Inorganica Chimica Acta, 45 (1980) L87–L88
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Quenching of the Emission of Tris(2,2'-bipyridine)ruthenium(II) by Substituted Bis(ethylenediamine) Complexes of Osmium

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Received April 12, 1980

Although quenching of the emission of excited tris(2,2'-bipyridine)ruthenium(II), $^*Ru(bpy)_3^{2+}$, has been studied in solution for a variety of species [1–5], little work has been done employing osmium ammines or saturated amines. The new series of bis(ethylenediamine)osmium complexes, *trans*-$OsO_2(en)_2^{2+}$ *cis*-$Os(en)_2H_2^{2+}$, and *cis*-$Os(en)_2Cl_2^+$ forms an unusual group of substrates that do quench $^*Ru(bpy)_3^{2+}$ effectively. This communication describes a determination of the rates at which $^*Ru(bpy)_3^{2+}$ is quenched by these species. A parallel is found between the relative quenching efficiencies and the susceptibilities of the complexes to oxidation or reduction.

Experimental

Materials

Tris(2,2'-bipyridine)ruthenium(II) chloride, obtained from G.E. Smith Chemical Co., was purified by two recrystallizations. *Trans*-dioxobis(ethylenediamine)oxmium(VI) chloride was prepared as described previously from osmium tetroxide (Engelhard Industries, Inc.) [6, 7]. The complex ion *cis*-dihydridobis(ethylenediamine)osmium(IV), $Os(en)_2H_2^{2+}$, was prepared in dilute HCl solution by reduction of the dioxo complex with zinc amalgam [6]. Solutions of this species used in the quenching experiments therefore contained nearly a threefold excess of aqueous zinc ion, relative to the dihydride. The chloride salt of *trans*-dichlorobis(ethylenediamine)osmium(III), $[Os(en)_2Cl_2]Cl\cdot H_2O$, was obtained by air oxidation of $Os(en)_2H_2^{2+}$ in aqueous, dilute HCl [8]. The oxidation was carried out after separating Zn(II) from the solution by ion exchange technique. After two recrystallizations, the dioxo and dichloro complexes gave uv spectra that were qualitatively and quantitatively in agreement with published values [6–8]. Although the dihydrido complex was not isolated as a solid it, too, gave spectra consistent with previously published data [6]. All three complexes are yellowish in solution and yellow or yellow-orange in crystalline form.

TABLE I. Quenching of $Ru(bpy)_3^{2+}$ Luminescence by Some Complexes of Osmium.[a]

Quencher Q	$10^{-2} \times K_{sv}$ (M^{-1})	k_q (M^{-1} s^{-1})[b]
$Os(en)_2O_2^{2+}$	10.0	1.67×10^9
$Os(en)_2H_2^{2+}$	1.37	2.28×10^8
$Os(en)_2Cl_2^+$	0.313	5.21×10^7

[a] 25 °C, μ = 0.5 *M*, 0.13 *M* HCl, 0.37 *M* NaCl, 9.6×10^{-6} *M* $[Ru(bpy)_3^{2+}]$. [b] τ_o = 0.6 μs.

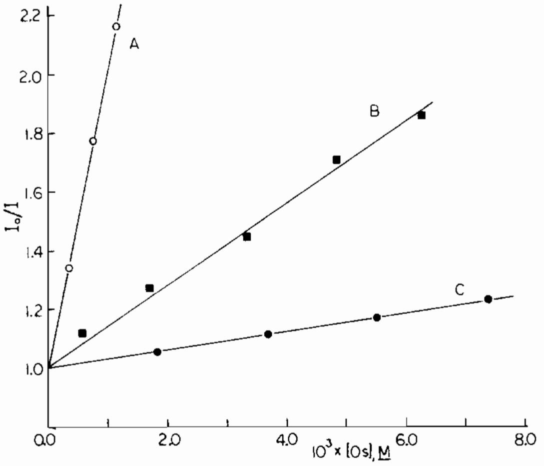

Fig. 1. Stern–Volmer plots for the quenching of $^*Ru(bpy)_3^{2+}$ emission (25 °C, 0.133 *M* HCl, 0.367 *M* NaCl): A, *trans*-$Os(en)_2O_2^{2+}$; B, *cis*-$Os(en)_2H_2^{2+}$; C, *trans*-$Os(en)_2Cl_2^+$.

Emission Intensity Measurements

The emission from the ruthenium(II) complex was monitored using a Perkin-Elmer Model MPF-4 fluorescence spectrometer equipped with a 150 W xenon lamp. Samples containing Ru(II) and quencher were excited at the absorbance maximum of the complex near 450 nm. The emission intensities were monitored at the wavelength of maximum emission (near 600 nm in the energy mode). All of the emission measurements were made in 1 cm^2 cells. Solutions of the complexes were bubbled with argon prior to use to remove oxygen. For the dihydrido complex, syringe transfer techniques were employed using platinum needles.

Results and Discussion

Stern–Volmer plots obtained from intensity measurements for the three osmium complexes are shown in Fig. 1. We note that no siginficant variation of the emission occurred during the time of the measurements, involving irradiation of the samples for up to one-half hour. This indicated that $Ru(bpy)_3^{2+}$ was not measurably consumed in the quenching process. The linearity of the plots is consistent with a dynamic quenching mechanism. In Table I are presented values of k_q which have been computed from the slopes of the Stern–Volmer plots, employing eqn. 1.

$$\frac{I_o}{I} = 1 + k_q\tau_o[Q] \qquad (1)$$

Mechanisms involving exciplex formation or static quenching are unlikely for these complexes. Therefore the possible quenching mechanisms involve energy transfer, eqn. (2), or redox reactions in which the excited state takes on or gives up an electron, as in eqns. (3) and (4), respectively.

$$^*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{2+} + Q^* \qquad (2)$$

$$^*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{+} + Q^+ \qquad (3)$$

$$^*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{3+} + Q^- \qquad (4)$$

A requirement for energy transfer is the existence of low-lying energy states in the quencher that are energetically accessible to excitation by $^*Ru(bpy)_3^{2+}$. We have sought but have not observed low energy bands in the visible regions of the spectra of the present series of osmium complexes. Moreover, it is known that the ligand field and charge transfer absorptions in the few existing analogous osmium ammines occur at wavelengths shorter than the $^*Ru(bpy)_3^{2+}$ emission [9]. Thus, no explicit support for an energy transfer quenching mechanism can be found for the quenchers studied here. However, we note that a given low-lying excited state need not be directly accessible from the ground state and, therefore, that an energy transfer mechanism is not obviated by the absence of a low energy absorption band. Emission from the bis(ethylenediamine)-osmium complex ions has not been observed.

In dealing with the question of electron transfer quenching, it is useful to consider first the redox capability of $^*Ru(bpy)_3^{2+}$ and second, the susceptibility of the osmium complex ions to oxidation and reduction. $E_{1/2}$ values for reduction and for oxidation of $^*Ru(bpy)_3^{2+}$ have been estimated as *ca.* 0.84 V [2, 10], $Os(en)_2O_2^{2+}$, the most efficient of the quenchers in Table I, is an oxidant which can be reduced by H_2/Pt but not by I^- in aqueous solution. Thus, $Os(en)_2O_2^{2+}$ is susceptible to reduction by $^*Ru(bpy)_3^{2+}$ with a driving force of at least 0.84 V. k_q for the quenching reaction is 1.2×10^9 M^{-1} s^{-1}, a specific rate which is consistent with a diffusion controlled reaction between two bipositive ions. This rapid reaction is tentatively ascribed to electron transfer quenching.

$Os(en)_2H_2^{2+}$ is an unusually stable metal hydride that does not react with aqueous hydrogen ion [6]. The dihydride is oxidized by O_2, I_3^- or electrochemically at *ca.* 0.2 V *vs.* NHE. Although this species is thermodynamically susceptible to oxidation by $^*Ru(bpy)_3^{2+}$, the rate of quenching is decreased fivefold in comparison with the dioxo species, and is slightly low in comparison with known values of k_q in redox quenching processes of comparable driving force (*ca.* 0.6 V) [4]. At this time the reactivity of the dihydrido species is not well-understood. However, it seems possible that the low value of k_q for this species reflects a mechanistic tendency for the hydride to act as a two-electron, rather than a one-electron, reducing agent.

The osmium(III) amine $Os(en)_2Cl_2^+$ has been examined by cyclic voltammetry in acidic solution. The complex presents a catalytic (H^+) reduction wave near –0.8 V relative to NHE and an irreversible anodic wave near 0.75 V. This species, therefore, also is subject to oxidation, and possibly to reduction, by $^*Ru(bpy)_3^{2+}$ but with substantially lower driving force than the dioxo and dihydrido species. The comparatively low value of k_q, 5.21×10^7 M^{-1} s^{-1}, for the osmium(III) complex is qualitatively consistent with the electrochemical observations. However, it is important to remember that since an energy transfer quenching mechanism may also be important, k_q may include a contribution from that mechanism.

Acknowledgements

This research was supported in part by the U.S. Energy Research and Development Administration, and partly by a University of Missouri Summer Faculty Fellowship. Dr. Gilbert Brown is thanked for his assistance with the cyclic voltammetry measurements and Dr. Norman Sutin is thanked for his kind hospitality at Brookhaven National Laboratory.

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