J. Electroanal. Chem., 244 (1988) 319–324
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary note

ELECTROGENERATED CHEMILUMINESCENCE

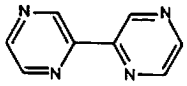
PART 51. THE TRIS(2,2′-BIPYRAZINE)OSMIUM(II) SYSTEM

CHI-WOO LEE, JIANGBO OUYANG and ALLEN J. BARD
Department of Chemistry, The University of Texas, Austin, TX 78712 (U.S.A.)

(Received 10th February 1988)

INTRODUCTION

We describe here a new polypyridyl osmium system, $Os(bpz)_3^{2+}$ (bpz = 2,2′-bipyrazine),



whose electrogenerated chemiluminescence (ECL), produced by alternate generation of oxidized and reduced reactants, is more intense than other known osmium(II) tris chelates and whose excited state lifetime is longer. The chemiluminescence that arises from the highly energetic and fast electron transfer reactions between two reactants generated at electrode surfaces, has been investigated extensively [1–3]. The best characterized metal chelate ECL system is probably $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) [2,4–6]. For comparison, we recently examined the related $Ru(bpz)_3^{2+}$ [3]. The electrochemical and ECL behavior of the $Ru(bpz)_3^{2+}$ system in general paralleled that of the corresponding bpy system with higher energies involved for identical electron transfer events. To see if the same parallelism would hold with osmium(II), we investigated the electrochemical and ECL behavior of $Os(bpz)_3^{2+}$ in acetonitrile (MeCN) media. An additional motivation for this study was the search for a useful ECL tag with emission at wavelengths significantly different from those of $Ru(bpy)_3^{2+}$. We have recently discussed the application of metal chelates as tags for analytical methods [7] and the availability of tags at different wavelengths would allow multiple tests to be carried out simultaneously.

Previous studies on the ECL of Os complexes have been reported [8]. The results showed that the ECL intensity was much higher than that of previously known tris polypyridyl osmium(II) complexes of bpy or phen (phen = 1,10-phenanthroline) and the excited state lifetime was much longer.

0022-0728/88/$03.50

EXPERIMENTAL

The bpz ligand was prepared by a literature method [9] and $Os(bpz)_3^{2+}$ by a method similar to one described for $Os(bpy)_3^{2+}$ [10]. Final purification of the dark-green product was effected by chromatography on alumina [11,12]. The tetrabutylammonium hexafluorophosphate (TBAFP) was obtained from Southwestern Analytical Chemicals (Austin, TX). HPLC grade MeCN (Fisher Scientific, Fair Lawn, NJ) was purified and dried by continuous refluxing, then distillation, from P_2O_5 under a nitrogen atmosphere. The solvent was degassed by freeze–pump–thaw cycles ($< 10^{-5}$ Torr) before it was transferred by bulb-to-bulb distillation under vacuum to an electrochemical cell containing the samples, which had been dried in advance under vacuum overnight. A two-compartment cell was used to carry out most experiments, except the coulometric measurements, where a three-compartment cell was employed. Three-electrode configurations were used with either a platinum disk, a platinum/mica [13], or a platinum foil as working electrode, platinum foil or vitreous carbon as auxiliary electrode and an Ag wire reference electrode. The silver quasi-reference electrode (AgRE) was separated from the working electrode chamber by a medium porosity frit, and the potential of AgRE was checked against the ferrocene/ferrocenium couple in the sample solution at the end of experiments [14]. Measured potentials were referenced to a saturated sodium calomel electrode (SSCE) using +0.31 V vs. SCE for the ferrocene/ferrocenium couple [15]. Electrochemical and ECL experiments were performed with a Princeton Applied Research (PAR) Model 175 Universal Programmer, Model 173 Potentiostat/Galvanostat and Model 179 digital coulometer. The ECL spectra were recorded using an Aminco-Bowman spectrometer with a Hamamatsu R928 photomultiplier tube. UV/Vis absorption spectra were obtained with a Hewlett-Packard Model 8450A dual-beam spectrometer. The excited state lifetime was measured by using Photochemical Research Associates Correlated Single-Photon Counting Apparatus as described earlier [16].

RESULTS AND DISCUSSION

Figure 1 shows a cyclic voltammogram (CV) recorded with 1 m*M* $Os(bpz)_3^{2+}$ in 0.1 *M* TBAFP + MeCN at a platinum working electrode. The peak separation for each wave was near 60 mV and the peak currents were similar in size for the four different cathodic and anodic waves, respectively. In addition, the ratios of cathodic to anodic peak currents in each pair of waves were equal to one. A separate coulometric measurement at constant potential (−0.75 V) confirmed that the number of electrons involved is one for the first reduction of $Os(bpz)_3^{2+}$. (During this bulk electrolysis, the solution color changed from green to dark red.) Thus, the three reduction and one oxidation processes are assigned to the 2+/+, +/0, 0/− and 2+/3+ couples, respectively. The general electrochemical pattern of the $Os(bpz)_3^{2+}$ system is very similar to that of $Os(bpy)_3^{2+}$ in MeCN, but there are important differences. The potentials for the reductions to the +, 0, and − species

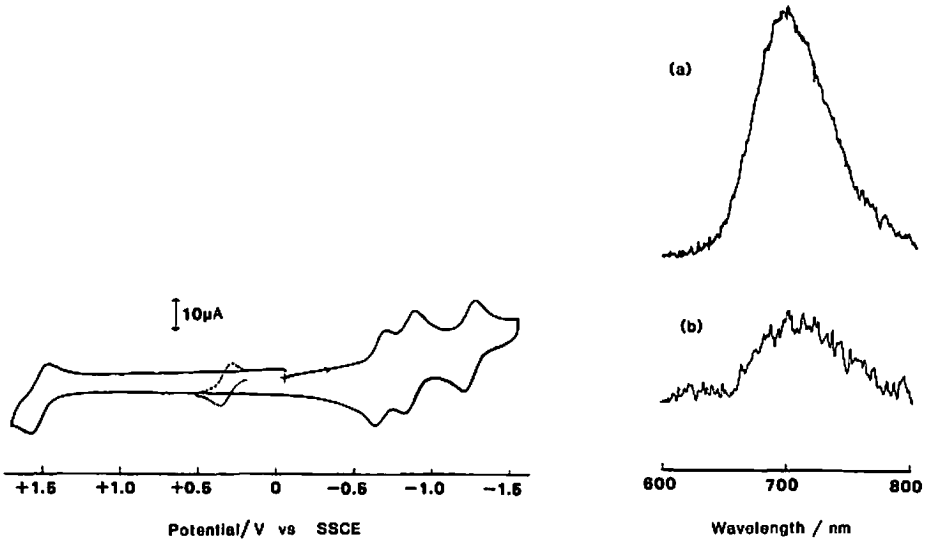


Fig. 1. Cyclic voltammogram of 1 m*M* $Os(bpz)_3PF_6$ at a Pt electrode in MeCN + 0.1 *M* TBAFP. Scan rate, 100 mV/s. The dotted portion shows the ferrocene/ferrocinium couple response.

Fig. 2. (a) Luminescence spectrum of 0.2 m*M* $Os(bpz)_3^{2+}$ in MeCN solution with excitation at 450 nm. (b) ECL emission spectrum for 1 m*M* $Os(bpz)_3^{2+}$ in 0.1 *M* TBAFP + MeCN solution using a cyclic square wave at 50 Hz between +1.7 V and −0.8 V vs. AgRE.

and the oxidation to the 3+ species were shifted to more positive values by potentials of 500 to 700 mV as compared to those for the bpy complex, indicating that the $Os(bpz)_3^{3+}$ species is a much stronger oxidant than is $Os(bpy)_3^{3+}$ and that the reduced species are milder reductants than the bpy ones. Thus, investigation of electron transfer chemistry of $Os(bpz)_3^{2+}$ can be conveniently explored in common non-aqueous solvents without being limited by solvent potential windows [17]. Electrochemical results are summarized, along with luminescence data, in Table 1. The data for the bpy and phen complexes of Os are also listed for comparison.

When the potential of the platinum electrode was pulsed at a frequency of 50 Hz between the anodic peak potential of oxidation and the cathodic peak potential of the first reduction in 1 m*M* $Os(bpz)_3^{2+}$ solution, ECL was observed with an emission maximum wavelength of 700 nm (Fig. 2b). (Less intense ECL was observed under identical conditions with the $Os(bpy)_3^{2+}$ or $Os(phen)_3^{2+}$ complexes [8].) ECL emission was also observed with higher pulsing frequencies and by stepping the potential between the anodic peak potential of oxidation and the cathodic peak potential of the second or third reduction waves. The observed ECL spectrum is very similar to the luminescence spectrum obtained in MeCN solution (Fig. 2a) with the same maximum wavelength at 700 nm. Based on these results, the electrogenerated species are believed to produce the emitting species $Os(bpz)_3^{2+*}$,

TABLE 1

Electrochemical and luminescence data for tris-polypyridyl complexes of osmium(II) [a]

Complex	$E^{\circ\prime}_{3+/2+}$/V	$E^{\circ\prime}_{2+/+}$/V	$E^{\circ\prime}_{+/0}$/V	$E^{\circ\prime}_{0/-}$/V	$\lambda_{max.ECL}$/nm [b]	$\lambda_{max.em}$/nm [b]	τ/μs [c]
$Os(bpy)_3^{2+}$	0.82	−1.26	−1.45	−1.76	720	724	0.02
$Os(phen)_3^{2+}$	0.86	−1.25	−1.42	−1.76	691	690	0.08
$Os(bpz)_3^{2+}$	1.52	−0.67	−0.86	−1.24	700	700	0.24

[a] At room temperature. All potentials are given vs. SSCE in acetonitrile. Data on bpy and phen complexes from refs. 12 and 13.

[b] In acetonitrile solution of 0.1 *M* tetrabutylammonium perchlorate or hexafluorophosphate.

[c] Excited state lifetime in acetonitrile.

with ECL generated by the same path as that proposed for $Ru(bpy)_3^{2+}$ and $Ru(bpz)_3^{2+}$:

$$Os(bpz)_3^{2+} + e^- \rightarrow Os(bpz)_3^{+}$$

$$Os(bpz)_3^{2+} - e^- \rightarrow Os(bpz)_3^{3+}$$

$$Os(bpz)_3^{+} + Os(bpz)_3^{3+} \rightarrow Os(bpz)_3^{2+*} + Os(bpz)_3^{2+}$$

Independent UV/Vis absorption experiments demonstrated that $Os(bpz)_3^{2+}$ absorbed electromagnetic radiation in a similar pattern as $Os(bpy)_3^{2+}$ [18–20] with wavelength maxima at 630, 558, 468, 412, 301, and 240 nm; these are blue-shifted from those observed with the bpy complex, indicating that higher energies are required for the equivalent charge transfer transitions with the $Os(bpz)_3^{2+}$ system. Time resolved emission measurements showed that the lifetime of $Os(bpz)_3^{2+*}$ was ca. 0.24 μs. It is interesting to note that $Os(bpz)_3^{2+*}$ shows a stronger ECL than $Os(bpy)_3^{2+*}$ and a longer lifetime, although the emission energy is nearly the same. Recently, Meyer [11] and Abruna [8] reported that a two- to three-order of magnitude longer excited state lifetime than that of $Os(bpy)_3^{2+}$ and stronger ECL were observed with $Os(bpy)_2(L)_2^{2+}$ systems (L = 1,2-bis-diphenylphosphinoethane, 1,2-bis-diphenylarsinoethane, etc.). However, theoretical analysis of these mixed ligand systems would not be as straightforward as with the trispolypyridyl complexes, $Os(bpy)_3^{2+}$ or $Os(phen)_3^{2+}$ because of their lower symmetry and heterogeneous ligand environments caused by the non-polypyridyl ligand coordination [19,21,22]. In this respect, the more symmetrical and single ligand species, $Os(bpz)_3^{2+}$, may offer a simpler exercise for theoretical understanding toward lengthening excited state lifetime and ECL properties of osmium(II) species. In addition, ECL was observed when the electrode potential was scanned to +1.4 V in 0.2 *M* phosphate (pH 7.0) aqueous solution of $Os(bpz)_3^{2+}$ (0.3 m*M*) and oxalate (30 m*M*). The reaction sequence in this case may be the same as that proposed for

$Ru(bpy)_3^{2+}/C_2O_4^{2-}$ systems as follows [7]:

$$Os(bpz)_3^{2+} \rightarrow Os(bpz)_3^{3+} + e^-$$

$$Os(bpz)_3^{3+} + C_2O_4^{2-} \rightarrow Os(bpz)_3^{2+} + C_2O_4^{\cdot -}$$

$$C_2O_4^{\cdot -} \rightarrow CO_2 + CO_2^{\cdot -}$$

$$Os(bpz)_3^{2+} + CO_2^{\cdot -} \rightarrow Os(bpz)_3^{+} + CO_2$$

$$Os(bpz)_3^{3+} + Os(bpz)_3^{+} \rightarrow Os(bpz)_3^{2+*} + Os(bpz)_3^{\cdot 2+}$$

Thus, the $Ox(bpz)_3^{2+}$ system appears promising as an analytical tag in the red region.

In conclusion, the tris-bipyrizine complex of Os(II) has the longest excited state lifetime among known osmium(II) tris chelates, and its ECL is one of the most intense.

ACKNOWLEDGEMENTS

The support of the Army Research Office and and the Robert A. Welch Foundation is gratefully acknowledged. We thank Prof. Steve E. Weber for allowing us to use his apparatus and Ms. Keiko Kamioka for helping us obtain excited state lifetimes.

REFERENCES

1 L.R. Faulkner and A.J. Bard in A.J. Bard (Ed.), Electroanalytical Chemistry, Vol. 10, Marcel Dekker, New York, 1977, p. 1
2 N.E. Tokel and A.J. Bard, J. Am. Chem. Soc., 94 (1972) 2862.
3 J. Gonzales-Velasco, I. Rubinstein, R.J. Crutchley, A.B.P. Lever and A.J. Bard, Inorg. Chem., 22 (1983) 822.
4 N.E. Tokel-Takavoryan, R.E. Hemingway and A.J. Bard, J. Am. Chem. Soc., 95 (1973) 652.
5 J.D. Luttmer and A.J. Bard, J. Phys. Chem., 85 (1981) 1155.
6 S.S. Glass and L.R. Faulkner, J. Phys. Chem., 85 (1981) 1159.
7 D. Ege, W.G. Becker and A.J. Bard, Anal. Chem., 56 (1984) 2413.
8 H.D. Abruna, J. Electroanal. Chem., 175 (1984) 321.
9 R.J. Crutchley and A.B.P. Lever, Inorg. Chem., 21 (1982) 2276.
10 J.G. Gaudiello, P.G. Bradley, K.A. Norton, W.H. Woodruff and A.J. Bard, Inorg. Chem., 23 (1984) 3.
11 E.M. Kober, B.P. Sullivan, W.J. Dressick, J.V. Caspar and T.J. Meyer, J. Am. Chem. Soc., 102 (1980) 7383.
12 C.-W. Lee, D.J. Ecker and K.N. Raymond, J. Am. Chem. Soc., 107 (1985) 6920 and references therein.
13 H.-Y. Liu, F.-R.F. Fan and A.J. Bard, J. Electrochem. Soc., 132 (1985) 2666.
14 G. Gritzner and J. Kuta, Pure Appl. Chem., 48 (1984) 462.
15 A.J. Bard and L.R. Faulkner, Electrochemical Methods, Wiley, New York, 1980, p. 701.
16 J.A. Delare, M.A.J. Rodgers and S.E. Weber, J. Phys. Chem., 88 (1984) 6219.
17 C.K. Mann in A.J. Bard (Ed.), Electroanalytical Chemistry, Vol. 3, Marcel Dekker, New York, 1969, p. 57.

18 F.H. Burstall, F.P. Dwyer and E.C. Gyarfas, J. Chem. Soc., (1950) 953.
19 F. Felix, J. Ferguson, H.U. Gudel and A. Ludi, Chem. Phys. Lett., 62 (1979) 153.
20 C. Creutz, M. Chou, T.L. Netzel, M. Okumura and N. Sutin, J. Am. Chem. Soc., 102 (1980) 1309.
21 S. Decurtins, F. Felix, J. Ferguson, H.U. Gudel and A. Ludi, J. Am. Chem. Soc., 102 (1980) 4102.
22 E.M. Cober and T.J. Meyer, Inorg. Chem., 21 (1982) 3967.