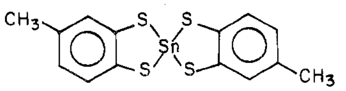
o-Phenylenedioxytin(II),[16] tin(II) oxalate,[15] and the tin(II) derivatives derived from mercaptoethanol and ethanedithiol exhibit Mössbauer resonances at room temperature, evidence generally considered to indicate strong polymeric lattices which contribute to large recoil-free fractions.[19] The recent observation of ambient-temperature tin-119m Mössbauer spectra for certain molecular solids[21] does not affect our conclusion which is based upon close analogies with other associated tin(II) solids whose structures are known.[22]

Ample evidence is available in the literature of tin structures[22] to support the idea of bridging oxygen and sulfur groups at ψ-trigonal-bipyramidal or φ-square-pyramidal tin(II) atoms to give association polymers in the solid state. The original molecules can, as in the case of the infusible *o*-phenylenedioxytin(II),[1] preserve their integrity in the crystal, sublime as the monomer, and be recovered unchanged from strongly donating solvents. The physical properties of the infusible derivatives containing carboxylic acid groups prepared here, in which the infrared ν(C=O) shifts to lower frequencies, argue likewise for a strongly associated solid through carbonyl oxygen atom bridging. Associated structures through oxygen atom bridging have also been proposed for the tin(II) dialkoxides[12,14] and diphenoxide,[8] with a double bridge proposed for tin(II) dimethoxide.[14] The products from mercaptoethanol and ethanedithiol, like the analogous material from ethylene glycol,[3] are presumably open-chain polymers with the backbone structure $[-ECH_2CH_2E'-Sn-]_n$ in which E = O, E′ = S and E = E′ = O,[3] S. The thioglycolate derivative, on the other hand, is more likely an associated solid made up of heterocyclic units linked together by carbonyl oxygen atom bridges. The related tin(II) oxalate apparently uses only one of its carbonyl oxygen atoms to bridge, the other remaining free.[15]

On prolonged standing in air, a resonance in the tin(IV) region appears in the Mössbauer spectra of the compounds studied here. However, one compound, 3,4-toluenedithiolatotin(II), is apparently much less stable than the others. When exposed to the atmosphere, a freshly prepared sample changes color from yellow to red within 1 day. No color change occurs when the compound is stored under nitrogen. The red color is characteristic of the spiro tin(IV) compound,[23] and 3,4-toluenedithiol is used in the colorimetric determination of tin.[24]



The red tin(IV) spirane is an associated polymer in the solid state. No other related tin(IV) dithiolato compounds, or the pyridine or dimethylformamide adduct of the spirane, exhibit the red color.[23]

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Registry No. $Sn(OMe)_2$, 37182-97-1; *o*-phenylenedioxytin(II), 1767-80-2; *o*-oxybenzoyloxytin(II), 28637-75-4; *o*-thiolatobenzoyloxytin(II), 64957-59-1; thiolatoethyleneoxytin(II), 64957-60-4; 3,4-toluenedithiolatotin(II), 42549-83-7; thioglycolatotin(II), 64957-61-5; 2,3-pyridinedioxytin(II), 64957-62-6; ethanedithiolatotin(II), 6570-39-4; $SnCl_2$, 7772-99-8; CH_3OH, 67-56-1; catechol, 120-80-9; salicylic acid, 69-72-7; *o*-mercaptobenzoic acid, 147-93-3; mercaptoethanol, 60-24-2; 3,4-toluenedithiol, 496-74-2; thioglycolic acid, 7283-42-3; 2,3-dihydroxypyridine, 16867-04-2; ethanedithiol, 107-21-1; ^{119}Sn, 14314-35-3.

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Kinetics and Mechanism of the Reduction of Bromate Ion by Hexachloroiridate(III)

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The bromate ion oxidation of metal ions has been studied with the reducing agents Ce(III),[1,2] Mn(II),[1,2] Np(V),[1-3] VO^{2+},[4,5] V^{3+},[6] V^{2+},[6] Fe^{2+},[7] $Fe(CN)_6^{4-}$,[8] $Fe(bpy)(CN)_4^{2-}$,[9] $Fe(bpy)_2(CN)_2$,[9] $Fe(bpy)_3^{2+}$,[9] $Ru(CN)_6^{4-}$,[10] Hg^0 (from disproportionation of Hg_2^{2+}),[11] and U^{4+}.[12] These reactions exhibit a remarkable variety of mechanistic behavior. The reactions with Ce(III), Mn(II), and Np(V) exhibit induction periods and autocatalysis, with rate laws independent of the metal ion, caused by the bromous acid reduction of bromate to give the reactive oxidant BrO_2.[1-3] The VO^{2+} reaction exhibits simple mixed-second-order kinetics but involves a disproportionation of bromous acid in competition with its reduction by VO^{2+}.[4] The reductions by V^{3+} and V^{2+} proceed in two consecutive steps with apparently complex mechanisms and were not studied completely.[6] The Fe^{2+} reduction follows simple mixed-second-order kinetics with a complex hydrogen ion dependence indicating the involvement of a binuclear steady-state intermediate.[7] The reactions with $Fe(CN)_6^{4-}$, $Fe(bpy)(CN)_4^{2-}$, $Fe(bpy)_2(CN)_2$, and $Ru(CN)_6^{4-}$ have both a direct path and an autocatalytic path caused by the Br^-–BrO_3^- reaction.[9] The $Fe(bpy)_3^{2+}$ reaction is also partially autocatalytic and involves reactions with both monomeric and dimeric Br(V) species.[9] The reactions with Hg^0 and U^{4+} follow simple kinetics, first-order in each reactant and possibly involve the transfer of two electrons.[11,12] We report here on the bromate oxidation of $IrCl_6^{3-}$, which also exhibits simple kinetics with no indication of complexities in the mechanism.

Experimental Section

The preparation and analysis of $HClO_4$,[13] $LiClO_4$,[13] and $NaBrO_3$[8] solutions and of $Na_3IrCl_6{\cdot}2H_2O$[14] have been described. Kinetics were determined under pseudo-first-order conditions with $[BrO_3^-]_0 \geq 5[IrCl_6^{3-}]_0$, such that $[BrO_3^-]$ varied by less than 4% during the course of the reaction. Ionic strength was maintained at 0.500 M by addition of $LiClO_4$. Temperature was maintained at 25.0 °C by circulating thermostated water through the cuvette holder. Components were thermostated prior to mixing and were placed in the cuvette holder at least 5 min prior to addition of the final reagent (usually $NaBrO_3$). Solid $Na_2IrCl_6{\cdot}2H_2O$ was added to the reaction solution and dissolved shortly before addition of the final reagent. The concentration was determined from the final absorbance attained at a wavelength of maximum absorbance for $IrCl_6^{2-}$.[15,16] Absorbance–time traces were obtained at 415 or 490 nm with a Varian Techtron 635 recording spectrophotometer and with a Gilford Model 240 spectrophotometer, equipped with a Varian A-25 recorder. Reaction solutions purged for 15 min with oxygen-free N_2[17] gave results identical with those obtained with air-saturated solutions, so most experiments were carried out in the presence of air.

Absorbance–time traces generally showed a small upward drift noticeable at the end of the reaction. This drift was not eliminated by using a completely independent set of reagents so it probably was not caused by an impurity. Solutions prepared by addition of Na_2IrCl_6 to BrO_3^- solutions showed very slow increases in absorbance. These increases were so small that quantitative comparisons could not be made however. Plots of log $(A_\infty - A_t)$ vs. time (where A = absorbance at the indicated time) were linear for several half-lives but showed upward curvature toward the end of the reaction. Most data were treated by the Guggenheim method,[18] with plots being linear for at least 3–4 half-lives. Where comparisons were possible, the two types of plots were in good agreement.

The stoichiometry was determined spectrophotometrically by addition of excess $IrCl_6^{3-}$ to an acidic BrO_3^- solution, giving a ratio of $[Ir(III)]/[Br(V)] = 5.84 \pm 0.06$. However, the kinetics were determined with BrO_3^- in excess, so the final product cannot be Br^- as these results would suggest but must be Br_2 since Br^- would react with BrO_3^- to give Br_2.[8] This was confirmed by addition of solid $Na_3IrCl_6{\cdot}2H_2O$ to an excess of BrO_3^-. The resulting solution was immediately extracted with CCl_4. The pale yellow extract was washed several times with deionized water and then reacted with aqueous sodium iodide, which changed the color of the CCl_4 layer to pink, confirming the presence of Br_2.

Results

Identification of Br_2 as the reaction product when BrO_3^- is present in excess over $IrCl_6^{3-}$ requires the stoichiometry

$$5IrCl_6^{3-} + BrO_3^- + 6H^+ = 5IrCl_6^{2-} + {}^1/_2Br_2 + 3H_2O \qquad (1)$$

The kinetics of this reaction were determined at 25.0 °C and 0.500 M ionic strength over the concentration ranges (0.4–8.0) × 10^{-4} M $IrCl_6^{3-}$, (0.3–40) × 10^{-3} M BrO_3^-, and 0.05–0.50 M H^+. Linear pseudo-first-order plots indicated the rate law

$$-d[IrCl_6^{3-}]/dt = k_1[IrCl_6^{3-}] \qquad (2)$$

Values of k_1 obtained for a variety of reactant concentrations are presented in Table I. Log–log plots[19] suggested that the reaction varied between zero- and first-order in $[BrO_3^-]$ and between zero- and second-order in $[H^+]$. Plots of k_1 vs. $[H^+]^2$ at constant $[BrO_3^-]$ were linear with intercepts independent of $[BrO_3^-]$ and slopes directly proportional to $[BrO_3^-]$, indicating the rate law

$$k_1 = k_0 + k_2[BrO_3^-][H^+]^2 \qquad (3)$$

The validity of this equation is confirmed by excellent linearity in a plot of k_1 vs. $[BrO_3^-][H^+]^2$, which is shown on a log–log scale in Figure 1. Least-squares analysis of all data in Table I gave the values $k_0 = (1.21 \pm 0.32) \times 10^{-3}$ s^{-1} and $k_2 = 50.8 \pm 0.4$ M^{-3} s^{-1}, which reproduce the observed values of k_1 with an average deviation of 6.5%.

Discussion

The minor term in the rate law, $k_0[IrCl_6^{3-}]$, is difficult to explain. It most probably originates from the very slow small absorbance increase superimposed on the absorbance–time traces for the BrO_3^-–$IrCl_6^{3-}$ redox reaction, but we have not been able to identify the chemical changes responsible. The rate constant $k_0 = 0.0012$ s^{-1} is too large by 2–3 orders of magnitude to be due to aquation of either $IrCl_6^{3-}$[20,21] or $IrCl_6^{2-}$,[22] and absorbance changes are in the wrong direction. Oxidation of bound chloride in $IrCl_6^{2-}$ by BrO_3^- is a possibility but a dependence on $[BrO_3^-]$, or possibly on $[Br_2]$,[23] would be expected. However, rate constants measured under conditions where the k_0 term made significant contributions indicated that this term is independent of $[BrO_3^-]$ and of $[Ir(III)]_0$ (and hence of $[Br_2]_\infty$). Photochemically induced reactions of $IrCl_6^{2-}$ are also possible[24,25] but would not be expected to be significant at the low light levels in the spectrophotometer. In any event, we do observe similar slow absorbance increases in $IrCl_6^{2-}$–BrO_3^- solutions, so this minor rate term probably is not directly involved in the mechanism for the redox reaction between $IrCl_6^{3-}$ and BrO_3^-.

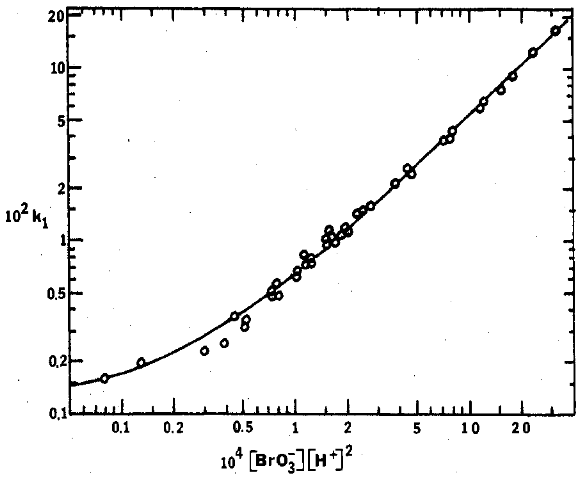

Figure 1. Plot of k_1 vs. $[BrO_3^-][H^+]^2$ on logarithmic scales. The line was calculated from eq 3 and the parameters given in the text.

The mechanism for the principal term in the rate law for the $IrCl_6^{3-}$–BrO_3^- reaction can be summarized as

$$BrO_3^- + 2H^+ \underset{}{\overset{K \ll 1}{\rightleftharpoons}} H_2BrO_3^+ \qquad (4)$$

$$IrCl_6^{3-} + H_2BrO_3^+ \xrightarrow{k_2'} IrCl_6^{2-} + H_2O + BrO_2 \qquad (5)$$

$$BrO_2 + 4IrCl_6^{3-} + 4H^+ \xrightarrow{\text{fast}} {}^1/_2Br_2 + 4IrCl_6^{2-} + 2H_2O \qquad (6)$$

Since the reaction was not partially or totally autocatalytic and complexities such as a dependence of the rate constant on the ratio $[BrO_3^-]_0/[Ir(III)]_0$ were not observed (as they were in the VO^{2+} reaction[4]), it is highly likely that eq 6 represents the stepwise reduction $BrO_2 \rightarrow HBrO_2 \rightarrow BrO \rightarrow HOBr \rightarrow Br_2$, involving the consumption of one $IrCl_6^{3-}$ in each step, rather than reactions between various bromine species. In this mechanism the observed parameter would then be given by $k_2 = 5k_2'K$ where the factor of 5 accounts for the consumption of 5 $IrCl_6^{3-}$ each time the rate-determining step (eq 5) occurs.

The rate laws for a large number of direct reductions of bromate ion by metal ion complexes can be accommodated by the equation

$$-d[BrO_3^-]/dt = (k + k_H[H^+]^2)[BrO_3^-][M^{n+}] \qquad (7)$$

Values for the parameters k and k_H at 25 °C are listed in Table II. We have speculated previously[8,9] that the parallel reactions of BrO_3^- and $H_2BrO_3^+$ (or BrO_2^+) may proceed by outer-sphere and inner-sphere mechanisms, respectively. However, rate correlations[9] based on Marcus theory[26] have

Table I. Rate Constants for the Reduction of BrO_3^- by $IrCl_6^{3-}$ at 25.0 °C and $I = 0.500$ M[a]

$10^3[BrO_3^-]$, M	$[H^+]$, M	$10^4[BrO_3^-]\cdot[H^+]^2$, M^3	10^2k_1, s^{-1} Obsd[b]	10^2k_1, s^{-1} Calcd[c]
3.00	0.500	7.50	3.86 ± 0.09 (4)	3.93
1.00	0.500	2.50	1.51 ± 0.05 (5)	1.39
0.800	0.500	2.00	1.12 ± 0.06 (8)	1.14
0.500	0.500	1.25	0.744 ± 0.036 (4)	0.756
0.300	0.500	0.750	0.510 ± 0.020 (2)	0.502
5.00	0.497	12.4	6.54	6.42
10.0	0.490	24.0	12.4	12.3
20.0	0.480	46.1	27.7	23.5
0.800	0.450	1.62	1.03 ± 0.08 (2)	0.944
0.500	0.450	1.01	0.66 ± 0.08 (2)	0.634
20.0	0.402	32.2	17.0 ± 0.2 (2)	16.5
5.00	0.402	8.08	4.36	4.23
3.00	0.397	4.73	2.44 ± 0.05 (3)	2.52
1.00	0.397	1.58	0.995 ± 0.005 (2)	0.924
0.800	0.397	1.26	0.780 ± 0.005 (4)	0.761
0.750	0.397	1.18	0.844 (2)	0.720
0.500	0.397	0.788	0.552 ± 0.023 (3)	0.521
20.0	0.301	18.1	9.00 ± 0.16 (2)	9.32
5.00	0.301	4.50	2.60	2.41
3.00	0.301	2.72	1.59 ± 0.07 (3)	1.50
0.800	0.301	0.752	0.489 ± 0.037 (4)	0.489
0.500	0.301	0.453	0.363	0.351
3.00	0.250	1.88	1.10 ± 0.02 (2)	1.08
2.50	0.250	1.56	1.06 (2)	0.913
40.0	0.198	15.7	7.28	8.10
30.0	0.198	11.8	5.87	6.12
20.0	0.198	7.84	3.85 ± 0.16 (2)	4.10
10.0	0.198	3.92	2.16 ± 0.06 (2)	2.11
5.00	0.198	1.96	1.19	1.12
4.00	0.198	1.57	0.984 ± 0.055 (2)	0.919
3.00	0.198	1.18	0.728 ± 0.011 (4)	0.720
2.00	0.198	0.784	0.465	0.519
1.00	0.198	0.392	0.249	0.320
10.0	0.150	2.25	1.43	1.26
7.50	0.150	1.69	1.17 ± 0.03 (2)	0.980
10.0	0.102	1.04	0.622 ± 0.009 (2)	0.649
5.00	0.102	0.520	0.354	0.385
20.0	0.100	2.00	1.13 ± 0.02 (3)	1.14
17.0	0.100	1.70	1.01 ± 0.01 (2)	0.985
3.00	0.100	0.300	0.225 ± 0.001 (2)	0.273
0.800	0.100	0.0800	0.160	0.161
20.0	0.051	0.520	0.310 ± 0.015 (2)	0.385
5.00	0.051	0.130	0.194	0.187

[a] $[IrCl_6^{3-}]_0 = (0.4\text{–}8.0) \times 10^{-4}$ M. [b] The uncertainties given are average deviations for a number (given in parentheses) of different determinations under the same conditions but with various $[IrCl_6^{3-}]_0$. [c] Calculated from $k_1 = 0.00121 + 50.8\cdot[BrO_3^-][H^+]^2$.

Table II. Values of k and k_H for the Reduction of BrO_3^- by Metal Ions at 25 °C[a]

Metal ion	k, M^{-1} s^{-1}	k_H, M^{-3} s^{-1}	Ionic strength, M	Ref
$Fe(CN)_6^{4-}$	0.00125	0.193	0.5 M	8
$Fe(bpy)(CN)_4^{2-}$	0.0062	0.227	0.5	9
$Fe(bpy)_2(CN)_2$	0.0295	0.755	0.5	9
$Fe(bpy)_3^{2+}$	⩽0.0042[b]	⩽0.15[b]	0.5	9
Fe^{2+}	0.372	*c*	0.5	7
VO^{2+}	4.93		2.0	4
U^{4+}	12.5	3.2	2.0	12
Hg^0	3.7[d]	2.0[d]	1.0	11
$IrCl_6^{3-}$		10.2	0.5	This work

[a] The parameters k and k_H are defined in eq 7. [b] Estimated values; the reaction follows a different rate law. [c] Another term with a complex $[H^+]$ dependence was also observed. [d] Corrected for disproportionation of Hg_2^{2+}.

suggested that both terms in the rate law are probably due to outer-sphere mechanisms for the Fe(II) complexes listed as the first four entries in Table II. The consistency of the k_H values, which vary by only a factor of about 60 while the k values vary by 4 orders of magnitude, is certainly suggestive of a common feature in all these mechanisms. This again supports the possbility of an inner-sphere mechanism for the k_H path with rate-limiting displacement of water. However, the oxygen-exchange rate, if expressed in terms of eq 7 with $M^{n+} = H_2O$, gives $k_H \approx 8 \times 10^{-5}$ M^{-3} s^{-1} as a limiting rate of substitution.[27] Another possibility is that the species $H_2BrO_3^+$ is so reactive with respect to reduction that its reactions are essentially diffusion-controlled outer-sphere processes, thus requiring that K be about 10^{-9}–10^{-11} M^{-2}, which is quite reasonable. In fact, if one uses the rule of thumb that an oxy acid of formula $XO_2(OH)$ has a first dissociation constant of about 10^3 M and that successive dissociation constants decrease by about a factor of 10^{-5}, then the formation constant of $H_2BrO_3^+$ would be estimated to be 10^{-3} $M^{-1} \times 10^{-8}$ $M^{-1} = 10^{-11}$ M^{-2}, in good agreement with the value required for diffusion-controlled redox reactions of $H_2BrO_3^+$ with metal ions.

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Registry No. BrO_3^-, 15541-45-4; $IrCl_6^{3-}$, 14648-50-1.

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Synthesis and Characterization of Some New Complexes of the Mo_2^{4+} Ion

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Complexes of the quadruply bonded Mo_2^{4+} ion often undergo ligand substitution without disruption of the metal–metal

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