Evidence for Inner- and Outer-sphere Mechanisms in the Reactions of Cr^{2+} with $IrCl_6^{2-}$ and Some Related Studies

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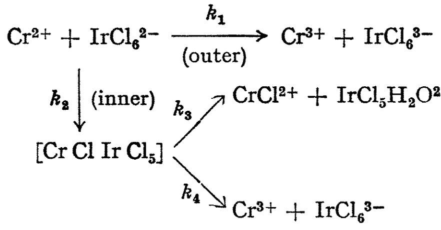
THE reaction of chromium(II) with hexachloroiridium(IV) was reported by Taube and Myers[1] to give a green intermediate of formula $[(H_2O)_5CrClIrCl_5]$; this they believed decomposed to give hexa-aquochromium(III) and hexachloroiridium(III) as final products. The reaction has been of considerable interest[2] because, according to the above interpretation, the bridging ligand remains attached to the reduced form after breakdown of the intermediate. It is now known that hexachloroiridium(III) ($k = 9{\cdot}4 \times 10^{-6}$ sec.$^{-1}$ at 25° for the replacement of the first chloride)[3] is more labile than monochloropenta-aquochromium(III) ($k = 2{\cdot}3 \times 10^{-7}$ sec.$^{-1}$ at 25°).[4] In view of this and current interest in reactions in which binuclear intermediates are formed,[5] the system seemed to merit further investigation.

In perchlorate media ($\mu = 1{\cdot}0$M) the disappearance of hexachloroiridium(IV) in the first stage (ϵ 4075 at 490 nm.) was too fast to follow by stopped-flow techniques. At 25° and with reactant concentrations *ca.* 10^{-4}M the rate constant is therefore $>10^6$ l.mole^{-1} sec.$^{-1}$. Excess of Cr^{2+} was generally avoided since there is a further reduction of hexachloroiridium(III) to either iridium or an oxide form. This reaction is considerably slower than the first stage and probably involves more than one step. From the rate of formation of the precipitate we estimate the half-life to be of the order of magnitude 1 min. The first-order decomposition of the binuclear intermediate was followed by conventional and (at 25°) stopped-flow techniques. At any one temperature, rate constants were found to be independent of the hydrogen-ion concentration, over the range 0·11—1·00M.

The cationic products were separated by ion-exchange techniques to give Cr^{3+} and $CrCl^{2+}$ in roughly equivalent amounts. In a typical experiment at 25° with initial reactant concentrations $[Cr^{2+}]$ 0·08M, $[IrCl_6^{2-}]$ 0·083M, and $[H^+]$ 0·63M, 98% of the chromium was recovered, 42% of this as $CrCl^{2+}$ and 58% as Cr^{3+}. The ratio of the two products is independent of the hydrogen-ion concentrations over the range 0·11—0·63M, but does show a temperature dependence. This and the fact that rate constants are independent of $[H^+]$ is important, because it suggests that the Cr^{3+} component is not formed *via* the intermediate $[(H_2O)_5Cr\,Cl\,Ir\,Cl_5]$. If it were, then higher rate constants and greater concentrations of Cr^{3+} would be expected at the lower hydrogen-ion concentrations. It has been shown that in the uncatalysed[4] and mercury(II)-catalysed[6] aquation of $CrCl^{2+}$ there are significant variations in rate constants over a similar range of $[H^+]$ (a factor of 2—3 in each case). We conclude therefore that the binuclear intermediate breaks down to give predominantly $CrCl^{2+}$ and $IrCl_5H_2O^{2-}$. There may be a small contribution from the parallel path giving Cr^{3+} and $IrCl_6^{3-}$, but the bulk of the Cr^{3+} is most likely formed in an outer-sphere path. Thus we might write



where there is evidence for steps k_1, k_2, and k_3, but k_4 makes little or no contribution. The latter was the path suggested by Taube and Myers.[1] At 25°, $\mu = 1{\cdot}0$M, $k_3 = 4{\cdot}23 \times 10^{-2}$ sec.$^{-1}$, and the activation parameters are $\Delta H_3^{\ddagger} = 21{\cdot}8$ ($\pm 1{\cdot}0$) kcal. mole^{-1} and $\Delta S_3^{\ddagger} = 8{\cdot}4$ ($\pm 3{\cdot}0$) e.u. In further experiments the products $IrCl_5H_2O^{2-}$ and $IrCl_6^{3-}$ were determined spectrophotometrically (*a*) directly and (*b*) by oxidizing with chlorine and using known spectra for the corresponding iridium(IV) complexes.[3] At any one temperature the ratio of the two was in good agreement with the ratio of $CrCl^{2+}$ to Cr^{3+}. The spectrum of the intermediate was obtained assuming that inner- and outer-sphere mechanisms are effective. It has general features (peaks at 354 nm., ϵ 560, and 400 nm., $\epsilon \sim 400$) which are not unlike those of hexachloroiridium(III) (358 nm., ϵ 74·5, and 417 nm., ϵ 87·5) and $CrCl^{2+}$ (428 nm., ϵ 20·4). Our experiments appear to rule out appreciable amounts of di- (and tri-) bridged intermediates, and there seems little doubt that the intermediate is in fact $[(H_2O)_5Cr\,Cl\,Ir\,Cl_5]$.

In the reactions of vanadium(III) and iron(II) with hexachloroiridium(IV) we were unable to detect binuclear intermediates by stopped-flow techniques. The product is in each case hexachloroiridium(III). The vanadium(III) reaction proceeds by an inverse hydrogen-ion-dependent path, which is not unreasonable since the product is the vanadyl ion, VO^{2+}. In this case the $[H^+]$-dependence does not constitute evidence for an inner-sphere mechanism or for hydroxy-bridging. At 25°, rate constants for the reaction of VOH^{2+} and Fe^{2+} with $IrCl_6^{2-}$ are $3{\cdot}8 \times 10^4$ and $3{\cdot}0 \times 10^6$ l.mole^{-1} sec.$^{-1}$, respectively. Alternatively the vanadium(III) reaction may be considered to be a reaction of V^{3+} with $IrCl_6^{2-}$, a proton being lost at an intermediate stage. For these reactions it is more difficult to decide whether the mechanisms are inner- and/or outer-sphere. The rate constant for the reaction of vanadium(II) with hexachloroiridium(IV) is $> 10^6$l.mole^{-1} sec.$^{-1}$ and it can be concluded that this reaction is of the outer-sphere type.

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[2] See, *e.g.* F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd edn., 1967, p. 468.

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