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Photoreduction of Nitric Acid by Electronically Excited Diplatinum(II,II) Pyrophosphite, $[Pt_2(P_2O_5H_2)_4]^{4-}$

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The reduction of HNO_3 (0.1 M) to NO_2^- by an electronically excited platinum complex is described; the intermediate products, $[Pt_2^{II,III}(P_2O_5H_2)_4]^{3-}$ and HNO_3^-, have been identified by transient absorption spectroscopy and quenching studies.

We describe here results for the reduction of nitric acid to nitrite ion by an electronically excited platinum complex, $[Pt_2(P_2O_5H_2)_4]^{4-}$, that is known to be a powerful reductant[1—9] in water upon excitation by irradiation. Nitric acid at a concentration of <1 M shows little oxidizing power and one-electron reduction of HNO_3 to HNO_3^- has only been reported in pulse radiolytic work.[10]

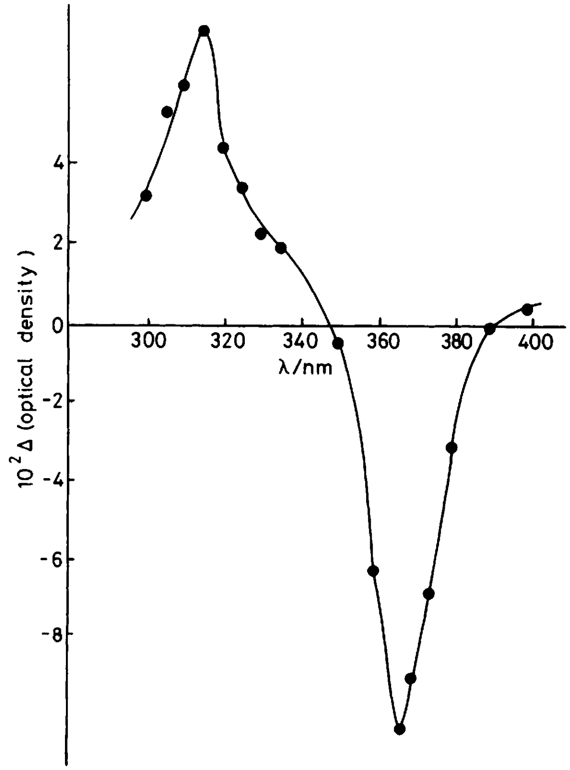

Figure 1. Transient absorption difference spectrum of $[Pt_2(P_2O_5H_2)_4]^{4-}$ in 0.1 M HNO_3 recorded 10 μs after the laser flash. Excitation, 355 nm; laser energy, ~1 mJ/cm² per pulse.

A degassed solution of $[Pt_2(P_2O_5H_2)_4]^{4-}$ in 0.1 M HNO_3 is stable in the dark for 1 h but gives an immediate transient signal upon excitation at 355 nm with a 8 ns Quanta-Ray DCR-2Nd:YAG laser. The transient absorption difference spectrum (Figure 1) recorded 10 μs after the laser flash shows intense absorption and bleaching at 317 and 367 nm respectively. The ratio of the magnitudes of the transient difference optical density at 317 and 367 nm is ~0.67, which closely matches the spectra for $[Pt_2^{II,III}(P_2O_5H_2)_4]^{3-}$ (ref. 7) and $[Pt_2^{II,III}(P_2O_5H_2)_4](Im)]^{3-}$ (Im = Imidazole) (ref. 11), generated by photoionization of $[Pt_2(P_2O_5H_2)_4]^{4-}$ and pulse radiolysis of $[Pt_2(P_2O_5H_2)_4(Im)_2]^{2-}$. With the laser energy

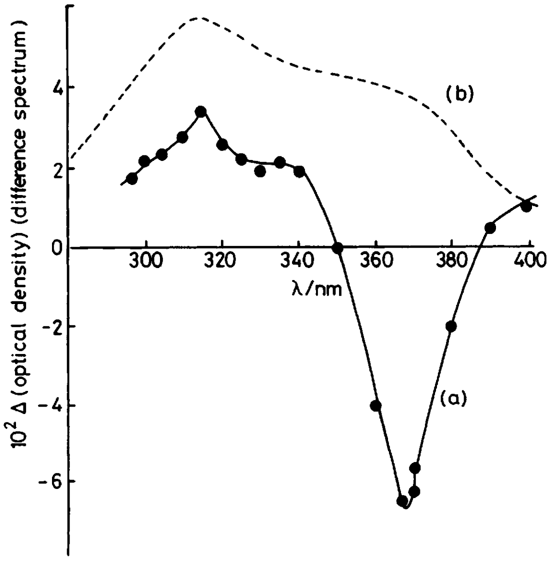

Figure 2. (a) Transient absorption difference spectrum of $[Pt_2(P_2O_5H_4)_4]^{4-}$ in 0.1 M HNO_3 recorded 100 ms after the laser flash. Excitation, 355 nm; laser energy, ~1 mJ/cm² per pulse. (b) U.v.–visible spectrum of $[Pt_2(P_2O_5H_2)_4(NO_2)_2]^{4-}$ in H_2O (arbitrary absorbance units).

employed in the experiment, in the absence of HNO_3, the production of $[Pt_2^{II,III}(P_2O_5H_2)_4]^{3-}$ through photoionization is insignificant. The phosphorescence lifetime of $[Pt_2(P_2O_5H_2)_4]^{4-}$ is 5.2, 2.8, 1.1, and 0.3 µs in 0.05, 0.1, 0.2, and 0.4 M nitric acid respectively (*cf.* 9.8 µs in distilled water).[3] The photoreaction is proton-assisted since in 0.1 M KNO_3 solution, little $[Pt_2^{II,III}(P_2O_5H_2)_4]^{3-}$ was produced under similar conditions and the phosphorescence lifetime of $[Pt_2(P_2O_5H_2)_4]^{4-}$ is only slightly affected by NO_3^- at pH 5—6. With the degree of dissociation of HNO_3 in 0.05—0.5 M reported by Davis *et al.*[12] a linear Stern–Volmer plot (τ_0/τ *vs.* concentration of undissociated HNO_3) was obtained. The bimolecular quenching rate constant for the $[Pt_2(P_2O_5H_2)_4]^{4-}$ triplet $[(d\sigma^*)^1(p\sigma)^1]$ by undissociated HNO_3 is calculated to be 5.2×10^8 mol^{-1} dm^3 s^{-1}. Thus the photoreaction immediate after the laser flash could be described as in equation (1).

$$[Pt_2(P_2O_5H_2)_4]^{4-} + HNO_3 \xrightarrow{h\nu} [Pt_2^{II,III}(P_2O_5H_2)_4]^{3-} + HNO_3^- \quad (1)$$

One-electron reduction of HNO_3 to HNO_3^- has previously been reported by Graetzel and co-workers in their pulse-radiolytic work.[10] No photoreaction was found upon flashing $[Pt_2(P_2O_5H_2)_4]^{4-}$ in 0.1 M $HClO_4$ or 0.1 M H_2SO_4.

The transient signal decays in a time-scale of 10 ms to a value different from that of the original baseline and then remains constant for seconds. Both the amplitude and the decay rate of the transient increase with the energy of the laser flash, indicating that the decay is a bimolecular process. The decay also fits bimolecular kinetics. Figure 2(a) and (b) illustrate the transient absorption difference spectrum recorded 100 ms after the flash, and the optical spectrum of an authentic sample of $[Pt_2(P_2O_5H_2)_4NO_2)_2]^{4-}$ in water. The two spectra are similar in the 300—340 nm region suggesting that Figure 2(a) corresponds to the optical spectrum of a dimeric platinum(III) complex containing axially co-ordinated NO_2^-.

The $[Pt_2^{III,III}(P_2O_4H_2)_4(H_2O)_2]^{2-}$ complex, which is the alternative photo-oxidized product, does not absorb appreciably at λ >300 nm.[13,14] That Figure 2(a) is due to $[Pt_2(P_2O_5H_2)_4(NO_3)_2]^{4-}$ is also unlikely since it is expected to have a similar optical spectrum to $[Pt_2(P_2O_5H_2)_4(H_2O)_2]^{2-}$. A possible scheme for the photoreduction is given in reactions (2)—(4).

$$[Pt_2(P_2O_5H_2)_4]^{4-} + HNO_3 \xrightarrow{h\nu} HNO_3^- + [Pt_2^{II,III}(P_2O_5H_2)_4]^{3-} \quad (2)$$

$$HNO_3^- + H^+ \xrightarrow{\text{fast}} NO_2 + H_2O \quad (3)$$

$$[Pt_2^{II,III}(P_2O_5H_2)_4]^{3-} + NO_2 \xrightarrow{H_2O} [Pt_2^{III,III}(P_2O_5H_2)_4(NO_2)(OH_2)]^{3-} \quad (4)$$

The generation of the novel HNO_3^- anion by the electronically excited $[Pt_2(P_2O_5H_2)_4]^{4-}$ further illustrates the rich photochemistry of this platinum complex.

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