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Energy transfer in the chemiluminescent system: Eu(II)/(III)–N_3^-–H_2O_2

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Abstract

Chemiluminescence (CL) in the systems containing Eu(II), Eu(III) ions and hydrogen peroxide has been investigated. Earlier results show that these systems are sources of excited Eu(III) ions and singlet oxygen generated in the recombination reactions of the hydroxyl radicals which originate from hydrogen peroxide decomposition. The excited Eu(III) ions undergo radiative deactivation. The addition of azide ions (N_3^-) to the Eu(II)/(III)–H_2O_2 system causes a significant increase in the chemiluminescence intensity and yield as a result of the energy transfer process from the dimers of singlet oxygen to Eu(III) ions. Taking into account the kinetic and spectral data obtained from the systems studied, the scheme of processes is proposed, and the quantum yield of chemiluminescence is estimated using the CL standard system: luminol–haemin–H_2O_2.

Keywords: Chemiluminescence; Azide; Europium; Energy transfer

1. Introduction

Chemiluminescence (CL) of lanthanide ions, in particular Eu(II) and Eu(III), has been studied for many years. It has been established that europium ions can be excited in the oxidation reaction with the use of hydrogen peroxide [1–3]. Also a possibility of energy transfer from dimers of singlet oxygen $^1\Delta_g^1\Delta_g(1,0)$ and $^1\Delta_g^1\Delta_g(0,0)$ to Eu(III) ions complexed with azide ligand N_3^- in the system Eu(II)+H_2O_2 has been indicated [4]. The role of the $(Eu–N_3)^{2+}$ complex as a sensitiser in the system Eu(II)/(III)–N_3^-–H_2O_2 and in the Fenton system (Fe(II)/(III)–H_2O_2) has been determined by measurement of the yield of CL versus concentrations of particular components for different pH. The CL spectra obtained testified to the presence of excited Eu(III) ions undergoing radiative deactivation as a result of the transitions $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$.

The aim of this work was to analyse the kinetics of $(Eu–N_3)^{2+}$complex formation and the influence of its presence on the course of CL of the system Eu(II)/(III)–N_3^-–H_2O_2, with energy transfer involved.

2. Experimental

The preparation of $EuCl_2$ solutions was described in earlier works [1,2] and the scheme of the experimental set-up is given in Ref. [4]. Solutions of all reagents were prepared using distilled water. Spectrophotometric measurements were made by means of a UV–2401 PC Shimadzu spectrophotometer.

3. Results and discussion

The absorption spectrum of Eu(II) ions in water environment reveals two bands with maxima at $\lambda = 248$ and 328 nm, ascribed to the electronic transitions $4f^7 \rightarrow 4f^6 5d$ [5]. In the concentration range 10^{-4}–10^{-2} $mol \cdot dm^{-3}$, for $\lambda = 248$ nm, the $EuCl_2$ solutions satisfied the Lambert–Beer law. The other components of the system studied, i.e. hydrogen peroxide and azide ions, at the concentrations used, did not give significant absorption signals for $\lambda = 248$ nm. This fact was used for determination of changes in the concentration of Eu(II) ions in the system studied. Fig. 1 presents the time changes in Eu(II) concentration calculated from the changes in intensity of the absorption band at 248 nm.

The course of the curve shown in Fig. 1 is the same for the reaction in the system Eu(II)/(III)–H_2O_2 and in Eu(II)/(III)–N_3^-–H_2O_2. This observation means that azide ions have no influence on the rate of Eu(II) ion oxidation so the hydrated europium ions are oxidised at the same rate as those complexed by N_3^-. On the basis of the con-

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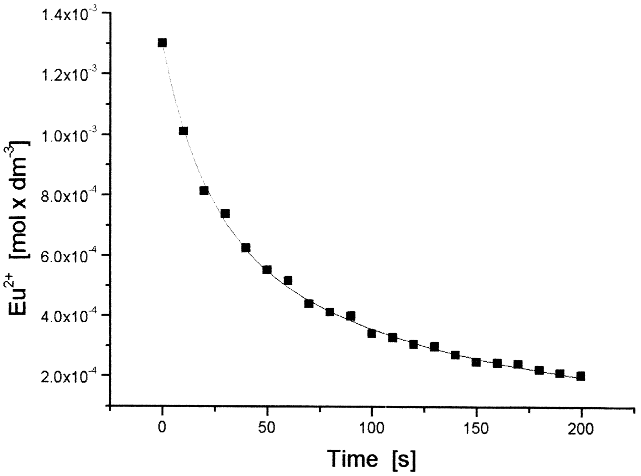

Fig. 1. Changes in the concentration of Eu(II) ions after addition of H_2O_2. The initial concentrations of the reagents were the same and equal to 1.3×10^{-3} mol×dm^{-3}.

centration changes of Eu(II) in time, a value of the oxidation rate for the total reaction:

$$2\mathrm{Eu(II)} + \mathrm{H_2O_2} \xrightarrow{k} 2\mathrm{Eu(III)} + 2\mathrm{HO}^-$$

was calculated for equimolar amounts of the reagents (Fig. 2) to be $k=10.35\pm0.15$ mol^{-1} s^{-1}.

As follows from earlier studies [4] in the chemiluminescent system Eu(II)/(III)–N_3^-–H_2O_2, the energy originating from dimers of singlet oxygen is accepted by the complex $(\mathrm{Eu{-}N_3})^{2+}$ appearing during oxidation of Eu(II), as well as singlet oxygen whose presence is a result of side radical reactions [6,7]. With the time of the reaction, the concentration of the energy acceptor ($(\mathrm{Eu{-}N_3})^{2+}$) increases and that of the energy donor $(^1O_2)_2$ decreases.

The time changes of CL intensity for the system Eu(II)/(III)–N_3^-–H_2O_2 are illustrated by curve 2 in Fig. 3.

Two phases can be distinguished in this CL. The first one from the beginning of the reaction to about 200 s, is characterised by increasing intensity of emission up to the maximum. This increase is a consequence of increasing concentration of the complex $(\mathrm{Eu{-}N_3})^{2+}$ [8,9], shown by curve 3 in Fig. 3. The two curves almost coincide in the first phase, to about 200 s, which confirms that the complex plays the role of the energy acceptor and, simultaneously, the CL emitter in the system. The second phase of the kinetic curve of CL, starting from about 200 s is characterised by a slow decrease in the emission intensity despite a high concentration of the energy acceptor. This fact can be explained by a decrease in the concentration of the energy donor, that is singlet oxygen. As follows from the CL duration, in spite of almost complete oxidation of $(\mathrm{Eu{-}N_3})^{+}$ to $(\mathrm{Eu{-}N_3})^{2+}$, the radical reactions continue for a relatively long time (about 1.5 h), until CL intensity reaches the background level, reproducing singlet oxygen in the system.

The processes taking place in the system Eu(II)/(III)–N_3^-–H_2O_2 can be described by the following equations, taking into account the above results; the kinetics of Eu(II) oxidation [1,2] is similar to the kinetics of the complex oxidation.

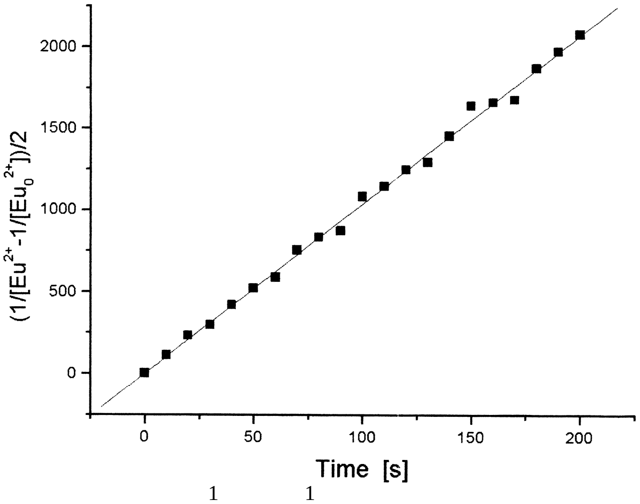

Fig. 2. The plot of $\dfrac{\dfrac{1}{[\mathrm{Eu(II)}]}-\dfrac{1}{[\mathrm{Eu(II)}]_0}}{2}=k\cdot t$ for the reaction of Eu(II) ions oxidation with H_2O_2. [Eu(II)], concentration of Eu(II) ions after time t; $[\mathrm{Eu(II)}]_0$, initial concentration of Eu(II) ions; k, rate constant of a second-order reaction.

3.1. Reactions for $(Eu{-}N_3)^{2+}$complex formation

$$(\mathrm{Eu{-}N_3})^{+} + \mathrm{H_2O_2} \rightarrow (\mathrm{Eu{-}N_3})^{2+} + \mathrm{HO}^{\cdot} + \mathrm{HO}^-$$

$$(\mathrm{Eu{-}N_3})^{+} + \mathrm{HO}^{\cdot} \rightarrow (\mathrm{Eu{-}N_3})^{2+} + \mathrm{HO}^-$$

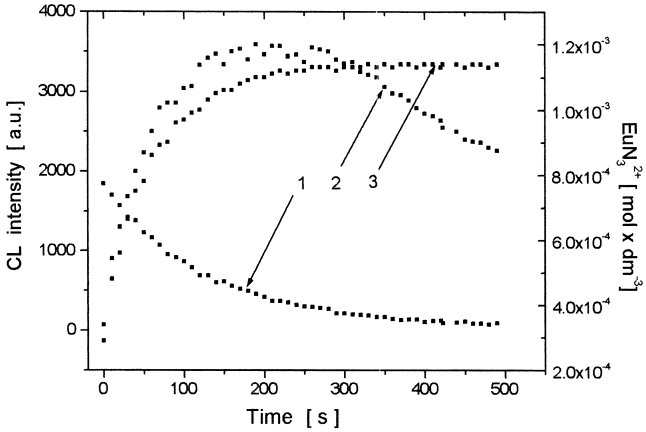

Fig. 3. The kinetic curves of CL in the systems: Eu(II)/(III)–H_2O_2 (curve 1), Eu(II)/(III)–N_3^-–H_2O_2 (curve 2) and changes in the concentration of $(\mathrm{Eu{-}N_3})^{2+}$ during the reaction (curve 3); pH 7.

3.2. Radical reactions reproducing singlet oxygen [6]

$$\mathrm{HO}^{\cdot}+\mathrm{H_2O_2}\rightarrow\mathrm{HO}_2^{\cdot}+\mathrm{H_2O};\ \mathrm{HO}_2^{\cdot}\leftrightarrow\mathrm{O}_2^{\cdot-}+\mathrm{H}^{+}$$

$$\mathrm{O}_2^{\cdot-}+\mathrm{HO}^{\cdot}\rightarrow\mathrm{HO}^{-}+{}^{1}\mathrm{O}_2;\ \mathrm{O}_2^{\cdot-}+\mathrm{O}_2^{\cdot-}\rightarrow\mathrm{HO}_2^{\cdot}+{}^{1}\mathrm{O}_2$$

$$\mathrm{HO}_2^{\cdot}+\mathrm{HO}_2^{\cdot}\rightarrow\mathrm{H_2O_2}+{}^{1}\mathrm{O}_2;\ \mathrm{O}_2^{\cdot-}+\mathrm{H_2O_2}\rightarrow\mathrm{HO}^{-}+\mathrm{HO}^{\cdot}+{}^{1}\mathrm{O}_2$$

3.3. Transfer of energy from singlet oxygen dimers to azide complex of europium (III) [4]

$$({}^{1}\mathrm{O}_2)_2+(\mathrm{Eu{-}N_3})^{2+}\rightarrow(\mathrm{Eu{-}N_3})^{2+}\cdots({}^{1}\mathrm{O}_2)_2\rightarrow((\mathrm{Eu{-}N_3})^{2+})^{*}+2\,{}^{3}\mathrm{O}_2$$

3.4. Radiative deactivation of the complex (emission bands for Eu(III) ions)

$$((\mathrm{Eu{-}N_3})^{2+})^{*}\rightarrow(\mathrm{Eu{-}N_3})^{2+}+h\nu(595\ \mathrm{nm},\ 615\ \mathrm{nm})$$

Quantum yield of CL of the system Eu(II)/(III)–N_3^{-}–$\mathrm{H_2O_2}$ was determined by comparing the integral intensity of CL of this system with that of the standard. The quantum yield reached a value of 2.7×10^{-10} and was almost two orders of magnitude higher than in the system without azide ions. The CL standard was the reaction of luminol with hydrogen peroxide catalysed with hemine, in a solution of pH 11.6 [10].

In conclusion, the azide ion plays a very important role in the chemiluminescence reaction in the Eu(II)/(III)–$\mathrm{H_2O_2}$. The mechanism of the chemiluminescence and its quantum yields have been determined. The kinetic analysis of the CL reaction has shown that the $(\mathrm{Eu{-}N_3})^{2+}$ complex, as an energy transfer acceptor from the singlet oxygen dimers, is the main chemiluminescence emitter.

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