reaction is consistent with the loss of translational entropy in bringing three species together to form the activated complex.

The equilibrium constant (K) of Cl_2 hydrolysis is the ratio of

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Table 3. Summary of Kinetic and Thermodynamic Parameters for Cl_2 Hydrolysis

	$\Delta H^{\ddagger}$,[a] kJ mol^{-1}	$\Delta S^{\ddagger}$,[a] J mol^{-1} K^{-1}
forward reacn	63 ± 2	−8 ± 4
reverse reacn	27 ± 1	−71 ± 9
	$\Delta H^{\ominus}$	$\Delta S^{\ominus}$
overall reacn[b]	33 ± 2	53 ± 6
std[c]	23.1	7.5

[a] Values at 15.0 °C for the range 0.0 to 30.0 °C at μ = 0.50 M. [b] Data obtained from the reversible kinetics study at μ = 0.50 M, 25.0 °C. [c] Standard thermodynamic data from ref 20 for overall reaction at μ = 0 M, 25.0 °C.

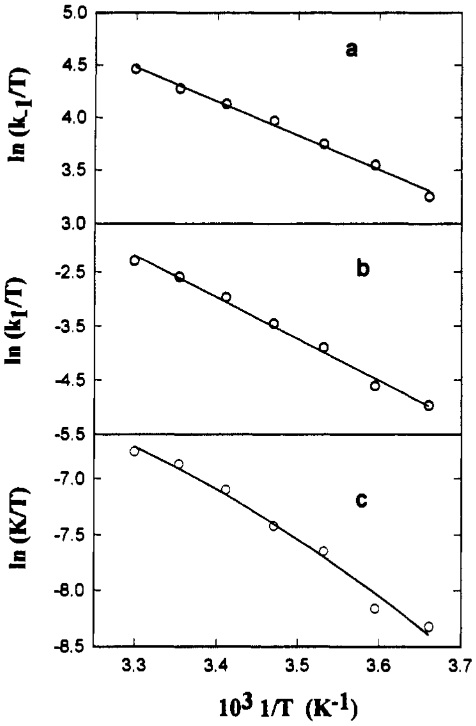

Figure 2. Plots to evaluate kinetic and thermodynamic parameters: (a) forward reaction between Cl_2 and H_2O (least-squares fit of eq 9 giving slope = −(7.8 ± 0.3) × 10^{-3} and intercept = (2.3 ± 0.1) × 10^1); (b) Reverse reaction of HOCl + H^+ + Cl^- (least-squares fit of eq 9 giving slope = −(3.2 ± 0.1) × 10^{-3} and intercept = (1.5 ± 0.4) × 10^1); (c) Equilibrium constants calculated from rate constants ($K = k_1/k_{-1}$). The solid curve is the best fit of the experimental data to a three-parameter polynomial.

k_1/k_{-1} and varies with temperature (eq 10),

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^{\ominus}(T)}{RT^2} \qquad (10)$$

where $\Delta H^{\ominus}$ is the enthalpy of reaction. Figure 2c shows that the plot of ln K vs $1/T$ is not linear; the curve shown is the best fit of the data to a three-parameter polynomial. The slope of the curve at each temperature corresponds to $\Delta H^{\ominus}$, and the results indicate that $\Delta H^{\ominus}$ varies with temperature. Connick and Chia also observed a rapid change of $\Delta H^{\ominus}$ with temperature for Cl_2 hydrolysis.[4,5] A plot of our $\Delta H^{\ominus}$ values (obtained from the slope of the curve at different temperatures in Figure 2c) against temperature in Figure 3 is linear. Therefore the partial molal heat capacity, ΔC_p, can be considered to be constant in the temperature range we studied. The ΔC_p value obtained from the slope of Figure 3 equals −537 ± 7 J mol^{-1} deg^{-1} at μ = 0.50 M. Connick and Chia[5] estimated a ΔC_p value for Cl_2 hydrolysis to be −376 J mol^{-1} deg^{-1} at μ = 0 M, 25 °C and reported their ΔC_p value to be −388 J mol^{-1} deg^{-1} at $\mu \approx 10^{-2}$ M, 25 °C. They suggested that the large negative value of ΔC_p for Cl_2 hydrolysis arises primarily from the large positive value of the aqueous partial molal heat capacity of Cl_2, i.e. 326 J mol^{-1} deg^{-1}. From his study of equilibria involving aqueous Cl_2, Liebhafsky[18] hypothesized the existence of two hydrates whose relative concentrations varied with temperature. Frank and Evans[19] proposed that nonpolar gases dissolved in water cause the formation of ordered arrangements of water around them, which forms icebergs, and the melting of icebergs with increasing temperature is the source of the large ΔC_p value. The significant difference between our ΔC_p value and the value of Connick and Chia is attributed to the effect of ionic strength. We will show later that there is a significant ionic strength effect on the rate constants and equilibrium constants of Cl_2 hydrolysis.

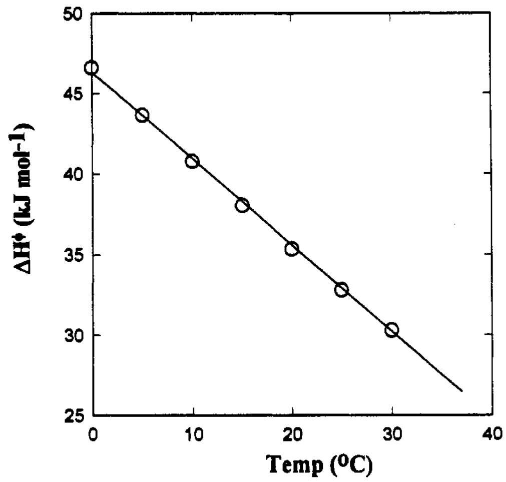

Figure 3. Variation of $\Delta H^{\ominus}$ with temperature for Cl_2 hydrolysis. The ΔC_p value determined by linear regression analysis is −(5.37 ± 0.07) × 10^2 J mol^{-1} deg^{-1}.

Table 4. Equilibrium Constants for Cl_2 Hydrolysis at 25 °C and Different Ionic Strengths

10^4K, M^2	μ, M	ref
5.05	0	20
5.21	0.035	5
7.7[a]	0.10	2
10.4 ± 0.7	0.50	this study
10.1	0.50	3

[a] Corrected from 20 °C.

The $\Delta H^{\ominus}$ value obtained from Figure 3 (where ΔC_p is taken into account) for the overall reaction of Cl_2 hydrolysis is 33 kJ mol^{-1} at 25.0 °C and μ = 0.50 M. The calculated $\Delta S^{\ominus}$ value is 53 J mol^{-1} K^{-1} (obtained from the equilibrium constant and the $\Delta H^{\ominus}$ value). These values are significantly different from the standard $\Delta H°$ and $\Delta S°$ values given in the literature, which are 23.05 kJ mol^{-1} and 7.48 J mol^{-1} K^{-1}, respectively.[20] This difference may be explained by ionic strength effects.

Ionic Strength Effect. Table 4 gives values of the equilibrium constants measured at different ionic strengths. The measured K value in this study (1.04 × 10^{-3} M, μ = 0.50 M, 25 °C) is about twice as large as the calculated equilibrium constant (5.05 × 10^{-4} M, μ = 0 M, 25 °C) from standard thermodynamic data. The data in Table 4 show a strong ionic strength dependence of the equilibrium constants. The Debye–Hückel–Brønsted–Davies equation[21,22] (eq 11) predicts the effect of ionic strength on the reverse reaction (Z_A = 1 and Z_B = −1) for a large variation of ionic strength (μ = 0 – 1 M), where k°_{-1} is the rate constant at μ = 0 M, and b is a constant. The forward rate constant, k_1, is

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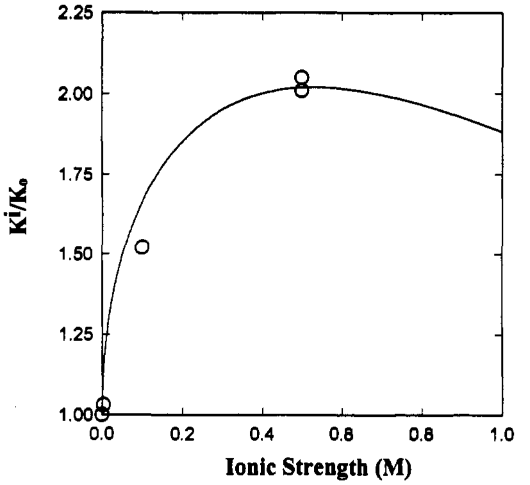


Figure 4. Ionic strength effect on the equilibrium constant of Cl_2 hydrolysis fit to the Debye–Hückel–Brønsted–Davies relationship for k_{-1} with $Z_A = 1$, $Z_B = -1$, and $b = 0.23$ at 25.0 °C.

$$\log k_{-1} = \log k_{-1}^{\circ} + 1.02 Z_A Z_B \left(\frac{\mu^{1/2}}{1 + \mu^{1/2}} - b\mu \right) \tag{11}$$

nearly independent of the ionic strength because all the species are neutral. The predicted equilibrium constant (K^1/K_0) as a function of μ is shown in Figure 4 when $b = 0.23$. The b value is obtained from the best fit of eq 11 using data in Table 4 and is within the range of typical values for this interaction coefficient.[21,22] Figure 4 shows that the calculated equilibrium constant as a function of ionic strength agrees well with the experimental points. Therefore, we conclude that the variation of the ionic strength contributes to the changes of the enthalpy and the entropy of hydrolysis compared to the standard thermodynamic quantities.

Cl_2 Hydrolysis in Buffer Solutions. Chlorine hydrolysis in the presence of a buffer occurs by two pathways (eqs 1 and 2). The rate expression of the hydrolysis reaction can be expressed by eq 12 (see Appendix), where K_a is the dissociation equilibrium

$$-\frac{d[Cl_2]}{dt} = \left(k_1 + k_{-1}[H^+][Cl^-] + \frac{k_{-2}[HA]_T(K_1 + [H^+][Cl^-])}{[H^+] + K_a} \right)([Cl_2] - [Cl_2]_\infty) \tag{12}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{13}$$

$$k_{obsd} = k_1 + k_{-1}[H^+][Cl^-] + \frac{k_{-2}[HA]_T(K_1 + [H^+][Cl^-])}{[H^+] + K_a} \tag{14}$$

constant of the acid HA (eq 13), K_1 is the equilibrium constant of Cl_2 hydrolysis (eq 1), and $[HA]_T = [HA] + [A^-]$. The concentrations of H^+ and Cl^- are unchanged for a given run so that the hydrolysis kinetics are reduced to a reversible pseudo-first-order expression in both reactions with k_{obsd} given by eq 14. Therefore, the rate constant of the reverse reaction, k_{-2}, for the buffer path can be calculated from the slope of a linear regression plot of k_{obsd} vs $[HA]_T$. The forward rate constant, k_2, is calculated by eq 15. Figures 5 and 6 show the plots of k_{obsd} vs $[HA]_T$ in

$$k_2 = \frac{K_1 k_{-2}}{K_a} \tag{15}$$

the presence of HSO_4^-/SO_4^{2-} and $H_3PO_4/H_2PO_4^-$, respectively, at $\mu = 0.50$ M and 15.0 °C. The total concentration of H^+ for both systems was maintained at 0.101 M. The results show reversible general-acid/base-assisted Cl_2 hydrolysis. By using the values of the equilibrium constants at 15 °C, $K_1 = 5.99 \times 10^{-4}$ M^2, $K_a = 0.0537$ M, $[H^+] = 0.101$ M, and $[Cl^-] = 0.0400$ M, the rate constants for the forward and reverse reactions are 32 ± 3 M^{-1} s^{-1} and (2.8 ± 0.5) × 10^3 M^{-2} s^{-1}, respectively, for HSO_4^-/SO_4^{2-}, and are 45 ± 3 M^{-1} s^{-1} and (1.3 ± 0.2) × 10^3 M^{-2} s^{-1}, respectively, for $H_3PO_4/H_2PO_4^-$ ($K_a = 0.0174$ M^{-1}).

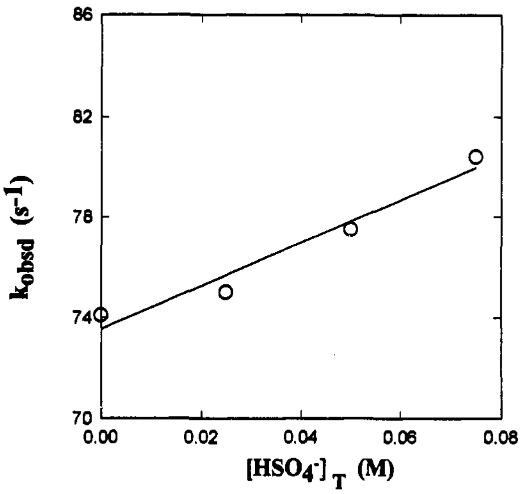


Figure 5. Dependence of reversible pseudo-first-order rate constants on $[HSO_4^-]_T$ for Cl_2 hydrolysis in HSO_4^- buffer. The experimental conditions are in Table 5.

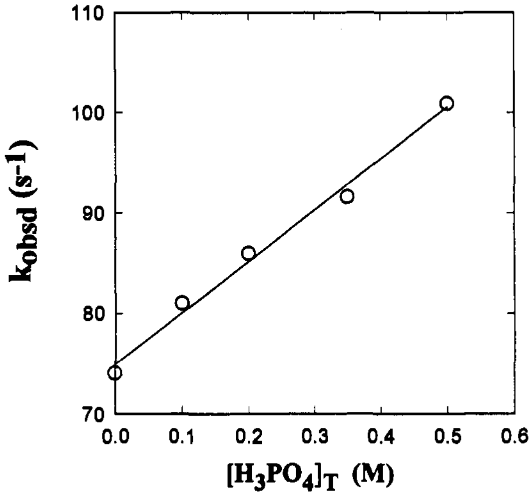
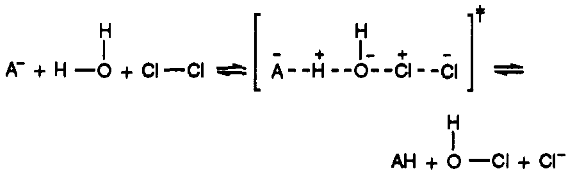


Figure 6. Dependence of reversible pseudo-first-order rate constants on $[H_3PO_4]_T$ for Cl_2 hydrolysis in H_3PO_4 buffer. The experimental conditions are in Table 5.

The general-base-assisted mechanism for the forward reaction consists of a Cl^+ transfer to OH_2 as a proton transfers to A^- in the transition state. The general-acid-assisted mechanism for the reverse reaction involves a Cl^+ transfer to Cl^- as a proton transfer occurs from HA to HOCl in the transition state (eq 16).



$$\mathrm{A^- + H{-}\overset{H}{\overset{|}{O}} + Cl{-}Cl \rightleftharpoons \left[\overset{-}{A}{\cdot\cdot}\overset{+}{H}{\cdot\cdot}\overset{H}{\overset{|}{\overset{-}{O}}}{\cdot\cdot}\overset{+}{Cl}{\cdot\cdot}\overset{-}{Cl} \right]^{\ddagger} \rightleftharpoons AH + \overset{H}{\overset{|}{O}}{-}Cl + Cl^-} \tag{16}$$

The mechanism of Cl_2 hydrolysis can be either a one-step reaction (eq 16), or a two-step reaction (eqs 3 and 4). These two mechanisms are kinetically indistinguishable. However, for both mechanisms, the rate constant is proportional to the strength of the acid or base in accordance with the Brønsted–Pedersen

Table 5. Summary of Constants for the Brønsted–Pedersen Relationship with $Cl_2(aq)$ Hydrolysis[a]

HA	p	q	pK_a, M	k_2, M^{-1} s^{-1}	k_{-2}, M^{-2} s^{-1}
H_3O^+	3	2	−1.74	1.6×10^{-1} [b]	1.5×10^4
HSO_4^-	1	4	1.27	3.2×10^1	2.8×10^3
H_3PO_4	3	2	1.75	4.5×10^1	1.3×10^3
$CH_2ClCOOH$[c]	1	2	2.81	9.7×10^1	2.9×10^{-1}
HCOOH[c]	1	2	3.72	1.2×10^2	1.2×10^{-1}
CH_3COOH[c]	1	2	4.76	9.4×10^2	2.8×10^{-2}

[a] Conditions: $[Cl^-] = 0.0400$ M; $[Cl_2]_T = 4.0 \times 10^{-3}$ M; $[H^+] = 0.101$ M; $\mu = 0.50$ M; 15.0 ± 0.1 °C. [b] $k_2 = k_1/55.5$ [c] Data obtained from refs 8 and 9 were corrected from 9.5 to 15.0 °C and to $\mu = 0.50$ M. The k_{-1} values were calculated from our K value and the pK_a value.

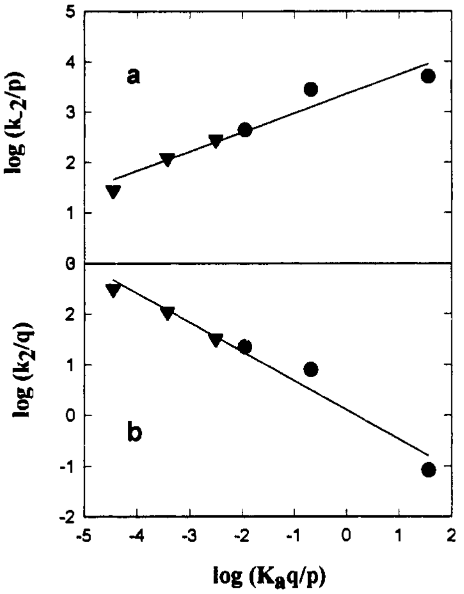


Figure 7. (a) Brønsted–Pedersen plot for the general-acid-assisted reverse reaction of Cl_2 hydrolysis: (●) this study; (▼) calculated from refs 8 and 9. The α value determined from the slope is 0.40 ± 0.05. (b) Brønsted–Pedersen plot for the general-base-assisted forward reaction of Cl_2 hydrolysis: (●) this study; (▼) calculated from refs 8 and 9. The β value determined from the slope is 0.58 ± 0.06.

equations (eqs 17 and 18),[23,24] where p is the number of equiva-

$$\log(k_2/q) = \log G_a - \beta \log(K_a q/p) \tag{17}$$

$$\log(k_{-2}/p) = \log G_b + \alpha \log(K_a q/p) \tag{18}$$

lent protons in acid HA, q is the number of sites that can accept a proton in the conjugate base A^-, α and β are the slopes which reflect the degree of proton transfer in the transition state, and G_a and G_b are constants. The α and β values range from 0 to 1, and theoretically $\alpha + \beta = 1$. Table 5 tabulates the k_2 and k_{-2} values for H^+, HSO_4^-, H_3PO_4, CH_3COO^-, $ClCH_2COO^-$, and $HCOO^-$. The values for the last three buffers are obtained from the results of Lifshitz and Perlmutter-Hayman[8,9] ($\mu = 0.05$–0.3 M, 9.5 °C) and corrected to $\mu = 0.50$ M and to 15.0 °C by eqs 9 and 11. This correction assumes that the activation enthalpy and entropy for Cl_2 hydrolysis in the presence of buffers (eq 2) is approximately the same as in eq 1. This assumption will not introduce appreciable error since we only need a small correction for the temperature change of 5.5 °C. Parts a and b of Figure 7 show Brønsted–Pedersen plots of $\log(k_2/q)$ and $\log(k_{-2}/p)$ vs $\log(K_a q/p)$ for the five buffers in Table 5. The resulting α and β values are 0.40 ± 0.05 and 0.58 ± 0.06, respectively. The sum of α and β is 0.98 ± 0.08, which is within the experimental error of the theoretical value. The smaller value of α compared to β shows that there is a smaller degree of proton transfer from HA to HOCl in the general-acid-assisted reverse reaction compared to the degree of the proton transfer from HOH to A^- in the general-base-assisted forward reaction.

Table 6. Rate Constants and Brønsted α Values for Acid-Assisted Reactions of HOCl and Halide Ions

reacn type	n[a]	α	k_{-1}, M^{-2} s^{-1}	ref
HA + HOCl + I^-	5.04	0.11	3.5×10^{11}	24
HA + HOCl + Br^-	3.89	0.27	1.3×10^6	28
HA + HOCl + Cl^-	3.04	0.40	1.5×10^4	this study

[a] Nucleophilicity of halide ion.

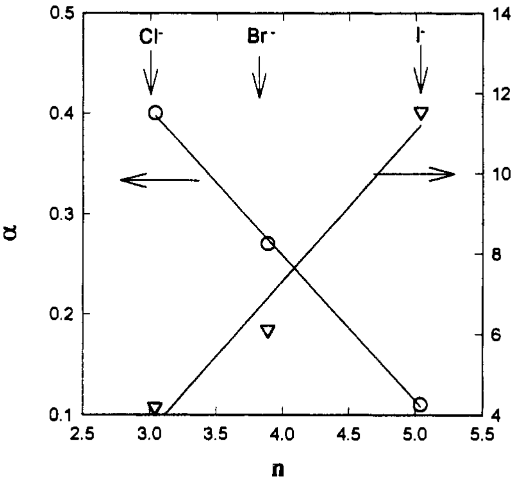


Figure 8. Correlation of the Brønsted α values for HA + HOCl + X^- with the nucleophilicity (n) of X^- (Cl^-, Br^-, I^-). The right hand ordinate shows the dependency of k_{-1} on n.

Extrapolation of Figure 7a to include hydroxide ion predicts a value of $k_2 = 10^{9.61}$ M^{-1} s^{-1} (15.0 °C, $\mu = 0.50$ M) for $A^- = OH^-$ in eq 16. This is based on $K_a = K_W/[H_2O] = 10^{-15.74}$, $q = 3$ for OH^-, and $p = 2$ for H_2O, where pK_w = 14.00 at 15 °C in 0.5 M $NaClO_4$.[25,26] Direct reaction with OH^-, without the intervening H_2O molecule, would be expected to occur at the diffusion-controlled limit in water ($k_D = 10^{9.8}$ M^{-1} s^{-1} at 15.0 °C),[27] Combination of these two OH^- pathways would predict a value of $10^{10.0}$ M^{-1} s^{-1} for k_{OH}, which is the value estimated by Eigen and Kustin[2] at 20 °C, $\mu = 0.1$ M, for the OH^- reaction with aqueous Cl_2 to form Cl_2OH^-. Contribution from this pathway is negligible under our acidic conditions. It would be very difficult to measure k_{OH} directly because of the accompanying heat of neutralization of acidic $Cl_2(aq)$ solutions and the need to avoid buffers.

Rate constants and α values for acid-assisted reactions of HOCl with different halide ions (X^-) are summarized in Table 6.[28,29] Previous studies[30] have shown that second-order rate constants for the reactions between HOCl + X^- follow the Swain–Scott relationship[31] (eq 19), where n is the nucleophilicity of X^- and

$$\log\left(\frac{k}{k_o}\right) = sn \tag{19}$$

s is the sensitivity of the reaction site. The sensitivity factor is

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extremely large for the HOCl + X^- reactions, where $s = 4.7$. As Table 6 and Figure 8 show, the third-order rate constants for H^+ + HOCl + X^- also increase with the nucleophilicity of X^- and the sensitivity factor is still large ($s = 3.8$). Figure 8 also shows that the Brønsted α values decrease linearly as the nucleophilicity of X^- increases. When the n values are large, the reactions are very favorable and the degree of proton transfer from HA is small because there is less need for acid assistance. On the other hand if the nucleophilicity is small the reaction needs a larger degree of assistance by proton transfer as reflected by larger α values. This is an interesting correlation between the role of general-acid assistance for proton transfer to oxygen and the role of the nucleophilicity of X^- as it reacts with the adjacent chlorine in HOCl.

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Appendix

Derivation of eqs 7 and 12. The rate expression for Cl_2 hydrolysis in the presence of H_3O^+/H_2O and HA/A^- (eqs 1 and 2) is given by eq 20. [HOCl] can be expressed by eq 21 and

$$-\frac{d[Cl_2]}{dt} = k_1[Cl_2] - k_{-1}[HOCl][H^+][Cl^-] + k_2[Cl_2][A^-] - k_{-2}[HOCl][HA][Cl^-] \quad (20)$$

substitution of eq 21 into eq 20 gives eq 22. The $[HOCl]_\infty$ value

$$[HOCl] = [Cl_2]_\infty + [HOCl]_\infty - [Cl_2] \quad (21)$$

$$-\frac{d[Cl_2]}{dt} = k_1[Cl_2] - k_{-1}[H^+][Cl^-]([Cl_2]_\infty + [HOCl]_\infty - [Cl_2]) + k_2[Cl_2][A^-] - k_{-2}[HA][Cl^-]([Cl_2]_\infty + [HOCl]_\infty - [Cl_2]) \quad (22)$$

can be expressed by eq 23 from the equilibrium in eq 1. Substitution of eq 23 into eq 22 gives eq 24. HA is in rapid

$$[HOCl]_\infty = \frac{K_1[Cl_2]_\infty}{[H^+][Cl^-]} \quad (23)$$

$$-\frac{d[Cl_2]}{dt} = k_1[Cl_2] - k_{-1}[H^+][Cl^-][Cl_2]_\infty - k_1[Cl_2]_\infty + k_{-1}[H^+][Cl^-][Cl_2] + k_2[Cl_2][A^-] - k_{-2}[HA][Cl^-][Cl_2]_\infty - \frac{K_1k_{-2}[Cl_2]_\infty[HA]}{[H^+]} + k_{-2}[HA][Cl^-][Cl_2] \quad (24)$$

equilibrium with H^+ and A^- (eq 25). Substitution of eq 25 into eq 24 and rearrangement leads to eq 26. The concentrations of

$$\frac{[H^+][A^-]}{[HA]} = K_a = \frac{K_1}{K_2} \qquad K_2 = \frac{k_2}{k_{-2}} \quad (25)$$

$$-\frac{d[Cl_2]}{dt} = (k_1 + k_{-1}[H^+][Cl^-] + k_2[A^-] + k_{-2}[HA][Cl^-])([Cl_2] - [Cl_2]_\infty) \quad (26)$$

HA and A^- can be expressed by eq 27. By substituting eq 27 into

$$[HA] = [HA]_T\frac{[H^+]}{[H^+] + K_a} \qquad [A^-] = [HA]_T\frac{K_a}{[H^+] + K_a} \quad (27)$$

eq 26 and by rearranging the resulting equation, we obtain eq 28,

$$-\frac{d[Cl_2]}{dt} = \left(k_1 + k_{-1}[H^+][Cl^-] + \frac{k_{-2}[HA]_T(K_1 + [H^+][Cl^-])}{[H^+] + K_a}\right)([Cl_2] - [Cl_2]_\infty) \quad (28)$$

which is the same as eq 12. If the concentrations of H^+ and Cl^- are constant, the reaction then becomes a reversible pseudo-first-order reaction with k_{obsd} as expressed in eq 14. In the absence of acid HA, the k_{obsd} dependence is the same as in eq 8.