Journal of Photochemistry and Photobiology A: Chemistry 154 (2003) 273–277

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Chemiluminescence as the energy transfer effect in the system Eu(III)–thenoyltrifluoroacetone–H_2O_2–NaOH

Małgorzata Kaczmarek, Krzysztof Staninski, Marian Elbanowski*

Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Received 6 June 2002; received in revised form 27 August 2002; accepted 10 September 2002

Abstract

Chemiluminescence (CL) of the water–ethanol solutions containing hydrogen peroxide, sodium hydroxide and europium(III) complex with thenoyltrifluoroacetone (TTA) was studied. It has been established that the introduction of europium(III) chelate into the system H_2O_2–NaOH caused an increase in the CL intensity and significantly extended its duration (up to a few hours). The dominant band in the emission spectrum has been the one at $\lambda \sim 600$ nm, which means that Eu(III) ions are the only emitters in the system H_2O_2–NaOH–europium(III) chelate. The study revealed a strong connection between the CL intensity and the concentrations of europium(III) chelate and hydrogen peroxide. These relations and a strong influence of the competitive ligand (aminopolycarboxylic acid) suggest that the excitation of Eu(III) ions takes place in the complex through the mediation of TTA ligand. A mechanism of the processes taking place in the system has been proposed, taking into account the process of energy transfer from the products of decomposition of hydrogen peroxide to the Eu(III) ions in the complex with TTA.

Keywords: Chemiluminescence; Europium ions; Thenoyltrifluoroacetone; Energy transfer

1. Introduction

Chemiluminescence (CL) can be emitted by a number of systems including oxygen or oxygen-containing compounds as oxidisers. Low intensities of CL were obtained for typical inorganic systems in which hydrogen peroxide got decomposed in a basic medium or it oxidised d-electron metal cations [1–3].

Studies of CL systems characterised by low intensity of emission require the use of sensitizers [4]. Thanks to their specific luminescence properties, the lanthanide ions, mainly europium(III) and terbium(III), have been successfully used as luminescence and CL probes [5–8]. The excited states of the lanthanide ions are non-radiatively quenched by the –OH oscillators of the solvent molecules coordinated in the inner coordination sphere of the metal ion [9]. The intensity of emission of the lanthanide ions can be significantly increased by complexing them with appropriate organic ligands [10–12].

In this paper a complex of europium(III) ions with thenoyltrifluoroacetone (TTA) was used as a sensitizer in the reaction system H_2O_2–NaOH, characterised by very low intensity of emission.

2. Experimental

Measurements of CL were performed using the apparatus for recording of ultraweak radiation, by the stationary method described in [13]. The absorption spectra were recorded by a spectrophotometer Shimadzu UV 2401 PC.

The reagents used were: TTA (pure for analysis, Fluka) diluted in 95% ethanol (pure for analysis); sodium hydroxide NaOH (pure for analysis, POCh); europium chloride(III) obtained by diluting europium oxide Eu_2O_3 (spectral purity, synthesised at our laboratory) in hydrochloric acid (spectral purity, Fluka); diethylenetriaminepentaacetic acid (DTPA) (pure for analysis, Fluka); hydrogen peroxide (30% solution, pure for analysis, Merck). Solutions of europium chelate with TTA were obtained by mixing europium chloride solutions with a solution of TTA at the molar ratio 1:1, 1:2, 1:3 and 1:4.

All CL measurements were performed in the same method. Hydrogen peroxide was added to a solution containing 1 ml, 0.1 mol/l NaOH and europium(III) chelate. The measurements were performed in water–ethanol solutions

---

* Corresponding author.

E-mail address: elbanmar@main.amu.edu.pl (M. Elbanowski).

1010-6030/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(02)00359-3

(1:1). For all solutions studied the kinetic curves of CL decay were determined and the CL light sums were calculated as the area under these curves ($S = \int_{t_0}^{t} I\,\Delta t$, where I is CL intensity and t is measurement duration).

3. Results and discussion

The intensity of CL emission appearing as a result of the reaction of decomposition of hydrogen peroxide in a basic environment in water and water–ethanol solutions was measured. The introduction of hydrogen peroxide to 0.01 mol/l NaOH solution caused a short-lived CL of low intensity. Similar effects were obtained for water–ethanol solutions. The kinetic curve of CL decay in the system H_2O_2–NaOH is shown in Fig. 1.

The low intensity CL emission appeared at the moment of introduction of H_2O_2 into NaOH solution, and then in the time of 4 min the CL signal reached the noise level.

The introduction of TTA into the system H_2O_2–NaOH caused a significant decrease in CL intensity and shortening of its duration. According to the earlier study of the reaction systems in which hydrogen peroxide is decomposed in a basic medium or under the influence of d-electron metals, the emitters in such systems are particles of singlet oxygen and their dimols [1–3]. Therefore, the fact of CL quenching by TTA implies that this compound is a quencher of the excited state of oxygen or its radicals appearing on decomposition of H_2O_2.

The intense and long-lived CL was obtained for the solutions containing NaOH, europium(III) complex with TTA and H_2O_2 (curves 2, 3, 4 and 5 in Fig. 1). The measurements were performed for the systems of the metal:ligand molar ratios of 1:1, 1:2, 1:3 and 1:4. The highest intensity of emission was recorded for the ratio Eu(III):TTA = 1:3. The character of the kinetic curve of CL, was similar for all the systems studied. The highest CL intensity was recorded at the moment of hydrogen peroxide introduction and then in the time of a few minutes its intensity significantly decreased, and after this period the CL decrease was much slower, so that the emission reached the noise level only after 5 h.

In order to identify the emitter in the system of europium(III) chelate–H_2O_2–NaOH, its spectral distribution was recorded by the method of cut-off filters (Fig. 2).

The emission spectra were recorded at 5, 60, 120 and 240 min after the introduction of H_2O_2 to the solution. All the emission spectra were similar and revealed only the band characteristic of Eu(III) ions with a maximum at $\sim \lambda = 600$ nm, assigned to the transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ [8]. This means that in the system studied the only emitter were europium(III) ions.

The CL characteristic of europium(III) ions obtained in the solutions containing the europium chelate complexes suggests that the complex with TTA plays an essential role in the excitation of Eu(III) ions. In order to determine the effect of the complex concentration on the intensity of emission of the system studied, the intensity of CL was measured in the systems containing H_2O_2 and NaOH at a constant concentration and europium chelate at different concentrations (Fig. 3).

With increasing concentration of the complex, the CL emission intensity increased. For the CL emission of these systems values of the light sums of CL (S) were calculated and as follows from Fig. 3, the light sum increases in proportion to the increase in the europium chelate concentration.

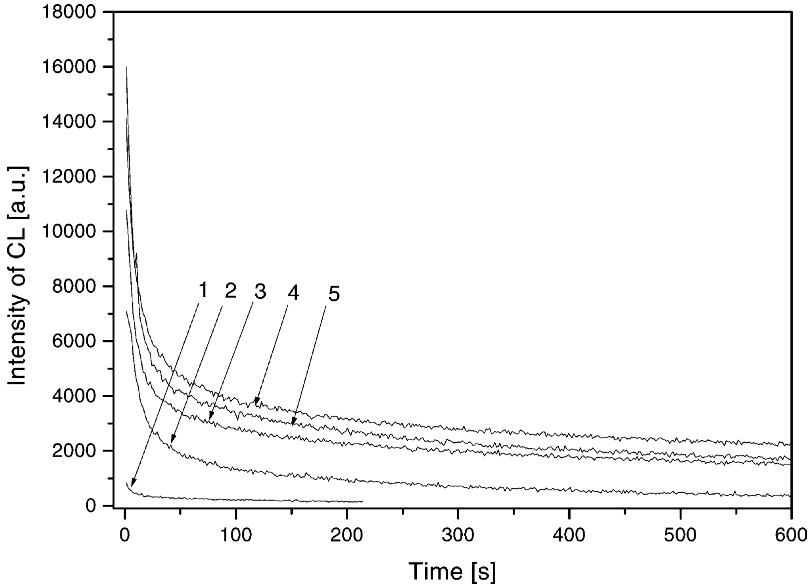

Fig. 1. The kinetic curves of CL decay in the systems: H_2O_2–NaOH (curve 1); Eu(III) chelate–H_2O_2–NaOH, for the Eu(III):TTA molar ratios 1:1 (curve 2); 1:2 (curve 3); 1:3 (curve 4); and 1:4 (curve 5) in water–ethanol solution. The concentration of Eu(III) ions was 5×10^{-4} mol/l; the initial concentration of $H_2O_2 = 2 \times 10^{-3}$ mol/l.

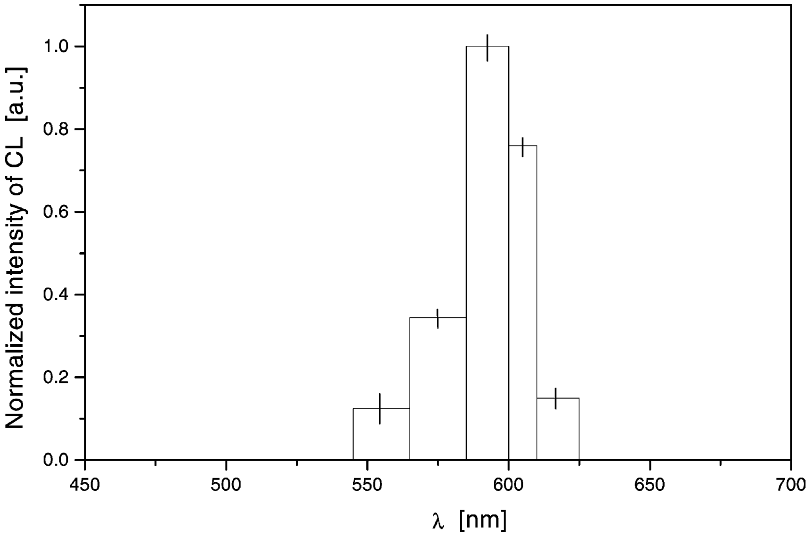

Fig. 2. Spectral distribution of CL of the system Eu(III) chelate–H_2O_2–NaOH.

Addition to the system europium(III) chelate–H_2O_2–NaOH of a ligand competitive towards TTA, e.g. DTPA, immediately resulted in a decrease in the CL intensity in proportion to the amount of the ligand added. This effect was a consequence of pushing out TTA from the coordination sphere of Eu(III) by the competitive DTPA ligand forming a more stable complex with europium ions [14]. The effect of the competitive ligand and a strong dependence of CL intensity of the system europium(III) chelate–H_2O_2–NaOH on the concentration of europium(III) chelate has shown that the excitation of Eu(III) ions takes place in the complex through a mediation of TTA.

The absorption spectra of the system europium(III) chelate–H_2O_2–NaOH were also taken before and after the addition of hydrogen peroxide (Fig. 4). The introduction of europium(III) ions to the solution of TTA resulted in the appearance of a band with a maximum at $\lambda \sim 350$ nm, characteristic of the europium chelate–TTA complex [15].

As follows from Fig. 4, the intensity of this band did not change after the introduction of H_2O_2, which means that the Eu–TTA complex does not undergo destruction under the effect of hydrogen peroxide.

In order to fully characterise the system europium(III) chelate–H_2O_2–NaOH the effect of hydrogen peroxide

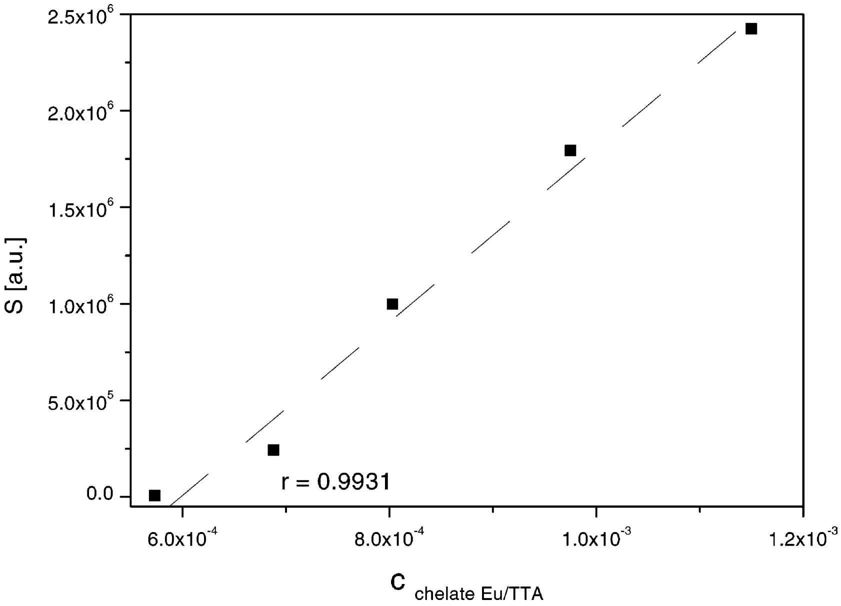

Fig. 3. The light sum of CL (S) of the system Eu(III) chelate–H_2O_2–NaOH vs. the concentration of $Eu(TTA)_3$; the initial concentration of H_2O_2 was 2×10^{-2} mol/l.

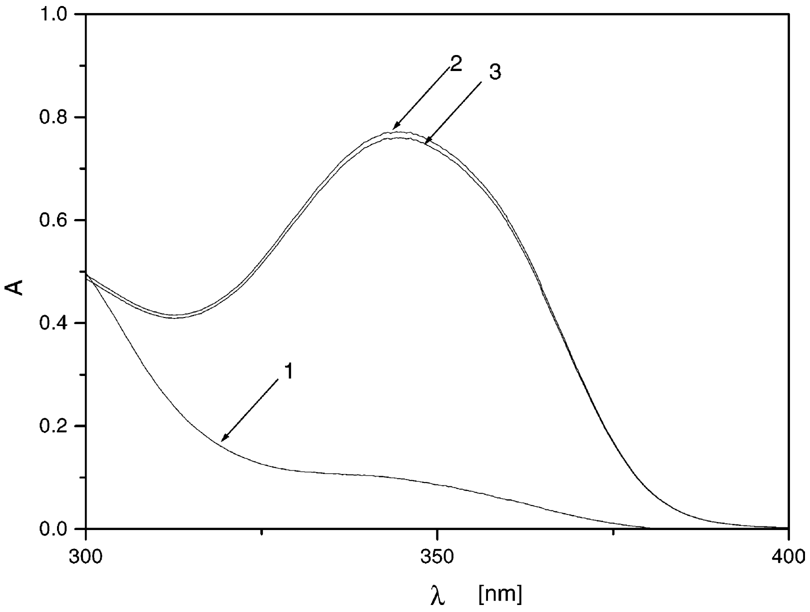

Fig. 4. The absorption spectrum of TTA (1) and the system Eu(III)–TTA (Eu(III):TTA molar ratio 1:1), before (2) and after (3) addition of hydrogen peroxide.

concentration on the intensity and duration of CL was also studied.

With increasing hydrogen peroxide concentration the intensity of CL emission typical of Eu(III) ions increased as did its duration. Irrespective of the concentration of H_2O_2 the shape of the kinetic CL curves was the same. A strong decrease in the CL emission intensity was recorded in 3 min and then it continued to decrease but much slower. In the system europium(III) chelate–H_2O_2–NaOH, the emission intensity reached the noise level after 5 h for H_2O_2 concentration of 2×10^{-3} mol/l and after 11 h for H_2O_2 concentration of 0.5 mol/l, while in the systems containing only H_2O_2 and NaOH in the same concentrations, the CL emission reached the noise level in 4 and 20 min, respectively. The H_2O_2 concentration dependence of the light sum of the system europium(III) chelate–H_2O_2–NaOH was linear in a wide range of H_2O_2 concentrations (2×10^{-3} to 0.5 mol/l) (Fig. 5).

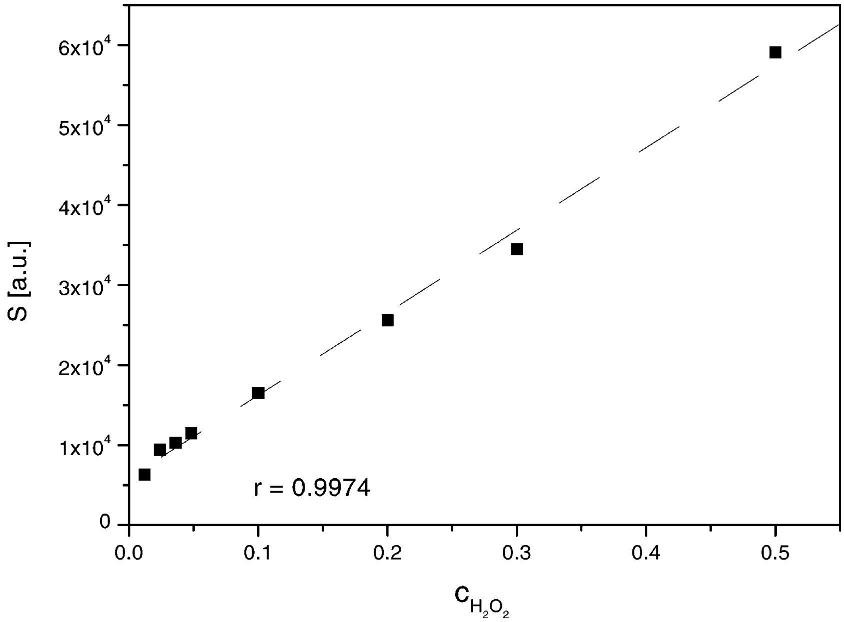

Fig. 5. The light sum of CL (S) of the system Eu(III) chelate–H_2O_2–NaOH vs. the concentration of hydrogen peroxide; the concentration of Eu(III) ions was 5×10^{-4} mol/l; the Eu(III):TTA molar ratio 1:3.

The results obtained: CL characteristic of Eu(III) ions in the system europium(III) chelate–H_2O_2–NaOH, a strong dependence of this CL intensity on the concentration of the europium(III) complex and the concentration of hydrogen peroxide and the quenching of CL of the system H_2O_2–NaOH by TTA, lead to a conclusion that the excitation of Eu(III) ions takes place as a result of the energy transfer from the products of hydrogen peroxide decomposition to the lanthanide ions in the complex with TTA. A phenomenon of energy transfer from the ligands to the lanthanide(III) ions, resulting consequently in a great enhancement of the Ln(III) ions luminescence, is well known [7,8,15–19].

The course of the processes is illustrated in the scheme below:

$$\mathrm{Eu/TTA} \xrightarrow{H_2O_2,\,{}^1O_2,\,OH^\bullet} [\mathrm{Eu/TTA}]^* \rightarrow [\mathrm{Eu}^*/\mathrm{TTA}] \rightarrow \mathrm{Eu/TTA} + h\nu\ (\lambda \sim 600\,\mathrm{nm})$$

4. Conclusion

In the hitherto studies the β-diketonates complexes of lanthanide ions have been used in the CL emitting systems in which dioxetanes and hydrazine underwent decomposition [8]. In this paper europium(III) chelate in the complex with TTA was used to study CL emission accompanying the decomposition of hydrogen peroxide in a basic medium. The excitation of europium(III) ions was achieved after the introduction of the lanthanide(III) complex into the system H_2O_2–NaOH. A strong increase in the intensity of CL characteristic of Eu(III) ions in the system europium(III) chelate–H_2O_2–NaOH relative to the CL emission of the system H_2O_2–NaOH proves that the complex of europium(III) chelate with TTA is an efficient sensitizer of CL accompanying decomposition of hydrogen peroxide in an basic medium.

Acknowledgements

This work was supported by the Polish State Committee for Scientific Research, Grant No. 3 T09A 105 19.

References

[1] D. Sławińska, Scientific Volumes of Technical University, Szczecin 101 (1968) 117.
[2] A.U. Khan, J. Am. Chem. Soc. 105 (1983) 7195.
[3] M. Yamada, A. Sudo, S. Suzuki, Chem. Lett. 6 (1985) 801.
[4] P.D. Wildes, E.H. White, J. Am. Chem. Soc. 93 (1971) 6286.
[5] M. Albin, W.D.W. Horrocks Jr., Inorg. Chem. 24 (1985) 895.
[6] M. Elbanowski, B. Mąkowska, J. Photochem. Photobiol. A: Chem. 99 (1996) 85.
[7] Y.B. Tsaplev, Zh. Fiz. Khim. 71 (1997) 730.
[8] M. Elbanowski, B. Mąkowska, K. Staninski, M. Kaczmarek, J. Photochem. Photobiol. A: Chem. 130 (2000) 75.
[9] W.D. Horroks Jr., D. Sudnick, J. Am. Chem. Soc. 101 (1979) 334.
[10] M. Elbanowski, S. Lis, J. Konarski, Monatsh. Chem. 120 (1989) 699.
[11] S.F. Zhou, Z. Li, Talanta 37 (1990) 341.
[12] S. Lis, J. Konarski, Z. Hnatejko, M. Elbanowski, J. Photochem. Photobiol. A: Chem. 79 (1994) 25.
[13] M. Elbanowski, K. Staninski, M. Kaczmarek, Acta Phys. Pol. A 90 (1996) 101.
[14] Critical Stability Constants, Plenum Press, New York, 1989.
[15] J. Georges, Anal. Chim. Acta 317 (1995) 343.
[16] S. Lis, Z. Hnatejko, B. Mąkowska, M. Elbanowski, J. Photochem. Photobiol. A: Chem. 150 (2002) 233.
[17] S.B. Meshkova, V.E. Kuzmin, Y.E. Shapiro, Z.M. Topilova, I.V. Yudanova, D.V. Bolshoi, V.P. Antonovich, Zh. Anal. Khim. 55 (2000) 118.
[18] B. Marciniak, G.L. Hug, J. Photochem. Photobiol. A: Chem. 78 (1994) 7.
[19] J.M. Lehn, Angew. Chem. Int. Ed. Engl. 29 (1990) 1304.