Detection of a Transient Rhenium(IV)-Amine Complex from Pulse Radiolysis Studies

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Reduction of dioxobis(diamine)rhenium(V) complexes with the aquated electron generates transient d^3 Re^{IV} complexes whose electronic spectra and rates of decay have been determined.

Dioxo complexes of Re^V and Tc^V with simple multidentate amines have been known for some time, although only the 1,2-diaminoethane (en) and 1,3-diaminopropane (pn) complexes with Re^V are well characterized.[1,2] The d^2 Re^V complex $[Re(en)_2O_2]Cl$ has been characterized by a crystal structure analysis, where a monomeric octahedral geometry with *trans*-oxo ligands and en chelates was established.[3] Raman spectroscopy indicates that this geometry persists in aqueous solution, and the Re^V complex undergoes ligand substitution (amine loss) only very slowly in neutral and dilute acid solution at ambient temperatures. Since d^3 is an inherently inert electronic configuration, and Re^{IV} complexes are known with mainly halide donor ligands,[4—6] it was of interest to investigate the one electron reduction of d^2 Re^V to d^3 Re^{IV} in dioxoamine complexes.

The voltammetry of $[Re(en)_2O_2]^+$ indicates that the behaviour of the Re^V–Re^{IV} couple is markedly pH dependent. At neutral pH, an irreversible reduction is seen at appreciably negative potentials [E_{pc} −1.45 V *vs.* standard calomel electrode (s.c.e.), cyclic voltammetry at hanging mercury drop electrode (h.m.d.e), pH 5.5]. In 1 M acid, where the complex exists as $[Re(en)_2(OH)(O)]^{2+}$, the reduction potential shifts by *ca.* +1 V, and is quasi reversible ($E_{\frac{1}{2}}$ −0.50 V *vs.* s.c.e., h.m.d.e., pH 1). Protonation/deprotonation shifts of *ca.* 1 V have been observed for other third row transition metal complexes recently, namely for Pt^{IV} and Os^{IV},[7] so this effect is not unique. Since coulometric reduction and reoxidation in 1 M acid does not produce a product with the initial absorption spectrum, the reduced complex is not stable on the coulometric timescale (min). In order to detect and characterize spectrophotometrically the Re^{IV} complex in neutral solution, and to determine the stability, we have employed the rapid timescale technique of pulse radiolysis.

A microanalytically pure sample of $[Re(en)_2O_2]Cl$ was prepared as previously described.[1] The complex in triply-distilled water ($[Re] \leqslant 10^{-3}$ M) was treated with a strong reducing agent, e_{aq}, using an N_2-purged solution containing 0.1 M t-butyl alcohol as a radical scavenger of OH. The 1 MeV pulse radiolysis facility, optical system, and process of kinetic analysis have been described previously.[8] The system was calibrated by thiocyanate dosimetry.[9] Initial and final optical density changes were measured at 5—20 nm intervals from signal-averaged data over the range 240—700 nm. This allowed measurement of the absorption spectra of the intermediate and decay products. The kinetics were followed at several wavelengths in the u.v.–visible region.

Reaction of $[Re(en)_2O_2]^+$ with the strong reducing agent e_{aq} (E° = −2.8 V) in water (pH *ca.* 6) proceeds with a formation constant $k_f = 2.3 \times 10^{10}$ dm^3 mol^{-1} s^{-1} to yield a transient with maxima at 500 (ε 150 dm^3 mol^{-1} cm^{-1}) and 330

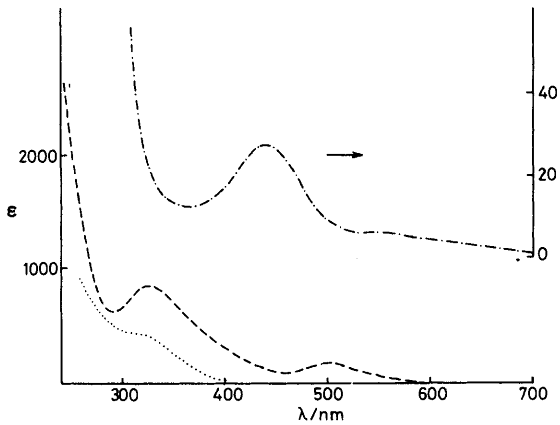

Figure 1. Electronic spectrum of *trans*-$[Re(en)_2O_2]^+$ precursor (-·-·-·-·-), the d^3 Re^{IV} intermediate (-------), and the decay product (···········).

nm (850), Figure 1. This transient decays by a first order pathway with a rate constant of 6×10^3 s^{-1} to a product which shows no measurable absorbance in the visible region beyond a shoulder near 320 nm. The analogue $[Re(pn)_2O_2]^+$ under similar conditions yields a transient with absorption maxima at 500 (ε 120) and 325 nm (1100), which decays with a rate constant of 9×10^3 s^{-1}.

Reaction of Re^V with e_{aq} can be considered to give either direct reduction of the metal centre to Re^{IV}, or to produce a Re^V ligand radical. Direct metal-centred reduction is usually preferred to the formation of unsaturated ligand radicals, at least with first row metal complexes. Further, ligand radicals yield strong absorption spectra in the u.v. region only. The observation of a transient with absorption maxima at 500 and 330 nm, and with ε values below 10^3 dm^3 mol^{-1} cm^{-1} is most consistent with the initial formation of a Re^{IV} complex. The presence of two maxima in these regions is not inconsistent with expectations for a d^3 metal ion with N and O donors. The stable monomeric octahedral complex *trans*-$Re(acac)_2Cl_2$ (acac = MeCOCHCOMe) exhibits bands in the visible region near 500 (ε 260), 420 (810), and 330 nm (1600);[5] although the tetragonally-distorted O_4Cl_2 donors cannot be directly compared with the presumed N_4O_2 donors in this case, the resemblances are notable. No stable Re^{IV} complexes with mixed N,O donors are known; the Re^{IV} complexes which are known and stable are usually monomeric and octahedral, and contain halide or mixed halide and O or P donors.

We assert that reaction of d^2 $[Re(diamine)_2O_2]^+$ complexes with e_{aq} generates a d^3 Re^{IV} species which decays with a half-life of <1 ms. The first order nature of the decay suggests that amine ligand loss may be rate determining. The nature of the decay product(s) has not been ascertained at present. The limited current knowledge of the amine co-ordination chemistry of rhenium does not permit ready identification of products, although perhaps polymeric species, or eventually hydrated ReO_2 on a longer timescale, could be expected.

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