solvated electrons are formed with a very small yield ($\phi < 10^{-4}$), if any at all, by this complex. Moreover, transient absorptions (500–600 nm) were observed in flash photolyses of deaerated solutions ($10^{-7} \leq [H^+] \leq 10^{-5}$ M; $[Cu(dmp)_2^+] \leq 3 \times 10^{-5}$ M) for excitations at $\lambda > 400$ nm. A second-order dependence in transient concentration (see Figure 3) was obtained for the decay, with a rate constant to extinction coefficient ratio of $k/\epsilon = 8.1 \times 10^5$ cm s^{-1} at 550 nm. Saturation of the solutions with N_2O had no effect on k/ϵ or on the yield of the species produced per flash. Since absorptions of the ligand radical anion (see reaction 12) are placed somewhere in this region,[20] one may assume that the observed species is generated in steps following the primary process as indicated in reactions 10–17. In this sequence the

$$Cu(dmp)_2^+ \xrightarrow{h\nu} CTTL \tag{10}$$

$$CTTL \rightsquigarrow Cu(cmp)_2^+ \tag{11}$$

$$CTTL \xrightarrow[-OH^-]{+OH_2} Cu(dmp)(dmpH\cdot)^{2+} \tag{12}$$

$$Cu(dmp)(dmpH\cdot)^{2+} \rightleftharpoons Cu(dmp)(dmp^-\cdot)^+ + H^+ \tag{13}$$

$$Cu(dmp)(dmp^-\cdot)^+ \rightarrow Cu(dmp)_2^+ \tag{14}$$

$$Cu(dmp)(dmpH\cdot)^{2+} \rightarrow Cu(dmp)^{2+} + dmpH\cdot \tag{15}$$

$$Cu(dmp)^{2+} + dmpH\cdot \rightarrow Cu(dmp)^+ + dmp + H^+ \tag{16}$$

$$dmpH\cdot + dmpH\cdot \rightarrow products \tag{17}$$

steps (10)–(15) are expected to be fast, following the excitation pulse, while (16) and (17) should be the observed reactions in flash photolyses experiments.

The distinct photochemical tendencies of the Cu(I) complexes indicated above show that reactive excited states with a different nature are populated in each case. The *absence of emission at room temperature* seems to be a good indication of the short life of the low-lying excited states. In such a case the direct oxidation–reduction reactions between these states and added substrates seem to be unlikely.[1] However, acid–base reactions of the excited state with solvent molecules (eq 12) are, probably, rapid enough for competition with nonradiative relaxation (eq 11).

The lowest energy absorption band (λ_{max} 450 nm, ϵ_{max} 7×10^3 M^{-1} cm^{-1}) of the $Cu(dmp)_2^+$ spectra was previously attributed to a charge transfer to ligand transition (CTTL).[21] Such assignment indicates that a CTTL state might be responsible for the photochemical behavior exhibited by $Cu(dmp)_2^+$. By contrast, the dissociation into solvated electrons in the primary process of cuprous halides might be used as an indication of a photoreactive charge transfer to solvent state (CTTS). The possibility of such transitions placed at 350–200 nm in the spectra of cuprous halides seems feasible from photochemical and spectroscopic models.[22] Moreover, the emission observed in glassy solutions (140 K) of cuprous halides[23] suggests that intramolecular excited states might be in the vicinity of the CTTS state. Although ligand to metal charge-transfer excited states are expected to be present, no photochemical evidence for their photoreactivity was obtained with these species.

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Registry No. $CuCl_3^{2-}$, 29931-61-1; $Cu(dmp)_2^+$, 21710-12-3.

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Kinetics of the Hexachloroiridate(III) Reduction of Iodate Ion

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As part of a study of the reactions of transition-metal complexes with oxyhalogen species, we have reported the reduction of BrO_3^- by $IrCl_6^{3-}$.[1] The kinetics were quite straightforward, with the principal term in the rate law being of the form $k[BrO_3^-][IrCl_6^{3-}][H^+]^2$. This rate law is in accord with the behavior expected for reactions of oxyanions.[2] The $IrCl_6^{3-}$ reduction of ClO_3^- has also been studied.[3] This reaction is first order in both $[IrCl_6^{3-}]$ and $[ClO_3^-]$ and exhibits a complex $[H^+]$ dependence, which appears minimally to require parallel reaction paths zero, first, and second order in $[H^+]$. We report here on the $IrCl_6^{3-}$ reduction of the third halate, iodate.

Experimental Section

The preparation of all reagents, procedures for measuring reaction rates, and data handling procedures have been described previously.[1,4] Ionic strength was maintained at 0.500 M by addition of $LiClO_4$, and pseudo-first-order conditions were maintained throughout. First-order plots were linear for >90% reaction.

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Table I. Pseudo-First-Order Rate Constants for Reduction of IO_3^- by $IrCl_6^{3-}$ at 25.0 °C and 0.500 M Ionic Strength

	$10^4 k_{obsd}$, s^{-1}								
	$[IO_3^-]_{total}$, M								
$[H^+]_{total}$, M	0.0025	0.0050	0.0100	0.0200	0.0300	0.0400	0.0500	0.0600	0.0700
0.0252	1.13	1.89	3.21	4.43	5.39	6.69	7.42	8.08	8.45
0.0504	2.14	4.03	6.76	9.95	12.0	15.4	17.3	18.8	19.9
0.102	4.33	8.11	14.6	24.8	30.7	37.4	44.9	50.8	52.5
0.150	8.43	13.1	24.3	42.3	54.6	64.2	68.6	78.9	89.5
0.197	9.96	18.4	32.6	56.8	77.7	87.5	97.9	103	125
0.252	12.9	23.7	43.9	77.9	103	122	137	159	163
0.300	17.1	30.3	52.1	83.3	127	149	163	177	181
0.347	17.6	34.1	62.7	116	145	173	189	211	238
0.402	23.3	39.8	74.4	130	188	211	233	263	288
0.499	24.1	46.8	87.8	143	208	254	273		

Iodate was reduced to I_2 regardless of which reactant was in excess. Spent reaction solutions having $[IO_3^-]_0 \gg [IrCl_6^{3-}]_0$ were extracted with CCl_4, resulting in a pink coloration due to I_2. Measurement of the absorbance change in a solution with $[IrCl_6^{3-}]_0 \gg [IO_3^-]_0$ indicated $[Ir(IV)]_\infty/[I(V)]_0 = 4.99$, consistent with the production of I_2. The stoichiometry is thus given by

$$5IrCl_6^{3-} + IO_3^- + 6H^+ = 5IrCl_6^{2-} + {}^1/_2 I_2 + 3H_2O \qquad (1)$$

Results

The kinetics of the reaction of $IrCl_6^{3-}$ with IO_3^- were determined at 25.0 °C and 0.500 M ionic strength over the initial concentration ranges (0.4–2.6) × 10^{-4} M $IrCl_6^{3-}$, (2.5–70) × 10^{-3} M IO_3^-, and 0.025–0.45 M H^+. Linear pseudo-first-order plots indicated the rate law:

$$-d[IrCl_6^{3-}]/dt = k_{obsd}[IrCl_6^{3-}] \qquad (2)$$

Values of k_{obsd} measured at various total concentrations of H^+ and IO_3^- are presented in Table I. Further interpretation of these data to formulate an equation describing the $[H^+]$ and $[IO_3^-]$ dependences of k_{obsd} must take into account the simultaneous existence of I(V) in two states of protonation:

$$HIO_3 \overset{K_a}{\rightleftharpoons} H^+ + IO_3^- \qquad (3)$$

Numerous determinations of K_a at 25.0 °C and extrapolated to zero ionic strength yield the value $K_a° = 0.167$ M.[5-10] Values determined in solutions of 1.00 M ionic strength are 0.470 M (in $LiClO_4$)[11] and 0.467 M (in HNO_3),[6] while values at about 0.50 M ionic strength are 0.396 M (in HCl),[6] 0.396 M (in HNO_3),[6] and 0.393 M (in HNO_3).[7] These results all fit quite well to the equation $\log K_a = 0.777 - 1.018I^{1/2}/(1 + 1.278I^{1/2})$, which gives $K_a = 0.400$ M at $I = 0.500$ M and 25 °C. This latter value was used in all further calculations.

The value of K_a along with the mass balance equations $[H^+]_{total} = [H^+] + [HIO_3]$ and $[IO_3^-]_{total} = [IO_3^-] + [HIO_3]$ were used to calculate the actual concentration of H^+ in each reaction solution. These corrections amounted to ≤8% when $[H^+]_{total} = 0.400$ M and ≤14% when $[H^+]_{total} = 0.0252$ M. It is to be expected that the term $(K_a + [H^+])^{-1}$ will be associated with $[IO_3^-]_{total}$ wherever it appears in the rate law.

$$[IO_3^-] = K_a[IO_3^-]_{total}/(K_a + [H^+]) \qquad (4)$$

$$[HIO_3] = [H^+][IO_3^-]_{total}/(K_a + [H^+]) \qquad (5)$$

At constant $[H^+]_{total}$, the value of k_{obsd} follows the equation

$$k_{obsd} = A[IO_3^-]_{total}/(1 + B[IO_3^-]_{total}) \qquad (6)$$

where A and B are $[H^+]$ dependent. Since $[IO_3^-]_{total}$ will necessarily have associated with it a term such as in eq 4 or 5, this equation can be further refined

$$k_{obsd} = A'[IO_3^-]_{total}(K_a + [H^+])^{-1}/\{1 + B'[IO_3^-]_{total}(K_a + [H^+])^{-1}\} \qquad (7)$$

Table II. Iodate Dependence of the Reduction of IO_3^- by $IrCl_6^{3-}$ at 25.0 °C and 0.500 M Ionic Strength[a]

$[H^+]_{total}$, M	A'', M^{-2} s^{-1}	A''/B'', M^{-1} s^{-1}	B'', M^{-1}
0.0252	0.680 ± 0.055	0.0563 ± 0.0040	30.2 ± 4.7
0.0504	0.729 ± 0.050	0.0715 ± 0.0053	25.5 ± 3.6
0.104	0.838 ± 0.034	0.112 ± 0.008	18.7 ± 2.0
0.150	1.10 ± 0.05	0.115 ± 0.007	23.8 ± 2.5
0.197	1.19 ± 0.06	0.121 ± 0.008	24.6 ± 2.8
0.252	1.33 ± 0.03	0.140 ± 0.005	23.8 ± 1.4
0.300	1.52 ± 0.07	0.118 ± 0.007	32.2 ± 3.4
0.347	1.58 ± 0.04	0.136 ± 0.006	29.0 ± 2.0
0.402	1.77 ± 0.06	0.145 ± 0.007	30.4 ± 2.5
0.449	1.88 ± 0.06	0.154 ± 0.011	30.6 ± 3.2

[a] Parameters are defined by eq 8.

Values of B' are reasonably independent of $[H^+]$, while A' has a $[H^+]$ dependence varying between first and second order. The last equation can be simplified by substituting from eq 4 and including a partial $[H^+]$ dependence for A'.

$$k_{obsd} = A''[H^+][IO_3^-]/(1 + B''[IO_3^-]) \qquad (8)$$

where $A'' = A'/K_a[H^+]$ and $B'' = B'/K_a$. Values of A'' and A''/B'' determined from the inverse of the linear least-squares intercepts and slopes of plots of $[H^+][IO_3^-]k_{obsd}^{-1}$ vs. $[IO_3^-]$ are given in Table II. The values of B'' obtained from these data are independent of $[H^+]$, with an average of 26.9 ± 4.3 M^{-1}. The values of A'' and of A''/B'' increase with increasing $[H^+]$, according to the equation

$$A''/B'' = k_1 + k_2[H^+]_{total} \qquad (9)$$

where linear least squares gives $k_1 = 0.0738 \pm 0.0074$ M^{-1} s^{-1} and $k_2 = 0.190 \pm 0.032$ M^{-2} s^{-1}. These parameters (k_1, k_2, and B'') substituted into eq 8–9 can reproduce the values of k_{obsd} with an average deviation of 8.3%. If data at the two lowest $[H^+]_{total}$, which show a marginally significant tendency to deviate from eq 9, are excluded, the average deviation drops to 4.5%.

A possible interpretation for the parameter B'' is the equilibrium constant K_f for formation of an Ir(III)–I(V) binuclear complex. The absorbances of Ir(III) solutions were measured as a function of $[IO_3^-]$ (with no added H^+, so the redox process was suppressed). The absorbance did increase slightly with increasing $[IO_3^-]$ as would be expected for a binuclear complex.[12] Values of the alleged K_f could be obtained as the ratio of the intercept to the slope of plots of the inverse of the absorbance change vs. the inverse of $[IO_3^-]$.[13] For [Ir(III)] < 3.5 × 10^{-3} M, the absorbance changes were very small, and K_f was within experimental error of zero. However, more concentrated solutions of Ir(III) yielded the value $K_f = 12 \pm 1$ M^{-1}, in reasonable agreement with the kinetic value, considering the small absorbance changes used; e.g., with 4.35 × 10^{-3} M Ir(III), the absorbance at 415 nm in a 1-cm cell varied from 0.400 with $[IO_3^-] = 0.0$ to 0.445 with $[IO_3^-] = 0.070$ M. With an extinction coefficient of 92 $M^{-1}\ cm^{-1}$ for $IrCl_6^{3-}$,[14] the extinction coefficient of the proposed species, $IrCl_6 \cdot IO_3^{4-}$, would be 114 $M^{-1}\ cm^{-1}$ at 415 nm.

Discussion

If the denominator term in $[IO_3^-]$ does indeed arise from a complex formation reaction, one possible mechanism for the $IrCl_6^{3-} + IO_3^-$ reaction is given by eq 10–13. This mechanism

$$HIO_3 \overset{K_a}{\rightleftharpoons} IO_3^- + H^+ \tag{10}$$

$$IrCl_6^{3-} + IO_3^- \overset{K_f}{\rightleftharpoons} IrCl_6 \cdot IO_3^{4-} \tag{11}$$

$$IrCl_6 \cdot IO_3^{4-} + H^+ \xrightarrow{k_1} Ir(IV) + I(IV) \tag{12}$$

$$IrCl_6 \cdot IO_3^{4-} + 2H^+ \xrightarrow{k_2} Ir(IV) + I(IV) \tag{13}$$

$$4Ir(III) + I(IV) \overset{\text{fast}}{\rightleftharpoons} 4Ir(IV) + I(0) \tag{14}$$

is consistent with those proposed for the ClO_3^- and BrO_3^- reactions, although several differences are apparent. In this mechanism, k_1, k_2, and K_a have the values given above and $K_f = B''$. There are numerous possible variations on this mechanism which are kinetically indistinguishable and equally consistent with the evidence at hand.[15,16] The absence of a first-order dependence on $[H^+]$ in the B'' term indicates that binuclear complex formation cannot involve HIO_3. However, the existence of a binuclear complex does not necessarily implicate its involvement as a reactant. Steps 12 and 13 could involve instead reactions between $IrCl_6^{3-}$ and HIO_3 (or $H_2IO_3^+$). The same form of rate law would be involved in each case although the identity of the parameters in the equation would differ. If the sum of terms in the denominator did not arise from binuclear complex formation, it would be necessary to devise a steady-state mechanism.[15,16] This does not seem very likely since such a mechanism would require $IrCl_6^{3-}$ to exist in two different forms with the second form participating as a steady-state intermediate.[16]

The existence of binuclear complexes of metal ions and iodate has some precedence. Complexes have been identified with the metal ions $Cr(H_2O)_6^{3+}$ (first and second formation constants 3.3 M^{-1} and 40 M^{-2}),[17] $Cr(NH_3)_5OH_2^{3+}$ (formation constant 11 M^{-1}),[18,19] *cis*-$Co(en)_2(H_2O)_2^{3+}$ (formation constant 2.3 M^{-1}),[19] and VO^{2+} (formation constants of 1.7 M^{-1} and 0.4 M^{-2}).[20] The formation of $H(IO_3)_2^-$ from HIO_3 and IO_3^- has also been proposed,[9] with a formation constant of 4.0 M^{-1} determined by potentiometric measurements and 3.0 M^{-1} by cryoscopic measurements. Thus it is not unreasonable to suggest the formation of a binuclear complex from $IrCl_6^{3-}$ and IO_3^-, although a formation constant of 27 M^{-1} does seem somewhat high considering the ionic charges of these species.

First-order and second-order hydrogen ion dependences are consistent with previous results on reactions of iodate. The reduction by $Fe(CN)_6^{4-}$ had a $[H^+]$ dependence identical with that observed here,[21] while the oxygen exchange between iodate and water follows a rate law containing these terms[22] as well as others.[23] The formation of $Cr(NH_3)_5IO_3^{2+}$ and of *cis*-$Co(en)_2(H_2O)IO_3^{2+}$ is first order in $[H^+]$,[19] and the reduction of IO_3^- by I^- is second order in $[H^+]$.[10,24] These results are all consistent with the general expectation for reactions of oxyanions,[2] as well as with the general observation[25] that when reactant and product differ in the number of protons, some of the protons are gained or lost prior to the rate-determining step.

The halate oxidations of $IrCl_6^{3-}$ all seem to have unique mechanistic features, although the occurrence of a net activation process

$$XO_3^- + IrCl_6^{3-} + 2H^+ \xrightarrow{k} \{H_2XO_3IrCl_6^{2-}\}^{\ddagger}$$

is a common feature of all three mechanisms. It is not possible to ascertain whether these activation processes all involve the same detailed steps or whether all the activated complexes have the same structures. Values of k calculated from appropriate combinations of rate parameters, with approximate corrections for the different conditions in the ClO_3^- study,[3] are 5×10^{-5}, 50, and 5 $M^- s^{-1}$ for X = Cl, Br, and I, respectively. These results are consistent with the general observation that IO_3^- and BrO_3^- oxidations are more facile than ClO_3^- oxidations, probably due to easier substitution on the larger and softer halogens.[2]

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Acidity of $B_5H_9^+$ and Stability of the B_5H_8 Radical

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A relatively unexplored area of boron chemistry is that concerned with the role of free radical intermediates. Especially scarce is information on the nature of radicals formed when a B–H bond is broken. The purpose of this paper is to report results of an experimental investigation of the stability of B_5H_8. Structural features of the B_5H_8 radical and the relevance of this species in the photochemistry of B_5H_9 will be noted.

Equilibrium studies of proton-transfer reactions in the gas phase have provided proton affinity data for a large number of stable molecules. For measurements of proton affinities of short-lived intermediates equilibrium techniques are gen-