Energy transfer process in the reaction system $\text{NH}_2\text{OH}\text{-NaOH}\text{-Cu(II)}\text{-Eu(III)}/\text{thenoyltrifluoroacetone}$

Stefan Lis and Małgorzata Kaczmarek

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

ABSTRACT. Chemiluminescence (CL) in the system containing hydroxylamine, sodium hydroxide, copper(II) ions and complex of europium(III) with thenoyltrifluoroacetone has been studied. A weak emission arises from hydroxylamine in the presence of copper(II) ions in a basic aqueous solution. Addition of europium(III) chelate to this system causes a significant increase in the chemiluminescence intensity. The dominant band observed in the emission spectrum occurs at $\lambda \sim 600\text{ nm}$, confirming that Eu(III) ions are the only emitters in the system studied. A strong correlation between the CL intensity and the concentrations of europium(III) chelate was observed. It means that europium(III) thenoyltrifluoroacetone complex does not influence the oxidation rate of hydroxylamine and indicates its important role in this reaction as a sensitiser. A possible mechanism of the chemiluminescence of the $\text{NH}_2\text{OH}\text{-NaOH}\text{-Cu(II)}\text{-Eu(III)}$ chelate system is presented.

1. INTRODUCTION

In our earlier works on the role of lanthanide ions in the processes of chemiluminescence [1, 2] it has been proved that excited Eu(III) ions can appear in the system containing hydrogen peroxide. Excited Eu(III) has been obtained in the reaction of Eu(II) oxidation by hydrogen peroxide [3, 4], and in the process of energy transfer from the excited reaction products generated in the decomposition reaction of hydrogen peroxide to complexed europium ions [5]. In aqueous solution Eu(III) is coordinated with nine water molecules, which provides an efficient pathway for radiationless deactivation of the excited states through vibronic coupling with the OH oscillators [6]. The emission intensity of the lanthanide ions can be significantly increased by complexing them with appropriate organic ligands [7–10].

In this paper a chelate of Eu(III) ions with thenoyltrifluoroacetone (TTA) was used as a sensitizer in the system $\text{NH}_2\text{OH}\text{-NaOH}\text{-Cu(II)}$, characterised by very low emission intensity.

2. EXPERIMENTAL

Measurements of chemiluminescence were performed using the system enabling of ultraweak radiation by the stationary method as described earlier [1]. Spectroscopic measurements were made by means of UV-2401 PC Shimadzu spectrophotometer.

Europium(III) chloride was obtained by dissolving Eu_2O_3 (99.99% Aldrich) in hydrochloric acid (spectral purity, Fluka). The other reagents used for this study were sodium hydroxide NaOH (pure for analysis, POCh), hydroxylamine hydrochloride (pure for analysis, Fluka), thenoyltrifluoroacetone TTA (pure for analysis, Fluka), copper chloride CuCl_2 (pure for analysis, Fluka). All solutions were prepared with the use of doubly dis-

tilled water, except of TTA, which was dissolved in 95% ethanol (pure for analysis). Solutions of Eu/TTA complex were obtained by mixing europium chloride solution with a solution of TTA at the molar ratio 1 : 1, 1 : 2, 1 : 3 and 1 : 4. The ethanol content in $> 1\%$ v/v did not affect the CL intensity.

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 ($S = \int_0^t I \Delta t$, where I —CL intensity, t —measurement duration). The spectra of chemiluminescence were recorded using the method of cut-off filters.

3. RESULTS AND DISCUSSION

The chemiluminescence emitted from the systems containing hydroxylamine and Cu(II) ions as catalyst and Eu/TTA complex in aqueous solution was studied.

The introduction of hydroxylamine into 0.01 mol/l NaOH solution induced a short-lived chemiluminescence of low intensity. The kinetic curve of CL decay in the system $\text{NH}_2\text{OH}\text{-NaOH}$ is shown in Figure 1.

The low intensity CL emission appeared at the moment of NH_2OH introduction into NaOH solution, then quickly attenuated to baseline in 2 min. The presence of Cu(II) ions in this system resulted in an increase of CL intensity, having the same duration (curve 2 in Figure 1).

The introduction of thenoyltrifluoroacetone into the $\text{NH}_2\text{OH}\text{-NaOH}\text{-Cu(II)}$ and $\text{NH}_2\text{OH}\text{-NaOH}$ systems caused a significant decrease in CL intensity and shortening of its duration. The intense and long-lived CL was obtained for solutions containing NaOH, Cu(II), Eu/TTA complex and NH_2OH (curve 3 in Figure 1). The intensity of CL was dependent on the Eu(III): TTA molar ratios. The highest emission intensity was observed

Figure 1. The kinetic curves of CL decay in the systems: $\text{NH}_2\text{OH}\cdot\text{NaOH}$ (curve 1), $\text{NH}_2\text{OH}\cdot\text{NaOH}\cdot\text{Cu(II)}$ (curve 2), $\text{NH}_2\text{OH}\cdot\text{NaOH}\cdot\text{Cu(II)}\cdot\text{Eu(III)}$ chelate (molar ratio $\text{Eu}:\text{TTA} = 1:3$, curve 3). The concentration of Eu(III) ions was $1 \times 10^{-3} \text{ mol/l}$, the initial concentration of $\text{NH}_2\text{OH} = 1 \times 10^{-3} \text{ mol/l}$, and $\text{Cu(II)} = 5 \times 10^{-6} \text{ mol/l}$.

Figure 2. Spectral distribution of CL of the systems: $\text{NH}_2\text{OH}\cdot\text{NaOH}\cdot\text{Cu(II)}\cdot\text{Eu(III)}$ chelate (B) and $\text{NH}_2\text{OH}\cdot\text{NaOH}\cdot\text{Cu(II)}$ (C).

in the case of the ratio $\text{Eu(III)}:\text{TTA} = 1:3$. The most intensive CL was recorded at the moment of hydroxylamine introduction and then the CL decrease was much slower than that observed in the primary system (without Eu(III) chelate).

In order to identify the emitter in the systems studied, their spectral distributions were recorded by the method of cut-off filters (Figure 2).

The emission spectra of the systems $\text{NH}_2\text{OH}\cdot\text{NaOH}\cdot\text{Cu(II)}$ and $\text{NH}_2\text{OH}\cdot\text{NaOH}$ were similar and revealed four

Figure 3. The light sum of CL (S) of the system $\text{NH}_2\text{OH}\cdot\text{NaOH}\cdot\text{Cu(II)}\cdot\text{Eu(III)}$ chelate versus the concentration of Eu(TTA)_3 . The initial concentration of NH_2OH was $1 \times 10^{-3} \text{ mol/l}$.

bands at 480, 520, 580 and 630 nm. According to the earlier studies of the reaction systems in which hydrogen peroxide is decomposed in a basic aqueous solution or under the influence of d-electron metals, the emitters in such systems are particles of singlet oxygen and their dimols with characteristic emission bands at 480, 520, 580, 633 and 703 nm [11–15]. The presence of four bands at the same wavelength in the CL-spectra of $\text{NH}_2\text{OH}\cdot\text{NaOH}\cdot\text{Cu(II)}$ and $\text{NH}_2\text{OH}\cdot\text{NaOH}$ indicates, that the emitters in these systems are dimols of singlet oxygen [$(^1\text{O}_2)_2$].

The emission spectrum of $\text{NH}_2\text{OH}\cdot\text{NaOH}\cdot\text{Cu(II)}\cdot\text{Eu(III)}$ chelate with a maximum at $\lambda \sim 600 \text{ nm}$, was similar to the fluorescence spectrum characteristic of Eu(III) ions, corresponding to the transitions of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ ($\lambda \sim 595 \text{ nm}$) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ($\lambda \sim 615 \text{ nm}$) [2, 7, 8, 16]. The width of the spectral region, obtained using the cut-off filters method, is equal to 10–20 nm. An accurate resolution of the two bands in the presented spectrum is not possible. This means that in the system studied the only emitter were europium(III) ions.

The chemiluminescence characteristic of Eu(III) ions obtained in the solutions containing the europium(III) 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 CL of the system studied, the intensity of CL was measured in the systems containing NH_2OH , NaOH and Cu(II) ions, at a constant concentration and europium chelate at different concentrations.

Figure 3 presents the dependence of the light sum CL of the $\text{NH}_2\text{OH}\cdot\text{NaOH}\cdot\text{Cu(II)}\cdot\text{Eu(III)}$ chelate system on the concentration of europium(III) complex

Figure 4. The kinetic curves of CL decay in the system $\text{NH}_2\text{OH}\text{-NaOH}\text{-Cu(II)-Eu(III)}$ chelate versus the time of introduction of Eu(III) chelate after the initiation of reaction. Curve 1— Eu(III) complex presence at the moment of initiation of reaction; curve 2 introduction after 60 s, curve 3—after 180 s and curve 4—after 300 s. The concentration of Eu(III) ions was $1 \times 10^{-3} \text{ mol/l}$, the initial concentration of $\text{NH}_2\text{OH} = 1 \times 10^{-3} \text{ mol/l}$, and $\text{Cu(II)} = 5 \times 10^{-6} \text{ mol/l}$.

(M : L molar ratio = 1 : 3). As follows from Figure 3 the increase in the light sum of CL is proportional to the increase in the Eu(TTA)_3 complex concentration.

In order to fully characterise the system $\text{NH}_2\text{OH}\text{-NaOH}\text{-Cu(II)-Eu(III)}$ chelate, the effect of the introduction time of europium(III) chelate into $\text{NH}_2\text{OH}\text{-NaOH}\text{-Cu(II)}$ system on the intensity and duration of CL was also studied (Figure 4).

Curve 1 in Figure 4 presents the CL decay of the system studied, in which europium(III) complex was present at the moment of introduction of NH_2OH (initiation of reaction). Introduction of the Eu(III) chelate at 1, 3, 5 minutes after the reaction initiation does not influence the CL intensity and duration. That means that europium(III) complex does not influence the rate of oxidation of hydroxylamine.

The absorption spectra of the system $\text{NH}_2\text{OH}\text{-NaOH}\text{-Cu(II)-Eu(III)}$ chelate were also recorded before and after the addition of hydroxylamine (Figure 5). The absorption spectra of individual reagents show that TTA absorbs in the 225–325 nm range. The formation of the chelate between Eu(III) ions and TTA is evidenced by a new absorption band which is red shifted with respect to that of the free ligand (with a maximum at $\lambda \sim 350 \text{ nm}$) [10, 17]. As shown in Figure 5, the intensity of this band did not change after the introduction of NH_2OH which means that the Eu-TTA complex does not undergo destruction under the effect of hydroxylamine.

The oxidation mechanism of hydroxylamine in basic solution and metal-ion-catalysed has been investi-

Figure 5. The absorption spectrum of TTA (1) and the system Eu-TTA ($\text{Eu(III)} : \text{TTA}$ molar ratio 1 : 1) before (2) and after (3) addition of hydroxylamine.

gated [18–22]. In basic aqueous solution NH_2OH exists in the form of NH_2O^- , which can be attacked by the dissolved oxygen [19]:

The formation of HO_2^- free radicals also included, the oxidation of metal-ion-catalysed hydroxylamines [20], according to the scheme:

The recombination reaction of free radicals generated singlet oxygen [23, 24]:

Both oxidation mechanisms of hydroxylamine indicate that dissolved oxygen plays an important role in the CL reaction. Therefore, the CL intensity of system $\text{NH}_2\text{OH}\text{-NaOH}\text{-Cu(II)-Eu(III)}$ chelate in dependence of time of argon bubbled through the solution was studied. The intensity of emission decreased with increasing time of argon bubbling. The results indicate that in the reactions above dissolved oxygen is an import factor in the free radical creation.

According to our earlier study of the reaction systems in which hydrogen peroxide is decomposed in