Research Article

Influence of Lanthanide(III) Ions on the Reaction System Tryptophan—H₂O₂—Fe(II)

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Chemiluminescence (CL) studies were carried out with luminescent lanthanide ions as probes to a tryptophan-oxidation reaction at pH ~ 6. The redox system consisted of tryptophan, hydrogen peroxide, and Fe(II) ions (catalysts of H₂O₂ decomposition). The luminescent lanthanide(III) ions used were Eu(III), Tb(III), Gd(III), and Dy(III). In the case of the reaction system with the Tb(III) ion a significant increase in the chemiluminescence intensity and its duration was observed over the other Ln(III) ions. The CL spectrum registered for this system shows emission bands typical of Tb(III) ions with maxima at $\lambda \sim 490$ and 550 nm, corresponding to the electronic transitions of $^5D_4 \rightarrow ^7F_6$ and $^5D_4 \rightarrow ^7F_5$, respectively. The presence of emission bands characteristic of the Ln(III) ions was also observed in the systems containing Eu(III) and Dy(III) ions. These studies revealed a strong influence of the chemiluminescence intensity associated with the tryptophan oxidation, on the concentration of Ln(III) ions. On the basis of the results obtained, a possible mechanism is proposed for reaction of the system: Ln(III)—tryptophan—H₂O₂—Fe(II), taking into consideration an energy transfer process from the tryptophan oxidation products to the Tb(III), Dy(III), or Eu(III) ions.

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1. INTRODUCTION

Due to their luminescent properties lanthanide(III) ions, particularly europium(III) and terbium(III), have been used in a large number of investigations involving systems of biological importance, including aminoacids and proteins [1–4]. In these studies an important role is played by processes of energy transfer from organic chromophors to the Ln(III) ions. Tryptophan, used in these investigations, is an aromatic aminoacid—a naturally occurring chromophor. Energy transfer from tryptophan to Ln(III) ions has been widely studied through the use of spectrofluorimetric methods in which the observed emission was the result of tryptophan excitation [3].

In this paper, the Ln(III) ions were used as probes to study the reaction system of Ln(III)—tryptophan—H₂O₂—Fe(II). Results of chemiluminescence, that is, CL intensities, obtained from the oxidation of tryptophan, strongly depend on the pH of the solutions. An intense luminescence intensity has been observed in strongly alkaline [5, 6] and strongly acidic media [7]. However, a smaller number of investigations refers to this reaction in solutions of pH near neutral because of the low luminescence intensities occurring

in these systems. In this paper studies of the reaction system containing tryptophan—H₂O₂—Fe(II) were carried out in solutions of pH ~ 6, using Tb(III), Dy(III), and Eu(III) ions as luminescent probes for chemiluminescence.

2. EXPERIMENTAL

Chemiluminescence measurements were performed on the experimental set-up presented in Scheme 1 that is sensitive to ultra-low intensity irradiation using the stationary method. The absorption spectra were measured by means of a Shimadzu UV-2401 PC spectrophotometer, and fluorescence spectra were recorded using a Perkin-Elmer MP3 spectrofluorimeter.

Chemicals used in this study were tryptophan (analytical grade, Fluka), tryptamine hydrochloride (analytical grade, Fluka) (Figure 1), chlorides of Eu(III), Tb(III), Gd(III), and Dy(III) obtained by dissolving an appropriate oxide (spectroscopically pure, prepared in the Laboratory of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, Poznań) in hydrochloric acid (spectroscopically pure, Fluka), hydrogen peroxide (30% solution, analytical grade, Merck), thenoyltrifluoroacetone TTA, (analytical grade,

SCHEME 1: Structure of tryptophan (a) and tryptamine (b).

FIGURE 1: Apparatus for measurement of chemiluminescence. AC: automatic counter C570, DS: discriminator, A: amplifier, C: measurement cell, F: filters, D: diaphragm, P: photomultiplier M12 FQC51, PA: preamplifier, HVS: high voltage supplier.

Fluka); NaOH (analytical grade); FeCl₂ (analytical grade, Fluka). All solutions were prepared with the use of doubly distilled water, except for TTA, which was dissolved in 95% ethanol (pure for analysis). Chelate solutions of europium(III) with TTA were obtained by mixing solutions of EuCl₃ and TTA in the molar ratio 1 : 3. The ethanol content in > 1% v/v did not affect the CL intensities.

All of the chemiluminescence studies were performed in the same manner. Hydrogen peroxide ($2 \cdot 10^{-2}$ mol/l) was added to solutions containing tryptophan or tryptamine ($1 \cdot 10^{-4}$ mol/l), Fe(II) ions ($6 \cdot 10^{-6}$ mol/l), and Ln(III) ($4 \cdot 10^{-5}$ to $1 \cdot 10^{-2}$ mol/l), or europium(III) chelates ($5 \cdot 10^{-6}$ to $1 \cdot 10^{-4}$ mol/l). The experiments were conducted in near neutral solutions (pH $\sim$ 6), because all initial solutions were adjusted to pH $\sim$ 6. This pH value was attained by the addition of NaOH or HCl solutions. For all solutions studied, curves of CL decay were obtained, and the CL light intensity sums were calculated as the area under these curves ($S = \int_{t_0}^t I_{CL} \Delta t$; where I_{CL} intensity, t -measurement duration).

3. RESULTS AND DISCUSSION

The chemiluminescence in the reaction systems under study arises as the result of tryptophan oxidation by hydrogen peroxide in the presence of terpositive lanthanide ions (Eu(III), Tb(III), Dy(III), and Gd(III)) in aqueous solutions at pH $\sim$ 6. The kinetic curves of CL decay in these systems are presented in Figure 2. In contrast, in the case of the reaction mixtures: H₂O₂–Fe(II)–Ln(III), where Ln = Eu, Tb, Gd, and Dy, no chemiluminescence was observed.

The fundamental system tryptophan–H₂O₂–Fe(II) shows a low intensity, short-lived chemiluminescence. This low intensity CL emission appeared at the moment of H₂O₂

FIGURE 2: The kinetic curves of CL decay in the systems: tryptophan–H₂O₂–Fe(II) (see curve 1), tryptophan–H₂O₂–Fe(II)–Dy(III) (see curve 2), tryptophan–H₂O₂–Fe(II)–Eu(III) (see curve 3), and tryptophan–H₂O₂–Fe(II)–Tb(III) (see curve 4). The concentration of Tb(III) and Eu(III) ions was $1 \cdot 10^{-3}$ mol/l, Dy(III) ions was $6 \cdot 10^{-3}$ mol/l, and the initial concentration of H₂O₂ = $2 \cdot 10^{-2}$ mol/l, tryptophan = $1 \cdot 10^{-4}$ mol/l.

being introducing into the solution under investigation. This CL emission intensity decayed to the baseline in 5 min. The presence of Gd(III) ions in this system caused no changes, while the presence of Tb(III), Dy(III), or Eu(III) resulted in an increase of CL intensity. The latter ions also lead to

considerable lengthening of the duration of the CL (up to 2 hours). The kinetic curves of CL decay were independent of the presence of the Ln(III) ion introduced. They all have a similar time dependence, that is, the same maximal intensity at the moment of the reaction initiation. Moreover, the measurements indicated that changes of pH in the range from 5.5 to 6.6 did not influence the CL intensity.

Spectral analysis of the chemiluminescence in the systems studied was performed using cut-off filters as described earlier [8]. Because of the very low CL intensity of the reaction mixture tryptophan—H₂O₂—Fe(II), its spectral distribution could only be measured using a 10-fold higher concentration of tryptophan and H₂O₂ than in the systems containing Ln(III) ions. The spectral distribution of the system tryptophan—H₂O₂—Fe(II) shows a broad emission band in the range of 430–520 nm with a maximum at ~460 nm (spectrum in, Figure 3(a)). This spectrum is consistent with the fluorescence spectrum of N-Formylkynurenine [9], which is presented in a series of publications as a product of tryptophan oxidation by H₂O₂ [5, 6, 10]. An identical spectrum was also recorded for this reaction mixture containing additionally Gd(III) ions. However, in the systems tryptophan—H₂O₂—Fe(II)—Eu(III), tryptophan—H₂O₂—Fe(II)—Tb(III), and tryptophan—H₂O₂—Fe(II)—Dy(III) recorded 3 min after introduction of H₂O₂, the CL spectra show, in addition to this band ($\lambda_{\text{max}} \sim 460$ nm), the luminescence bands characteristic of the Ln(III) ions with maxima at $\lambda \sim 600$ nm for Eu(III), 550 nm for Tb(III), and 580 nm for Dy(III), respectively [11] (Figure 3). The CL spectra recorded at longer times following the introduction of H₂O₂ show only the bands characteristic for lanthanide(III) ions, which indicates that the long-lived CL occurring in the systems of tryptophan—H₂O₂—Fe(II)—Ln(III) is due to the Ln(III) emission.

In order to determine the role of the Ln(III) ions in the reaction mixtures, measurements were made of the fluorescence decays of tryptophan in solutions with and without Ln(III) ions. In addition, studies were made of chemiluminescence in systems containing the same initial concentrations of tryptophan and H₂O₂ and various concentrations of the Ln(III) ions. In aqueous solutions, tryptophan emits fluorescence with a maximum at $\lambda \sim 360$ nm [6]. For all of the reaction systems, tryptophan—H₂O₂—Fe(II) and tryptophan—H₂O₂—Fe(II)—Ln(III), the same fluorescence decay of the tryptophan band was observed after addition of H₂O₂ (Figure 4). A very strong tryptophan emission decay was observed in the time period ~100 after the reaction initiation. Following this initial time period, the tryptophan emission decay was much slower as seen in Figure 4. The fluorescence decays obtained for tryptophan in the reaction mixtures are in agreement with the kinetics of the CL decays in these systems.

In the reaction mixtures of tryptophan—H₂O₂—Fe(II)—Ln(III), an increase in the emission intensity with an increase in the Ln(III) concentration was observed; a particularly striking increase occurred in the case of Tb(III). The maximal value of the light-intensity sum in the system was observed for the molar ratio tryptophan: Tb(III) = 1 : 40

FIGURE 3: The spectral distribution of chemiluminescence of the systems: tryptophan—H₂O₂—Fe(II) (a), tryptophan—H₂O₂—Fe(II)—Tb(III) (b), tryptophan—H₂O₂—Fe(II)—Eu(III) (c), and tryptophan—H₂O₂—Fe(II)—Dy(III) (d).

(Figure 5). A similar tendency was found for Dy(III) ions. However, in the case of the tryptophan—H₂O₂—Eu(III), an increase of the CL intensity was observed up to the molar ratio Eu(III): tryptophan = 1 : 1. However, increases in the Eu(III) concentration did not influence the CL intensity.

The spectral distributions of the CL from the systems contained the bands characteristic of the trivalent lanthanide ions. This observation suggests that the CL intensity increases were related to the emission of the Ln(III) ions. However, independent of the concentrations of the Ln(III) ions, the CL decay profiles were the same as in the fundamental

FIGURE 4: The fluorescence spectrum of tryptophan in the system tryptophan— H_2O_2 — Fe(II) — Tb(III) before introduction of H_2O_2 (1); and 100 s (2), 300 s (3), 500 s (4), and 1000 s (4) after introduction of H_2O_2 . The initial concentration of $\text{H}_2\text{O}_2 = 1 \cdot 10^{-1}$ mol/l, tryptophan = $1 \cdot 10^{-3}$ mol/l.

FIGURE 5: Light sum of system tryptophan— H_2O_2 — Fe(II) — Ln(III) versus the concentration of Ln(III) ions. The initial concentration of $\text{H}_2\text{O}_2 = 2 \cdot 10^{-2}$ mol/l, tryptophan = $1 \cdot 10^{-4}$ mol/l.

system. The lack of an influence of the Ln(III) ions on the decay of the tryptophan fluorescence band following addition of H_2O_2 and the observation that the CL kinetic curves of the systems with and without Ln(III) ions are of the same shape independent of the Ln(III) concentration prove that the emission from these systems is related to the H_2O_2 oxidation of tryptophan and that the kinetics of this process are independent of the Ln(III) ions.

Aminoacids form complexes with the Ln(III) ions in aqueous solutions, independent of the metal: ligand ratio, but mainly ML species are created [12–15]. Furthermore, in systems generating excited carbonyl groups (decay of dioxethans) [16] in the presence of either uncomplexed Eu(III) and Tb(III) ions, excitation of Ln(III) was achieved only in the case of Tb(III) . These two observations from the literature [12–16] suggest that the differences observed in our luminescence intensities between Tb(III) and Eu(III) ions are likely the result of energy transfer only to complexed Eu(III) —tryptophan ions in the system containing Eu(III) .

In order to confirm the role of Eu(III) —tryptophan complexes in the observed chemiluminescence and studies using tryptamine were carried out. Tryptamine contains in its structure an imidazole ring (similar to tryptophan), which is sensitive to oxidation by H_2O_2 . However, in solutions of $\text{pH} < 9$, tryptamine does not form complexes with the Ln(III) ions because the amino group of tryptamine is protonated. The system tryptamine— H_2O_2 — Fe(II) shows very low emission intensity which is also of short duration. Introduction of Eu(III) ions into this reaction mixture did not cause any changes, but the presence of Tb(III) resulted in an increased emission intensity characteristic of the Tb(III) ions. Lack of Eu(III) emission in solutions of tryptamine— H_2O_2 — Fe(II) — Eu(III) supports the notion that energy transfer from the excited $(\text{C}=\text{O})^*$ groups to Eu(III) takes place in the complexes of Eu(III) —tryptophan. In contrast to Eu(III) systems, there was excitation of uncomplexed Tb(III) ions in the system tryptamine/ H_2O_2 . This observation along with the observations of maximal emission intensities in the tryptophan— H_2O_2 — Fe(II) — Ln(III) ($\text{Ln} = \text{Tb, Dy}$) systems even when there was a considerable excess of Tb(III) and Dy(III) relative to tryptophan prove that energy was being transferred from the excited carbonyl groups to the uncomplexed Tb(III) and Dy(III) ions. The significantly lower emission intensities seen in the systems with Dy(III) compared to the ones with Tb(III) are related to the differences in the intrinsic emission quantum yields of these two ions.

In order to confirm that excited organic molecules $(\text{C}=\text{O})^*$ participate in the energy transfer process, studies using the Eu(III) /TTA chelate were carried out. β -diketonate complexes of Ln(III) ions, among them TTA, are widely utilized in studies involving interactions between excited organic ligands and metal complexes [17–20]. A good energy matching between the triplet states of TTA ($\sim 20300 \text{ cm}^{-1}$ [21]) and excited products of the dioxane decomposition enables an efficient triplet—triplet energy transfer. The excitation of europium is the result of the intermolecular energy transfer (triplet—triplet) from the excited $(\text{C}=\text{O})^*$ groups to the ligand TTA (complexed with Eu), and consequently the intramolecular energy transfer to Eu(III) [4]. Introduction of this chelate into the fundamental system, as presented in Figure 6, stimulated an increase in the CL intensity. The emission intensity in a solution containing the Eu/TTA complex was 70 times higher than in a system containing the same concentration of Eu(III) concentration, and it was 30 times higher than in a solution with Tb(III) ions.

FIGURE 6: The kinetic curve of CL decay in the tryptophan— H_2O_2 — Fe(II) — Eu(III) /TTA system (a) and spectral distribution of CL (b). The concentration of Eu(III) ions was $1 \cdot 10^{-4}$ mol/l, the molar ratio $\text{Eu} : \text{TTA} = 1 : 3$, and the initial concentration of $\text{H}_2\text{O}_2 = 2 \cdot 10^{-2}$ mol/l, tryptophan = $1 \cdot 10^{-4}$ mol/l.

SCHEME 2

A spectral distribution of the tryptophan— H_2O_2 — Eu(III) /TTA reaction mixture contained only the characteristic luminescence band of the Eu(III) ion (spectrum in Figure 6(b)), which was the only emitter in this system.

Taking into consideration the results of our previous studies in which Eu/TTA was used as an effective sensitizer of the H_2O_2 decay in a strongly alkaline solution [22], studies were carried out in the $\text{Eu(III)/TTA—H}_2\text{O}_2$ system at pH of ~ 6 . In these experiments the complex concentrations ranged from $5 \cdot 10^{-5}$ to $3 \cdot 10^{-4}$ mol/l. The CL intensity could not be detected for lower concentrations of Eu(III)/TTA , and, even for the concentration of $3 \cdot 10^{-4}$ mol/l, the CL intensity was very weak. After introducing tryptophan ($2 \cdot 10^{-4}$ mol/l) into these systems, the CL intensity increased by two orders of magnitude. A linear dependence was observed for the CL intensity of the system tryptophan— H_2O_2 — Eu(III)/TTA as a function of the tryptophan concentration. In these experiments the initial concentration of hydrogen peroxide and chelate was held constant while the tryptophan concentra-

tion varied between $5 \cdot 10^{-6}$ and $1 \cdot 10^{-4}$ mol/l. The presence of Eu(III)/TTA complex in these reaction mixtures was confirmed on the basis of its absorption band at $\lambda_{\text{max}} = \sim 350$ nm [21–23]. The absorption spectra of the reaction mixture before and after introducing H_2O_2 were similar. Because the 350 nm absorbance of tryptophan and H_2O_2 is very small in the concentration ranges used, obtaining comparable absorption values for this wavelength in the mixture after the reaction proves that the Eu(III)/TTA concentration is constant during this process.

The mechanism for the oxidation of tryptophan using hydrogen peroxide or peroxyntrous acid ONOOH has been discussed in several papers, and it can be presented as in Scheme 2 [6, 24].

The mechanism describing the processes under study is proposed and presented in Scheme 3. This scheme takes into consideration the tryptophan—oxidation mechanism in Scheme 2, and our chemiluminescence results where emissions were observed with Eu(III) , Tb(III) , and Dy(III) but

SCHEME 3: Processes occurring in the reaction system of tryptophan—H₂O₂—Fe(II)—Ln(III).

none was seen with Gd(III), which has a high lying emitting level ($\sim 32000 \text{ cm}^{-1}$) that is located above the singlet and triplet states of most organic ligands.

4. CONCLUSIONS

In this work ions of Eu(III), Tb(III), Dy(III), and Gd(III) were used for the studies of chemiluminescence accompanying the reaction of tryptophan oxidation by hydrogen peroxide in solution at pH 6. Strong chemiluminescence intensities characteristic of Eu(III) and Tb(III) ions in the systems of tryptophan—H₂O₂—Fe(II)—Ln(III) compared to the emission from the system tryptophan—H₂O₂—Fe(II) prove that the Ln(III) ions play a role as energy mediators of the CL accompanying tryptophan oxidation by hydrogen peroxide. In the case of Eu(III), the energy transfer process from the excited carboxylic groups to the Eu(III) ion occurs within the Eu(III)—tryptophan complex (pathway B in Scheme 3) whereas, in the system with Tb(III) ions, energy transfer also occurs with the involvement of uncomplexed Tb(III) ions (pathways B and C, Scheme 3).

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