Oxidation of Hexachloroiridate(III) by OH. Evidence for both Inner and Outer Sphere Electron Transfer Pathways

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Summary Two rate processes have been observed by optical pulse radiolysis studies for the oxidation of hexachloroiridate(III) by OH in the pH range 3·0—4·5 and the rate constant for the faster process, $k_1 = 1{\cdot}3 \times 10^{10}$ l mol^{-1} s^{-1}, which comprises both inner and outer sphere electron transfer pathways was found to be independent of pH, whereas the rate constant for the slower process, $k_2 = 1{\cdot}2 \times 10^5\,[H^+]$ l mol^{-1} s^{-1}, showed a first-order dependence on the hydrogen ion concentration

OXIDATION of labile metal ions such as Tl^+, Ag^+, Sn^{2+}, and Cu^{2+} by OH in aqueous solution has recently been shown to occur *via* adduct formation rather than outer sphere electron transfer[1] With co-ordination-saturated inert metal complexes, oxidation by OH may occur by outer sphere processes or by oxidation of the ligand and/or inner sphere processes[2] No direct evidence for an inner sphere electron transfer pathway in the oxidation of co-ordination-saturated metal complexes by OH is known,[3] although it has been suggested on energetic grounds[2] Reactions (1)—(3) have been shown to occur[4] in the oxidation of Cl^- by OH It is thought that similar intermediates

$$OH + Cl^- \rightleftharpoons ClOH^- \qquad (1)$$

$$ClOH^- + H^+ \rightarrow H_2O + Cl \qquad (2)$$

$$Cl + Cl^- \rightarrow Cl_2^- \qquad (3)$$

may occur in the oxidation of inert metal complexes containing $\mathrm{Cl^-}$ as the ligand and so we reinvestigated the reaction of OH with $\mathrm{IrCl_6^{3-}}$.[5] Thermal aquation reactions of $\mathrm{IrCl_6^{3-}}$ and $\mathrm{IrCl_6^{2-}}$ are slow under our experimental conditions.[6]

Studies of the spectral changes of the products observed on γ-radiolysis of $\mathrm{N_2O}$-saturated aqueous solutions containing 3×10^{-4}M $\mathrm{IrCl_6^{3-}}$ in the pH range 3·0—4·5 show that the formation of $\mathrm{IrCl_6^{2-}}$ is quantitative according to equation (4).

$$\mathrm{OH} + \mathrm{IrCl_6^{3-}} \longrightarrow \mathrm{IrCl_6^{2-}} + \mathrm{OH^-} \qquad (4)$$

Aqueous solutions containing $1{\cdot}0$—$3{\cdot}0 \times 10^{-4}$ M $\mathrm{IrCl_6^{3-}}$ in the pH range 3·0—4·5 and saturated with $\mathrm{N_2O}$ were irradiated with electron pulses from an Arco LP-7 Linear Accelerator. Data aquisition was achieved by the computer-controlled pulse radiolysis apparatus previously described.[7] The spectra observed 10 μs and 70 ms after the pulse are shown in the Figure. The rate of formation of the initial intermediate was independent of pH and the second order rate constant observed for this process was $k_1 = 1{\cdot}3 \times 10^{10}\ \mathrm{l\ mol^{-1}\ s^{-1}}$. The spectrum obtained 10 μs after the pulse is different from that of $\mathrm{IrCl_6^{2-}}$ and that reported by Broskiezwicz.[5]† The rate of formation of the final product produced from the initial intermediate was first order in $\mathrm{H^+}$ concentration and the second order rate constant, k_2, observed for this process was $1{\cdot}2 \times 10^5\ [\mathrm{H^+}]\ \mathrm{l\ mol^{-1}\ s^{-1}}$. The spectrum of the final product agrees very well with the spectrum of $\mathrm{IrCl_6^{2-}}$. The following reactions, equation (5), *via* an inner sphere pathway (I.S.) can account for both the kinetic processes observed.

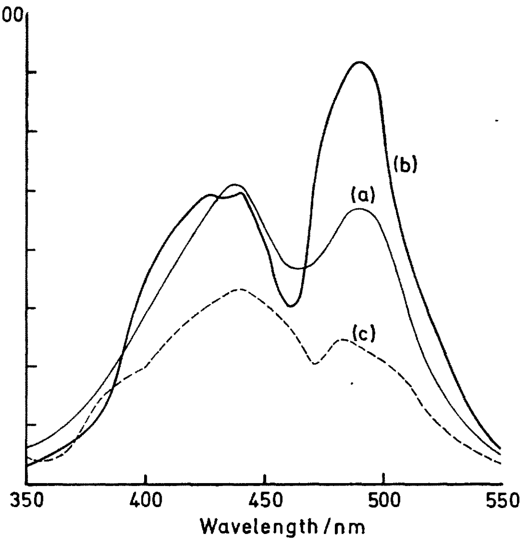
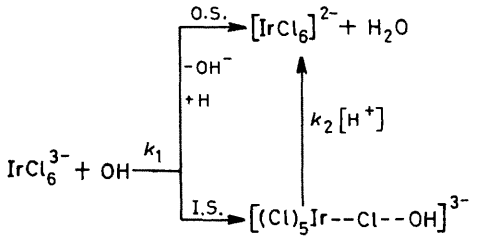


FIGURE. Absorption spectra from the pulse radiolysis of $\mathrm{IrCl_6^{3-}}$ saturated with $\mathrm{N_2O}$ taken (a) 10 μs and (b) 70 ms after the pulse; (c) corrected spectrum of (a) from the contribution of $\mathrm{IrCl_6^{2-}}$ (see text).

$$\mathrm{IrCl_6^{3-}} + \mathrm{OH} \xrightarrow{k_1} [(\mathrm{Cl})_5\mathrm{Ir} - - \mathrm{Cl} - - \mathrm{OH}]^{3-} \xrightarrow[k_2]{+\mathrm{H^+}} \mathrm{IrCl_6^{2-}} + \mathrm{H_2O} \qquad (5)$$

The possibility of any contribution by a direct outer sphere electron transfer pathway (O.S.) as shown in the Scheme was tested by a conductometric pulse radiolysis experiment on $\mathrm{IrCl_6^{3-}}$ solutions saturated with $\mathrm{N_2O}$ at pH 3·0. This experiment showed a decrease in conductivity for 10 μs after the pulse. The rate of decrease agreed within ±5% of the rate of the fast process, k_1, observed in the optical experiments. If the oxidation of $\mathrm{IrCl_6^{3-}}$ by OH were to occur *via* an inner sphere pathway, no conductivity changes would have been expected. By comparison with the conductivity changes observed for the oxidation of hydroxycyclohexadienyl radicals by $\mathrm{IrCl_6^{2-}}$, the conductivity changes observed in this experiment correspond to *ca.* 35% of the total yield of OH. The large changes in conductivity observed can only be attributed to the direct outer sphere electron transfer process to the extent of *ca.* 35%. The absorption spectrum of the intermediate after correcting for the contribution from $\mathrm{IrCl_6^{2-}}$ is shown in Figure 1c.



SCHEME

For the first time, direct evidence for both inner and outer sphere electron transfer pathways for the oxidation of an inert metal complex by OH is established. The formation of the intermediate and its pH-dependent decay as shown for the inner sphere pathway is very similar to that observed for the oxidation of the free ligand, $\mathrm{Cl^-}$, by OH, shown in equations (1) and (2).

We thank the Office of Basic Energy Sciences of the Department of Energy for support.

(*Received*, 20*th December* 1979; *Com.* 1324.)

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† The origin of the difference is not known; the purity of $\mathrm{IrCl_6^{3-}}$ used in our experiments was found to be 98%.

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[3] An OH adduct as an intermediate was formulated (E. S. Floryan and P. Pageberg, *Int. J. Radiat. Phys. Chem.*, 1976, 425) in the oxidation of tris (1,10-phenanthroline)iron(II) by OH. In this system hydroxyl radical adds to the pyridine or benzene ring. Formation of an OH adduct has been suggested in the oxidation of $\mathrm{PtCl_4^{2-}}$ by OH [R. K. Broszkiewicz, Proc. Fourth Tihany Symposium on Radiation Chemistry, (Keszthdy, Hungary), eds. P. Hedvig and R. Schillerl, Akado Kiado, Budapest, 1977, p. 765—75].

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