One-electron Reduction of Tris(bipyridyl) Complexes of Cobalt(III) and Chromium(III)

By MORTON Z. HOFFMAN*
(*Department of Chemistry, Boston University, Boston, Massachusetts* 02215 *and Pioneering Research Laboratory, U.S. Army Natick Laboratory, Natick, Massachusetts* 01760)

and M. SIMIC
(*Radiation Biology Laboratory, University of Texas, Austin, Texas* 78712 *and Pioneering Research Laboratory, U.S. Army Natick Laboratory, Natick, Massachusetts* 01760)

Summary The reaction of e^-_{aq} with $Co(bipy)_3^{3+}$ and $Cr(bipy)_3^{3+}$ produces an intense transient absorption at 300 nm which decays *via* first-order kinetics with $k = 3{\cdot}5\ s^{-1}$; the intermediates are not excited spin states of the metal centres nor can they be described simply as radical anions of the pyridyl ligands.

WALTZ and PEARSON[1] observed a weak transient absorption at $\lambda > 400$ nm upon the reaction of e^-_{aq} with $Co^{III}(bipy)_3^{3+}$ (bipy = 2,2′-bipyridyl) using pulse radiolysis techniques. The transient reacted rapidly with O_2 and $Co^{III}(bipy)_3^{3+}$ ($k \sim 10^9$ M s^{-1}) and was suggested to be $Co^{II}(bipy)_3^{3+}$ with the metal centre in its low-spin $t_{2g}^6 e_g$ electronic configuration. The final product was high-spin ($t_{2g}^5 e_g^2$) $Co^{II}(bipy)_3^{2+}$. More recently, Baxendale and Fiti[2] repeated these experiments and made similar spectral observations at $\lambda > 400$ nm. They concluded that the transient was the electron-adduct to the ligand, $Co^{III}(bipy)_2(bipy^-)^{2+}$.

We have examined the reaction of e^-_{aq} and $Co^{III}(bipy)_3^{3+}$ by pulse radiolysis[3,4] using relatively low concentrations (4×10^{-5} M) of $Co^{III}(bipy)_3^{3+}$ in order to investigate the spectral region $\lambda < 400$ nm and have observed an intense absorption band at λ_{max} 300 nm with ϵ_{max} $4{\cdot}2 \times 10^4$ M^{-1} cm^{-1}. Identical transient absorptions were obtained using CO_2^- and Me_2COH radicals as the reductants ($k = 7 \times 10^9$ M^{-1} s^{-1}). The transient absorptions in all cases decayed *via* pH-(0·5—10·5) and substrate-independent (1—5 × 10^{-5} M) first-order kinetics with $k = 3{\cdot}5\ s^{-1}$. The final product was identified spectrally as $Co^{II}(bipy)_3^{2+}$; the *G*-value of Co^{II} formation from the continuous radiolysis of Co^{III}-$(bipy)_3^{3+}$ in 0·1 M $HClO_4$ and 0·2 M propan-2-ol was 6·2 indicating that quantitative reduction occurs. When $Cr^{III}(bipy)_3^{3+}$ reacts with these reducing agents, a transient absorption is observed that is virtually identical with that obtained from $Co^{III}(bipy)_3^{3+}$; the decay of this intermediate is first order with $k = 3{\cdot}5\ s^{-1}$.

These results are to be compared with those obtained from the reaction of e^-_{aq} with bipy. The electron adduct to the free ligand has an intense absorption maximum at λ 365 nm with ϵ_{max} 3·0 × 10^4 $M^{-1}\ cm^{-1}$ at pH 9 and λ 375 nm at pH 4 with ϵ_{max} 4·5 × 10^4 $M^{-1}\ cm^{-1}$. It should be noted that CO_2^- and Me_2COH do not react at a measurable rate ($k < 10^6\ M^{-1}\ s^{-1}$) with bipy but react fairly rapidly ($k = 3 \times 10^8\ M^{-1}\ s^{-1}$) with its protonated forms. This electron adduct decays *via* pH-dependent second-order kinetics. Although the electron adduct to bipy reacts with *p*-benzoquinone to produce the semiquinone by electron transfer, the electron added to the complexes cannot be recovered by the quinone.

The following conclusions can be drawn from these results:

(i) The transient we observe at 300 nm is completely unrelated to the transient observed previously;[1,2]

(ii) The intensity of the 300 nm transient absorption establishes that it arises from the major reaction;

(iii) The weak absorption at $\lambda > 400$ nm is the result of a very minor process involving e^-_{aq}, as with an impurity, or, alternatively, is due to the reaction of another primary radical, such as H atoms, with the complex;

(iv) The transient intermediate cannot be attributed to an excited spin state of the reduced metal centre nor can it be described simply as a free radical co-ordinated to the metal centre in its higher oxidation state;

(v) The one-electron reduction of these complexes proceeds *via* the addition of an electron to an orbital of the ligand which, although possessing characteristics similar to those of the state populated upon electron addition to the free ligand (as evidenced by the intense u.v. absorption), is sufficiently perturbed by interaction with the metal centre to cause a blue-shift of the absorption spectrum and lack of reactivity with quinone;

(vi) The nature of the intermediate (spectrum and decay kinetics) appears to depend on the fact that the metal centre has a +3 charge, not on the detailed electronic structure of the metal;

(vii) The decay of the intermediate represents intramolecular transfer of the added electron to the metal centre with the extremely low rate indicative of the barriers to the process.

We thank the National Science Foundation and National Institutes of Health for financial support and Dr. E. Hayon of the U.S. Army Natick Laboratories for the use of the pulse radiolysis apparatus.

(*Received*, 30*th May* 1973; *Com.* 755.)

[1] W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, 1969, **73**, 1941.
[2] J. H. Baxendale and M. Fiti, *J.C.S. Dalton*, 1972, 1995.
[3] M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, 1972, **92**, 1757.
[4] M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 3794.