Chemiluminescence of $Ru(bpy)_3^{2+*}$ in the reaction of electron transfer from Ph_3CNa to $Ru(bpy)_3^{3+}$ in a solution

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Conditions for the generation of the $Ru(bpy)_3^{3+}$ complex in organic solvents (Me_3CN or $MeNO_2$) in the presence of small amounts of H_2SO_4 were found. Chemiluminescence was observed in the reaction of $Ru(bpy)_3^{3+}$ with Ph_3Na in a THF—MeCN mixture. The chemiluminescence emitter was identified as $Ru(bpy)_3^{2+*}$. This emitter forms in the excited state in the elementary reaction of electron transfer from the Ph_3C^- anion to $Ru(bpy)_3^{3+}$.

Key words: chemiluminescence, photoluminescence, ruthenium complex, organometallic compounds.

Redox reactions of heterovalent ruthenium complexes are among the best studied chemiluminescent systems.[1—3] The $Ru(bpy)_3^{3+}$ complex is generally prepared by oxidation of $Ru(bpy)_3^{2+}$ (bpy — α,α'-bipyridyl) with lead dioxide in aqueous solutions of acids because attempts to obtain $Ru(bpy)_3^{3+}$ in organic solvents have been unsuccessful.[4] More recently, it has been demonstrated that $Ru(bpy)_3^{3+}$ can be prepared in organic solvents but in an acidic medium.[5,6] The specificity of operations with organometallic compounds does not allow one to use aqueous solutions as a medium as well as to use acids because they are highly aggressive with respect to organometallic compounds. Therefore, it was of interest to find out whether it is possible to prepare the $Ru(bpy)_3^{3+}$ complex in an organic medium and whether this complex can participate in chemiluminescent reactions with organometallic compounds.

Experimental

The solvents (MeCN, $MeNO_2$, and THF) used in this work were purified according to a known procedure.[7] H_2SO_4 of high purity grade and doubly distilled water was used. The $Ru(bpy)_3Cl \cdot 6H_2O$ complex was synthesized according to a procedure reported previously.[8] The $Ru(bpy)_3^{3+}$ complex was prepared by dissolving a weighed sample of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ in MeCN or $MeNO_2$ in an argon atmosphere followed by addition of the oxidant PbO_2 (0.1 mmol) and concentrated H_2SO_4 (to $[H_2SO_4] = 10^{-3}$ mol L^{-1}) to the reaction solution ($[Ru] = 10^{-3}$ mol L^{-1}, $V = 10$ mL). The formation of the $Ru(bpy)_3^{3+}$ complex was monitored spectrophotometrically (Specord M-40) taking into account a decrease in the intensity of absorption bands of $Ru(bpy)_3^{2+}$ as well as taking into account a decrease in the intensity of photoluminescence of the $Ru(bpy)_3^{2+}$ complex ($\lambda_{max} = 608$ nm) measured on a spectrofluorometer assembled on the basis of a MDR-23 scanning monochromator. Ph_3CNa was prepared by the reaction of sodium amalgam with Ph_3CCl in THF under argon. Chemiluminescence was recorded on an instrument reported previously[3] after addition of an aliquot of solutions of the $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ complexes to a solution of Ph_3CNa in a glass chemiluminescence cell under argon. The chemiluminescence spectra were measured using a set of cutoff light filters.

Results and Discussion

Photoluminescence of $Ru(bpy)_3^{3+}$ compounds is absent and observed only in the case of the $Ru(bpy)_3^{2+}$ complex. Therefore, the $Ru(bpy)_3^{2+}$—$Ru(bpy)_3^{3+}$ conversions in the course of oxidation can be monitored taking into account a decrease in the intensity of photoluminescence of the $Ru(bpy)_3^{2+}$ complex. In special experiments, it was established that a decrease in the intensity of photoluminescence is not caused by quenching of $Ru(bpy)_3^{2+*}$ with lead dioxide or acid. The addition of even a large excess of the oxidant PbO_2 to a solution of the $Ru(bpy)_3^{2+}$ complex in MeCN or $MeNO_2$ in the absence of acid afforded only a small amount of the $Ru(bpy)_3^{3+}$ complex, which is manifested in an insignificant decrease in the intensity of photoluminescence (Fig. 1, curve *2*). This photoluminescence decay is attributable to oxidation of $Ru(bpy)_3^{2+}$ according to the following equation

$$2\ Ru(bpy)_3^{2+} + PbO_2 + 4\ H^+ \rightleftharpoons$$

$$\rightleftharpoons 2\ Ru(bpy)_3^{3+} + Pb^{2+} + H_2O. \qquad (1)$$

Protons required for the oxidation arise apparently

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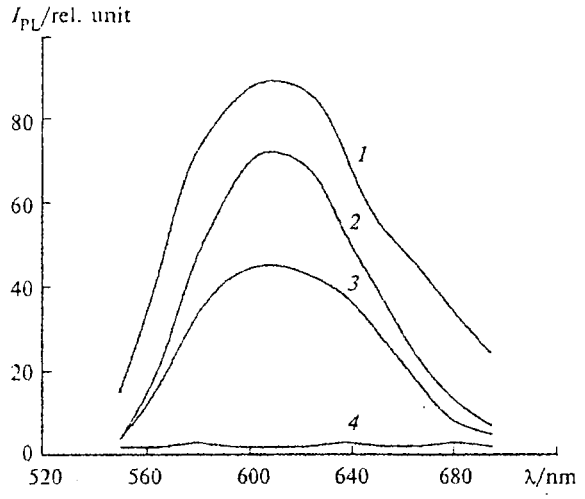

Fig. 1. Photoluminescence (PL) spectra of solutions of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ in MeCN at 298 K: *1*, $Ru(bpy)_3Cl_2 \cdot 6H_2O$ = 10^{-5} *M*; after addition of PbO_2 (0.1 mmol) (*2*), H_2SO_4 (10^{-4} *M*) (*3*), and $[H_2SO_4] = 10^{-3}$ *M* (*4*).

due to the interaction of PbO_2 with traces of water, which are hard to remove:

$$PbO_2 + H_2O \rightleftharpoons H_2PbO_3, \qquad (2a)$$

$$H_2PbO_3 \rightleftharpoons H^+ + HPbO_3^-. \qquad (2b)$$

The initial hexahydrate $Ru(bpy)_3Cl_2 \cdot 6H_2O$ can serve as an alternative source of protons.

When the acid was added to a solution of $Ru(bpy)_2^{2+}$ containing PbO_2 (0.1 mmol) until the H_2SO_4 : $Ru(bpy)_3^{3+}$ ratio became equal to 10, the intensity of photoluminescence decreased more substantially (see Fig. 1, curve *3*). Although the amount of the acid was substantially larger than that corresponding to the stoichiometry of reaction (1), the complete transformation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ was not achieved. In this case, the intensity of photoluminescence decayed virtually immediately after addition of a portion of the acid and then the intensity of photoluminescence remained unchanged. It appeared that for complete oxidation of $Ru(bpy)_3^{2+}$ to occur, it is necessary to add the acid in the ratio H_2SO_4 : $Ru(bpy)_3^{3+}$ = 100, *i.e.*, a 50-fold excess of H_2SO_4 with respect to the stoichiometry of Eq. (1) is required.

Since the content of the acid in the solution was very small ([MeCN] : $[H_2SO_4] = 2 \cdot 10^4$), reaction (1) proceeded virtually in an organic medium. The concentration of H_2SO_4 in the solution (10^{-3} mol L^{-1}) was two orders of magnitude lower than that of Ph_3CNa, which was used in the reaction with the $Ru(bpy)_3^{3+}$ complex. This amount of the acid in the reaction with Ph_3CNa gave substantially less intense chemiluminescence than that observed in the reactions of organometallic compounds with the $Ru(bpy)_3^{3+}$ complex.

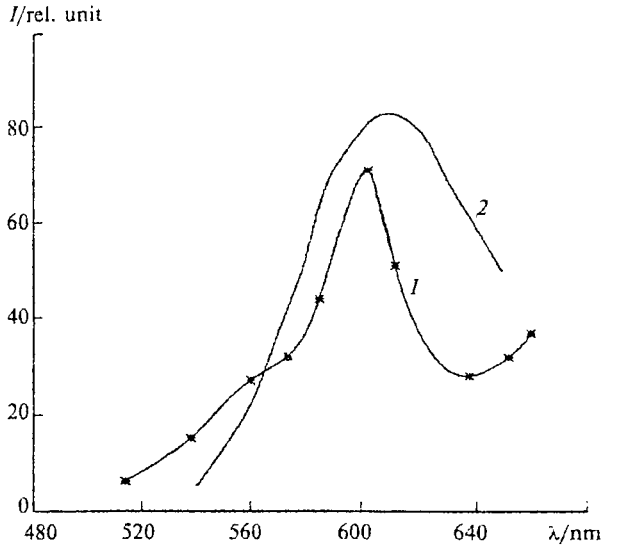

Fig. 2. Chemiluminescence spectrum (*1*) obtained during oxidation of Ph_3CNa (10^{-1} *M*) in THF with the $Ru(bpy)_3^{3+}$ complex (10^{-4} *M*) and the photoluminescence spectrum (*2*) of an acetonitrile solution of $Ru(bpy)_3^{2+}$ (10^{-4} *M*), λ_{exc} = 365 nm, T = 298 K.

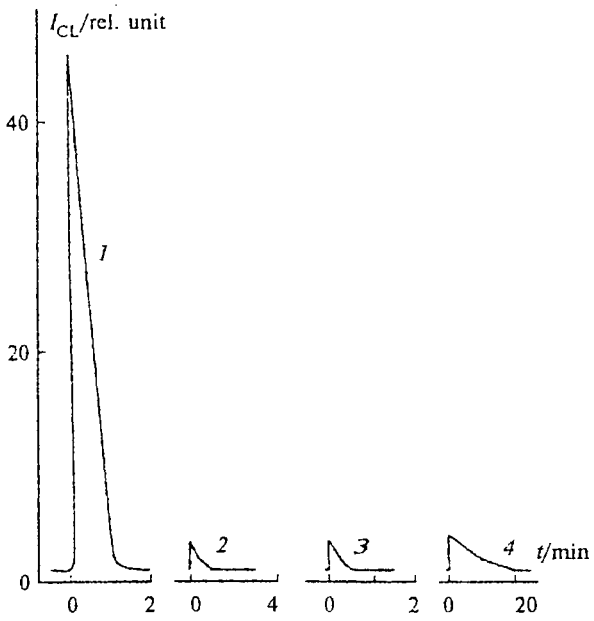

Fig. 3. Change in the intensity of chemiluminescence with time when a solution of Ph_3CNa (10^{-1} *M*) in THF was added to acetonitrile solutions: *1*, $Ru(bpy)_3^{3+}$ (10^{-4} *M*); *2*, H_2SO_4 (10^{-2} *M*); *3*, $Ru(bpy)_3^{2+}$ (10^{-4} *M*); and *4*, with the solvent (MeCN).

Therefore, we found the conditions for the generation of the $Ru(bpy)_3^{3+}$ complex in an organic solvent, which allow one to use this complex as a reagent in chemiluminescent redox reactions with organometallic compounds.

Recently it has been reported[9] that chemiluminescence was observed during oxidation of the radical ion

of the aromatic polycyclic hydrocarbon Na^+R^- with the $Ru(bpy)_3^{3+}$ complex. The chemiluminescence spectrum consists of a short-wavelength structure band due to radiation from singlet molecules of aromatic hydrocarbons ($^1R^*$) and a long-wavelength diffuse band of luminescence from $Ru(bpy)_3^{2+*}$.

We observed chemiluminescence during oxidation of Ph_3CNa with the $Ru(bpy)_3^{3+}$ complexes in a THF solution whose spectrum differs substantially from that obtained previously[9] because the former occurs due to emission of only one luminescence emitter. The chemiluminescence spectrum, which was measured with the use of cutoff light filters because of its low intensity, is observed in the red region and correlates well (Fig. 2) with the photoluminescence spectrum of an acetonitrile solution of the $Ru(bpy)_3^{2+}$ complex. This means that the $Ru(bpy)_3^{2+*}$ complex, which is formed in the electron-transfer reaction, can serve as the chemiluminescence emitter.

$$Ph_3C^-Na + Ru(bpy)_3^{3+} \rightarrow [Ph_3C^-Na^+...Ru(bpy)_3^{3+}] \rightarrow \rightarrow Na^+ + Ru(bpy)_3^{2+} + Ph_3C^{\cdot}. \quad (3)$$

The free energy of reaction (3), which was calculated with the use of electrochemical redox potentials,[10,11] is 2.32 eV. This provides excitation of $Ru(bpy)_3^{2+}$ (2.10 eV); however, this value is insufficient for population of the emitting level of $(Ph_3C^{\cdot})^*$ (2.37 eV). Although the energy deficiency of reaction (3) is small (0.05 eV), the absence of characteristic luminescence from the trityl radical indicates that this radical is not formed in the excited state.

Since even traces of O_2 afford $(Ph_3C^{\cdot})^*$ as a result of autooxidation of $Ph_3C^-Na^+$ and the energy of the excited state of $(Ph_3C^{\cdot})^*$ is higher than that of $Ru(bpy)_3^{2+*}$, the possibility of generation of $Ru(bpy)_3^{2+*}$ not only according to reaction (3) but also *via* the energy transfer from the excited radical must not be ruled out

$$(Ph_3C^{\cdot})^* + Ru(bpy)_3^{2+} \rightarrow Ph_3C^{\cdot} + Ru(bpy)_3^{2+*}. \quad (4)$$

It is also conceivable that $Ru(bpy)_3^{2+}$ forms according to reaction (3) in the ground rather than in an excited state and it is excited only through reaction (4).

To test these ways of excitation of the chemiluminescence emitter, we carried out a series of control experiments (Fig. 3). Curves *2—4* were obtained in the reactions of solutions of Ph_3CNa in THF with sulfuric acid in acetonitrile (curve *2*), with a solution of the $Ru(bpy)_3^{2+}$ complex (curve *3*), and with the solvent (acetonitrile) as such (curve *4*). It can be seen that luminescence is observed in the presence of even acetonitrile alone. Consequently, triphenylmethyl sodium is actually oxidized by traces of O_2. Chemiluminescence that appears during the interaction of sulfuric acid with THF (see Fig. 3, curve *2*) is also insignificant and makes no noticeable contribution to the total luminescence. In two cases (curves *3* and *4*), the intensity of chemiluminescence is virtually identical, which indicates that the energy transfer from the excited radical to $Ru(bpy)_3^{2+}$ does not occur.

This conclusion is confirmed by the results of an experiment in which a solution of the $Ru(bpy)_3^{2+}$ complex was added to a cell containing a solution of Ph_3CNa, which exhibits luminescence during oxidation with an air stream. In the case of energy transfer, an increase in the intensity should be observed against the background of a chemiluminescence decay, the kinetics of chemiluminescence being unchanged. However, no changes in the intensity of chemiluminescence were observed when the $Ru(bpy)_3^{2+}$ complex was added to the reaction solution.

The results obtained in this work suggest that the generation of the chemiluminescence emitter, $Ru(bpy)_3^{2+*}$, occurs in the elementary reaction of electron transfer from the Ph_3C^- anion to $Ru(bpy)_3^{3+}$.

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