Chemiluminecsence in the oxidation of Na_2C_{60} by the $(NH_4)_2Ce(NO_3)_6$ complex in THF

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Chemiluminescence (λ_{max} = 790 nm) in the oxidation of fulleride Na_2C_{60} by the $(NH_4)_2Ce(NO_3)_6$ complex in THF was found. The $^3C_{60}{}^*$ triplet of fullerene formed in the transfer of an electron from the intermediate $C_{60}{}^-$ anion to Ce^{IV} was suggested to be the chemiluminescence emitter.

Key words: fullerene, triplet, chemiluminescence, anions.

We have previously reported[1,2] chemiluminescence (CL) arisen in the ozonolysis of solutions of C_{60}, whose emitters are excited ketones $^*O{=}C_{60}{=}[O]_m$ (λ_{max} = 685 nm). In this work, we found CL (λ_{max} = 790 nm) in the oxidation of Na_2C_{60} (henceforth **1**) by the $(NH_4)_2Ce(NO_3)_6$ complex (henceforth Ce^{IV}) in THF.

Experimental

Commercial fullerene containing 99.9% C_{60} and $Ce(NO_3)_3 \cdot 6H_2O$ (reagent grade) were used. The Ce^{IV} complex was synthesized by a previously described procedure.[3] THF was refluxed and distilled with sodium benzophenone ketyl. A solution of **1** in THF was prepared using a known procedure[4] by the reaction of a suspension of C_{60} (0.025 mmol) and sodium amalgam (0.5 mmoles of Na) at 300 K in an Ar atmosphere. The concentration of **1** was determined after the hydrolysis of an aliquot of the prepared solution by titration with an HCl fixanal. A solution of the oxidant was prepared by the dissolution of a weighed sample of Ce^{IV} in THF. The precipitate that formed was separated by filtration and analyzed for the presence of C_{60} by the IR spectra (KBr). A solution of the oxidate was analyzed for C_{60} and Ce^{IV}, Ce^{III} by the IR and UV spectra, respectively. A decrease in $[Ce^{IV}]$ in the solution after the reaction was found by the titration of Ce^{IV} with a solution of $Ce(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Mohr's salt) in the presence of *o*-phenanthroline.[5] Absorption spectra were measured on Specord IR-75 (IR region), Specord M-40 UV—VIS (layer thickness 0.012 cm), and SF-16 (2.0 cm) (UV region) spectrophotometers. CL spectra, due to a low intensity and a short duration of emission, were detected using boundary light filters on a stop-flow setup according to a procedure described previously.[6] Photoluminescence (PL) spectra of a toluene solution of C_{60} were measured at 77 K on an Aminko-Bowman spectrofluorimeter and using boundary light filters on a minifluorimeter with PL excitation by an LGI-23 laser.

Results and Discussion

Ten min after the beginning of the synthesis of **1**, the solution becomes greenish-blue, and 30 min after it gains an intense red color, and bands at 829 and 945 nm, which are characteristic[7] of the $C_{60}{}^{2-}$ dianion and coincide with the absorption bands of $C_{60}{}^{2-}$ obtained[4] by another method in DMF, appear in the absorption spectrum (Fig. 1). When solutions of **1** and Ce^{IV} in THF are mixed, rapidly decaying CL (40 s, $I_{max} = 1.1 \cdot 10^8$ photon s^{-1} mL^{-1}) appears accompanying by a decrease in the intensity of the bands at 829 and 945 nm (see Fig. 1). The UV spectrum also exhibits a decrease in the intensity of the characteristic[8] absorption band of Ce^{IV} at 322.5 nm and the appearance of the absorption bands of Ce^{III} (248, 252, 257, 265, 269.8 (sh), and 272 nm).

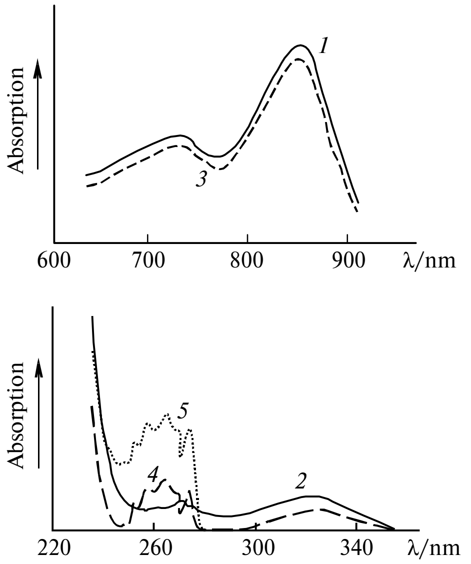

Fig. 1. Absorption spectra of solutions for the oxidation of Na_2C_{60} with the Ce^{IV} complex in THF: *1* and *2*, starting THF solutions of Na_2C_{60} ($4 \cdot 10^{-3}$ mol L^{-1}) and Ce^{IV} ($2 \cdot 10^{-2}$ mol L^{-1}), respectively; *3*, solution of Na_2C_{60} in DMF (Ref. 4); *4*, solution after the reaction; and *5*, solution of $Ce(NO_3)_3 \cdot 6H_2O$ in THF ($6 \cdot 10^{-3}$ mol L^{-1}).

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The indicated maxima coincide with the absorption maxima of a solution of $Ce(NO_3)_3 \cdot 6H_2O$ in THF (see Fig. 1). The bands at 527, 577, 1183, and 1429 cm^{-1} characteristic[9] of C_{60} were found in the IR absorption spectrum of the precipitate formed in the reaction. These bands are absent from the remaining solution, *i.e.*, all fullerene is precipitated from the solution. Thus, C_{60} and Ce^{III} compounds are the main stable reaction products.

The maximum in the CL spectrum at 790 nm (Fig. 2) corresponds to that in the phosphorescence (PS) spectrum of a solution of C_{60} vitrified[10] at 77 K and is shifted toward the long-wave region as compared to the fluorescence of a toluene solution of C_{60} (720—750 nm)[10] (see Fig. 2). Since the temperature (300, 77 K) and nature of the solvent (toluene, cyclohexane) have no effect[10—13] on the position of the fluorescence maximum of C_{60} in the region of 690—750 nm, we may accept that the emission of $^1C_{60}{}^*$ is not manifested during the reaction. We failed to detect the photoluminescence of solutions (300, 77 K) of the starting reactants and Ce^{III} in the region of CL emission. Reference experiments showed no CL in the region of CL emission when a solution of the Ce^{IV} complex and THF contacted with sodium amalgam under the conditions identical to those of synthesis of **1** were mixed. These facts suggest that the intermediate reaction product $^3C_{60}{}^*$ is the CL emitter. A decrease in the Ce^{IV} concentration in the reaction of titration with Mohr's salt is equal to 40%, *i.e.*, 2 moles of Ce^{IV} are consumed per mole of **1**. Experiments with $^3C_{60}{}^*$ quenching by dioxygen[14] gave an additional evidence for the formation of $^3C_{60}{}^*$ in the reaction. For example, when an O_2 flow is passed through the reaction solution followed by stopping the flow, a sharp decrease and an increase in the CL intensity are sequentially observed. The obtained results propose the following scheme of the studied redox reaction:

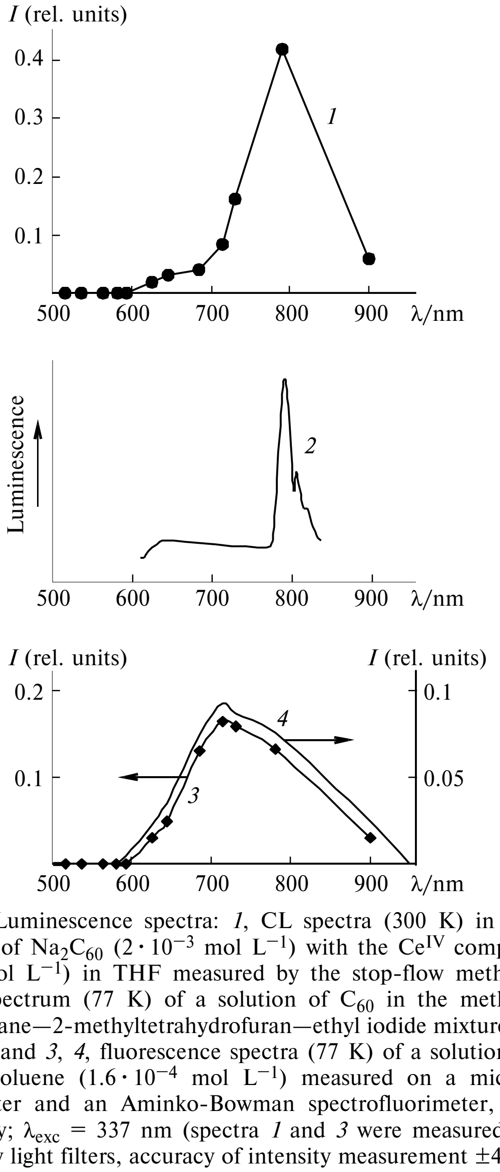
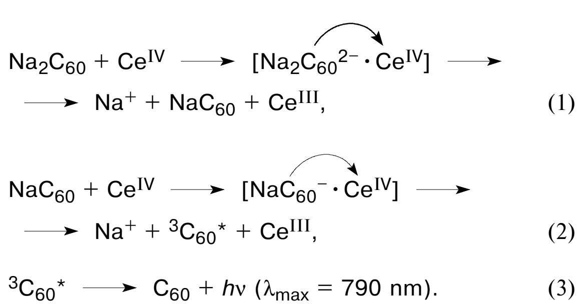


Fig. 2. Luminescence spectra: *1*, CL spectra (300 K) in the reaction of Na_2C_{60} ($2 \cdot 10^{-3}$ mol L^{-1}) with the Ce^{IV} complex (10^{-2} mol L^{-1}) in THF measured by the stop-flow method; *2*, PS spectrum (77 K) of a solution of C_{60} in the methylcyclohexane—2-methyltetrahydrofuran—ethyl iodide mixture by Ref. 10; and *3*, *4*, fluorescence spectra (77 K) of a solution of C_{60} in toluene ($1.6 \cdot 10^{-4}$ mol L^{-1}) measured on a microfluorimeter and an Aminko-Bowman spectrofluorimeter, respectively; λ_{exc} = 337 nm (spectra *1* and *3* were measured by boundary light filters, accuracy of intensity measurement ±4%).



$$Na_2C_{60} + Ce^{IV} \longrightarrow [Na_2C_{60}{}^{2-} \cdot Ce^{IV}] \longrightarrow Na^+ + NaC_{60} + Ce^{III}, \quad (1)$$

$$NaC_{60} + Ce^{IV} \longrightarrow [NaC_{60}{}^{-} \cdot Ce^{IV}] \longrightarrow Na^+ + {}^3C_{60}{}^* + Ce^{III}, \quad (2)$$

$$^3C_{60}{}^* \longrightarrow C_{60} + h\nu\ (\lambda_{max} = 790\ \text{nm}). \quad (3)$$

At stage (1) an electron is transferred from $C_{60}{}^{2-}$ to Ce^{IV} to form the $C_{60}{}^{-}$ anion and Ce^{III}. We believe that $^3C_{60}{}^*$ is formed at stage (2) during the transfer of an electron from the $C_{60}{}^{-}$ intermediate to another molecule of the Ce^{IV} complex. The free energies of reactions (2) estimated from the known electrochemical redox potentials of cerium[15] and fullerene[16] are the following:

$$\Delta G°(1) = E(Ce^{III}/Ce^{IV}) - E(C_{60}{}^{2-}/C_{60}{}^{-}) = [1.7 - (-0.72)] = 2.42\ (\text{eV}),$$

$$\Delta G°(2) = E(Ce^{III}/Ce^{IV}) - E(C_{60}{}^{-}/C_{60}] = [1.7 - (-0.44)] = 2.14\ (\text{eV}).$$

The energy of reaction (2) is enough for the formation of the $^1C_{60}{}^*$ singlet (2.01 eV)[16] rather than $^3C_{60}{}^*$ (1.56 eV).[16] Therefore, $^3C_{60}{}^*$ can be formed by both the electron transfer (reaction (2)) and intersystem crossing $^1C_{60}{}^* \rightarrow {}^3C_{60}{}^*$. However, the generation of the CL emitter, triplet $^3C_{60}{}^*$, by the crossing is improbable because only fullerene fluorescence is observed upon the photoexcitation of C_{60}.[10,11] Moreover, for the detection of PS, even at 77 K EtI should be introduced[10] into the solution to accelerate the conversion $^1C_{60}{}^* \rightarrow {}^3C_{60}{}^*$. Any intermediate compounds of C_{60} and Ce appeared in the excited state due to high values of the thermal effects of stages (1) and (2) (2.42 and 2.14 eV, respectively) can be an alternative source of CL. However, this energy for the formation of $(Ce^{III})^*$ is insufficient: 3.4 eV are needed.[8]

It seems that stage (2) is still the source of $^3C_{60}^*$ generation. This conclusion is confirmed by weak CL in the same spectral region when Ce^{IV} is mixed with a greenish-blue solution containing only the anion in the NaC_{60}^- form (910, 1075 nm).[4] Note in conclusion that the emission of $^3C_{60}^*$ at room temperature has not been detected previously.[10—13]

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