Production of Platinum(III) by Flash Photolysis of $PtCl_6^{2-}$

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Summary The absorption of light in the ligand-to-metal charge-transfer band of $PtCl_6^{2-}$ causes both photoaquation to $PtCl_5OH^{2-}$ and photoreduction to a Pt^{III} complex, $PtCl_4^-$.

The photochemistry of platinum(IV) halide complexes, PtX_6^{2-}, is not well understood. The photoexchanges of chloride ion with $PtCl_6^{2-}$[1,2] and of bromide ion with $PtBr_6^{2-}$[3] involve chain reactions with very large quantum yields. The chain carriers in both reactions have been suggested to be Pt^{III} species, PtX_5^{2-}, produced by photochemical reduction of the Pt^{IV} complexes. Recently the photochemistry of $PtBr_6^{2-}$ and PtI_6^{2-} was investigated.[4] Aquation was the only process observed and the quantum yield was independent of wavelength in both the charge-transfer and *d–d* bands of the complexes. We have observed both photoreduction, producing a Pt^{III} species, and photoaquation in the flash photolysis of $PtCl_6^{2-}$.

Solutions of Na_2PtCl_6 (5×10^{-5}M) were photolysed in the presence of Cl^- (10^{-3}—10^{-1}M) and H^+ (10^{-5}—10^{-1}M). The light from the $Xe–O_2$ flash lamp is essentially a continuum, but at $PtCl_6^{2-}$ concentrations of 5×10^{-5}M, light absorption in the photolysis cell by the charge-transfer band of the complex (λ_{max} 262 nm, ϵ 24,500)[5] is about 50 times greater than absorption by the *d–d* band (λ_{max} 353 nm, ϵ 490).[5]

A transient absorption was observed in the wavelength range 350—450 nm. The absorption decayed with a lifetime of about 0·1 s and the spectrum of the transient is shown in the Figure. This spectrum was obtained 50 ms after the flash. The absorption due to the transient decayed by a second-order process and plots of (absorbance)$^{-1}$ against time were linear to >90% reaction. Pt^{III} species have been observed in the pulse radiolysis of $PtCl_4^{2-}$ and $PtCl_6^{2-}$:[6]

$$PtCl_4^{2-} + OH \rightarrow Pt^{III} + OH^-$$

$$PtCl_6^{2-} + e^-_{aq} \rightarrow Pt^{III}$$

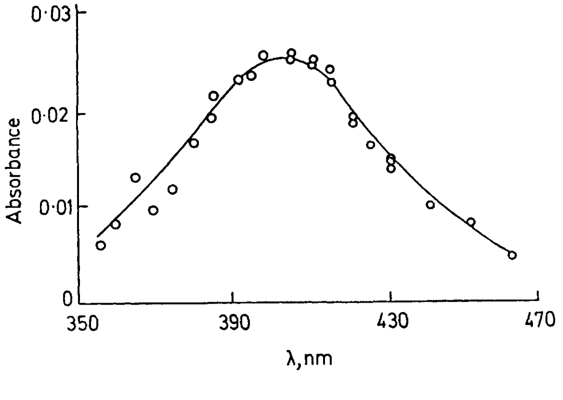

Figure. *Spectrum of the* Pt^{III} *complex formed by flash photolysis of* 5×10^{-5} M $PtCl_6^{2-}$ *in the presence of* 10^{-3}M Cl^-. *Spectrum taken* 50 ms *after the flash.*

The spectrum of the Pt^{III} complex obtained 25 μs after the radiation pulse is virtually identical with the spectrum shown in the Figure. Pt^{III} is expected to disproportionate [equation (1)] and the second-order decay of the transient

$$Pt^{III} + Pt^{III} \rightarrow Pt^{II} + Pt^{IV} \qquad (1)$$

can be identified with this reaction. The extinction coefficient of the Pt^{III} complex at 410 nm is $3{\cdot}7 \times 10^3$ [6] and we find the second-order rate constant $2k_1$ to be $4{\cdot}6 \pm 0{\cdot}4 \times 10^6$ l mol^{-1} s^{-1} at *ca.* 20° (pH 5·8 and ionic strength 10^{-3} mol l^{-1}). The relatively slow rate of the disproportionation reaction indicates that Pt^{III} is almost certainly the long-lived chain carrier responsible for the large quantum yields of the halide ion—PtX_6^{2-} photoexchanges.

Flash photolysis of the Na_2PtCl_6 solutions containing 10^{-3}M or more Cl^- also produced $\cdot Cl_2^-$ radical-ions. $\cdot Cl_2^-$ can be generated by the flash photolysis of Cl^- solutions alone:[7]

$$Cl_{aq}^- \xrightarrow{h\nu} \cdot Cl + e^-_{aq}$$

$$\cdot Cl + Cl^- \rightleftharpoons \cdot Cl_2^-$$

In our experiments the light from the flash lamp was filtered to remove light of $\lambda < 230$ nm before it was absorbed by the solution. Under these conditions no $\cdot Cl_2^-$ is produced from solutions of Cl^- alone, and the $\cdot Cl_2^-$ we have observed must be produced by the photolysis of the $PtCl_6^{2-}$.

$\cdot Cl_2^-$, and Pt^{III} leading eventually to Pt^{II}, were not the only products of photolysis. The fall in the $PtCl_6^{2-}$ concentration resulting from the flash was much greater than the Pt^{III} produced. The spectrum of the solutions after flashing showed two isosbestic points at 214 and 245 nm, which correspond to the production of the aquated product, $PtCl_5OH^{2-}$. The ratio of the quantum yields for photoaquation ($PtCl_5OH^{2-}$) and photoreduction (Pt^{III}) was about 10:1. This ratio is probably dependent on the wavelength in the same way as for the cobalt(III) acidoammines.[8]

We have found that the Pt^{III} reacts with Fe^{2+} to give Fe^{3+} [equation (2)] and k_2 is $2{\cdot}8 \pm 0{\cdot}3 \times 10^6$ l mol^{-1} s^{-1} at

$$Pt^{III} + Fe^{2+} \rightarrow Pt^{II} + Fe^{3+} \qquad (2)$$

an ionic strength of 2×10^{-3} mol l^{-1}. We have used the dependence of k_2 upon ionic strength to establish the charge on the Pt^{III} complex. The limiting slope of the plot of log k_2 *versus* $(I)^{1/2}$ is -2, and the charge on the Pt^{III} complex is therefore -1. The most likely species is $PtCl_4^-$ Adams *et al.*[6] reported that the reduction of $PtCl_6^{2-}$ by e^-_{aq} initially produces $PtCl_6^{3-}$ and suggested that this dissociates to the five-co-ordinate complex $PtCl_5^{2-}$. It seems more likely that $PtCl_6^{3-}$ would lose two Cl^- rapidly to give $PtCl_4^-$ because the d^7 Pt^{III} would favour a square-planar structure[9] with two highly labile apical positions, and the spectra of the Pt^{III} produced by photoreduction or by reduction with aquated electrons are the same.

The sequence of reactions in the photoreduction of $PtCl_6^{2-}$ in the ligand-to-metal charge-transfer band must be

$$PtCl_6^{2-} \xrightarrow{h\nu} PtCl_5^{2-} + \cdot Cl$$

followed by the two very fast reactions

$$PtCl_5^{2-} \rightarrow PtCl_4^{-} + Cl^{-}$$

$$\cdot Cl + Cl^{-} \rightleftarrows \cdot Cl_2^{-}$$

The photoaquation reaction

$$PtCl_6^{2-} \xrightarrow{h\nu} PtCl_5OH^{2-} + H^{+} + Cl^{-}$$

is considerably more efficient than the photoreduction and the ratio of the quantum yields for reduction and aquation may represent the fraction of the excited $PtCl_6^{2-}$ ions which do not undergo efficient energy transfer processes to the excited triplet state from which aquation may occur.

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