Chemiluminescence in the oxidation of sodium anthracenide and pyrenide by a Ru^{III} complex

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Chemiluminescence (CL) during oxidation of organosodium compounds of anthracene and pyrene in THF by a Ru(bpy)$_3^{2+}$ complex was studied. Excited singlet states of anthracene and pyrene (^{1}R*) and a Ru(bpy)$_3^{2+*}$ complex were identified as CL emitters. A mechanism for the generation of the excited states in electron transfer reactions resulting in the formation of Ru(bpy)$_3^{2+*}$ and triplet states of hydrocarbons (^{3}R*) was proposed. The direct formation of a singlet state from the radical anion is energetically impossible. Therefore ^{1}R* is generated in the triplet-triplet annihilation $^3R^* + {}^3R^* \longrightarrow {}^1R^* + R$, whereas Ru(bpy)$_3^{2+*}$ can be formed in the reaction of Ru(bpy)$_3^{3+}$ with Ru(bpy)$_3^{1+}$ or by the energy transfer from ^{1}R* to Ru(bpy)$_3^{2+}$.

Key words: chemiluminescence, organosodium compounds, oxidation by oxygen, excited singlet states.

Previously, we have reported the chemiluminescence (CL) of ionic organosodium derivatives Na$^+$R$^{\cdot-}$ of polycyclic aromatic hydrocarbons, when they react with such oxidants as XeF$_2$,[1] O$_2$,[2] and a complex of Ce(IV) [3] in a solution of THF, which results in formation of different radiating centers (CL emitters), depending on the nature of oxidants.

For the first time, such luminescent systems producing ^{1}R* states or triplet molecules ^{3}R* as products of redox reactions were detected in the study of electrochemiluminescence (ECL) of hydrocarbons, where luminescence occurs upon annihilation of oppositely charged ions generated on the electrodes during elecrolysis conducted with alternating current.[4–6] Later, purely chemical sources of luminescence were revealed, such as redox reactions of ionic organosodium compounds of the Na$^+$R$^{\cdot-}$ type with a series of electron acceptors.[7–9]

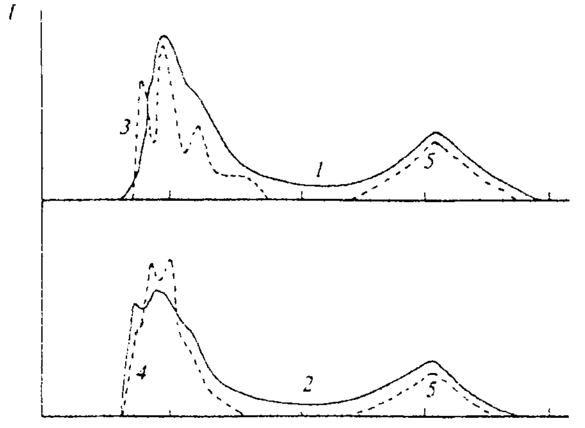

Fig 1. The spectra of CL of sodium anthracenide (*1*) and sodium pyrenide (*2*) in THF, measured using an MZD-2 M monochromator during interaction with a Ru(bpy)$_3^{3+}$ solution in CH$_3$CN. The spectra of CL of anthracene in THF (λ_{exc} = 253 nm) (*3*), of pyrene (λ = 300 nm) in THF (*4*), of Ru(bpy)$_3^{2+}$ solutions, and Ru(bpy)$_3^{3+}$ + Ru(bpy)$_3^{2+}$ solutions (λ = 453 nm) in CH$_3$CN (*5*).

The present work deals with the study of a new CL reaction of Na$^+$R$^{\cdot-}$ (where R is anthracene or pyrene) occurring when Na$^+$R$^{\cdot-}$ is oxidized by a complex of trivalent ruthenium Ru(bpy)$_3^{3+}$ in THF.

Experimental

Compounds Na$^+$R$^{\cdot-}$ were synthesized by the reaction of metallic Na with sublimed anthracene or pyrene in THF under argon.[7] A solution of a Ru(bpy)$_3^{3+}$ complex in CH$_3$CN was obtained according to the procedure[10] by oxidation of a Ru(bpy)$_3^{2+}$ solution (prepared by dissolution of Ru(bpy)$_3$Cl$_2\cdot$6H$_2$O) with cerium ammonium nitrate or lead dioxide. The techniques of measurements of CL are described in Ref. 7.

Results and Discusion

A bright CL visible to the naked eye is observed upon mixing Na$^+$R$^{\cdot-}$ solutions in THF with a Ru^{III} solution in CH$_3$CN. The CL spectrum (Fig. 1) contains two components: a structural one in the ultraviolet-blue range and a diffusional one in the red range. The short-wave component coincides with fluorescence (FL) of

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the corresponding hydrocarbon and is due to the radiation of singlet-excited hydrocarbons $^1R^*$. The «red» component coincides with the FL spectrum of the solution of the Ru^{II} complex and is caused by luminescence of the $Ru(bpy)_3{}^{2+*}$ complex with λ_{max} = 610 nm; a relative part of the emission of the excited states of $^1R^*$ is higher than $Ru(bpy)_3{}^{2+*}$ states (Fig. 1).

All possible exothermic redox reactions of the reagents involved in the process are shown in Scheme 1.

Scheme 1

$$Na^+R^{\dot{-}} + Ru^{III} \longrightarrow Na^+ + {}^3R^* + Ru^{II} \qquad (1)$$

$$Na^+R^{\dot{-}} + Ru^{III} \longrightarrow Na^+ + R + Ru^{II*} \qquad (2)$$

$${}^3R^* + {}^3R^* \longrightarrow {}^1R^* + R \qquad (3)$$

$$Na^+R^{\dot{-}} + Ru^{II} \longrightarrow Na^+ + R + Ru^{I} \qquad (4)$$

$$Ru^{I} + Ru^{III} \longrightarrow Ru^{II} + Ru^{II*} \qquad (5)$$

$${}^1R^* + Ru^{II} \longrightarrow R + Ru^{II*} \qquad (6)$$

$${}^1R^* \longrightarrow R + h\nu_1 \text{ (short-wave CL)} \qquad (7)$$

$$Ru^{II*} \longrightarrow Ru^{II} + h\nu_2 \text{ (long-wave CL)} \qquad (8)$$

Evaluation of the heat effects of reactions (1)—(5), which was performed from the balances of electrochemical redox potentials according to the equation[11]

$$\Delta H(D^-...A^+) = E_{1/2}(A/A^+) - E_{1/2}(D^-/D) + 0.2 \text{ eV}$$

(where D^- is an electron donor and A^+ is an electron acceptor) demonstrated that even the most high-exothermic reaction (1) (ΔH = 2.97 eV for anthracene and 3.1 eV for pyrene) is unable to form hydrocarbon singlets (3.28 and 3.34 eV, respectively). The deficiency in energy is equal to 0.31 eV for anthracene and 0.24 eV for pyrene. But the spectrum unambiguously attests to the emission of $^1R^*$. The sole energy source of $^1R^*$ formation is the annihilation of triplets (3) resulting from reaction (1), whose energy makes the formation of $^3R^*$ possible (1.82 and 2.1 eV for anthracene and pyrene, respectively). It should be noted that the triplet-triplet annihilation as a source for formation of hydrocarbon singlets in energy-deficient systems was postulated earlier.[11] A low-intensity emission of hydrocarbon excimers $^1(R \cdot R)^*$ was also registered[11] for certain hydrocarbons. The absence of excimer radiation in the system studied (Fig. 1) suggests the almost complete absence of O_2 under experimental conditions: even the presence of small amounts of O_2 in $Na^+R^{\cdot -}$ solutions leads to CL, whose spectrum consists of one structureless band typical of excimers. The primary electron transfer can lead to the excitation of a ruthenium complex (reaction (2)). Simultaneous formation of $^3R^*$ and $Ru(bpy)_3{}^{2+*}$ in the same act is impossible for lack of energy. But the generation of $Ru(bpy)_3{}^{2+*}$ can occur during other processes. The presence of FL in the initial solution of the oxidant suggests that this solution contains two forms of ruthenium: Ru^{II} and Ru^{III}. That is why, besides the reduction of Ru^{III} to Ru^{II} according to reaction (1), the reduction of Ru^{II} to Ru^{I} according to reaction (4) can also occur (in conformity with redox potentials of the system). The generation of a «red» CL emitter can be provided by an interaction between ruthenium forms of different valence in reaction (5), which was identified earlier[6] as a stage of emitter formation in ECL during electrolysis of a $Ru(bpy)_3Cl_2$ solution in CH_3CN with the alternating current. The energy transfer in reaction (6) also cannot be excluded as a source of $Ru(bpy)_3{}^{2+*}$ formation because the radiation level of $^1R^*$ is much higher in energy than that of $Ru(bpy)_3{}^{2+*}$. Both processes, (5) and (6), probably are sources of excitation of $Ru(bpy)_3{}^{2+*}$.

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