Kinetics of Oxidation of Transition-metal Ions by Halogen Radical Anions. Part IV.[1] The Oxidation of Vanadium(II) and Chromium(II) by Di-iodide, Dibromide, and Dichloride Ions Generated by Pulse Radiolysis

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The radical ions I_2^-, Br_2^-, and Cl_2^-, generated by nanosecond pulse radiolysis of solutions containing the halide ions, oxidise vanadium(II) to vanadium(III) and chromium(II) to chromium(III). At 22 ± 3 °C and $I = 0{\cdot}5$ mol l^{-1} rate constants for the reactions $X_2^- + V^{2+}{}_{aq} \longrightarrow V^{3+}{}_{aq} + 2X^-$ are $(1{\cdot}43 \pm 0{\cdot}2) \times 10^8$, $(1{\cdot}48 \pm 0{\cdot}2) \times 10^9$, and $(1{\cdot}95 \pm 0{\cdot}2) \times 10^9$ l mol^{-1} s^{-1} (X = I, Br, and Cl) and the reaction mechanism is outer sphere in all cases. Corresponding rate constants for the reactions $X_2^- + Cr^{2+}{}_{aq} \longrightarrow [Cr(OH_2)_5X]^{2+} + X^-$ are $(1{\cdot}5 \pm 0{\cdot}2) \times 10^9$, $(1{\cdot}9 \pm 0{\cdot}2) \times 10^9$, and $(2{\cdot}4 \pm 0{\cdot}3) \times 10^9$ l mol^{-1} s^{-1}. The reaction mechanisms were established by gamma-radiolysis and flash-photolysis experiments. The reaction between the ions Cl_2^- and $Cr^{2+}{}_{aq}$ proceeds by parallel inner- and outer-sphere paths with approximately equal probability. The radical ions I_2^- and Br_2^- react with $Cr^{2+}{}_{aq}$ ions entirely by inner-sphere paths.

OXIDATIONS of transition-metal ions by the halogen radical anions X_2^- (X = I, Br, or Cl) are particularly simple examples of one-electron oxidation by ligands. For the ions $Mn^{2+}{}_{aq}$ and $Co^{2+}{}_{aq}$ an inner-sphere reaction path is preferred,[1,2] but oxidation of $Fe^{2+}{}_{aq}$ by Cl_2^- ions takes place by parallel inner- and outer-sphere paths.[3] Rates of substitution are approximately the same for the ions $Mn^{2+}{}_{aq}$, $Fe^{2+}{}_{aq}$, and $Co^{2+}{}_{aq}$, and standard free energies of the reactions with X_2^- ions range from −147 ($Fe^{2+} + Cl_2^-$) to −21 kJ mol^{-1} ($Mn^{2+} + Br_2^-$). The reactions of the ions $V^{2+}{}_{aq}$ and $Cr^{2+}{}_{aq}$ with X_2^- extend the range of parameters (substitution rate and standard free energy of reaction) likely to influence the rates and mechanisms of metal-ion oxidations by these ligands. Substitution rates of $V^{2+}{}_{aq}$ and $Cr^{2+}{}_{aq}$ ions are *ca.* 10^2 and $>10^9$ l mol^{-1} s^{-1} respectively and the standard free-energy change for reaction of the ions Cr^{2+} and Cl_2^- is −263 kJ mol^{-1}.

The halogen radical anions are possible intermediates in the reduction of halogen or trihalide ions by V^{2+} and Cr^{2+} ions. A rapid reaction between free halogen atoms (which would in fact be present as X_2^-) and V^{2+} ions was proposed in the oxidation of V^{2+} by I_2 and Br_2.[4] Direct evidence of this reaction mechanism was not obtained but activation enthalpies were lower than for substitution reactions of $V^{2+}{}_{aq}$ ions. Bromine and iodine oxidise $Cr^{2+}{}_{aq}$ ions by inner-sphere reactions,[5] the products being $[Cr(OH_2)_5Br]^{2+}$ and $[Cr(OH_2)_5I]^{2+}$. With chlorine as oxidant both $[Cr(OH_2)_5Cl]^{2+}$ and $Cr(OH_2)_6{}^{3+}$ are produced.[5,6] The kinetic paths for these reactions have not been established and the role of the halogen radical ions in determining the reaction mechanism is not known.

EXPERIMENTAL

Solutions of V^{II} in perchloric acid were prepared from V^{IV} solutions by reduction with zinc amalgam. The V^{IV} solutions were prepared by dissolving V_2O_5 in 1M-NaOH, acidifying with 1M-$HClO_4$, and reducing to V^{IV} with SO_2. The acid concentration in V^{IV} solutions was determined with a pH meter using calibrating solutions of known acid concentration (*ca.* 0·1M) and ionic strength (adjusted with $NaClO_4$). Acid concentration in V^{II} solutions was calculated by assuming that the only change in $[H^+]$ on reduction was that due to formation of V^{II}. Acid concentrations may therefore be uncertain by up to 5%. Solutions of Cr^{II} in perchloric acid were prepared by reducing solutions of Cr^{III} perchlorate (G. F. Smith) with zinc amalgam. The acid concentration in Cr^{III} solutions was determined in the same way as in V^{IV} solutions. Acid concentration in Cr^{II} solutions was calculated from that in Cr^{III} solutions by assuming that 1 mole of H^+ ion was consumed in reduction of each mole of Cr^{III}. We have shown previously that Zn^{2+} ion added to the solutions by the reduction with zinc amalgam does not react with halogen radical anions.[3]

The reductions of V^{IV} and Cr^{III} were carried out on degassed solutions by shaking with zinc amalgam in glass syringes (20 or 50 cm^3) fitted with B5 capillary cones. After ejection of the amalgam stock V^{II} and Cr^{II} solutions could be stored in capped syringes for several days without oxidation. The V^{II} and Cr^{II} solutions were diluted, mixed with halide-ion solutions, and injected into radiolysis cells using the standard Argonne syringe technique.[7] Stock V^{II} and Cr^{II} solutions were analysed by injecting aliquot portions into Fe^{III} solutions and titrating the Fe^{II} produced with $KMnO_4$. The stock solutions were between 10^{-3} and 10^{-2}M in metal ion and *ca.* 0·1M in H^+ ion.

AnalaR sodium halides were used to prepare halide-ion solutions. Acid concentrations and ionic strengths were adjusted with AnalaR perchloric acid and sodium perchlorate. Solutions were prepared from water distilled from potassium permanganate and potassium dichromate and deaerated by bubbling with high purity argon or helium.

The flash photolysis apparatus and procedures have been described previously.[3] Preliminary pulse-radiolysis experiments were carried out with the 1·5 MeV Van de Graaff accelerator pulse-radiolysis facility at the Australian Atomic Energy Research Establishment, Lucas Heights,

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Australia. The main series of pulse-radiolysis experiments was carried out with the 3 MeV Van de Graaff accelerator and 22 MeV linear accelerator pulse-radiolysis facilities of the Chemistry Division, Argonne National Laboratory, Argonne, U.S.A. Electron pulses were 5—33 ns long and the dose per pulse was *ca.* 10^{21} eV l^{-1}. Irradiations were carried out at room temperature (*ca.* 22 °C). The halogen radical anion absorbance was measured at wavelengths between 300 and 400 nm using a pulsed xenon lamp as light source. *Ca.* 10μM concentrations of radical ions were produced by an electron pulse. At least three oscilloscope traces of light absorbance against time were analysed for each set of experimental conditions.

γ-Irradiations were carried out with a 1 000 Ci ^{60}Co source. Standard iron(II) sulphate dosimetry was used. Deaerated solutions containing Cr^{II} and halide ions were prepared and irradiated in glass syringes. The oxidation of Cr^{II} by halogen was investigated at acid and halide-ion concentrations as close as possible to those used in the ^{60}Co irradiations. Deaerated halogen and Cr^{II} solutions were prepared and mixed in syringes. After irradiation or halogen oxidation, excess of Cr^{II} was oxidised by shaking the solutions in air and chromium(III) products [penta-aquohalogenochromium(III) ions, hexa-aquochromium(III) ions, and polynuclear chromium(III) species] were separated on a Sephadex SP-C25 ion-exchange column using $HClO_4$ as eluting agent. The products were identified by their absorption spectra and the concentration of each product was determined spectrophotometrically as chromate after oxidation with H_2O_2.

Production of X_2^- *Radical Anions.*—The X_2^- (X = I, Br, or Cl) ions were produced by reaction between OH radicals and halide ions in both pulse-radiolysis and ^{60}Co γ-radiolysis experiments. The reactions between OH and X^- have complex mechanisms,[8-10] but at constant [H^+] can be represented by equations (1) and (2) (X = I, Br, or Cl).

$$H^+ + OH + X^- \xrightarrow{k_1} H_2O + X \qquad (1)$$

$$X + X^- \overset{k_2}{\rightleftharpoons} X_2^- \qquad (2)$$

The observed rate constant k_1 is dependent on [H^+]. Concentrations of H^+ and halide ions in the irradiated solutions were *ca.* 0·1M. At these concentrations, and V^{II} and Cr^{II} concentrations of *ca.* 10^{-3}M, the rates of reactions (3)

$$OH + M^{II} \xrightarrow{k_3} M^{III} + OH^- \qquad (3)$$

were very much slower than those of (1). Rate constants for reactions (2) are very high (*ca.* 10^{10} l mol^{-1} s^{-1}) and the rate of production of X_2^- radical anions was much faster than the rate of their reaction with the metal ions. Pulse radiolysis of halide-ion solutions in the absence of V^{II} and Cr^{II} showed that formation of X_2^- ions was complete at the end of a 5 ns electron pulse under our conditions. At the end of the electron pulse the predominant reactive species in solution were H atoms and X_2^- radical anions.

When no metal ions were present, the radical anions disappeared by disproportionations (4) (X = I, Br, or Cl)

$$X_2^- + X_2^- \xrightarrow{k_4} X_3^- + X^- \qquad (4)$$

and by reactions (5). Reactions (4) and (5) only competed

$$H + X_2^- \xrightarrow{k_5} H^+ + 2X^- \qquad (5)$$

with those of V^{2+}_{aq} and Cr^{2+}_{aq} with X_2^- ions [reactions (6)] at low metal-ion concentrations. At metal-ion concen-

$$X_2^- + M^{II} \longrightarrow M^{III} + 2X^- \qquad (6)$$

trations greater than *ca.* 10^{-3}M disappearance of the absorbance due to the X_2^- ions followed a pseudo-first-order rate law, as [M^{2+}] $\gg$ [X_2^-]. At metal-ion concentrations less than 10^{-3}M the disappearance of X_2^- ions was of mixed first and second order and pseudo-first-order rate constants for reactions (6) were calculated by a numerical integration procedure, using appropriate values for k_4 and k_5.

H Atoms can oxidise Fe^{II} to Fe^{III}.[11] The corresponding oxidations of V^{II} and Cr^{II} have been inferred.[12] If H atoms reacted with the metal ions in our solutions, the reduction in V^{II} and Cr^{II} concentrations due to these reactions was negligible and the reactions did not interfere with measurements of the rates of reactions (6). At high V^{II} and Cr^{II} concentrations ($\geqslant 10^{-2}$M) reactions (3) competed with (1) and yields of X_2^- ions decreased, but this did not affect the rates of reactions (6) and reduction in concentrations of V^{2+} and Cr^{2+} ions caused by reactions (3) was insignificant in comparison with other sources of error in the kinetic experiments.

In flash-photolysis experiments halogen radical ions were produced by absorption of light from the flash by acid solutions of the halide ions, reactions (7) (X = I, Br, or Cl) and (2). The electrons were scavenged by H^+ ions

$$X^-_{aq} \xrightarrow{h\nu} X + e^-_{aq} \qquad (7)$$

[reaction (8)].

$$e^-_{aq} + H^+ \longrightarrow H \qquad (8)$$

RESULTS

Reactions of X_2^- *Radical Anions with* V^{2+} *Ions.*—Preliminary experiments in which halogen radical anions were produced by flash photolysis of halide ions showed that I_2^-, Br_2^-, and Cl_2^- reacted with V^{2+}_{aq} with rate constants greater than 10^8 l mol^{-1} s^{-1}. The kinetics of reactions (6) (M = V; X = I, Br, or Cl) were most conveniently studied at relatively high (*ca.* 10^{-3}M) V^{II} concentrations due to difficulties of V^{II} analysis at low concentrations, and nanosecond pulse radiolysis was used to generate the X_2^- ions in order to follow the correspondingly short reaction times. Deaerated solutions containing the halide ions (0·1), acid (0·1), and vanadium(II) (10^{-4}—10^{-2}M) were irradiated.

No absorbance due to vanadium(III) reaction products was observed at wavelengths between 300 and 500 nm. The pulsed-light source used in the spectrophotometric detection system limited observations to periods of 100 or 200 μs following the electron pulse, and noise levels in the wide-band detection system prevented reliable detection of species with absorption coefficients less than *ca.* 500 l mol^{-1} cm^{-1}. Reactions (6) were pseudo-first-order because the V^{II} concentrations were much greater than those of the X_2^- ions. Second-order rate constants (Table 1) were obtained from straight-line plots (Figure 1) of the pseudo-first-order rate constants against [V^{2+}].

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At the highest V^{II} concentrations, V^{2+} ions competed effectively [reaction (3)] with X^- ions [reactions (1)] for OH radicals. The yield of X_2^- ions at the end of the electron pulse under these conditions was reduced by this competition and because the rate of reaction (6) was high enough for X_2^- to react appreciably with V^{2+} ions during the pulse. The decrease in the Br_2^- radical-ion yield at several V^{II} concentrations was used to estimate the rate constant for reaction (3) (M = V); $k_3(V^{II})$ is *ca.* 10^{10} l mol^{-1} s^{-1}. The rate constant k_3 can only be estimated from these measurements because results of recent studies [9] of reactions between OH radicals and Br^- ions, which lead to formation of Br_2^- radical ions, show that simple competition kinetics do not apply to this system. The complexity of the OH–X^- reactions makes them unsuitable to use in competition studies of rates of OH radical reactions.

TABLE 1

Rates and mechanisms of $M^{2+} + X_2^-$ (X = I, Br, or Cl) reactions

Reaction	Mechanism [a]	ΔG^0 / kJ mol^{-1}	k (25 °C) / l mol^{-1} s^{-1}	k (H_2O exchange) / s^{-1}
$V^{2+} + Cl_2^-$ [b]	O.s.–diffusion	−241	$(1.95 \pm 0.2) \times 10^9$	0.9×10^2 [c]
$V^{2+} + Br_2^-$ [b]	O.s.–diffusion	−191	$(1.48 \pm 0.2) \times 10^9$	
$V^{2+} + I_2^-$ [b]	O.s.	−116	$(1.43 \pm 0.2) \times 10^8$	
$Cr^{2+} + Cl_2^-$ [b]	O.s.–diffusion	−263	$(2.4 \pm 0.3) \times 10^9$	8×10^9 [d]
$Cr^{2+} + Cl_2^-$ [b]	I.s.–diffusion	−263	$(2.4 \pm 0.3) \times 10^9$	
$Cr^{2+} + Br_2^-$ [b]	I.s.–diffusion	−213	$(1.9 \pm 0.2) \times 10^9$	
$Cr^{2+} + I_2^-$ [b]	I.s.–diffusion	−138	$(1.5 \pm 0.2) \times 10^9$	
$Mn^{2+} + Cl_2^-$ [e]	I.s.–electron-transfer	−72	8.5×10^6	2.3×10^7 [f]
$Mn^{2+} + Br_2^-$ [e]	I.s.–electron-transfer	−21	6.3×10^6	
$Fe^{2+} + Cl_2^-$ [g]	O.s.	−147	1.0×10^7	3.2×10^6 [h]
$Fe^{2+} + Cl_2^-$ [g]	I.s.–substitution	−147	4.0×10^6	
$Fe^{2+} + Br_2^-$ [g]	I.s.–substitution	−97	3.6×10^6	
$Fe^{2+} + I_2^-$ [i]	I.s.–substitution	−22	3.6×10^6	
$Co^{2+} + Cl_2^-$ [j]	I.s.–substitution	−33	1.4×10^6	2×10^6 [k]

[a] O.s.–diffusion and i.s.–diffusion refer to outer sphere– and inner sphere–diffusion controlled mechanisms respectively. I.s.–electron-transfer and i.s.–substitution refer to inner sphere–electron-transfer controlled and –substitution controlled mechanisms respectively. [b] This work. Activation parameters were not determined for these diffusion-controlled reactions. [c] Ref. 18. [d] Ref. 20. [e] Ref. 1. [f] M. Grant, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 1971, **10**, 71. [g] Ref. 3. [h] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307. [i] Ref. 23. [j] Ref. 2. [k] J. P. Hunt, *Co-ordination Chem. Rev.*, 1971, **7**, 1.

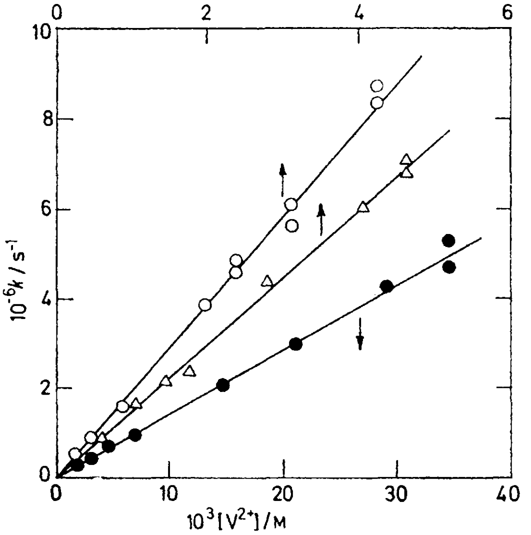

FIGURE 1 Dependence of pseudo-first-order rate constants on $[V^{2+}]$ for reactions of V^{2+} with I_2^- (●), Br_2^- (△), and Cl_2^- (○) at 22 ± 3 °C. The error in individual points is ±15%

Reactions of X_2^- Radical Anions with Cr_2^+ Ions.—Preliminary flash-photolysis and pulse-radiolysis experiments showed that Cr^{II} was oxidised by X_2^- radical ions with rate constants in excess of 10^8 l mol^{-1} s^{-1}. The rates of reactions (6) (M = Cr; X = I, Br, or Cl) were studied by pulse radiolysis in deaerated solutions containing the halide ions (0·1), acid (0·1), and chromium(II) (10^{-4}—10^{-2}M).

No absorbance due to chromium(III) reaction products was observed between 300 and 500 nm when the radical ions reacting with Cr^{2+}_{aq} ions were Br_2^- or Cl_2^-. The possible inner-sphere reaction products $[Cr(OH_2)_5Cl]^{2+}$ and $[Cr(OH_2)_5Br]^{2+}$ have absorption coefficients of less than 10 l mol^{-1} cm^{-1} in this wavelength region and were undetectable. When I_2^- radical ions reacted with Cr^{2+}_{aq} ions an absorption at 300 nm was observed after decay of the I_2^- ion absorbance. This absorption was identified as being due to the $[Cr(OH_2)_5I]^{2+}$ ion in the flash-photolysis experiments described below.

Pseudo-first-order rate constants for reactions (6) were calculated from the decay kinetics of the X_2^- ions and are shown plotted against chromium(II) concentration in Figure 2. Second-order rate constants (Table 1) for re-

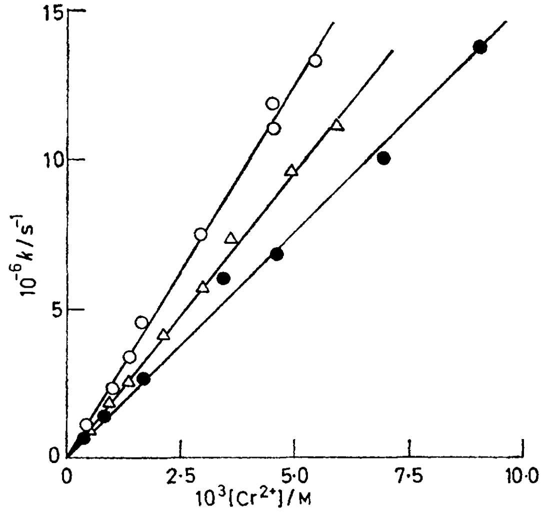

FIGURE 2 Dependence of pseudo-first-order rate constants on $[Cr^{2+}]$ for reactions of Cr^{2+} with I_2^- (●), Br_2^- (△), and Cl_2^- (○) at 22 ± 3 °C. The error in individual points is ±15%

actions (6) were calculated from gradients of the straight lines in Figure 2. The yields of the radical anions were reduced at the highest Cr^{II} concentrations because reaction (3) (M = Cr) competed with reactions (1). From this reduction, the rate constant for reaction (3) is estimated to be *ca.* 10^{10} l mol^{-1} s^{-1}. Samuni *et al.*[13] obtained a value of $1\cdot2 \times 10^{10}$ l mol^{-1} s^{-1} for k_3 from competition between Cr^{II} and SCN$^-$ ions for OH radicals, but neither reactions (1) (X = I, Br, or Cl) nor that between OH radicals and SCN$^-$ ions are suitable for use in competition studies of rates of OH radical reactions.

Products of $Cr^{2+}{}_{aq}$–X_2^- *Reactions.*—The Cr^{III} reaction products from (6) (X = I, Br, or Cl) could not be definitely identified in pulse-radiolysis experiments because of the small concentrations produced. The products were therefore investigated in experiments in which solutions containing Cr^{2+} and X$^-$ ions were irradiated with ^{60}Co γ-rays. Because the Cr^{III} species are substitution inert the reaction products can be identified after irradiation by ion-exchange separation. The chemical form of Cr^{III} produced is dependent on the mechanism of reactions (6). The product will be $Cr(OH_2)_6^{3+}$ ions if the reactions are outer sphere, $[Cr(OH)_2)_5X]^{2+}$ ions if inner sphere. Polynuclear Cr^{III} species are produced by oxidation of Cr^{2+} by oxidants such as ClO_3^-, ClO_2^-, and ClO$^-$ (ref. 6) but are unlikely to be produced by reactions (6).

Solutions of $Cr^{2+}{}_{aq}$ and X$^-$ ions were irradiated under conditions in which all OH radicals produced in the primary radiolysis step were converted to X_2^- ions. The yield of X_2^- ions was equal to that of OH radicals and $G(X_2^-) = G(OH)$. Conditions were also adjusted so that the only significant reaction of X_2^- ions was with $Cr^{2+}{}_{aq}$. The yield of $[Cr(OH_2)_5X]^{2+}$ ions, $G\{[Cr(OH_2)_5X]^{2+}\}$, when compared with $G(OH)$, is a direct measure of the extent of the inner-sphere reaction. Possible reactions of the OH radicals are (1) and (3) (M = Cr). In 0·1M-acid, values of k_1 are $1\cdot1 \times 10^9$, $4\cdot4 \times 10^9$, and $3\cdot4 \times 10^{10}$ l mol^{-1} s^{-1} for X = Cl,[8] Br,[10] and I [14] respectively, and k_2 is *ca.* 10^{10} l mol^{-1} s^{-1}. In order to ensure that $G(X_2^-) = G(OH)$ the concentration of halide ions in the irradiated solutions was 50 times that of chromium(II), so that >90% of the OH radicals reacted with the halide ions. In 0·1M-acid H atoms $[G(H) = g(e^-{}_{aq}) + g(H)]$ may react with X_2^- ions [reactions (5)] reducing $G(X_2^-)$, with Cr^{III} species reducing $G(Cr^{III})$ [reaction (9)], or with Cr^{II} [reaction (10)] increasing $G(Cr^{III})$.

$$H + Cr^{III} \longrightarrow Cr^{II} + H^+ \qquad (9)$$

$$H + H^+ + Cr^{II} \longrightarrow Cr^{III} + H_2 \qquad (10)$$

The concentration of Cr^{II} was made large enough (4×10^{-3}M) in the experiments for the X_2^- radical ions to react with $Cr^{2+}{}_{aq}$ and not with H atoms or by second-order disproportionation [reactions (4)]. Reaction (10) produces only aquochromium(III) species and does not influence the yield of $[Cr(OH_2)_5X]^{2+}$ ions. Secondary reaction of H atoms with $[Cr(OH_2)_5X]^{2+}$ ions produced by an inner-sphere path of reaction (6) (M = Cr) will reduce $G\{[Cr(OH_2)_5X]^{2+}\}$ [reaction (9)]. The solutions used in the γ-radiolysis experiments therefore contained $Cr^{3+}{}_{aq}$ ions so that the rate of reaction (11) was much faster than that of (12), and H atoms were effectively scavenged by $Cr^{3+}{}_{aq}$ ions.

$$H + Cr^{3+}{}_{aq} \longrightarrow Cr^{2+}{}_{aq} + H^+ \qquad (11)$$

$$H + [Cr(OH_2)_5X]^{2+} \longrightarrow Cr^{2+} + X^- + H^+ \qquad (12)$$

Deaerated solutions of the ions X$^-$ (0·2—0·4M) (X = Br or Cl), H$^+$ (0·1M), Cr^{3+} (2×10^{-2}M), and Cr^{2+} (4×10^{-3}M) were irradiated at room temperature (*ca.* 20 °C). Deaerated solutions of the ions I$^-$ (0·2M), H$^+$ (0·2M), Cr^{3+} (2×10^{-2}M), and Cr^{2+} (4×10^{-3}M) were irradiated at 0 °C in order to reduce the rate of aquation of the inner-sphere product $[Cr(OH_2)_5I]^{2+}$. The yields of penta-aquohalogenochromium(III) complexes are given in Table 2. The value of $G(X_2^-)$ (X = I, Br, or Cl) should be 2·95, the value of $G(OH)$ in 0·1M-acid.[16] If the reaction between the radical anions and $Cr^{2+}{}_{aq}$ ions were entirely inner sphere, $G\{[Cr(OH_2)_5X]^{2+}\}$ would also be 2·95. Within experimental error, the reaction between Br_2^- and $Cr^{2+}{}_{aq}$ ions is entirely inner sphere. The reaction between Cl_2^- ions and $Cr^{2+}{}_{aq}$ is partly inner and partly outer sphere. The mechanism of the I_2^- ion reaction with $Cr^{2+}{}_{aq}$ ions cannot be determined with certainty from these experiments. Some inner-sphere oxidation of Cr^{2+} ions does take place, but the apparent ratio of the inner-sphere to the outer-sphere path (*ca.* 1 : 2) is low because of aquation of the $[Cr(OH_2)_5I]^{2+}$ ions produced. The aquation reaction of the ion $[Cr(OH_2)_5I]^{2+}$ has a half-life of *ca.* 12 h at 0 °C. Irradiation times were *ca.* 24 h and aquation also occurred during separation on the ion-exchange column.

TABLE 2

Yields of inner-sphere (CrX^{2+}) and outer-sphere (Cr^{3+}) products from $Cr^{2+} + X_2^-$ and $Cr^{2+} + X_2$ reactions (X = I, Br, or Cl)

Reaction	Cr^{3+} Yield	CrX^{2+} Yield	Inner-sphere path (%)
Cr^{2+}–Cl_2^- [a]	$1\cdot55 \pm 0\cdot3$	$1\cdot40 \pm 0\cdot3$	47 ± 10
Cr^{2+}–Cl_2 [b]	26 ± 5	74 ± 5	74 ± 10
Cr^{2+}–Br_2^- [a]	$0\cdot55 \pm 0\cdot4$	$2\cdot40 \pm 0\cdot4$	80 ± 12
Cr^{2+}–Br_2 [b]	2 ± 2	98 ± 2	98 ± 4
Cr^{2+}–I_2^- [a]	$2\cdot10 \pm 0\cdot4$	$0\cdot85 \pm 0\cdot4$	29 ± 12 [c]
Cr^{2+}–I_2^- [d]	$0\cdot05 \pm 0\cdot05$	$1\cdot00 \pm 0\cdot05$	100 ± 5
Cr^{2+}–I_2 [b]	5 ± 5	95 ± 5	95 ± 10

[a] Measured in steady-state γ-radiolysis experiments in which $G(X_2^-) = G(OH) = 2\cdot95$. Yields are expressed as $G(Cr^{3+})$ and $G(CrX^{2+})$; $G(Cr^{3+}) = 2\cdot95 - G(CrX^{2+})$. The solutions contained X$^-$ (0·2—0·4M), H$^+$ (0·1—0·2), Cr^{3+} (2×10^{-2}), and Cr^{2+} (4×10^{-3}M) ions. [b] Measured at the same concentrations of X$^-$, H$^+$, Cr^{3+}, and Cr^{2+} ions as in the γ-radiolysis experiments. Yields are expressed as percentages of the total Cr^{III} yields. [c] Measured at 0 °C. The low value of $G(CrI^{2+})$ is due to aquation of the CrI^{2+} complex. [d] Measured 50 μs after flash photolysis of solutions containing I$^-$ (0·2), H$^+$ (0·1), Cr^{3+} (10^{-2}M), and Cr^{2+} (5×10^{-3}M) ions. The yield of CrI^{2+} is expressed as a fraction of the yield of I_2^- produced by the flash and the yield of Cr^{3+} obtained by difference.

The mechanism of reaction (6) (M = Cr, X = I) was established in flash-photolysis experiments. The solutions were similar to those used in the steady-state radiolysis experiments and contained the ions I$^-$ (0·2M), H$^+$ (0·1M), Cr^{3+} (10^{-2}M), and Cr^{2+} (5×10^{-3}M). The H atoms produced by the flash [reaction (8)] were scavenged by Cr^{3+} ions. The I_2^- radical ions produced by the flash reacted with Cr^{2+} ions with a half-life of *ca.* 100 ns [reaction (6)]. A long-lived transient absorbance ($t_{\frac{1}{2}} >$ several minutes) was observed and the spectrum of the transient recorded 50 μs after the flash is shown in Figure 3. The absorbance was due to the $[Cr(OH_2)_5I]^{2+}$ ion and the yield of the complex

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was compared with that of the I_2^- radical ion produced by the flash in solutions from which chromium(II) was absent. The results are included in Table 2, and show that the reaction between I_2^- radical ions and Cr^{2+}_{aq} is inner sphere.

Because of the significance of the mechanism of oxidation of Cr^{2+}_{aq} ions by free halogen or trihalide ion for our systems, we reinvestigated the stoicheiometry of these reactions under the same conditions of acid and halide-ion concentration used in the radiolysis experiments. The results are included in Table 2, and confirm previous observations that oxidation of Cr^{II} by Br_2 or I_2 is essentially completely inner sphere, but that oxidation by Cl_2 is partly inner and partly outer sphere.[5,6]

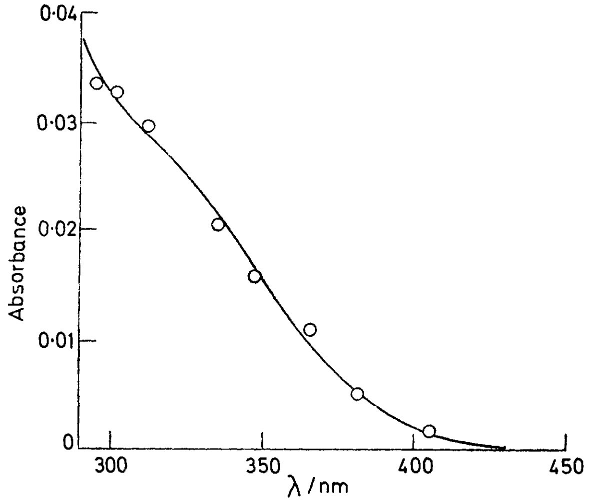

FIGURE 3 Spectrum of the transient observed after flash photolysis of $0{\cdot}2\text{M-}I^-$, $0{\cdot}1\text{M-}H^+$, $10^{-2}\text{M-}Cr^{3+}$, and $5 \times 10^{-3}\text{M-}Cr^{2+}$ solutions (○) 50 μs after the flash. (——), Spectrum of the complex CrI^{2+}

DISCUSSION

Vanadium(III) products of the oxidation of V^{2+}_{aq} by halogen radical ions could not be observed in pulse-radiolysis experiments and therefore the mechanisms of reactions (6) ($M = V$; $X = I$, Br, or Cl) are not known directly. Steady-state irradiation experiments cannot be used to distinguish between the inner- and outer-sphere mechanisms because of the lability of vanadium(III) species. The mechanism of reactions (6) ($M = V$) is readily inferred from a comparison of the rates of the oxidation reactions and rates of substitution reactions of V^{2+} ions.

Rates of formation and aquation of vanadium(II) complexes are relatively slow. The rate of substitution of SCN^- ions into V^{2+}_{aq} is *ca.* 28 l mol^{-1} s^{-1} at 25 °C[17] and the rate of water exchange in V^{2+}_{aq} ions is 90 s^{-1} (ref. 18). Rates of substitution of X_2^- radical ions into other bivalent transition-metal aquo-ions are approximately the same as those of anions such as Cl^-.[2,3] Halogen radical ions are therefore likely to substitute into V^{2+}_{aq} ions with rate constants of the order of 10^2 l mol^{-1} s^{-1}, that is six or seven orders of magnitude more slowly than observed rates of oxidation of V^{2+} ions by the radical anions. On the time scales of the oxidation reactions V^{2+}_{aq} ions are inert to substitution and reactions with the halogen radical anions must therefore proceed by outer-sphere mechanisms (13).

$$X_2^- + V^{2+}_{aq} \longrightarrow V^{3+}_{aq} + 2X^- \qquad (13)$$

Rate constants (Table 1) for reactions (13) ($X = I$, Br, or Cl), show that these reactions are close to being diffusion controlled and rates of the electron-transfer processes are not directly measurable. If the rate of diffusion is k_d and that of electron transfer is k_{et} then the observed rate constant for reactions (13), k_{obs}, is given[19] by equation (14). The difference in standard free

$$1/k_{obs} = (1/k_{et}) + (1/k_d) \qquad (14)$$

energies of oxidation of V^{2+} ions by Cl_2^- and Br_2^- radical ions is 50 kJ mol^{-1}. The dependence of electron-transfer rates for outer-sphere reactions on the standard free energy of reaction is well established but the observed rate constants k_{13} ($X = Br$) and k_{13} ($X = Cl$) are the same within experimental error. If these reactions are diffusion controlled k_d [equation (14)] will be the dominant factor in the observed rate constants and the lack of dependence of k_{obs} on ΔG^0 is explained. For the reaction between V^{2+} ions and I_2^- radical ions, ΔG^0 is -116 kJ mol^{-1} and the observed rate constant is an order of magnitude smaller than those for the reactions with Cl_2^- and Br_2^- ions. In this case k_{et} must be the more important term in equation (14). Diffusion rates for Cl_2^- and Br_2^- ions might be expected to differ and this difference should be reflected in rate constants ($k_{obs} = k_d$) for reactions of the radical ions with V^{2+}_{aq} ions, but we have observed only small differences in the rates of other diffusion-controlled (or near diffusion-controlled) reactions of the halogen radical ions. For example, at 25 °C and $I = 0{\cdot}2$ mol l^{-1}, rate constants (k_4) and activation enthalpies for disproportionation of the radical ions are $5{\cdot}2 \times 10^9$ ($\Delta H^\ddagger$ 10) and $5{\cdot}3 \times 10^9$ l mol^{-1} s^{-1} ($\Delta H^\ddagger$ 11 kJ mol^{-1}) for Cl_2^- and Br_2^- ions respectively.

Identification of the inert chromium(III) products of the oxidation of Cr^{2+}_{aq} ions by halogen radical ions in steady-state ^{60}Co γ-radiolysis and flash-photolysis experiments directly establishes the mechanisms of these reactions (Table 2). The reactions of Cr^{2+}_{aq} ions with I_2^- and Br_2^- radical ions have entirely inner-sphere mechanisms (15) ($X = I$ or Br). The reaction of

$$X_2^- + Cr^{2+}_{aq} \longrightarrow [Cr(OH_2)_5X]^{2+} + X^- \quad (15)$$

Cr^{2+}_{aq} ions with Cl_2^- ions takes place with equal probability by inner- and outer-sphere paths.

For inner-sphere reactions which are diffusion controlled it is difficult to distinguish between substitution controlled and electron-transfer controlled mechanisms. Rates of substitution of simple anions into Cr^{2+}_{aq} ions are unknown. The rate of water exchange in Cr^{2+}_{aq}

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ions[20] is *ca.* 8×10^9 s^{-1}. For substitution reactions taking place by an Eigen–Wilkins mechanism,[21] in which ion-pairing precedes substitution, with ion-pairing constants between 0·1 and 10 l mol^{-1}, second-order substitution rates would lie between 10^9 and 10^{10} l mol^{-1} s^{-1}, but interpretation of the mechanism in terms of such successive reaction steps in a situation controlled by the encounter rate, where the average residence time of either water molecules or anions in the inner-co-ordination sphere of the metal ion is *ca.* 10^{-10} s, is invalid. The substitution rate of 2,2′-bipyridyl (bipy) into Cr^{2+}_{aq} to form the $Cr(bipy)^{2+}$ ion[22] is $3{\cdot}5 \times 10^7$ l mol^{-1} s^{-1}, considerably slower than the rates of reactions (6) ($M = Cr$), but rates of formation of chelate complexes are not necessarily good guides to rates of substitution of unidentate anions. The intimate details of inner sphere–diffusion controlled oxidation–reduction reactions of this kind are not accessible to direct experimental test. Although we conclude that rates of substitution of the halogen radical ions into Cr^{2+}_{aq} are $\geqslant 2 \times 10^9$ l mol^{-1} s^{-1}, we cannot distinguish between inner sphere–substitution controlled and electron-transfer controlled mechanisms.

Both the inner- [reaction (15), $X = Cl$] and outer-sphere [reaction (16)] paths for the Cr^{2+}_{aq}–Cl_2^- ion reaction are diffusion controlled, and k_{obs} [equation (14)]

$$Cl_2^- + Cr^{2+}_{aq} \longrightarrow Cr(OH_2)_6^{3+} + 2Cl^- \qquad (16)$$

cannot be split into rate constants for these paths as was possible for the Fe^{2+}_{aq}–Cl_2^- reaction.[3] Reactions (15) and (16) occur with equal probability and the entropies of activation and encounter distances must be the same. The observation of a diffusion-controlled reaction with two distinct intimate paths [reactions (15) and (16)] is unusual. As both paths are equally probable, it is likely that reaction occurs on the first encounter of the reactants in the solvent cage, and the choice between inner- and outer-sphere paths is determined by the geometry of the encounter. The chromium(II) hexa-aquo-ion is highly distorted ($t_{2g}^3e_g^1$). Approach by a Cl_2^- ion on a face of the distorted octahedron may lead to outer-sphere electron transfer, while attack in the region of a vertex of the octahedron will lead to inner-sphere electron transfer. Because of the high rate of water exchange in the Cr^{2+}_{aq} ion the barrier to approach at a vertex is no greater than that at an octahedral face and so we observe inner- and outer-sphere paths occurring with about equal probability.

The oxidation of V^{2+}_{aq} ions by halogens and trihalide ions has been investigated by Malin and Swinehart.[4] The rates of the reactions are very much slower than those of the corresponding halogen radical ion reactions and have abnormally low observed energies of activation (*ca.* 20 kJ mol^{-1}) which approach those for diffusion-controlled reactions in water, even though the rate constants are only about an order of magnitude greater than rates of substitution into V^{2+}_{aq} ions. The suggested mechanism involves the halogen radical ions as intermediates [reactions (17), (2), and (13)]. In the reactions

$$X_2 + V^{2+}_{aq} \longrightarrow V^{3+}_{aq} + X^- + X \qquad (17)$$

of V^{2+} with Br_2 and Cl_2 there was some evidence of formation of an intermediate. In view of the diffusion-controlled rate constants for reaction (13) the stationary-state concentrations of X_2^- ions in the experiments of Malin and Swinehart cannot have exceeded *ca.* 5×10^{-9}M. Another intermediate species must therefore be responsible for the anomalous absorbance, and the low activation energies may indicate an undetected equilibrium step involving this intermediate.

γ-Radiolysis of solutions of Cr^{II} and chloride ions has been investigated previously;[12] Cr^{3+}_{aq}, $CrCl^{2+}$, and $CrOCr^{4+}$ ions were produced on irradiating solutions of Cr^{2+}_{aq} ions containing Cl^- ions and high (up to 2·8M) concentrations of $HClO_4$. The relative yields of Cr^{III} species depended on the ratio $[Cl^-] : [ClO_4^-]$. Our value for $G(CrCl^{2+})$ (Table 2) is approximately half that of Lykourezos *et al.*[12] in 0·4M-Cl^- and 0·56M-H^+ solutions, but considerable oxidation of Cr^{II} by H atoms and radiolytic decomposition products of ClO_4^- occurred in their solutions. The previous value for the ratio $k_3 : k_6$ ($M = Cr$, $X = Cl$) is also in error, due to the assumption that oxidation of Cr^{2+}_{aq} by Cl_2^- ions is entirely inner sphere.

The reactions of the halogen radical ions with Cr^{2+}_{aq} ions are analogous to those with Fe^{2+}_{aq}, where the reactions with I_2^- (ref. 23) and Br_2^- (ref. 3) ions are entirely inner sphere and that with Cl_2^- ions is partly inner and partly outer sphere at 25 °C. Evidence of dual mechanisms for oxidation of Cr^{2+}_{aq} ions by chlorine oxidants is not confined to our measurements. The oxidation of Cr^{2+}_{aq} ions by Cl_2 produces both Cr^{3+}_{aq} and $[Cr(OH_2)_5Cl]^{2+}$ ions, as well as some $CrOCr^{4+}$ ions. At acidities close to those in our experiments (0·55M-$HClO_4$) Thompson and Gordon[6] found that relative yields of chromium(III) species in the oxidation of Cr^{2+}_{aq} ions by Cl_2 were Cr^{3+}_{aq} (23%), $CrCl^{2+}$ (68%), and binuclear species (10%). The yield of $[Cr(OH_2)_5Cl]^{2+}$ ions increased as the ratio $[Cl^-] : [Cl_2]$ increased, reaching 78% at a ratio of 4·6 : 1. These results are in agreement with the present work if it is assumed that the mechanism of Cr^{II} oxidation is similar to that of the Fe^{II}[24] and V^{II}[4] oxidations, involving reaction (18) followed by (2), (15), and (16). If reaction (18) is 100% inner

$$Cl_2 + Cr^{2+}_{aq} \longrightarrow Cr^{III} + Cl + Cl^- \qquad (18)$$

sphere, then as reactions (15) (inner-sphere path) and (16) (outer-sphere path) take place with equal probability, the overall yield of the inner-sphere product, $[Cr(OH_2)_5Cl]^{2+}$, will be $75 \pm 5\%$, in agreement with

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the results of Thompson and Gordon. The rate constant for reaction (18) is $9{\cdot}7 \times 10^3$ l mol^{-1} s^{-1} and since this is very much lower than the rate of substitution into Cr^{2+}_{aq} ions, reaction (18) can be classified as inner sphere–electron-transfer controlled as is that between Fe^{2+}_{aq} ions and Cl_2. Our observations and those of previous workers[5] show that the yield of inner-sphere chromium(III) products is close to 100% in the oxidation of chromium(II) by I_2 and Br_2, in agreement with our observations that reaction (6) (M = Cr, X = I or Br) is entirely inner sphere [reaction (15)] if the reaction sequence is the same as that proposed for the Cr^{II}–Cl_2 reaction.

We found no evidence for the production of dihalogenochromium(III) species in steady-state irradiation experiments. This indicates that the halogen radical anions cannot act as chelating groups in the oxidation and that halogen–halogen bond fission accompanies the electron-transfer process.

Rate constants, standard free-energy changes, and mechanisms of reactions of the bivalent first-row transition-metal ions from vanadium to cobalt with halogen radical ions are summarised in Table 1. The mechanism of the reactions is largely determined by the rate of substitution into the metal ion and is independent of the standard free-energy change. Only for V^{2+}_{aq}, which has the smallest substitution rate and largest activation energy for substitution (57 kJ mol^{-1}), are the reactions entirely outer sphere. The importance of substitution processes which precede or accompany reductions of transition-metal ions by oxidisable ligands has been emphasised by McAuley,[25] and it is obvious that this is also true for oxidation of transition-metal ions by ligands such as the halogen radical anions. Even for diffusion-controlled oxidations of Cr^{2+}_{aq} ions with $-\Delta G^0$ as large as 263 kJ mol^{-1} (Cr^{2+}–Cl_2^-) the dominant mechanism is inner sphere. For the Cr^{2+}_{aq}–Br_2^- reaction for example, where ΔG^0 is −213 kJ mol^{-1}, there must be a barrier to outer-sphere electron transfer at least 6 kJ mol^{-1} higher than that for the inner-sphere path as no outer-sphere path was observed.

The reaction of V^{2+}_{aq} with I_2^- ions is anomalous in that ΔG^0 is −116 kJ mol^{-1} and is 31 kJ mol^{-1} more positive than ΔG^0 for the outer-sphere reaction between Fe^{2+}_{aq} and Cl_2^- ions, but the rate constant is 100 times greater than that of the Fe^{2+}–Cl_2^- reaction. For such similar reactions the Marcus theory of outer-sphere electron-transfer reactions suggests that the V^{2+}_{aq}–I_2^- reaction should be considerably slower than that of Fe^{2+}_{aq}–Cl_2^-. It is possible that the outer-sphere path for the Fe^{2+}_{aq}–Cl_2^- reaction is one involving relatively large work terms and strong interactions, as the rate is approximately the same as that of the inner-sphere path, while the V^{2+}_{aq}–I_2^- reaction approximates better to the weak interaction case.

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