# Kinetics of Oxidation of Transition-metal Ions by Halogen Radical Anions. Part II.[1] The Oxidation of Cobalt(II) by Dichloride Ions Generated by Flash Photolysis

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The radical anion $Cl_2^-$, generated by flash photolysis of solutions containing $Cl_3^-$, oxidizes cobalt(II) to cobalt(III). At 25 °C and $I$ = 0·3M, the rate constant is $(1{\cdot}4 \pm 0{\cdot}2) \times 10^6$ l mol$^{-1}$ s$^{-1}$ ($\Delta H^‡ = 29 \pm 4$ kJ mol$^{-1}$ and $\Delta S^‡ = -31 \pm 10$ J K$^{-1}$ mol$^{-1}$). The reaction is inner sphere–substitution controlled, the initial product being $CoCl^{2+}$ which is not labile on the time scale of the oxidation reaction.

THE oxidation of halide ions to halogens and the reduction of halogens to halide ions take place in one electron-transfer steps and the radical ions $X_2^-$ (X = Cl, Br, or I) are important intermediates in these reactions. Rate constants (*ca.* $10^{10}$ l mol$^{-1}$ s$^{-1}$) and equilibrium constants ($\geqslant 10^5$ l mol$^{-1}$) for equilibrium (1) (X = Cl, Br, or I) are sufficiently large that halogen atoms are not normally the reactive intermediates in halogen redox reactions. The radical anions $Br_2^-$ and $Cl_2^-$ are intermediates in the oxidation of $Br^-$ by $Mn^{3+}$ (ref. 2) and $Co^{3+}$,[3] of $Cl^-$ by $Co^{3+}$,[4,5] and in the reduction of

$$X + X^- \rightleftharpoons X_2^- \qquad (1)$$

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$Cl_2$, $Br_2$, and $I_2$ by $V^{2+}$.[6] Oxidation of the metal ion in oxidation state II by the halogen radical ion has been proposed, but not directly demonstrated, in these systems. Oxidations of ligands by metal ions have been extensively investigated,[7] but comparatively few ligand reductions by metal ions are known. The oxidation of the complex Co(*trans*-[14]diene)$^{2+}$ (*trans*-[14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene) by halogen radical ions has recently been reported.[8]

In Part I of this series [1] it was shown that the oxidation of $Fe^{2+}$ by $Br_2^-$ occurs through an inner sphere–substitution controlled mechanism, but that the oxidation of $Fe^{2+}$ by $Cl_2^-$ takes place by both inner- and outer-sphere paths at 25 °C. The present work establishes the importance of the reaction of $Cl_2^-$ with $Co^{2+}$ in the oxidation of $Cl^-$ by $Co^{3+}$ and suggests that, for transition-metal ions with high substitution rates, the rate of metal–ligand electron-transfer reactions is controlled by the substitution rate. The ions $Fe^{2+}_{aq}$ and $Co^{2+}_{aq}$ have approximately the same substitution rates ($10^6$—$10^7$ l mol$^{-1}$ s$^{-1}$) and, although the free-energy changes for oxidation by $Cl_2^-$ differ by 104 kJ mol$^{-1}$, both reactions are inner sphere–substitution controlled.

## EXPERIMENTAL

Solutions of $Co^{II}$ were prepared from the perchlorate (Fluka) and were standardized by electrodeposition. AnalaR sodium halide salts were used to prepare the halide-ion solutions. Acid concentrations and ionic strengths of the solutions were adjusted with perchloric acid (AnalaR) and sodium perchlorate (Fluka). Chlorine used in the preparation of solutions of $Cl_3^-$ was prepared by the oxidation of sodium chloride (AnalaR) and was vacuum distilled. The hydrogen peroxide used was inhibitor-free (Laporte). All other materials were of AnalaR grade purity. Solutions were prepared in water distilled from alkaline potassium permanganate and acidified potassium dichromate.

The flash-photolysis apparatus and experimental procedure have been described previously.[1] In the kinetic experiments the change in concentration of the radical ion with time was recorded as the change in absorbance at 366 nm. At least three oscilloscope traces were analysed for each set of experimental conditions. Preliminary experiments showed that the reactions of the radical ions were not affected by the presence or absence of dissolved oxygen in the solutions and most experiments were carried out on aerated solutions. When the metal ions reacted with the radical anions reaction (2) competed with disproportionation (3), and the rate of disappearance of $Cl_2^-$ was given by equation (4). The metal-ion concentration was very much greater than that of the radical anion and the reaction of $Co^{II}$ with $Cl_2^-$ was pseudo-first order.

$$Cl_2^- + Co^{II} \xrightarrow{k'} Co^{III} + 2Cl^- \qquad (2)$$

$$Cl_2^- + Cl_2^- \xrightarrow{k''} Cl_3^- + Cl^- \qquad (3)$$

$$-d[Cl_2^-]/dt = k'[Co^{II}][Cl_2^-] + k''[Cl_2^-]^2 \qquad (4)$$

The rate of disappearance of $Cl_2^-$ was mixed first and second order and the pseudo-first-order rate constants were calculated using a numerical integration procedure and the separately measured rate constant for the disproportionation.[1]

*Production of* $Cl_2^-$ *Radical Anions*.—The radical anion $Cl_2^-$ was produced by flash photolysis of trichloride ions [9] in most of the experiments. This eliminated kinetic complications caused by reaction of the metal ions with $e^-_{aq}$ to produce $Co^+$ when the radical anions were produced by photolysis of halide ions.[10] Flash photolysis (with light from the flash lamp filtered to eliminate wavelengths <220 nm) of solutions containing $Cl_3^-$ produced 10μM concentrations of $Cl_2^-$ in the presence of $Co^{II}$ [reactions (5) and (1) (X = Cl)]. The concentrations of halide ion, halogen, and acid in equilibrium with the trihalide ion were chosen to minimize the equilibrium concentrations of hypohalite ion in the solutions. Photolysis of hypohalite ions [11] produces hypohalite radicals which interfere with the reactions of the radical anions.

$$Cl_3^- \xrightarrow{h\nu} Cl_2^- + Cl \qquad (5)$$

In experiments in which the absorbance of the halogen or trihalide ion interfered with measurement of the spectra of reactants or products, OH radicals were used to produce the radical ions. Flash photolysis of $10^{-3}$M-$H_2O_2$ solutions containing halide ions produced 20μM concentrations of the OH radical [equation (6)], which reacted with chloride ion * to produce the radical ion [reactions (7) and (1) (X = Cl)]. The ratio of the concentration of the halide ion to that of the cobalt(II) ion was kept high in these solutions to minimize reaction of the OH radicals with $Co^{II}$. The hydrogen peroxide concentration was sufficiently low for reaction (8) not to interfere. Hydrogen peroxide solutions were not used in the kinetic studies because of the reaction between the radical anions and hydrogen peroxide.

$$H_2O \xrightarrow{h\nu} 2OH \qquad (6)$$

$$OH + Cl^- \longrightarrow OH^- + Cl \qquad (7)$$

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \qquad (8)$$

## RESULTS

The standard reduction potential of $Br_2^-$ is estimated to be +1·77 V, just smaller than that of $Co^{3+}_{aq}$ (+1·85 V), and the equilibrium constant for reaction (9) is *ca.* 5 × $10^{-2}$ mol l$^{-1}$. There was no evidence of reaction between $Br_2^-$ and $Co^{2+}_{aq}$ after flash photolysis of solutions containing

$$Br_2^- + Co^{2+}_{aq} \longrightarrow Co^{III} + 2Br^- \qquad (9)$$

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* The reaction between OH and $Cl^-$ to produce $Cl_2^-$ is more complex than we have represented it,[12] but at our $Cl^-$ and $H^+$ concentrations the stoicheiometry is that given by the equations and the half-lives for $Cl_2^-$ formation were less than 1μs.

[6] J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, 1969, **8**, 1407.

[7] A. McAuley, *Co-ordination Chem. Rev.*, 1970, **5**, 245; 'Inorganic Reaction Mechanisms,' ed. J. Burgess, Specialist Periodical Report, The Chemical Society, London, 1971, vol. 1, p. 30.

[8] S. D. Malone and J. F. Endicott, *J. Phys. Chem.*, 1972, **76**, 2223.

[9] L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, 1957, **61**, 1089.

[10] A. T. Thornton and G. S. Laurence, *Chem. Comm.*, 1970, 443.

[11] N. K. Bridge and M. S. Matheson, *J. Phys. Chem.*, 1960, **64**, 1280.

[12] M. Anbar and J. K. Thomas, *J. Phys. Chem.*, 1964, **68**, 3829.

*ca.* $3 \times 10^{-5}$M-$Br_3^-$ ($10^{-1}$M-$Br^-$, $5 \times 10^{-5}$M-total $Br_2$, and $10^{-1}$M-$H^+$) and $10^{-1}$M-$Co^{2+}$. Within experimental error (±5%), the rate of disappearance of $Br_2^-$ was the same in these solutions as that in solutions of the same ionic strength which contained no cobalt(II). The disproportionation reactions of the halogen radical anions have rate constants of *ca.* $5 \times 10^9$ l $mol^{-1}$ $s^{-1}$ and set limits to reactions of the radical anions with substrates which can be studied. The rate of the reaction must be $>10^4$ l $mol^{-1}$ $s^{-1}$ and the reaction must have an equilibrium constant large enough to ensure that an appreciable fraction of the radical anions is consumed at equilibrium. Our failure to observe reaction between $Br_2^-$ and $Co^{2+}$ is probably due to the unfavourable equilibrium constant. No reaction could be detected between $I_2^-$ ($E^0$ +1·0 V) and $Co^{2+}$.

The radical ion $Cl_2^-$ reacts with $Co^{2+}_{aq}$ [equation (10)].

$$Cl_2^- + Co^{2+}_{aq} \longrightarrow Co^{III} + 2Cl^- \qquad (10)$$

The rate of disappearance of $Cl_2^-$ after flash photolysis of $Cl_3^-$ increased when $Co^{2+}$ was present in the solutions and a transient absorbance at 270 nm was observed after the $Cl_2^-$ absorbance had decayed. The spectrum of the transient was measured in solutions in which $Cl_2^-$ was generated by flash photolysis of $H_2O_2$–$Cl^-$ mixtures ($10^{-3}$M-$H_2O_2$, $10^{-1}$M-$Cl^-$, and $10^{-1}$M-$H^+$). The cobalt(II) concentration in the solutions was $10^{-1}$M and the half-life of the $Cl_2^-$ radical ion was *ca.* 10 μs. The transient spectrum, 100 μs after the flash, is shown in Figure 1. The ratio of the chloride- to the cobalt-ion concentrations ensured that less than 1% of the OH radicals generated by photolysis of $H_2O_2$ reacted with $Co^{2+}$. When solutions of $H_2O_2$ ($10^{-3}$M) and $Co^{2+}$ ($10^{-1}$M) without chloride ion were flashed, a weaker transient absorbance was observed at shorter wavelengths. This was produced by the reaction between the OH radicals and $Co^{2+}$ [equation (11)] and the spectrum

$$OH + Co^{2+}_{aq} \longrightarrow Co^{III} + OH^- \qquad (11)$$

of the aquocobalt(III) product is compared with the spectrum of $Co^{3+}_{aq}$ in Figure 1.

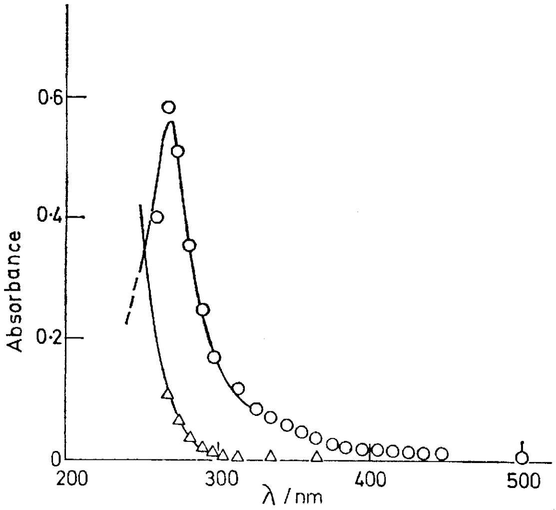

FIGURE 1 Spectra of the products of the reactions of $Co^{2+}$ with $Cl_2^-$ and OH taken 100 μs after the flash: (○), product of the flash photolysis of solutions containing $10^{-3}$M-$H_2O_2$, $10^{-1}$M-$Cl^-$, $10^{-1}$M-$H^+$, and $10^{-1}$M-$Co^{II}$ (the solid line represents the spectrum of $CoCl^{2+}$ normalized to our absorbance at 270 nm); (△), product of the flash photolysis of solutions containing $10^{-3}$M-$H_2O_2$, $10^{-1}$M-$H^+$, and $10^{-1}$M-$Co^{II}$ (the solid line represents the spectrum of $Co^{3+}$)

The transient absorbance which results from the reaction of $Cl_2^-$ and $Co^{2+}_{aq}$ is due to the cobalt(III) chloro-complex $CoCl^{2+}$. The spectrum of $CoCl^{2+}$ has been measured in stopped-flow experiments[13] but the absorption coefficients are not known. The stopped-flow spectrum normalized to our absorbance value at 300 nm is included in Figure 1, and the spectra are clearly the same. Assuming a 1 : 1 stoicheiometry between the yields of $Cl_2^-$ and $CoCl^{2+}$ in our experiments, the absorption coefficient of $CoCl^{2+}$ at the absorption maximum (270 nm) is 5000 ± 2000 l $mol^{-1}$ $cm^{-1}$. The main contribution to the error in the absorption coefficient is the difficulty of determining the initial $Cl_2^-$ yield under conditions in which the half-life of $Cl_2^-$ was 10 μs.

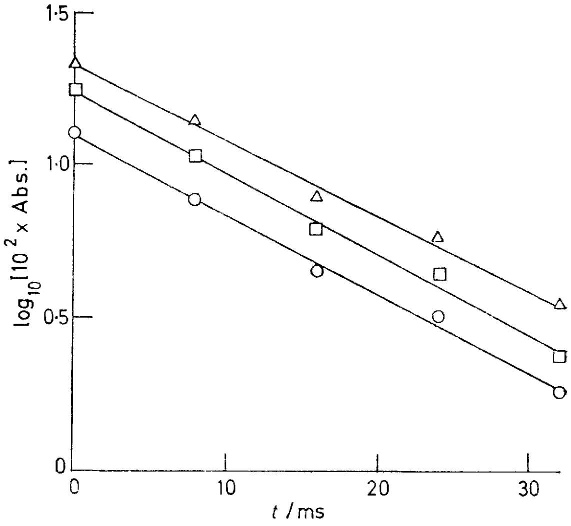

FIGURE 2 Relaxation kinetics of $CoCl^{2+}$ formed by the reaction of $Co^{2+}$ and $Cl_2^-$ at 25 °C. The solutions contained $10^{-3}$M-$H_2O_2$, $10^{-1}$M-$Cl^-$, $10^{-1}$M-$H^+$, and $10^{-1}$M-$Co^{II}$ at $I = 0·5$M and (△), 297, (□), 303, and (○), 313 nm

The $CoCl^{2+}$ absorbance decayed with first-order kinetics and plots of log (Absorbance) against time are shown in Figure 2. The first-order rate constant in $10^{-1}$M-$Cl^-$ and $10^{-1}$M-$H^+$ at 25 °C and $I = 0·44$M was 59 ± 2 $s^{-1}$. This value is in excellent agreement with the rate of approach to equilibrium of reaction (12) under the same conditions,

$$Co^{3+}_{aq} + Cl^- \rightleftharpoons CoCl^{2+} \qquad (12)$$

57 $s^{-1}$, calculated from the results of McAuley *et al.*[13] The reduction of $Co^{III}$ by chloride ion is very much slower in these solutions.

The presence of $CoCl^{2+}$ less than 100 μs after the flash, and the decay of $CoCl^{2+}$ by reaction (12), prove that $CoCl^{2+}$ and not $Co^{3+}_{aq}$ is the initial product of the reaction between

$$Cl_2^- + Co^{2+}_{aq} \xrightarrow{k_{13}} CoCl^{2+} + Cl^- \qquad (13)$$

$Cl_2^-$ and $Co^{2+}_{aq}$. If the initial product was $Co^{3+}_{aq}$, $CoCl^{2+}$ could only be formed by reaction (12), with a half-life of *ca.* 10 ms under our conditions. Because initially all the cobalt(III) produced by reaction (13) is in the form of $CoCl^{2+}$, we observe the dissociation of $CoCl^{2+}$ until the equilibrium concentration is reached.

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[13] A. McAuley, M. N. Malik, and J. Hill, *J. Chem. Soc.* (*A*), 1970, 2461.

The rate of reaction (13) was studied in solutions in which $Cl_2^-$ was generated by flash photolysis of $Cl_3^-$. The solutions contained *ca.* $10^{-4}$M-$Cl_3^-$ ($10^{-1}$M-$Cl^-$, $5 \times 10^{-3}$M-$Cl_2$, and $10^{-1}$M-$H^+$) and the cobalt(II) concentration was varied from $10^{-2}$ to $5 \times 10^{-2}$M. The kinetics of the $Cl_2^-$ decay were mixed first and second order because of competition between the pseudo-first-order reaction (13) ($[Co^{2+}] \gg [Cl_2^-]$) and the second-order disproportionation of $Cl_2^-$. Pseudo-first-order rate constants obtained for reaction (13) are plotted against cobalt(II) concentration in Figure 3. The rate constants are a good linear function of the cobalt(II) concentration and the plot shows no curvature even at the highest cobalt(II) concentrations. The second-order rate constant for reaction (13), $k_{13}$, calculated from the gradient in Figure 3 is $(1{\cdot}4 \pm 0{\cdot}2) \times 10^6$ l mol$^{-1}$ at 25 °C. The temperature dependence of $k_{13}$ was determined by measuring the rate constants at constant $Co^{II}$ concentration and several temperatures. Second-order rate constants are given in Table 1 together with the activation parameters.

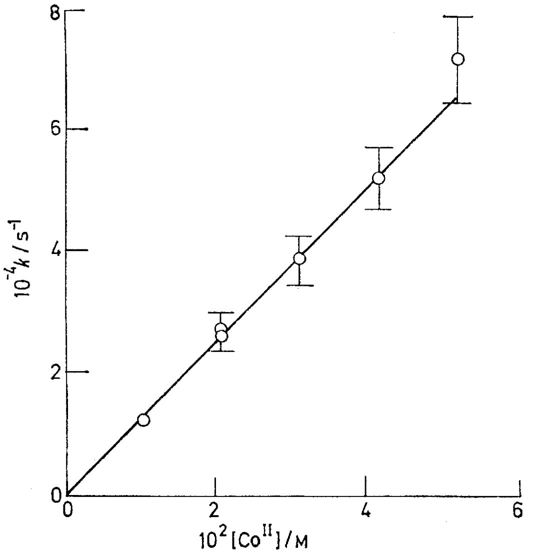

FIGURE 3 Dependence of the pseudo-first-order rate constant for the reaction of $Co^{2+}$ and $Cl_2^-$ on the $Co^{II}$ concentration, at 25 °C. The solutions contained *ca.* $10^{-4}$M-$Cl_3^-$ ($10^{-1}$M-$Cl^-$, $5 \times 10^{-2}$M-$Cl_2$, and $10^{-1}$M-$H^+$) and $I = 0{\cdot}3$M

TABLE 1

Rate constants for the reaction $Cl_2^- + Co^{2+} \longrightarrow CoCl^{2+} + Cl^-$ at 0·1M-$HClO_4$ and $I = 0{\cdot}3$M

| Temp./°C | 13·5 | 22·0 | 31·5 | 41·5 |
|---|---|---|---|---|
| $10^{-6}k$/l mol$^{-1}$s$^{-1}$ | 0·82±0·1 | 1·29±0·1 | 1·80±0·2 | 2·16±0·2 |

$\Delta H^{\ddagger} = 29 \pm 4$ kJ mol$^{-1}$ $\Delta S^{\ddagger} = -31 \pm 10$ J K$^{-1}$ mol$^{-1}$

## DISCUSSION

The observation that $CoCl^{2+}$ is the primary reaction product in the oxidation of $Co^{2+}_{aq}$ by $Cl_2^-$ proves that this reaction, like those between $Fe^{2+}_{aq}$ and halogen radical anions, is inner sphere, and there was no evidence of an outer-sphere path. We were unable to distinguish between inner sphere–substitution controlled and inner sphere–electron-transfer controlled mechanisms by direct experimental observation, but the intimate mechanism may be inferred from the rate constant and activation enthalpy. The rate constant $k_{13}$ is $1{\cdot}4 \times 10^6$ l mol$^{-1}$ s$^{-1}$ at 25 °C and the water-exchange rate[14] for $Co^{2+}_{aq}$ is *ca.* $2 \times 10^6$ s$^{-1}$. Substitution at $Co^{2+}_{aq}$ and other bivalent transition-metal ions is essentially controlled by the rate of loss of water from the first co-ordination sphere, and the substitution rate will be of the same order of magnitude as the water-exchange rate. The activation enthalpy for water exchange has been measured several times and the values cover a range of 12 kJ mol$^{-1}$. The value of 43 kJ mol$^{-1}$ obtained in two different laboratories[14,15] is probably the most reliable. For the inner sphere–substitution controlled reaction between $Br_2^-$ and $Fe^{2+}_{aq}$ the activation enthalpy is also *ca.* 10 kJ mol$^{-1}$ smaller than the activation enthalpy for water exchange on the metal ion. If the inner-sphere reaction is electron-transfer controlled, the activation enthalpy must be greater than that for substitution. We conclude therefore that the $Co^{2+}_{aq}$–$Cl_2^-$ reaction is definitely substitution controlled.

The inner-sphere reactions of $Cl_2^-$ with $Fe^{2+}_{aq}$ and $Co^{2+}_{aq}$ are both substitution controlled despite the 108 kJ mol$^{-1}$ difference in the overall free-energy changes for the reactions. A parallel outer-sphere path of lower activation energy was found in the $Fe^{2+}_{aq}$–$Cl_2^-$ system.[1] The influence of the free-energy change for the reaction is much larger for outer- than for inner-sphere oxidations and an outer-sphere mechanism cannot compete with the inner-sphere path for the $Co^{2+}$–$Cl_2^-$ reaction.

Unlike the oxidation of $Fe^{II}$ to $Fe^{III}$, the oxidation of $Co^{II}$ (high spin) to $Co^{III}$ (low spin) must involve a change in spin multiplicity. The lifetime of the $Co^{III}$ transition involving the change of spin multiplicity is however short enough (<10 μs) for this not to be the rate-determining process. In the reduction of $Co(bipy)_3^{3+}$ (bipy = 2,2′-bipyridine) by $e^-_{aq}$ a transient intermediate with a lifetime of *ca.* $10^{-4}$ s was identified[16] as an excited ($t_{2g}^6e_g^1$) state of $Co(bipy)_3^{2+}$. We find that the spectrum of the $CoCl^{2+}$ product of reaction (13), 50 μs after the flash, is identical with the spectrum of ground-state $CoCl^{2+}$ (Figure 1) formed by the reaction of $Co^{3+}$ with $Cl^-$. Our results suggest that changes in the spin multiplicity of cobalt are not necessarily a barrier to rapid electron transfer. The reactions of $Cl_2^-$, $Br_2^-$, and $I_2^-$ with the complex Co(*trans*-[14]-diene)$^{2+}$ (*trans*-[14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene) are very fast ($10^9$—$10^{10}$ l mol$^{-1}$ s$^{-1}$) and both the $Co^{II}$ and $Co^{III}$ complexes are low spin. Malone and Endicott[8] did not definitely distinguish between inner- and outer-sphere mechanisms for the Co(*trans*-[14]diene)$^{2+}$ oxidations. The rate of exchange of $H_2O$ in the axial positions is likely to be very high. The rate of water exchange for $Ni^{II}$ and $Co^{II}$ complexes increases rapidly as the number of water molecules co-ordinated to the

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[14] J. P. Hunt, *Co-ordination Chem. Rev.*, 1971, **7**, 1.

[15] A. M. Chmelnik and D. Fiat, *J. Chem. Phys.*, 1967, **47**, 3986.

[16] W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, 1969, **73**, 1941.

metal decreases[14] and may be as large as $10^9$ s$^{-1}$ for the complex Co(*trans*-[14]diene)$^{2+}$. The rates of oxidation of the Co(*trans*-[14]diene)$^{2+}$ complex by the halogen radical anions are almost independent of the reduction potentials of the latter, and the rates of the $Co^{2+}$–$Cl_2^-$ and Co(*trans*-[14]diene)$^{2+}$–$I_2^-$ reactions (for which the overall free-energy changes are the same) differ by three orders of magnitude. The halogen radical anions must react with both Co(*trans*-[14]diene)$^{2+}$ and $Co^{2+}_{aq}$ by a common inner sphere–substitution controlled mechanism.

We have estimated the standard reduction potentials for reactions involving the radical anions $Cl_2^-$, $Br_2^-$, and $I_2^-$ from the standard free energies of formation of the halide ions,[17] the free energies of hydration of the appropriate inert gases, and the equilibrium constants[18] for the reaction (1) (X = Cl, Br, or I). After this work was completed Malone and Endicott published similar estimates.[8] We have checked our estimates against available kinetic data. The combination of our data for the rate of the $Co^{II}$–$Cl_2^-$ reaction with the rate of the reverse reaction (the reduction of $Co^{III}$ by $Cl^-$) confirms the estimate of $E^0$, +2·3 V, for the reduction of $Cl_2^-$. The estimate of $E^0$ for the reduction of $Br_2^-$, +1·8 V, agrees with the value obtained by combining the rate of reduction[2] of $Mn^{III}$ by $Br^-$ with the rate constant for oxidation[19] of $Mn^{II}$ by $Br_2^-$. Recent reduction potentials for $Cl_2^-$, $Br_2^-$, and $I_2^-$, obtained by a combination of pulse radiolysis and polarography in solutions of halide ions[20] cannot be reconciled with the experimental observations of the oxidations of metal ions by the halogen radical anions.

The standard reduction potential of the hydroxyl radical has been estimated to be +2·0 V in basic solution,[21] and recent investigations of the equilibria between OH and the halide ions allow the reduction potentials of $Cl_2^-$ and $Br_2^-$ to be calculated in terms of $E^0$ for OH. The equilibrium constant for reaction (15)

$$OH + e^- \longrightarrow OH^- \qquad (14)$$

$$OH + 2Cl^- \rightleftharpoons OH^- + Cl_2^- \qquad (15)$$

has been measured[18a] and is $10^{-5}$ l mol$^{-1}$. Equilibrium constants for reactions (16) and (17) involving OH and $Br^-$ in basic solution have been measured by Behar.[22]

$$OH + Br^- \rightleftharpoons BrOH^- \quad K = 2{\cdot}9 \times 10^3 \text{ l mol}^{-1} \qquad (16)$$

$$BrOH^- + Br^- \rightleftharpoons OH^- + Br_2^- \quad K = 3{\cdot}7 \qquad (17)$$

Using these equilibrium constants the standard reduction potentials of $Cl_2^-$ and $Br_2^-$ are +2·3 and +1·8 V, again in agreement with the estimated values in Table 2.

The reaction between $Co^{II}$ and $Cl_2^-$ accounts for the retardation by $Co^{II}$ of the rate of reduction of $Co^{3+}$ by $Cl^-$. The scheme is reaction (12) followed by reactions (18) and (19). The dependence of the overall rate on the $Co^{II}$ concentration is complex and the reaction is not integral order in $Cl^-$.

TABLE 2

Standard reduction potentials involving halogen radical anions

| Reaction | X = Cl | Br | I |
|---|---|---|---|
| $X + e^- \rightleftharpoons X^-$ | +2·59 | +2·08 | +1·31 |
| $X_2 + e^- \rightleftharpoons 2X^-$ | +2·29 | +1·77 | +1·00 |
| $X_2 + e^- \rightleftharpoons X_2^-$ | +0·43 | +0·41 | +0·06 |
| $\frac{1}{2}X_2 + e^- \rightleftharpoons X^-$ | +1·36 | +1·09 | +0·53 |

Values (in volts), estimated from available thermodynamic data, are considered to be within ±0·05 V of the true values. For $Cl_2^-$ and $Br_2^-$, values calculated using independent kinetic data agree with those in the Table to within ±0·05 V.

$$CoCl^{2+} + Cl^- \rightleftharpoons Co^{II} + Cl_2^- \qquad (18)$$

$$Co^{3+} + Cl_2^- \longrightarrow Co^{II} + Cl_2 \qquad (19)$$

The overall second-order rate constant[5] for the reduction of $Co^{III}$ at 25 °C and 1M-$H^+$ is 1·3 l mol$^{-1}$ s$^{-1}$ and at this temperature the rate constant[13] for formation of $CoCl^{2+}$ is 35 l mol$^{-1}$ s$^{-1}$. The equilibrium constant at 25 °C is 31 l mol$^{-1}$ and at the low $Cl^-$ concentrations used by Sramkova *et al.*[5] the rates of reaction (12) and (18) are comparable. A full kinetic analysis suggests that the reason for the apparent limit to the retardation due to $Co^{II}$, reached at $Co^{II}$ concentrations of *ca.* $10^{-2}$M, is not the proposed formation of $Co^{II}$ chloro-complexes ($K_{CoCl^+}$ *ca.* 0·3 l mol$^{-1}$)[23] but that reaction (19) can become rate determining as the $Co^{II}$ concentration is increased. Although the measured rate constant for the $Co^{III}$ reduction cannot be simply identified with that for the reverse of reaction (13), the rate of this reaction must be within a factor of 10 of 1·3 l mol$^{-1}$ s$^{-1}$ in order to account for the observed chloride-ion dependence. We can therefore estimate $E^0$ for the reduction of $Cl_2^-$ by combining this rate constant with our rate constant for reaction (13) ($k_{13} = 1{\cdot}4 \times 10^6$ l mol$^{-1}$ s$^{-1}$) and the standard reduction potential for $Co^{3+}_{aq}$, +1·85 V. The standard reduction potential for $Cl_2^-$ calculated in this way is +2·2 ± 0·06 V, in excellent agreement with the value estimated from thermodynamic data, +2·3 V.

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