Brief Communications

Regeneration of the $Ru(bipy)_3Cl_2$ excitation under chemiluminescence activation in the reaction of diphenylmethane autooxidation in an alkaline medium

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The effect of the $Ru(bipy)_3Cl_2$ [Ru^{II}] complex on chemiluminescence in the autooxidation of diphenylmethane in the presence of Bu^tOK was studied. The luminescence increases due to the participation of an activator in the redox processes. The excitation of the R^{II} complex occurs in the stage of oxidation by the superoxide anion of the Ru^I complex formed by the one-electron reduction of the initial Ru^{II} by anions.

Key words: chemiluminescence, $Ru(bipy)_3Cl_2$, diphenylmethane, autooxidation, electron-transfer.

Excitation of the $Ru(bipy)_3Cl_2$ complex (henceforth Ru^{II}) in luminescence reactions usually occurs during the reactions of $Ru(bipy)_3^{3+}$ (Ru^{III}) with reducing agents such as hydrazine,[1] a solvated electron,[2] or coordination compounds of transition metals.[3] It has recently been observed that the formation of electron-excited Ru^{II} during the oxidation of organoaluminum compounds (OAC) by xenon difluoride in the presence of ruthenium complexes also occurs at the stage of one-electron reduction by the starting OAC of the oxidized form of the activator, Ru^{III} formed in the reaction of Ru^{II} with XeF_2 or the $XeF^\cdot$ radical.[4] The Ru^{II} complex can also be excited during the one-electron oxidation of Ru^I.[5] In this case, it occurs upon the oxidation of electrochemically generated Ru^I by the 10-methylphenothiazine radical cation.

In this work, we studied the excitation of Ru^{II} during the activation of chemiluminescence (CL) in the diphenylmethane autooxidation in the presence of Bu^tOK in DMSO through the stage of formation of the reduced form of the activator, Ru^I.

Experimental

Diphenylmethane was purified by recrystallization from hexane. Bu^tOK was synthesized from Bu^tOH and potassium. DMSO was purified by the standard procedure[6] and dried with 4A sieves. NaO_2 was obtained according to the known procedure.[7] CL was measured on an installation similar to that described previously.[8] Absorption spectra were recorded on a Specord M-40 spectrophotometer, and fluorescence (FL) spectra were recorded on a Hitachi MPF-4 spectrofluorimeter.

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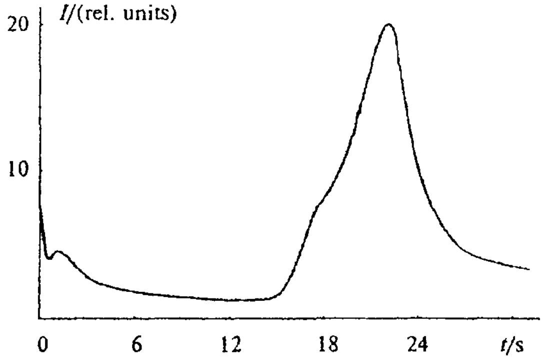

Fig. 1. Change in time of CL during autooxidation of Ph_2CH_2 in an alkaline medium in the presence of Ru^{II}. $[Ph_2CH_2] = 2.5 \cdot 10^{-3}$ mol L^{-1}; $[Ru^{II}] = 1 \cdot 10^{-3}$ mol L^{-1}; $[Bu^tOK] = 0.067$ mol L^{-1}; DMSO, 298 K.

Results and Discussion

CL appears on mixing of a solution of Ph_2CH_2 and Bu^tOK in DMSO (through which O_2 is bubbled) with a solution of Ru^{II} (Fig. 1). The spectrum of the CL observed (Fig. 2) coincides with the FL spectrum of the solution after the end of the reaction and corresponds to the FL spectrum of Ru^{II}. The electron-excited Ru^{II*} complex is the CL emitter. As shown previously,[9] in the absence of Ru^{II} a relatively weak CL of the product of oxidation of diphenylmethane (triplet benzophenone (^3BP)) is observed, whose intensity (I_{CL}) decreases exponentially with time. If Ru^{II} was excited only due to the energy transfer from ^3BP, the shape of the kinetic curve would be the same as in the absence of Ru^{II}. However, as seen in Fig. 1, the addition of the activator changes substantially the CL kinetics: a maximum appears in the kinetic curve.

Thus, the luminescence of Ru^{II} observed is mainly due to its chemical excitation in redox reactions occurring in the system under study. The electron-excited Ru^{II} complex can be formed either in the reduction of Ru^{III} or due to the oxidation of Ru^I. In this system, superoxide anion is the strongest oxidant, and its redox potential ($E_0(O_2^-/O_2^{2-}) = 1.72$ V)[10] is quite enough for the oxidation of Ru^{II} ($E_0(Ru^{III}/Ru^{II}) = 1.23$ V).[11] In an alkaline medium, the Ru^{III} formed transforms rapidly into Ru^{II}, and this process is accompanied by light emission.[1]

At the same time, Ru^{II} can be reduced to Ru^I (E_0 $(Ru^I/Ru^{II}) = -1.03$ V)[5] by the Ph_2CH^- ($E_{0,red} = -1.14$ V)[12] and Bu^tO^- anions present in this system. In fact, after mixing of solutions of Bu^tOK, Ph_2CH_2, and Ru^{II} in DMSO in an argon atmosphere, the absorption spectrum of the reaction mixture changes. The intensity of the characteristic band of Ru^{II} ($\lambda_{max} = 453$ nm) decreases gradually, and new bands appear ($\lambda_{max,1} = 358$, $\lambda_{max,2} = 495$ nm, Fig. 3), which, as known,[13] belong to the Ru^I complex. Gradual accumulation of Ru^I in the system studied, which is indicated by the spectrophotometric data, most likely results in the induction period on the kinetic curve of CL intensity (see Fig. 1).

The transformation of Ru^{II} into Ru^I also occurs in the absence of Ph_2CH_2. In this case, the Bu^tO^- anion is a reductant (see Ref. 14), and the reaction proceeds much more slowly.

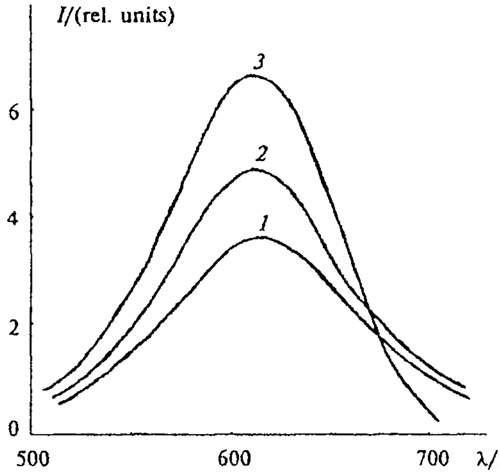

Fig. 2. CL spectra of autooxidation of Ph_2CH_2 in an alkaline medium in the presence of Ru^{II} (*1*) and of the reaction $Ph_2CH_2 + Bu^tOK + Ru^{II} + NaO_2$ in argon (*2*), as well as FL of Ru^{II} (10^{-5} mol L^{-1}) in DMSO (*3*). $[Ph_2CH_2] = 2.5 \cdot 10^{-3}$ mol L^{-1}; $[Bu^tOK] = 0.067$ mol L^{-1}; $[Ru^{II}] = 1 \cdot 10^{-3}$ mol L^{-1}.

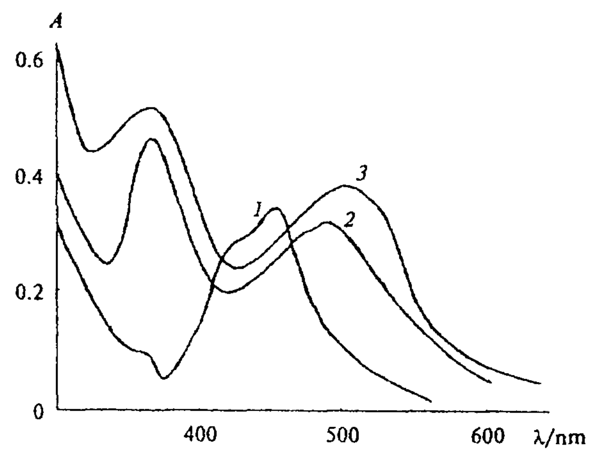

Fig. 3. Absorption spectra of a solution of Ru^{II} in DMSO (*1*); reaction mixture $Ph_2CH_2 + Bu^tOK + Ru^{II}$ in argon (*2*, *3*). $[Ph_2CH_2] = 2.5 \cdot 10^{-3}$ mol L^{-1}; $[Bu^tOK] = 0.067$ mol L^{-1}; $[Ru^{II}] = 1 \cdot 10^{-3}$ mol L^{-1}; DMSO, 298 K.

The Ru^I formed is rapidly oxidized by O_2 molecules and the O_2^- superoxide ion again to Ru^{II}.[15] In the reaction $Ru^I + O_2^-$

$$E_0(O_2^-/O_2^{2-}) - E_0(Ru^I/Ru^{II}) = 1.72 - (-1.03) = 2.75\ (V)$$

the excitation of Ru^{II} is quite possible ($E(Ru^{II*}/Ru^{II}) = 2.12$ V).[16] At the same time, in the reaction of Ru^I with oxygen

$$E_0(O_2/O_2^-) - E_0(Ru^I/Ru^{II}) = 0.56 - (-1.03) = 1.59\ (V),$$

i.e., Ru^{II*} is not formed.

The possibility of transformation of Ru^I into Ru^{II*} *via* the reaction with the superoxide ion is confirmed by detection of CL (with $\lambda_{max} = 610$ nm) observed during mixing of solutions of Ru^I and NaO_2 (see Fig. 2).

Thus, taking into account the results obtained previously,[7] we can offer the following reaction scheme:

$$Ph_2CH_2 + Bu^tO^- \rightarrow Ph_2CH^- + Bu^tOH,$$

$$Ru^{II} + Ph_2CH^- \rightarrow Ru^I + Ph_2CH^{\bullet},$$

$$Ph_2CH^- + O_2 \rightarrow Ph_2CH^{\bullet} + O_2^{\bullet -},$$

$$Ph_2CH^- + O_2^{\bullet -} \rightarrow Ph_2CH^{\bullet} + O_2^{2-},$$

$$Ph_2CH^{\bullet} + O_2 \rightarrow Ph_2CHOO^{\bullet},$$

$$Ru^I + O_2 \rightarrow Ru^{II} + O_2^{\bullet -},$$

$$Ru^I + O_2^{\bullet -} \rightarrow Ru^{II*} + O_2^{2-},$$

$$Ru^{II*} \rightarrow Ru^{II} + h\nu_{610\ nm},$$

$$Ph_2CHOO^{\bullet} + O_2^- \rightarrow Ph_2CHOO^- + O_2,$$

$$Ph_2CHOO^- \rightarrow Ph_2C{=}O + OH^-,$$

$$2Ph_2CHOO^{\bullet} \rightarrow Ph_2C{=}O^* + Ph_2CHOH + O_2,$$

$$Ru^{II} + O_2^{\bullet -} \rightarrow Ru^{III} + O_2^{2-},$$

$$Ru^{III} + Bu^tO^- \rightarrow Ru^{II*} + Bu^tO^{\bullet}.$$

When both oxidant and reductant are present in the system studied, the Ru^{II} complex can multiply transit to the excited state. Thus, the Ru^{II} excitation is regenerated, which can occur *via* two routes:

$$Ru^{II} \rightarrow Ru^I \rightarrow Ru^{II*},$$

$$Ru^{II} \rightarrow Ru^{III} \rightarrow Ru^{II*}.$$

Further studies are necessary to reveal a ratio between these processes and their relative contribution to the total CL intensity.

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