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TEMPERATURE DEPENDENCE OF ECL EFFICIENCY OF TRIS(BIPYRIDINE)Ru(II) COMPLEX

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Temperature dependence of ecl efficiency(η) and that of phosphorescence quantum yield(ϕ_p) of tris(bipyridine)Ru(II)-acetonitrile system have been investigated. Both η and ϕ_p increased with lowering temperature, while the ratio η/ϕ_p remained nearly constant. The value of η reached ca. 7 % at 0°C. Based on these results the ecl generation mechanism is discussed.

Photochemical and photoelectrochemical properties of tris(bipyridine)Ru complex have been studied with much interest in recent years.[1] It has been verified that the CT triplet state of this complex emits photons as phosphorescence with relatively high quantum yield.[2),3)] Tokel and Bard first reported the electrochemiluminescence (ecl) of the $Ru(bipy)_3^{2+}$-acetonitrile system and assigned its emission to the phosphorescence from the CT triplet state of the complex.[4] They reported the value of 5-6 % as an ecl efficiency for this system.[5] Such a realtively high ecl efficiency was attributed to the direct formation of the excited triplet state via electron transfer between +1 and +3 species as follows.

$$R^+ + R^{3+} \xrightarrow{k_1} {}^1(R^{2+})^* + R^{2+} \quad (1)$$

$$\xrightarrow{k_2} {}^3(R^{2+})^* + R^{2+} \quad (2)$$

$$\xrightarrow{k_3} 2R^{2+} \quad (3)$$

$${}^1(R^{2+})^* \longrightarrow {}^3(R^{2+})^* \quad (4)$$

$${}^3(R^{2+})^* \longrightarrow R^{2+} + h\nu \quad (5)$$

However, no further quantitative discussion has been made until present time. We report here a large temperature dependence of the ecl efficiency of $Ru(bipy)_3^{2+}$-acetonitrile system and give a semi-quantitative discussion concerning the possibility of formation of triplet state by the +1, +3 annihilation reaction on the basis of experimental results.[6]

Figure 1 shows the experimental setup for the measurement of ecl efficiency and its temperature dependence. Ecl efficiency η was measured by means of a calibrated photomultiplier Hamamatsu R374 with a 0.5x0.5 cm^2 aperture assembled on an integrating box whose inner wall was coated with a TiO_2 paint having an almost flat reflection characteristics within the visible light region. The light collecting efficiency of the integrating box was calculated to give 1.17×10^{-4} by the use of a small tungsten lamp as a nearly non-directional light source. The average quantum

efficiency of the photomultiplier was calculated to give 1.92 % based on the spectral sensitivity of the photomultiplier and the corrected emission spectrum of $Ru(bipy)_3^{2+}$ complex. Thus, the number of emitted photons could be obtained from the photo-output of the photomultiplier.

$Ru(II)(bipy)_3(ClO_4)_2$ was synthesized and purified according to the literature.[7] $Ru(II)(bipy)_3(ClO_4)_2$(2mM)-TBAP(0.04M)-acetonitrile system was electrolyzed with a square voltage wave with two platinum wire electrodes. Faradaic current was separated from the total current by a modified Pighin's method.[8] For the temperature control in the ecl cell, water thermostated by a Haake Circulator Model FKN was circulated in the outer jacket of the cell. In the steady state, the temperatures of inside of the cell and that of inside of the outer jacket were the same within experimental error. Ecl measurement was carried out after several freeze-pump-thaw cycles to eliminate the influence of O_2. The value of the phosphorescence quantum yield of Ru complex was determined using rhodamine B as a standard material (ϕ_f=0.61 in ethanol at room temperature[9]). The shape of the emission spectrum showed no change within the temperature range studied (0-40 °C).

Figure 2 shows the temperature dependence of the ecl efficiency η of the Ru complex system at 24 Hz. The value of η at 20 °C was 4 %, which compares well with that reported by Tokel-Takvoryan et al.[5] As Fig. 3 shows, η depends on the square wave frequency in a similar manner with the rubrene ecl system as reported by Pighin.[8] The value of η extrapolated to 0 Hz (η_0) was 1.13 times that at 24 Hz. Temperature dependence of this factor could be regarded to be small enough. Hence the maximum value of η experimentally accessible in the present work (at 0 °C and 0 Hz) is 7.0 % which is, to our knowledge, one of the highest ecl efficiencies ever reported.[10]

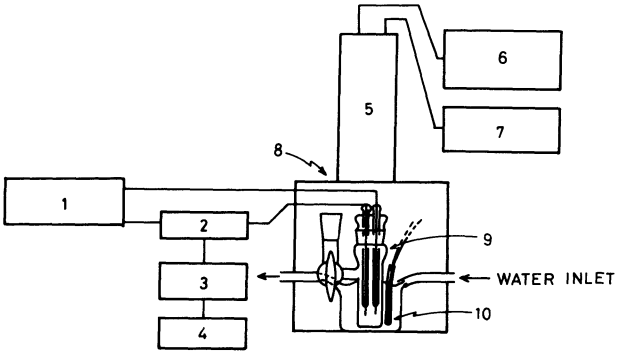

Fig. 1 Block diagram for the measurement of ecl efficiency: 1, function generator; 2, amplifier; 3, rectifier; 4, recorder; 5, photomultiplier; 6, high voltage source; 7, recorder; 8, integrating box; 9, ecl cell; 10, thermocouple.

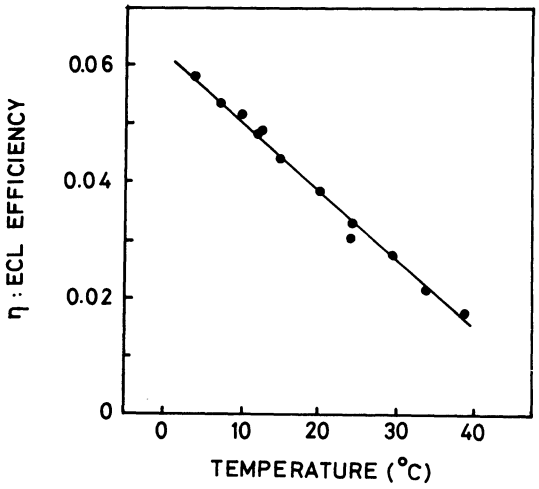

Fig. 2 Temperature dependence of ecl efficiency at 24 Hz.

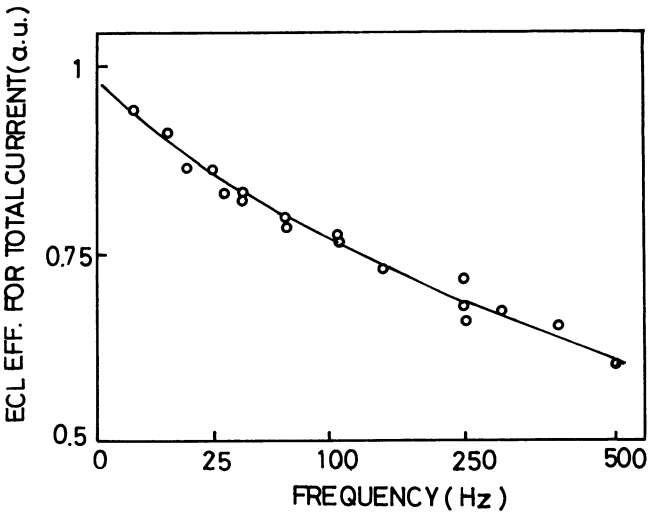

Fig. 3 Dependence of ecl efficiency on the square wave frequency.

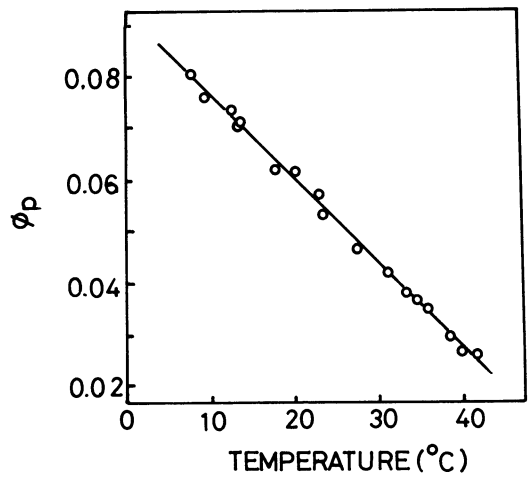

Fig. 4 Temperature dependence of ϕ. [Ru complex]=5.0×10^{-5} M. The ϕ_p for a 2mM Ru complex solution, employed in ecl experiments, showed the same temperature dependence.

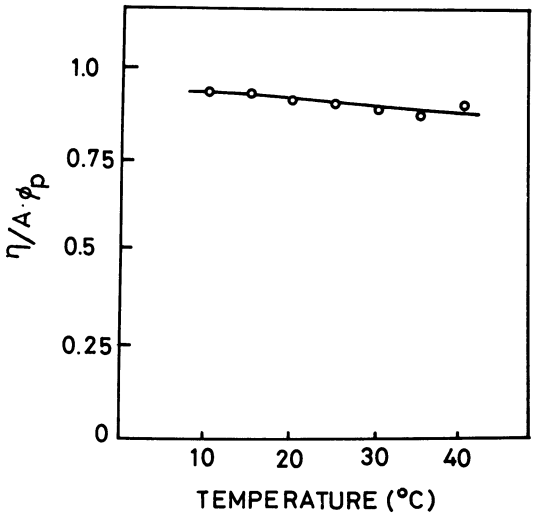

Fig. 5 Temperature dependence of $\eta_0/A\cdot\phi_p$.

Figure 4 shows the temperature dependence of the phosphorescence quantum yield ϕ_p. It increases with lowering temperature just like as η. The values of ϕ_p measured in this work in acetonitrile are larger than those in H_2O[3] and smaller than those in D_2O.[3] The presence of TBAP had no effect on ϕ_p.

Considering the reaction sequence (1)-(5), the following formula for η is obtained.

$$\eta = A\cdot\frac{k_1 + k_2}{k_1 + k_2 + k_3}\cdot\phi_p \qquad (6)$$

Here, A is a correction factor due mainly to the emission loss by the reflection of the electrode surface. In deriving the above equation, we regarded the efficiency of the intersystem crossing (eq. (4)) to be almost unity according to the literature.[10] Figure 4 shows the temperature dependence of $\eta_0/A\cdot\phi$ ($=(k_1+k_2)/(k_1+k_2+k_3)$). Here, we set A=0.8 following the estimation by Keszthelyi et al.[11], taking into account only the emission loss by the reflection of Pt (reflectance=0.6[11]). The value $\eta_0/A\cdot\phi$ is nearly constant in this temperature region (Fig. 5). This result indicates that the increase of η with lowering temperature uniquely reflects the increase of ϕ_p (i.e., increase in the triplet lifetime of the Ru complex.) We obtain $(k_1+k_2):k_3=11.5$ employing the value of $\eta_0/A\cdot\phi_p=0.92$ at lower temperatures.

Although the value of $(k_1+k_2):k_3$ is not sufficiently precise because of the

possible errors in estimating A,[12] it is evident that the emitting triplet state is produced with high efficiency, close to unity, by the 1+, 3+ annihilation reaction (2), and that the dominant factor determining η is ϕ_p in the present ecl system. Factors which increase ϕ_p, therefore, may cause a further increase in η. An increase in ϕ will be possible by replacing the ligands or by deuterium substitution in ligands and/or in the solvent.[3]

REFERENCES AND NOTES

1) C. T. Lin and N. Sutin, J. Phys. Chem., 80 97 (1976).
2) G. D. Hager, R. J. Watts, and G. A. Crosby, J. Amer. Chem. Soc., 97 7037 (1975).
3) J. Van Houten and R. J. Watts, J. Amer. Chem. Soc., 98 4853 (1976).
4) N. E. Tokel and A. J. Bard, J. Amer. Chem. Soc., 94 2862 (1972).
5) N. E. Tokel-Takvoryan, R. E. Hemingway, and A. J. Bard, J. Amer. Chem. Soc., 95 6582 (1973).
6) Just prior to submitting this manuscript we became aware through private communications of similar studies being carried out by William L. Wallace and Allen J. Bard at the University of Texas at Austin with conclusions similar to the ones reported here. Both groups have also examined the temperature dependence of the ecl efficiency of 9,10-diphenylanthracene, again with similar results. We thank proffessor Bard for a preprint of his work on the $Ru(bipy)_3^{2+}$ system.
7) F. H. Burstall, J. Chem. Soc. [London] 1936 173.
8) A. Pighin, Can. J. Chem., 51 3467 (1973).
9) E. N. Viktorova and I. A. Hofman, Zh. Fiz. Khim., 39 2643 (1965).
10) F. E. Lytle and D. M. Hercules, J. Amer. Chem. Soc., 91 253 (1969).
11) C. P. Keszthelyi, N. E. Tokel-Takvoryan, H. Tachikawa, and A. J. Bard, Chem. Phys. Letters, 15 219 (1973).
12) C. P. Keszthelyi, N. E. Tokel-Takvoryan, and A. J. Bard, Anal. Chem., 47 249 (1975).
13) a) Here we assume that the emission loss due to radical re-discharge is negligible,[14] though an earlier work by Schwartz and Robinson[15] led to a correction factor of 0.828 for this effect.
    b) A re-absorption process, causing a shift of the emission spectrum by the filtering effect,[12] was taken into account in estimating the average quantum efficiency of the photomultiplier. A re-emission process[10] was regarded to be negligible for the low values of ϕ_p.
14) A. J. Bard, private communication.
15) P. M. Schwartz, R. A. Blakely, and B. B. Robinson, J. Phys, Chem., 13 1862 (1972).

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