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# Evidence for a Two-Electron Transfer Using Cr(II) as a Reductant

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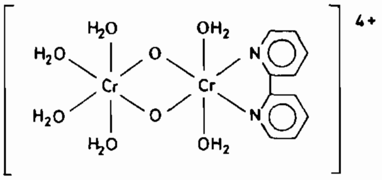
In a previous communication [1] and paper [2] we produced evidence that 2,2′-bipyridine (bipy) coordinated to a metal oxidant, may be transferred to Cr(II) during the act of electron transfer, either as a result of inner-sphere attack at a monodentate ligand or as a consequence of strong complexation between the free ligand and the labile Cr(II) centre.

We now wish to report a different manifestation of 2,2′-bipyridine serving as a bridging ligand. In the Cr(II) reduction of $[Co(bipy)_3]^{3+}$, the reaction product is a very stable chromium dimer containing a single 2,2′-bipyridine ligand indicating that two electrons must have been transferred to the cobalt oxidant. To the best of our knowledge, there is no precedent for such a curious reaction, although Kupferschmidt and Jordan [3] have recently reported the formation of chromium dimers and trimers with reduction of the double bond in the reaction between $[Co(NH_3)_5NCCH{=}CHCN]^{3+}$ and Cr(II).

The initial reduction occurred too quickly to be observed on the stopped-flow instrument and we may set a lower limit of $k = 1.28 \times 10^4\ M^{-1}\ s^{-1}$ (25.0 °C, $\mu = 1.0$ M ($LiClO_4$), $[H^+] = 0.10$ M) for this reaction. A complex series of at least four rapid steps (depending on the wavelength used) was subsequently observed on the stopped-flow instrument. Analytically pure samples of the oxidant were used in these studies. The cobalt complex was carefully ion-exchanged and was recrystallised twice from double-distilled deionised water using $NaClO_4$ as the precipitating agent. This was done to ensure that all traces of extraneous ions were removed. Several different preparations gave the same reproducible kinetic results.

The product analysis studies were done by mixing known amounts of Cr(II) and $[Co(bipy)_3]^{3+}$ in 0.10 M $HClO_4$ under an argon atmosphere for a few seconds and then aerating for five minutes to oxidise any Cr(II) which may remain. The reaction mixture was subsequently diluted with water and was placed on a Sephadex SP-120 cation-exchange column. If these studies were run under stoicheiometric conditions (1:1 ratio of Co(III) to Cr(II)), a red chromium-containing species was obtained in 98% yield. It had a 4+ charge, as determined by its ion-exchange behaviour. However, only 70 ± 5% of the $[Co(bipy)_3]^{3+}$ was used up in these experiments, suggesting that at least in one pathway, more than one equivalent of Cr(II) was required to reduce the Co(III) complex. If the experiments were done with a two-fold excess of Cr(II) over Co(III), no $[Co(bipy)_3]^{3+}$ remained on the ion-exchange column, indicating that the reaction was complete under these conditions. The UV–Vis spectrum of the red chromium species was obtained and extinction coefficients were calculated by analysing aliquots of these solutions using a standard chromate method [4]: $\lambda_{max}(nm)(\epsilon_{max}(M^{-1}\ cm^{-1}))$, 538 (21 ± 1), 442sh(23 ± 1), 412sh(59 ± 4), 390sh(82 ± 7), 247(5,900 ± 400), 307(8,500 ± 700). It was also necessary to determine the ratio of 2,2′-bipyridine to chromium(III) in the product. This was done by taking aliquots of a solution containing the red chromium species and analysing for the chromium content [4], then taking another aliquot of the same solution and analysing for 2,2′-bipyridine. To analyse for 2,2′-bipyridine, the solution was decomposed using zinc–mercury amalgam under an inert argon atmosphere to give the labile Cr(II) metal ion and free 2,2′-bipyridine. After the decomposition was complete (≃24 h), excess sodium carbonate was added to convert the chromium complex to the insoluble hydroxide. Upon sitting for a further ≃24 h, the chromium decomposition process was found to be complete. The free ligand was extracted into hexane and was analysed spectrophotometrically. Triplicate determinations of the chromium and 2,2′-bipyridine contents of the product obtained from separate experiments showed that there were two chromium metal ions for each 2,2′-bipyridine in the red complex. The most probable structure, which must have a 4+ charge to satisfy the ion-exchange observations is the hydroxo-bridged dimer, A.



**A**

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We were unable to prepare the red complex **A** by substitution of bipy on $[Cr(OH_2)_6]^{3+}$ nor by quenching $[Cr(OH_2)_6]^{2+}$ in the presence of bipy. Quenching experiments were performed using both the stoichiometric ratio (1:2) of bipy to $[Cr(OH_2)]^{2+}$ and various excesses of the free ligand. In all cases, the only bipy-containing complexes obtained in reasonable yields were $[Cr(OH_2)_4bipy]^{3+}$, a purple compound, $[Cr(OH_2)_2(bipy)_2]^{3+}$, reported earlier [5] or $[Cr(bipy)]_3$, a yellow species. These studies indicate that the red dimer, **A**, can only be prepared by electron transfer.

This reaction differs from that studied by Kupferschmidt and Jordan [3] in that in the fumaronitrile system, the kinetics showed stepwise reductions to give initially the expected product, $[(OH_2)_5\text{-}CrNCCH{=}CHCN]^{3+}$ which rapidly aquated to give $[Cr(OH_2)_6]^{3+}$ and the free ligand. The dimer arose as a result of attack of excess Cr(II) on the double bond of the free ligand. In the present work, it appears that the second electron transfer step leading to the dimer is faster than the first so no intermediate is formed, and there is no evidence for reduction of the ligand in **A**.

These experiments indicate that electron transfer reactions involving metal chelates may be subject to much greater mechanistic variation than had previously been suspected. Not only may 2,2′-bipyridine serve as a bridging ligand, but also we find that multi-electron transfer may occur when the bridging ligand is capable of existing, at least temporarily, as a coordinated radical.

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