in analogy with $pK_a = 4.65$ for $(nta)Co^{III}-CH_2OH^-(aq)$.[26] If this suggestion is correct, then the correct description of the observed transient in the pH range 5–8 is $(nta)Cu^{III}-CH_2O^{2-}(aq)$ and this formula should replace that of $(nta)Cu^{III}-CH_2OH^-(aq)$ throughout.

Finally, we checked whether similar intermediates are formed by analogous free radicals. The results (Table III) point out that analogous intermediates are indeed formed in the reactions of $\cdot CH(CH_3)OH$, $\cdot C(CH_3)_2OH$, and $\cdot CH_3$ free radicals with $Cu^{II}(nta)^-(aq)$. The specific rates of reaction of $\cdot CH(CH_3)OH$ and $\cdot C(CH_3)_2OH$ with $Cu^{II}(nta)^-(aq)$ are lower than those of $\cdot CH_2OH$ in analogy with the specific rates of these radicals with $Cu^{2+}(aq)$.[4] The absolute rates of reaction are also similar. On the other hand, the specific rate of reaction of $\cdot CH_3$ with Cu^{II}-$(nta)^-(aq)$ is considerably higher than that with $Cu^{2+}(aq)$.[5] This result is in accord with expectations as the nta ligand stabilizes the tervalent transient complex.

The transient complexes $(nta)Cu^{III}-CH(CH_3)OH^-(aq)$ and $(nta)Cu^{III}-C(CH_3)_2OH^-(aq)$ reduce $Cu^{II}(nta)^-(aq)$ somewhat

faster than $(nta)Cu^{III}-CH_2OH^-(aq)$. This result is in accord with the redox potentials of the $\cdot CH_2OH$, $\cdot CH(CH_3)OH$, and $\cdot C$-$(CH_3)_2OH$ free radicals.[27] Due to the low rates of reaction of the last two free radicals with $Cu^{II}(nta)^-$ we were unable to determine the yield of CH_3CHO and $(CH_3)_2CO$ in these systems.[28]

The transient complex $(nta)Cu^{III}-CH_3^-(aq)$ decomposes in a process that seems to obey a first-order rate law with $k = 10 \pm 3$ s^{-1}. However, due to the low absorption coefficient of this transient we did not study its properties in detail.

Registry No. Co(NH$_3$)$_6^{3+}$, 14695-95-5; Ru(NH$_3$)$_6^{3+}$, 18943-33-4; Fe(CN)$_6^{3-}$, 13408-62-3; $\cdot CH_2OH$, 2597-43-5; $\cdot C(CH_3)_2OH$, 5131-95-3; $\cdot CH_3$, 2229-07-4; $\cdot CH(CH_3)OH$, 2348-46-1.

(26) Meyerstein, D.; Schwarz, H. A. submitted for publication *J. Am. Chem. Soc.*

(27) Endicott, J. F. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, R. D., Eds.; Wiley: New York, 1975; pp 90–92.

(28) Acetaldehyde and acetone are products of the reaction mixture. This is however no proof for the suggested mechanism as they might be formed in the competing reaction $2CR_1R_2OH \rightarrow CR_1R_2O + CHR_1R_2OH$.

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Kinetics of the Iodine Monochloride Reaction with Iodide Measured by the Pulsed-Accelerated-Flow Method

Dale W. Margerum,* Peter N. Dickson, Julius C. Nagy, Krishan Kumar, Conrad P. Bowers, and Kimber D. Fogelman

The reaction $ICl + I^- \rightarrow I_2 + Cl^-$ is extremely rapid and is irreversible, so that it cannot be studied by either stopped-flow or relaxation methods. The kinetics are determined by measurement of the reactions of dichloroiodate(I) with iodide, $ICl_2^- + 2I^- \rightarrow I_3^- + 2Cl^-$, by the pulsed-accelerated-flow method, where the pseudo-first-order rate constants (k_r) range from 3800 to 70 000 s^{-1}. The rates are first order in ICl_2^- concentration, and the k_r values are proportional to the I^- concentration, inversely proportional to the Cl^- concentration, and independent of H^+ concentration (0.10–1.00 M). The resolved second-order rate constant for the reaction of ICl with I^- equals 1.1 (±0.1) $\times$ 10^9 M^{-1} s^{-1} (25.0 °C, $\mu = 1.0$).

Introduction

Eigen and Kustin[1] determined the kinetics of halogen hydrolysis by the temperature-jump relaxation technique. This method also was used to determine rate constants of triiodide ion formation and dissociation.[2] However, the hydrolysis and redox kinetics of interhalogen species have not been examined. This is because most of the reactions are not reversible and therefore are not suitable for relaxation techniques. Furthermore, the reactions are too rapid to study by stopped-flow methods. The development of the pulsed-accelerated-flow (PAF) method[3-5] permits reactions to be studied that have half-lives as short as 4 μs. This makes it possible to study reactions that are 3 orders of magnitude faster than can be studied by stopped-flow methods, without the reversibility required by relaxation methods.

In recent studies of the reactions of chloramines with iodide ion, a Cl^+ transfer to give ICl as an intermediate is proposed.[6]

It is therefore of special interest to know how rapidly iodide ion reacts with iodine monochloride. The reaction may be viewed as a redox process with a transfer of I^+ or as a substitution reaction around I^+, where I^- replaces Cl^-. Much less attention has been paid to atom-transfer reactions than to electron-transfer reactions.[7] Knowledge of the kinetics and mechanisms of reactions between halide ions and interhalogens or halogens is limited. The PAF method can provide important new information in this area.

Iodine monochloride is not stable in aqueous solution, but dichloroiodate(I), ICl_2^-, forms readily and is very stable in solutions where the HCl concentration is 0.5 M or greater.[8] The equilibrium constant, K_1, for eq 1 is 6.0 $\times$ 10^{-3} M.[9] The UV spectrum

$$ICl_2^- \rightleftharpoons ICl + Cl^- \quad K_1 \qquad (1)$$

of ICl_2^- has characteristic absorption bands at 224 nm ($\epsilon = 47\,500$ cm^{-1} M^{-1}) and at 343 nm ($\epsilon = 243$ cm^{-1} M^{-1}).[8] A molar absorptivity value of 275 cm^{-1} M^{-1} has also been reported for the 343-nm band.[10] The equilibrium constant, K_h, for the hydrolysis

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

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

(3) Jacobs, S. A.; Nemeth, M. T.; Kramer, G. W.; Ridley, T. Y.; Margerum, D. W. *Anal. Chem.* 1984, 56, 1058–1065.

(4) Nemeth, M. T.; Fogelman, K. D.; Ridley, T. Y.; Margerum, D. W. *Anal. Chem.*, in press.

(5) Nagy, J. C.; Dickson, P. N.; Margerum, D. W., to be submitted for publication.

(6) Kumar, K.; Day, R. A.; Margerum, D. W. *Inorg. Chem.*, in press.

(7) Taube, H. In *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; ACS Symposium Series 198; American Chemical Society: Washington, DC, 1982; pp 151–179.

(8) Cason, D. L.; Neumann, H. M. *J. Am. Chem. Soc.* 1961, 83, 1822–1828.

(9) Faull, J. H. *J. Am. Chem. Soc.* 1934, 56, 522–528.

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of ICl (eq 2), calculated from electrode potentials[11] is 1.1×10^{-4}

$$ICl + H_2O \rightleftharpoons HOI + H^+ + Cl^- \quad K_h \qquad (2)$$
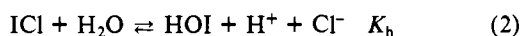
M^2 at 25 °C. Hence, combinations of high H^+ and Cl^- concentrations will give ICl_2^- as the predominant species in solution. The existence of trichloroiodate(I), ICl_3^{2-}, has been inferred,[12] but the original work is still unpublished. The same authors later quote K_1 values[11] based on the absence of ICl_3^{2-}.
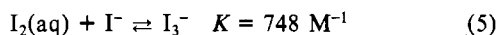
Dichloroiodate(I) rapidly oxidizes iodide (eq 3). In acidic

$$ICl_2^- + 2I^- \rightleftharpoons I_3^- + 2Cl^- \qquad (3)$$
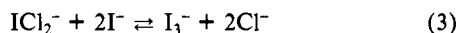
solutions, where the hydrolysis of I_2 (eq 4) is negligible,[13] the

$$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+ \quad K = 3.13 \times 10^{-13} \; M^2 \quad (4)$$

product exists in three forms: I_3^-, $I_2(aq)$, and I_2Cl^-. The distribution of these three species is dictated by the iodide and chloride concentrations (eq 5[14] and 6[8]). Triiodide ion has an

$$I_2(aq) + I^- \rightleftharpoons I_3^- \quad K = 748 \; M^{-1} \qquad (5)$$

$$I_2(aq) + Cl^- \rightleftharpoons I_2Cl^- \quad K = 1.7 \; M^{-1} \qquad (6)$$

intense absorption maximum at 350 nm ($\epsilon = 25\,800 \; cm^{-1} \; M^{-1}$),[15] whereas the other species have much less intense bands in the visible region: I_2Cl^- at 437 nm ($\epsilon = 1100 \; cm^{-1} \; M^{-1}$)[8] and $I_2(aq)$ at 460 nm ($\epsilon = 731 \; cm^{-1} \; M^{-1}$).[15] The equilibrium constant for eq 3 (calculated from eq 1, 2, 4, and 5) is 2×10^9, so that the reaction behaves as though it is irreversible.
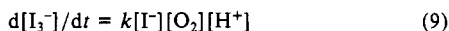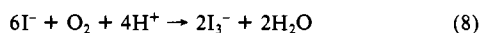
In this work, the kinetics of reaction 3 are studied as a function of I^-, Cl^-, and H^+ concentrations by use of the PAF method.

Experimental Section

A 0.030 M stock solution of ICl_2^- was prepared[16] by addition of NaI to a solution of primary standard grade $NaIO_3$ in 2 M HCl. Two moles of NaI was added for each mole of $NaIO_3$ (eq 7). The concentration

$$6H^+ + 6Cl^- + 2I^- + IO_3^- \rightarrow 3ICl_2^- + 3H_2O \qquad (7)$$
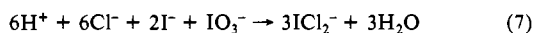
of the stock solution of ICl_2^- was checked spectrophotometrically, and our results indicate that $\epsilon = 275 \; cm^{-1} \; M^{-1}$ is the more appropriate value at 343 nm. The ICl_2^- solution was diluted into the reaction medium just prior to the kinetics experiments. Stock solutions of NaI were prepared from the solid and were standardized[17] by oxidation of iodide to iodate with bromine (excess bromine was removed by boiling), followed by titration with a solution of standardized $Na_2S_2O_3$. Dilutions of the iodide stock solution into 1.0 or 0.10 M H^+ were made immediately before use to minimize formation of iodine from the reaction of iodide with dissolved oxygen (eq 8 and 9, where $k = 1.3 \times 10^{-4} \; M^{-1} \; s^{-1}$ at 25.0 °C, $\mu = 1.0$).

$$6I^- + O_2 + 4H^+ \rightarrow 2I_3^- + 2H_2O \qquad (8)$$

$$d[I_3^-]/dt = k[I^-][O_2][H^+] \qquad (9)$$

We verified the value of the third-order rate constant for eq 9 because units were not reported for the rate constant in the original work.[18]

The $HClO_4$, H_2SO_4, and HCl solutions used in this study were standardized against NaOH, which has been standardized with primary standard potassium hydrogen phthalate. The absorbance (350 nm) of solutions of NaI in $HClO_4$ was greater than that of NaI solutions prepared in HCl. The $HClO_4$ was found to contain a trace oxidant, in addition to dissolved oxygen, which caused rapid formation of iodine in solutions of iodide. This oxidant concentration is $\sim10^{-5}$ M in concentrated $HClO_4$ (70%, Fisher Scientific). Stock solutions of $HClO_4$ were

Figure 1. Experimental data for the reaction of ICl_2^- solutions with I^- obtained by the pulsed-accelerated-flow method. The solid lines are least-squares fits. Values of k_r: (A) $3.87 \; (\pm0.05) \times 10^3 \; s^{-1}$; (B) $14.0 \; (\pm0.2) \times 10^3 \; s^{-1}$; (C) $37 \; (\pm2) \times 10^3 \; s^{-1}$.

purged with Ar just prior to reactant preparation to remove most of the oxidant, which may be traces of Cl_2 that are formed in the commercial distillation of $HClO_4$.[19] For experiments in 1.00 M H^+, a combination of $HClO_4$ and HCl was used to give the desired Cl^- concentrations. For experiments with 0.10 M Cl^- (1.0 M H^+), H_2SO_4 was used instead of $HClO_4$ to avoid interference from the oxidant that remained in the $HClO_4$. These solutions had 0.84 M H_2SO_4 and 0.10 M HCl to give 1.0 M H^+ and $\mu = 1.06$ (based on $pK_a = 1.1$ for H_2SO_4).

The studies at 0.1 M H^+ used HCl with NaCl and $NaClO_4$ to give the desired Cl^- concentration and to maintain an ionic strength of 1.00. We found that solutions of $NaClO_4$ prepared from the recrystallized salt gave more reproducible results than solutions prepared directly from $HClO_4$ and Na_2CO_3. This may also be related to the trace oxidant present in concentrated perchloric acid.

Solutions used in the PAF instrument were filtered through 0.45 -μm Triton-free Millipore Type HA filters and were degassed by aspiration for at least 10 min.

Spectra of the ICl_2^- solutions and data for the reactions of NaI with oxygen and the trace oxidant in $HClO_4$ were obtained with a Perkin-Elmer 320 UV–vis spectrophotometer.

A *pulsed-accelerated-flow spectrometer* was used to acquire the kinetics data. The kinetics of I_3^- formation from ICl_2^- solutions and I^- were monitored at 350 nm. The PAF spectrometer employs integrating observation[20,21] during continuous-flow mixing of short duration (a 0.4-s pulse). The purpose of the pulsed flow is to conserve reagents.[3,4] The reactants were observed along the direction of flow from their point of mixing to their exit from the observation tube (1.0 cm). A twin-path mixing/observation cell made from poly(vinyl chloride) was used.[4] The flow was accelerated during the pulse to give a linear velocity ramp,[3] and 250 measurements of the transmittance were taken as the flow velocity in the observation tube changed from 3.0 to 12.5 m s^{-1}. The velocity variation permits the chemical reaction rate process to be resolved from the mixing rate process.[3,4] The method of observation, the efficient mixing, and the variation of flow velocity permits the accurate measurement of first-order rate constants as large as 180 000 s^{-1}.[4,5] This is a factor of 10^3 larger than can be measured by typical stopped-flow methods. Solution reservoirs, drive syringes, and the mixing/observation cell were thermostated at 25.0 (±0.2) °C with a circulating water bath. Reactant solutions were drawn directly from the reservoirs into the drive syringes through Teflon tubing.

The fundamental relationship used in the analysis of first-order PAF data is given in eq 10, where M is the defined absorbance ratio, A_v is the

$$M_{exptl} = \frac{A_v - A_\infty}{A_0 - A_\infty} = \frac{1 - e^{-Y}}{Y}; \quad Y = \frac{bk_{app}}{v} \qquad (10)$$

absorbance of the reaction mixture at a given instantaneous velocity, A_∞ is the absorbance at infinite time, A_0 is the absorbance at time zero, k_{app} is the apparent rate constant (s^{-1}), b is the reaction path length (=0.010 m), and v is the solution velocity in the observation tube (m s^{-1}).[20,21] All absorbances are measured in the PAF spectrometer. The apparent rate

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(12) Desideri, P. G.; Lepri, L.; Heimler, D. In *Encyclopedia of the Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, 1973; Vol. 1, pp 119–121.

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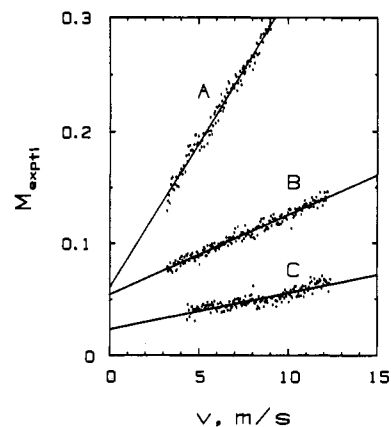
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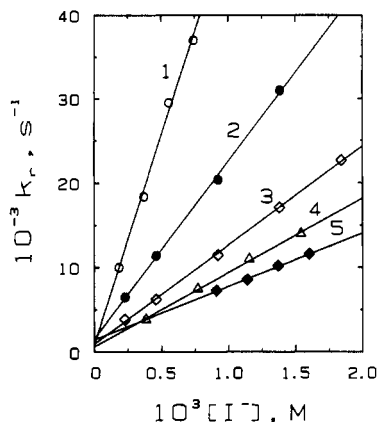
Figure 2. Pseudo-first-order rate constant vs. $[I^-]$ for the reaction of ICl and I^- in 1.00 M H^+. Cl^- concentrations: (1) 0.10 M; (2) 0.25 M; (3) 0.50 M; (4) 0.75 M; (5) 1.00 M.

constant, k_{app}, is related to the reaction rate constant, k_r (s^{-1}), and a mixing rate constant, k_{mix} (s^{-1}), by eq 11.[3,4] The mixing rate constant,

$$\frac{1}{k_{app}} = \frac{1}{k_{mix}} + \frac{1}{k_r} \quad (11)$$

k_{mix}, depends on the velocity, as shown in eq 12, where k_m is a mixing

$$k_{mix} = k_m v \quad (12)$$

constant (m^{-1}). Typically, k_m is greater than 1700 m^{-1} and v is 3.0–12.5 m s^{-1}. Thus for first-order rate constants greater than 4000 s^{-1}, $\exp(-Y)$ $\ll$ 1 in eq 10 and the model simplifies to eq 13. In the present study,

$$M_{exptl} = \frac{A_v - A_\infty}{A_0 - A_\infty} = \frac{1}{Y} = \frac{v}{bk_{app}} \quad (13)$$

$\exp(-Y)$ is generally less than 0.01 at all velocities up to 12.5 m s^{-1}, but for a few reactions with k_r values near 4000 s^{-1}, a lower velocity maximum, 9 m s^{-1}, was used to ensure that $\exp(-Y) < 0.04$. Substitution of eq 11 and 12 into eq 13 yields eq 14, where M_{exptl} is a linear fuction of

$$M_{exptl} = \frac{A_v - A_\infty}{A_0 - A_\infty} = \frac{1}{bk_m} + \frac{v}{bk_r} \quad (14)$$

velocity for fast reactions. Plots of M_{exptl} vs. v have slopes of $1/bk_r$ and intercepts of $1/bk_m$ for first-order reactions, as shown in Figure 1. The experimental data for the kinetics of I_3^- formation from solutions of ICl_2^- and I^- obey the model of eq 14 over the entire range of rate constants studied. The pseudo-first-order rate constants reported in this work are obtained from the slopes of linear regressions of M_{exptl} vs. v plots in accord with eq 14.

Results and Discussion

The reaction of ICl_2^- solutions with iodide was studied in aqueous media with H^+ concentrations of 1.0 or 0.10 M and chloride ion concentrations between 0.10 and 1.00 M. The reaction was studied under pseudo-first-order conditions with I^- and Cl^- in large excess. The product of the reaction is iodine, which exists in three forms: I_3^-, $I_2(aq)$, and I_2Cl^-. The ratios of these product species depend on the I^- and Cl^- concentrations. The product distribution (calculated from the equilibrium constants in eq 5 and 6) varies from 9 to 42% I_3^-, 9 to 55% I_2Cl^-, and 26 to 77% $I_2(aq)$. Under all experimental conditions the reaction is irreversible. The observed absorbance increase depends primarily on the I_3^- formation.

The reaction is first-order in $[ICl]_T$ (=$[ICl]$ + $[ICl_2^-]$). The observed rate constants at each chloride concentration increase linearly with iodide concentration (see Table I and Figure 2 for 1.0 M H^+ and Figure 3 for 0.10 M H^+) and are described by eq 15. The value of k_{II} decreases with increasing chloride con-

$$k_r = k_I + k_{II}[I^-] \quad (15)$$

centration. However, there is no trend in k_I, the intercept of the iodide dependencies. The average value of k_I is 1.0 (± 0.4) × 10^3 s^{-1} for the 1.00 M H^+ data, but k_I is statistically zero for the 0.10 M H^+ data. Initially we thought that the k_I term was caused by the hydrolysis of ICl, followed by rapid reaction with I^-. However, the lack of chloride suppression of k_I and the disap-
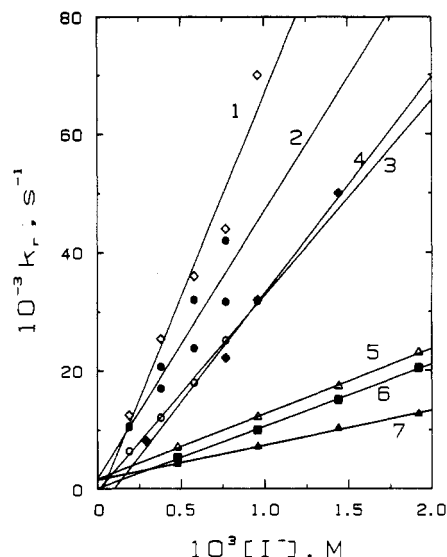

Figure 3. Pseudo-first-order rate constants vs. $[I^-]$ for the reaction of ICl and I^- in 0.10 M H^+. Cl^- concentrations: (1) 0.10 M; (2) 0.14 M; (3) 0.20 M; (4) 0.26 M; (5) 0.50 M; (6) 0.76 M; (7) 1.00 M.
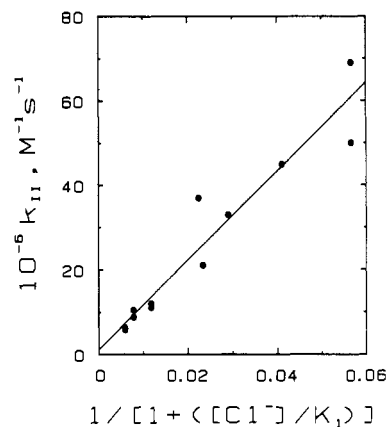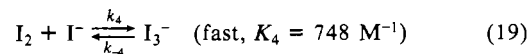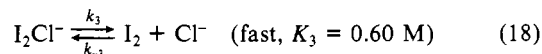

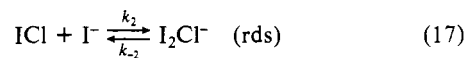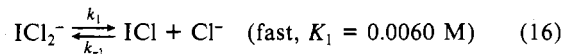**Figure 4.** Second-order rate constants from the iodide dependence (k_{II}) vs. $1/[1 + ([Cl^-]/K_1)]$ for the reaction of ICl_2^- and I^- for both the 1.00 M H^+ and 0.10 M H^+ experiments.

pearance of appreciable k_I values for reactions studied in 0.10 M H^+ make this unlikely. When we combine all the rate data, k_I = 400 ± 1500 s^{-1}, and we are forced to conclude that the k_I term is so uncertain that it must be neglected.

The proposed mechanism is given in eq 16–19. This mechanism

$$ICl_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ICl + Cl^- \quad (fast, K_1 = 0.0060 \text{ M}) \quad (16)$$

$$ICl + I^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} I_2Cl^- \quad (rds) \quad (17)$$

$$I_2Cl^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} I_2 + Cl^- \quad (fast, K_3 = 0.60 \text{ M}) \quad (18)$$

$$I_2 + I^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} I_3^- \quad (fast, K_4 = 748 \text{ M}^{-1}) \quad (19)$$

leads to the rate expression in eq 20, which gives the relationship

$$-\frac{d[ICl]_T}{dt} = \frac{k_2[I^-]}{1 + ([Cl^-]/K_1)}[ICl]_T \quad (20)$$

between k_{II} and Cl^- concentrations in eq 21. Figure 4 is a plot

$$k_{II} = \frac{k_2}{1 + ([Cl^-]/K_1)} \quad (21)$$

of k_{II} against $1/[1 + ([Cl^-]/K_1)]$, where the line is the least-squares fit. This fit gives an intercept with a value of (1 ± 3) × 10^6 M^{-1} s^{-1}. This is a small contribution to the measured rate constants, and the uncertainty is so great that the intercept is taken

Table I. Pseudo-First-Order Rate Constants for the Reaction of ICl_2^- with Excess I⁻ in the Presence of Excess Cl⁻ Measured by the PAF Technique[a]

[Cl⁻], M	10^3[I⁻], M	$10^{-3}k_r$,[b] s⁻¹	[Cl⁻], M	10^3[I⁻], M	$10^{-3}k_r$,[b] s⁻¹
		[H⁺] = 1.00 M (HClO₄, HCl), μ = 1.00			
1.00	0.91	7.28 (0.06)	0.50	0.46	6.23 (0.07)
1.00	1.14	8.56 (0.08)	0.50	0.92	11.5 (0.2)
1.00	1.37	10.2 (0.1)	0.50	1.38	17.1 (0.3)
1.00	1.60	11.6 (0.1)	0.50	1.84	22.7 (0.7)
0.75	0.38	3.87 (0.05)	0.25	0.23	6.5 (0.1)
0.75	0.77	7.49 (0.06)	0.25	0.46	11.4 (0.2)
0.75	1.16	11.0 (0.1)	0.25	0.92	20.4 (0.4)
0.75	1.54	14.0 (0.2)	0.25	1.38	31 (1)
0.50	0.23	3.85 (0.09)			
		[H⁺] = 1.00 M (HCl, H₂SO₄), μ = 1.06			
0.10	0.18	10.0 (0.2)	0.10	0.56	30 (1)
0.10	0.37	18.4 (0.5)	0.10	0.74	37 (2)
		[H⁺] = 0.10 M (HCl), μ = 1.00 (HCl, NaCl, NaClO₄)			
1.00	0.48	4.3 (0.4)	0.20	0.38	12.1 (0.2)[c]
1.00	0.96	7.19 (0.06)	0.20	0.58	18.0 (0.4)[c]
1.00	1.44	10.30 (0.09)	0.20	0.77	25.2 (0.7)[c]
1.00	1.92	12.7 (0.1)	0.20	0.96	31.8 (0.9)[c]
0.76	0.48	5.33 (0.04)	0.14	0.19	10.6 (0.2)[d]
0.76	0.96	10.0 (0.1)	0.14	0.19	10.5 (0.3)[d]
0.76	1.44	15.1 (0.2)	0.14	0.38	17.0 (0.4)[d]
0.76	1.92	20.5 (0.4)	0.14	0.38	20.7 (0.6)[d]
0.50	0.48	7.1 (0.7)	0.14	0.58	23.8 (0.6)[d]
0.50	0.96	12.2 (0.2)	0.14	0.58	32 (1)[d]
0.50	1.44	17.4 (0.3)	0.14	0.77	32 (1)[d]
0.50	1.92	23.1 (0.5)	0.14	0.77	42 (1)[d]
0.26	0.29	8.2 (0.1)	0.10	0.19	12.5 (0.5)[c]
0.26	0.77	22.2 (0.5)	0.10	0.38	25.4 (0.9)[c]
0.26	0.96	32 (1)	0.10	0.58	36 (3)[c]
0.26	1.44	50 (2)	0.10	0.77	44 (4)[c]
0.20	0.19	6.4 (0.1)[c]	0.10	0.96	70 (10)[c]

[a] 25.0 ± 0.2 °C, $[ICl]_T$ = 3.0 × 10⁻⁵ M, λ = 350 nm. [b] Each k_r value is a composite of two or three runs, and the value in parentheses is the standard deviation from the slope of M_{exptl} vs. v plots. [c] Recrystallized NaClO₄ was used. [d] Duplicate determinations were performed on different days by use of different solutions and separate determinations of A_0, A_∞, and A_v.

Table II. Resolved Rate Constants[a] for the Reaction of ICl_2^- with I⁻

[Cl⁻], M	$10^{-6}k_{II}$, M⁻¹ s⁻¹	$10^{-3}k_I$, s⁻¹	[Cl⁻], M	$10^{-6}k_{II}$, M⁻¹ s⁻¹	$10^{-3}k_I$, s⁻¹
		[H⁺] = 1.00 M			
1.00	6.4 (0.2)	1.4 (0.3)	0.25	21.1 (0.5)	1.5 (0.5)
0.75	8.8 (0.3)	0.6 (0.3)	0.10	50 (3)	0.7 (1.3)
0.50	12 (2)	0.9 (0.2)			
		[H⁺] = 0.10 M			
1.00	5.9 (0.2)	1.5 (0.2)	0.20	33 (1)	-0.3 (0.6)
0.76	10.5 (0.2)	0.1 (0.3)	0.14	45 (6)	1 (3)
0.50	11.1 (0.2)	1.6 (0.3)	0.10	69 (9)	-2 (6)
0.26	37 (2)	-3 (2)			

[a] $-d[ICl]_T/dt = (k_I + k_{II}[I^-])[ICl_2^-]_T$; [H⁺] = 1.00 M; $[ICl]_T = 3 \times 10^{-5}$ M; λ = 350 nm; 25.0 ± 0.2 °C; μ = 1.0.

as zero. The slope from the simple linear regression or a linear regression through the origin gives a k_2 value of (1.1 ± 0.1) × 10⁹ M⁻¹ s⁻¹.

The calculated equilibrium constant for k_2/k_{-2} is 7.3 × 10⁸ M⁻¹, so k_{-2} is only 1.5 s⁻¹. By contrast, a dilution experiment with the PAF method shows k_3 to be very large (>5 × 10⁴ s⁻¹), so the dissociation of I_2Cl^- to I_2 and Cl⁻ is many orders of magnitude faster than its dissociation to ICl and I⁻. The proposed Cl⁻ preequilibration step in the mechanism requires $k_{-1}[Cl^-] \gg k_2[I^-]$. For [Cl⁻] = 0.10 M, [I⁻] = 10⁻³ M, and k_2 = 1.1 × 10⁹ M⁻¹ s⁻¹, this means that $k_{-1} \gg 1.1 \times 10^7$ M⁻¹ s⁻¹ and $k_1 \gg 6.6 \times 10^4$ s⁻¹. Since the largest value of k_r measured is 7.0 × 10⁴ s⁻¹, the requirement is met. All reactions have a first-order dependence in iodide; hence, k_{-1} must be between 10⁸ M⁻¹ s⁻¹ and the diffusion limit (6 × 10⁹ M⁻¹ s⁻¹).

Comparisons may be made between the rate constants determined in this study and rate constants for similar reactions of other halogen species. The rate constant k_2 for iodide transfer to ICl is 1.1 × 10⁹ M⁻¹ s⁻¹, whereas the rate constant k_4 for the reaction iodide with I_2 is 6.2 × 10⁹ M⁻¹ s⁻¹. The fact that ICl reacts 5.6 times more slowly than I_2 with I⁻ might seem surprising because the iodine atom in the polar I–Cl molecule would be expected to be more susceptible to nucleophilic attack than the iodine atoms in the covalent I–I molecule. However, iodine monochloride is more strongly hydrated than I_2 as evidenced by their $\Delta G°$ of hydration values[11] (-9.28 and -2.94 kJ, respectively). thus, ICl may be less reactive with iodide because of a more strongly associated water molecule. Chloride ion suppresses the I⁻ reaction with ICl much more than it suppresses the I⁻ reaction with I_2, because $K_1 \ll K_3$. Our results show that after the rate-determining step rapid equilibration occurs among I_2Cl^-, $I_2(aq)$, and I_3^-.

Another interesting comparison is the k_{-2} value of 1.5 s⁻¹ for the process I–I–Cl⁻ → I⁻ + ICl, which is very small compared to the k_{-4} value of 8.5 × 10⁶ s⁻¹ for the process I–I–I⁻ → I⁻ + I–I. It is obviously more difficult to dissociate I⁻ from the I⁺ center in I_2Cl^- than it is to dissociate I⁻ from I_3^-. On the other hand, the value for k_3 is larger than 5 × 10⁴ s⁻¹ for the process I–I–Cl⁻ → I–I + Cl⁻, despite the fact that ICl(g) bond dissociation energy[22] is 50.5 kcal mol⁻¹ compared to the I_2(g) dissociation energy[23] of 36.4 kcal mol⁻¹. However, for I_2Cl^- in aqueous solution the k_{-2} step is thermodynamically less favorable than the k_3 step by a factor of 2.3 × 10⁻⁹.

Under the conditions of these experiments, we did not find evidence for an appreciable rate of hydrolysis of ICl to give IOH (eq 2). The rate of reaction of IOH with I⁻ in acid (eq 22) is very

$$HOI + I^- + H^+ \rightarrow I_2 + H_2O \qquad (22)$$
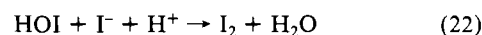
fast[1] and has a third-order rate constant equal to 4.4 × 10¹² M⁻²

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s^{-1}. Under our conditions this reaction would have a diffusion-controlled rate. Therefore, the rate of I_2 formation via eq 2 and 22 would depend only on the rate of hydrolysis of ICl ($=k_h[ICl]$). Accordingly, $k_I \approx k_h K_1/[Cl^-]$, but we did not observe a reciprocal $[Cl^-]$ dependence for k_I. If k_I were as large as 400 s^{-1}, then k_h could be between 7×10^3 s^{-1} for 0.1 M Cl^- and 7×10^4 s^{-1} for 1 M Cl^-. These values seem unreasonably large compared to hydrolysis rate constants of 28.6, 110, and 3.0 s^{-1} for Cl_2, Br_2, and I_2, respectively.[1] Thus, at present the rate of hydrolysis of ICl is not known.

Another possible path for the formation of I_2 in the absence of added I^- is the disproportionation of ICl. However, this rate depends on $[ICl]^2$ and is much too slow[24] to account for the k_I term.

A path for the direct attack of I^- on ICl_2^- to give I_2Cl^- and Cl^- is omitted from the mechanism because of the large uncertainty of the value, $(1 \pm 3) \times 10^6$ M^{-1} s^{-1}, for this second-order rate constant. A $I_2Cl_2^{2-}$ transition state would require a central iodine atom with six electron pairs (three nonbonding pairs around I^+ and three bonding electron pairs from one I^- and two Cl^- ions). This would be expected to be very unfavorable in contrast to the five electron pairs around the central iodine in I_2Cl^-, where structure I corresponds to the geometry expected from valence

shell electron pair repulsion theory.[25]

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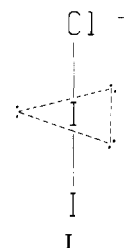
Conclusion

The PAF method is used to study the kinetics of irreversible atom-transfer reactions that are too fast to study by stopped-flow methods. Reaction rate constants from 3800 to 70 000 s^{-1} have been measured for the reaction of ICl_2^- solutions with I^-. In this study, it has been shown that the reaction of I^- with ICl has a second-order rate constant of 1.1×10^9 M^{-1} s^{-1}, whereas the rate constant for the reaction of I^- with ICl_2^- is at least 1000 times smaller.

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Notes

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Kinetic Study of the Conversion of cis-Diaqua(1,4,7,10-tetraazacyclotridecane)nickel(II) to the Planar Complex[1]

Anne M. Martin, Kenneth J. Grant, and E. Joseph Billo*

The recent publication by Hay and Akbar Ali[2] of some rates of cis-to-planar interconversion of the Ni(II) complex of the macrocyclic ligand 1,4,7,10-tetraazacyclotridecane (13aneN$_4$, structure I) prompts us to report our extensive investigation of

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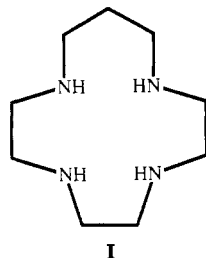
the same system. We find that, during the conversion of cis-Ni(13aneN$_4$)(H$_2$O)$_2^{2+}$ to the planar complex Ni(13aneN$_4$)$^{2+}$, a transient species, identified as a configurational isomer of planar Ni(13aneN$_4$)$^{2+}$, is observed. Similar configurational isomers have been postulated in the similar reaction of the corresponding cis-Ni(14aneN$_4$)(H$_2$O)$^{2+}$ complex,[3] but the Ni(II)–13aneN$_4$ system is the first in which such isomers have been observed as intermediates during the course of the reaction. We therefore report

our preliminary findings despite the fact that some aspects of the mechanism remain to be elucidated.

Experimental Section

The ligand 13aneN$_4$ was synthesized by following the method of Fabbrizzi[4] and isolated as the tetrahydrochloride salt. The ligand was converted to the nickel complex; well-formed yellow crystals of Ni(13aneN$_4$)(ClO$_4$)$_2$ were obtained and were recrystallized from hot water. Aqueous solutions of the complex exhibited the reported λ_{max} at 425 nm,[4] characteristic of square-planar nickel(II).

The cis complex, cis-Ni(13aneN$_4$)(H$_2$O)$_2^{2+}$, was generated in solution according to our earlier procedure[5] by adding a slight excess of ethylenediamine to form the mixed-ligand complex Ni(13aneN$_4$)(en)$^{2+}$, followed by acidification to yield the folded complex cis-Ni(13aneN$_4$)(H$_2$O)$_2^{2+}$. A few rates were measured by using cis-Ni(13aneN$_4$)Cl$_2$, prepared by our earlier procedure.[5]

Rates of interconversion of cis-Ni(13aneN$_4$)(H$_2$O)$_2^{2+}$ were measured by following the increase in absorbance at 425 or 430 nm. Rates were measured at 25 °C and, with the exception of a few rates at pH values below 1, at $I = 0.10$ (NaClO$_4$). Hydrogen ion and hydroxide ion concentrations were obtained from measured pH by using the following relationships: $-\log [H^+] = \text{pH} - 0.10$ and $K_w = 13.78$ (25 °C, 0.10 M NaClO$_4$).

Results and Discussion

The d–d spectrum of cis-Ni(13aneN$_4$)(H$_2$O)$_2^{2+}$ is similar to that of other cis-Ni^{II}N$_4$O$_2$ chromophores,[6] with bands at the following wavelengths (ϵ, M^{-1} cm^{-1}, in parentheses): 340 nm (15), 535 nm (9), 900 nm (18). cis-Ni(13aneN$_4$)(H$_2$O)$_2^{2+}$ spontaneously isomerizes to the stable planar complex Ni(13aneN$_4$)$^{2+}$.

At pH values below approximately 6 the interconversion reaction exhibits biphasic first-order kinetics (see Figure 1). Rate constants for the two reactions were obtained by standard methods.[7] From pH 1 to 4 the second reaction is some 50 times slower than the first, which enabled us to record the spectrum of the solution during the fast reaction with essentially no in-

(1) Presented in part at the 186th National Meeting of the American Chemical Society, Washington, DC, Aug 1983.

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