

Luminescence Characterisation of the Reaction System Histidine–KBrO₃–Tb(III)–H₂SO₄

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Abstract Chemiluminescence of the system containing Tb(III) ions, histidine and bromate ions in acid solution was studied. The kinetic curves and CL emission spectra of the system were discussed. The emission spectrum of the histidine–Tb(III)–KBrO₃–H₂SO₄ system revealed two emission maxima at ~490 and 550 nm, characteristic of Tb(III) ions. Values of lifetimes of the Eu(III) excited states in Eu(III)–histidine system have shown that the histidine formed ML and ML₂ complexes in neutral solution and did not make them in acidic environment. On the basis of the results, a possible mechanism of reaction system: histidine–Tb(III)–KBrO₃–H₂SO₄ is presented.

Keywords Chemiluminescence · Lanthanide(III) · Histidine · Energy transfer

Introduction

Chemiluminescence emission (CL) can be generated in many systems comprising oxygen or oxygen-containing compounds as oxidisers. The emission accompanying reactions of oxidation involving hydrogen peroxide or KMnO₄ is well recognised, while only a few authors have been interested in the systems with KBrO₃ as an oxidising factor [1–3]. The investigation of the chemiluminescence systems characterised by low intensity of emission is performed with the use of sensitisers being mostly organic fluorophores [4] and lan-

thanide ions [5–9] because of their luminescence properties. In water solutions lanthanide ions occur as aqua-complexes and their emission states are strongly quenched by the –OH oscillators from the water molecules. The quenching rate of luminescence is proportional to the number of water molecules in the first coordination sphere of the metal ion [10, 11] and the complex formation with ligands significantly extends the lifetime of the lanthanide ion excited state [12, 13].

This paper reports a chemiluminescence (CL) study of the reaction system: histidine–KBrO₃–Tb(III)–H₂SO₄ and the complex formation between Ln(III) ions and histidine. The amino acid used in the study is exogenic and in living organisms it is a source of histamine responsible for the allergic response. In the systems with KMnO₄ this amine acid undergoes deamination and decarboxylation [14, 15]. The kinetic curves of CL and CL spectral distribution were recorded. On the basis of the results it has been possible to propose mechanisms of the processes taking place in the system: histidine–KBrO₃–Tb(III)–H₂SO₄, taking into regard the energy transfer from the products of histidine oxidation reaction to Tb(III) ions as sensitiser.

Experimental

Chemiluminescence was recorded using the apparatus recording an ultraweak emission (Fig. 1) and spectral analysis of CL was obtained by using the cut-off filters method [16].

The process of chemiluminescence was each time initiated by adding a solution of histidine (or histamine or oxalic acid or creatinine) to the solution containing the ions Tb(III), KBrO₃ and H₂SO₄. The excited state lifetime of Eu(III) ion for different molar ratios of Eu(III): histidine

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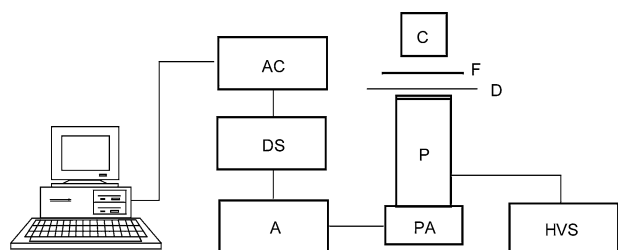


Fig. 1 Apparatus for measurement of chemiluminescence. AC: automatic counter C570; F: filters; HVS: high voltage supplier; DS: discriminator; D: diaphragm; A: amplifier; P: photomultiplier M12 FQC51; C: measurement cell; PA: preamplifier

was measured by a dye laser described earlier [17, 18]. The complexation of Ln(III) ions by histidine was studied by measuring the lifetimes of Eu(III) ions in solutions containing EuCl_3 and histidine at different molar ratios and at pH of 1.5 and 6.9. The value of pH was adjusted by adding HCl or NaOH. The lifetimes of Eu(III) ion were also measured using $\text{Eu}_2(\text{SO}_4)_3$ and histidine at different molar ratios in 0.5 mol/l H_2SO_4 , so in the same conditions as those of the chemiluminescence measurements. The lifetimes were calculated using the formula $n_{\text{H}_2\text{O}} = (1.05 \cdot 1/\tau) - 0.7$ [13]. All the reagents used were of purity not lower than analytical grade.

Results and discussion

Chemiluminescence of the systems containing histidine, Tb(III) ions and KBrO_3 as an oxidiser in the presence of sulphuric acid was studied. Figure 2 presents the CL kinetic curves of the system histidine– KBrO_3 – H_2SO_4 recorded in the presence and in the absence of Tb(III) ions. The emission generated on the reaction of histidine oxidation by potassium bromate is characterised by very low intensity and short duration. The emission at the level of the background was obtained in about 120 s after the reaction initiation, that is introduction of histidine into the reaction system (curve 1 in Fig. 2).

The introduction of Tb(III) ions into the system resulted in a strong increase in the emission intensity and a change in the kinetic curve character (curve 2 in Fig. 2). The maximum on the kinetic curve recorded for the system histidine–Tb(III)– KBrO_3 – H_2SO_4 was reached in about 45 s after the reaction initiation. Spectral analysis of CL of the systems studied was obtained by using the cut-off filters method. Regarding very low intensity of emission from the system histidine– KBrO_3 – H_2SO_4 , its spectral distribution was measured for higher concentrations of potassium bromate and 2 orders of magnitude higher concentration of histidine than those used in the systems with the Tb(III) ions.

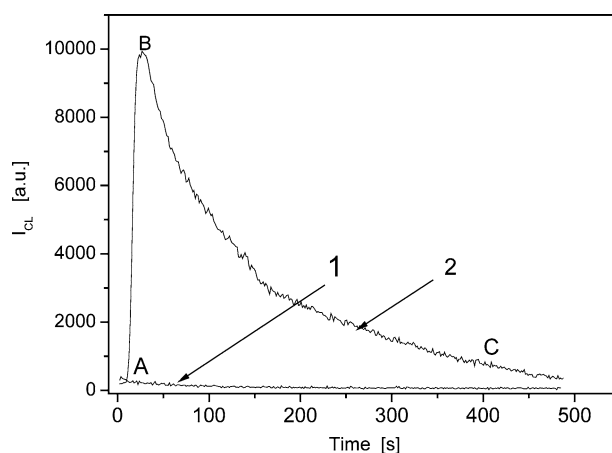


Fig. 2 Kinetic curves of CL of the systems histidine– KBrO_3 – H_2SO_4 (curve 1) and histidine– KBrO_3 –Tb(III)– H_2SO_4 (curve 2); the initial concentration: $c_{\text{KBrO}_3} = 0.06$ mol/l; $c_{\text{histidine}} = 0.001$ mol/l; $c_{\text{Tb(III)}} = 0.15$ mol/l; 0.5 mol/l H_2SO_4

The spectrum shows a broad emission band in the range 400–500 nm, with a maximum for $\sim \lambda = 450$ nm, which is typical of the CL systems with the compounds containing excited carbonyl groups as emitters [19, 20]. Figure 3 presents the CL spectral distribution of the solution containing Tb(III) ions.

The spectral distribution of CL shows the bands with maximums at $\lambda \sim 490$ nm and $\lambda \sim 550$ nm, so the emission bands typical of the Tb(III) ions [21]. The presence of these bands proves that in the system histidine–Tb(III)– KBrO_3 – H_2SO_4 the emitters are the excited lanthanide ions. The CL spectrum recorded and the fact that no emission was recorded of the mixture of Tb(III)– KBrO_3 – H_2SO_4 , suggest that the excitation of Tb(III) ions in the reaction system with histidine can be result of the energy transfer from the histidine

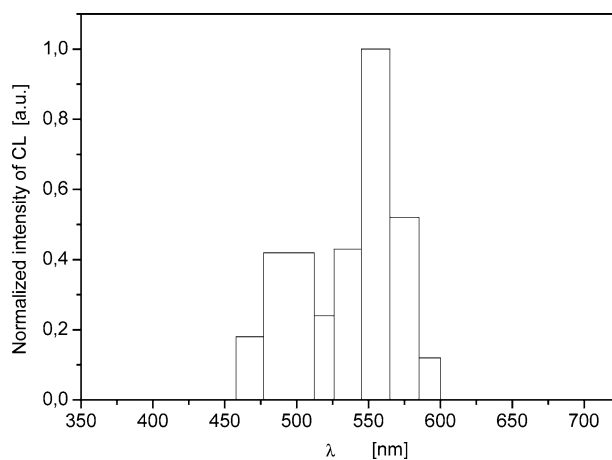


Fig. 3 The CL spectral distribution of the system histidine–Tb(III)– KBrO_3 – H_2SO_4

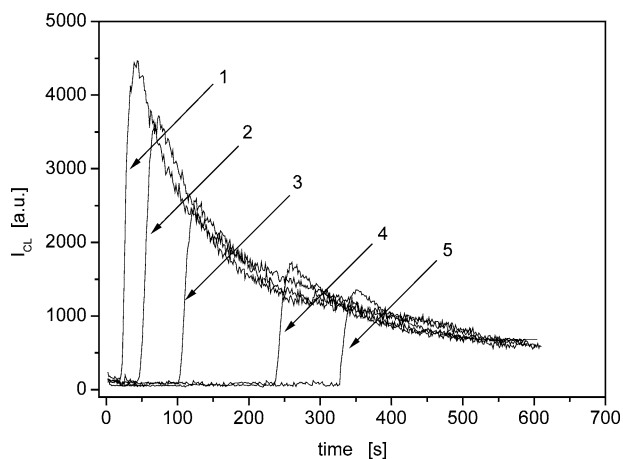


Fig. 4 Kinetic CL curves for the system histidine–KBrO₃–Tb(III)–H₂SO₄ versus the time of Tb(III) ions introduction after the reaction initiation; curve 1—Tb(III) present already at the moment of reaction initiation; curve 2—Tb(III) introduced 60 s after reaction initiation, curve 3—Tb(III) introduced 120 s after reaction initiation; curve 4—Tb(III) introduced 250 s after reaction initiation, curve 5—Tb(III) introduced 320 s after reaction initiation. The initial concentration $c_{\text{KBrO}_3} = 0.06 \text{ M}$; $c_{\text{histidine}} = 0.0005 \text{ mol/l}$; $c_{\text{Tb(III)}} = 0.15 \text{ mol/l}$; $0.5 \text{ mol/l H}_2\text{SO}_4$

oxidation products to Tb(III). In order to identify the role of the lanthanide ion in the reaction mixture studied, the process of Ln(III) complexation with histidine was studied and CL measurements with the Tb(III) ions added to the reaction mixture histidine–KBrO₃–H₂SO₄ were performed at different times after the reaction initiation (introduction of histidine), Fig. 4.

Spectral analysis of the process of Ln(III) complexation with histidine was based on measurements of the lifetimes of the Eu(III) excited states. The measurements were performed for the solutions containing Eu(III) ions (instead of Tb³⁺ ions) at different molar ratios of Ln(III): histidine of 1:0, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6 and 1:10 in solutions of pH = 1.5 and 6.9 and in the environment of 0.5 mol/l H₂SO₄. The luminescence lifetimes and hydration numbers, calculated as described in [22], are presented in Table 1.

The hydration number ($n_{\text{H}_2\text{O}}$) depends on pH and the metal:ligand molar ratio. In solutions of pH = 1.5 the value of $n_{\text{H}_2\text{O}}$ is 9.0 ± 0.5 irrespective of the ligand concentration, which indicates that no complexes between Ln(III) ions and histidine are formed. In solutions of higher pH the values of $n_{\text{H}_2\text{O}}$ decreased with increasing the ligand concentration. Analysis of the data presented in Table 1 shows that the ML complex dominates in the solutions with a smaller excess of histidine, while the species ML₂ dominates in those with a significant excess of histidine.

For europium (III) sulphate in 0.5 mol/l H₂SO₄ the value of $\tau = 134 \mu\text{s}$, indicates the presence of the species

Table 1 Luminescence lifetimes of Eu(III) (τ) and the hydration number of Eu(III) ions ($n_{\text{H}_2\text{O}}$) for different molar ratios of metal: ligand in solutions containing Eu(III) chloride and Eu(III) sulphide (VI), $c_{\text{Eu(III)}} = 0.01 \text{ mol/l}$

Metal:ligand molar ratio	pH	τ (ms)	$n_{\text{H}_2\text{O}}$
EuCl ₃ :histidine			
1:0	4.5	0.109	8.9
1:1	6.9	0.127	7.6
1:2	6.9	0.128	7.5
1:3	6.9	0.133	7.2 ML
1:4	6.9	0.140	6.8
1:5	6.9	0.147	6.4
1:6	6.9	0.152	6.2
1:10	6.9	0.175	5.3 ML ₂
Eu ₂ (SO ₄) ₃			
1:0	0.5 M H ₂ SO ₄	0.134	7.1
1:2	0.5 M H ₂ SO ₄	0.139	7.0
1:6	0.5 M H ₂ SO ₄	0.135	7.1

[Eu(H₂O)₇(SO₄)⁺]. The presence of sulphate ions in the inner coordination sphere of the lanthanide ion has been also reported by Tanaka and Berthoud [23, 24]. The lifetimes of Eu(III) in all solutions containing Eu(III) sulphate and histidine in 0.5 mol/l H₂SO₄ take similar values, which means that in the presence of sulphuric acid histidine does not form complexes with Ln(III) ions.

Curve 1 in Fig. 4 presents the CL decay for the system with Tb(III) ions present at the moment of the reaction initiation, curves 2, 3, 4 and 5 show the CL decay for the systems with Tb(III) introduced at 60, 120, 250 and 320 s after the reaction initiation. As follows from Fig. 4 irrespective of the moment of Tb(III) introduction, the character of the kinetic CL curves is similar, which indicates that the lanthanide ions have no effect on the rate of the histidine oxidation with potassium bromate.

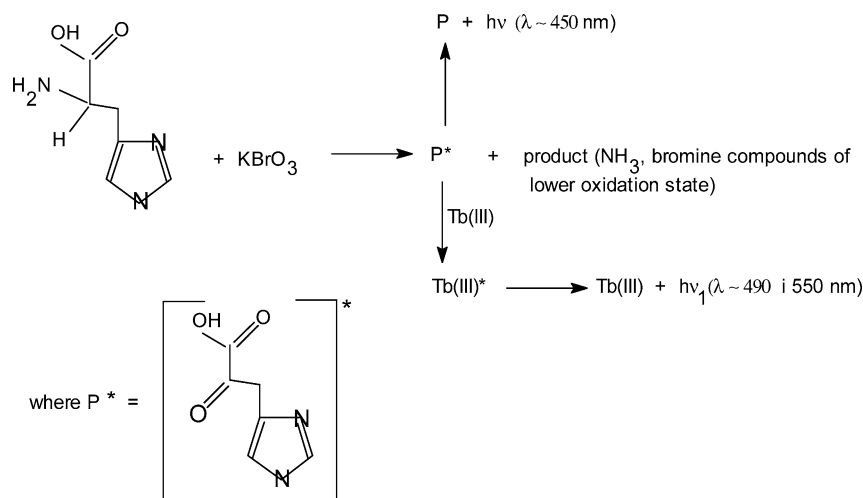
Moreover, the intensity of CL has been found to depend on Tb(III) ions concentration and satisfy the equation describing the sensitised luminescence [25, 26]:

$$1/\Phi_A = 1/\eta_A (1 + 1/K_{SV} [A])$$

where Φ_A is the quantum yield of sensitised luminescence of the acceptor that can be replaced by intensities, η_A the acceptor emission yield, K_{SV} the rate constant of energy transfer.

A linear relation of $1/I_{\text{CL}}$ on $1/[A]$ is obtained for Tb(III) ions concentrations from $6 \cdot 10^{-3}$ to $7.5 \cdot 10^{-2} \text{ M}$. This linear relation and the fact that Tb(III) ions have no effect on histidine oxidation by potassium bromate indicates that the Tb(III) ions act as activators in the system histidine–Tb(III)–KBrO₃–H₂SO₄. For this reaction mixture the

following scheme of the processes taking place in it can be proposed:



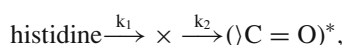
In order to identify product P^* the CL of systems with compounds containing exclusively carboxyl groups (oxalic acid) or the imidazole ring and $-\text{NH}_2$ group (creatinine, histamine) was studied. The systems of oxalic acid (creatinine, histamine)– KBrO_3 – H_2SO_4 generated emission of very low intensity and short duration. Introduction of Tb(III) ions to the above systems changed only the character of CL curves for the system of oxalic acid and histamine. The presence of Tb(III) ions in the system with creatinine did not produce any changes in the shape and intensity of the CL curves. The kinetic curves of the solutions oxalic acid– Tb(III) – KBrO_3 – H_2SO_4 , histamine– Tb(III) – KBrO_3 – H_2SO_4 , similarly as those of the systems with histidine, show a maximum at from 50 to 100 s after the reaction initiation, i.e. introduction of oxalic acid or histamine. For the solutions with oxalic acid the intensity of CL was about 50 times lower than that in the systems with histidine and 71 times lower than that in the system with histamine. The emission spectra obtained for the systems oxalic acid– Tb(III) – KBrO_3 – H_2SO_4 and histamine– Tb(III) – KBrO_3 – H_2SO_4 , are typical of terbium(III) ions.

In living organisms amino acids undergo oxidation under the effect of enzymes dehydrogenases and liases, leading to their deamination and decarboxylation [27]. Deamination of an amino acid gives ammonia and an appropriate ketoacid: $\text{R}-\text{CH}(\text{NH}_2)-\text{COOH} \rightarrow \text{R}-\text{C}=\text{O}-\text{COOH} + \text{NH}_3$, whose presence has been detected in CL systems containing amino acids and $\text{Ru}(\text{bipy})^{3+}$ [28]. Oxalic acid, in the redox mixtures (e.g. with KMnO_4 or $\text{Ru}(\text{bipy})^{3+}$, is oxidised to CO_2 [15, 29] and histamine undergoes deamination giving aldehyde as an intermediate product. The presence of the aldehyde has been confirmed in the IR spectra [30]. The post-reaction mixture of the solutions histidine (histamine, oxalic acid)– KBrO_3 – $(0.5 \text{ M})\text{H}_2\text{SO}_4$ was studied

by IR spectrophotometry. The IR spectra were the same for the systems of histidine (histamine)– KBrO_3 – $(0.5 \text{ M})\text{H}_2\text{SO}_4$. Analysis of the IR spectra indicated the occurrence of deamination in the solution with histamine and deamination together with decarboxylation in the system with histidine.

The CL characteristic of Tb(III) ions recorded only for the systems with histidine and histamine along with the fact that no CL was recorded for the system with creatinine means that formation of the product P^* is not related to the transformations of the imidazole ring. On the other hand, much greater intensity of emission obtained in the systems histidine– Tb(III) – KBrO_3 – H_2SO_4 , histamine– Tb(III) – KBrO_3 – H_2SO_4 than in the system oxalic acid– Tb(III) – KBrO_3 – H_2SO_4 proves that formation of P^* is related mainly to the process of deamination. Moreover, taking into regard the fact that the uncomplexed terbium(III) ions were obtained in the CL systems generating excited carbonyl groups [20] and the spectrum of the system histidine– KBrO_3 – H_2SO_4 , the P^* species can be concluded to be excited carbonyl groups.

As follows from analysis of the CL kinetic curve of the system histidine– Tb(III) – KBrO_3 – H_2SO_4 (curve 2 in Fig. 2), the excited species P^* is formed as a result of a few subsequent reactions. In the AB section the intensity of CL strongly increases and then in the subsequent section BC it decreases. On the basis of the kinetic curve the reaction rate constants characterising the reactions corresponding to AB and BC sections were calculated to be $k_1 = 0.0930 \text{ s}^{-1}$ and $k_2 = 0.0086 \text{ s}^{-1}$, respectively. Because of a great excess of KBrO_3 relative to histidine, these reactions are of pseudo-first order. The formation of the excited product P^* can be described by the following scheme:



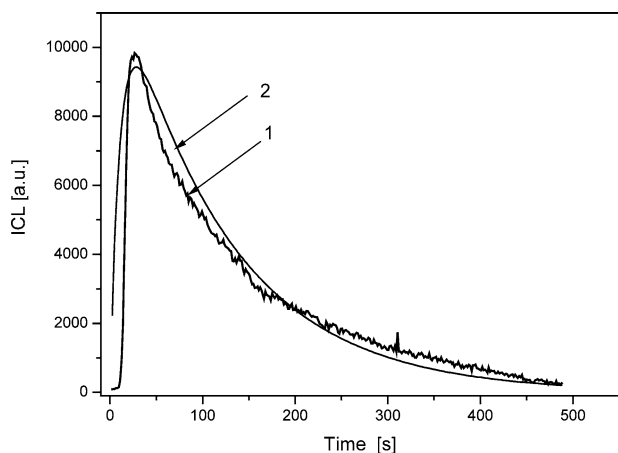


Fig. 5 Kinetic curves of CL of the system histidine–Tb(III)–KBrO₃–H₂SO₄, Experimental – curve 1; Calculated from equation (1) – curve 2. The simulation was performed for the initial concentration of histidine of 0.001 mol/l

where X is the intermediate product reaching a maximum concentration at the point B of the kinetic curve characterising the reactions in the system histidine–Tb(III)–KBrO₃–H₂SO₄. However, the intermediate product could not be identified. The reaction rate constant values imply that its formation is faster than the reaction of its decomposition with release of ($>C=O$)*. The kinetics of the process can be described by the following formula, typical for subsequent reactions:

$$I_{CL} = \beta [\text{histidine}] \frac{k_1}{k_2 - k_1} (\exp(-k_1 t) - \exp(-k_2 t)) \quad (1)$$

where β is the instrumental constant of 1.2×10^7 , [histidine] the initial concentration of histidine in the system studied, k_1 the rate constant of formation of X , k_2 the rate constant of decomposition of X .

The theoretical time dependence of CL for the system studied is in good agreement with the experimental data (Fig. 5).

Conclusion

The system histidine–KBrO₃–H₂SO₄ belongs to the group of reaction systems generating ultra-weak emission characteristic of excited carbonyl species forming mainly on deamination. Effective activators of this system are Tb(III). The lanthanide ions do not form complexes with histidine in a strongly acidic environment, whereas in the solutions of pH ~ 7 the formation of two types of complexes ML and ML₂ has been detected, depending on the molar ratio metal:ligand. The simulation of CL of the system histidine–Tb(III)–KBrO₃–H₂SO₄ (Fig. 5) with the help of equation (1) provided satisfactory results, close to the experimental

course of CL, despite significant approximations (first order of the reactions and assumption that at high concentrations of the activator almost all excited molecules transfer energy to the activator).

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