A comparative study on chemiluminescence propperties of some inorganic systems

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Abstract. Chemiluminescence (CL) of selected inorganic reaction systems, generating ultraweak photon emission, has been studied. The kinetics of the systems and their emission spectra have been characterised by measurements with the use of the stationary and the flow methods of CL recording. The systems studied contained cations at different oxidation degree such as $Fe^{2+\backslash 3+}$, $Cu^{+\backslash 2+}$, $Co^{2+\backslash 3+}$, $Eu^{2+\backslash 3+}$, CLO^- anions and hydrogen peroxide without organic sensitisers. On the basis of the analysis of the spectra, in particular systems emitters have been identified and mechanisms of the reactions have been proposed. The effect of carbonate and azide ions and propylene carbonate on the yield of CL and spectral characterisation of the systems studied has been evidenced and discussed. A possibility of the application of the systems $Eu^{3+}\backslash N_3^-\backslash H_2O_2$ and $Co^{2+}\backslash$propylene carbonate$\backslash H_2O_2$ for analytical purposes has been considered.

1. INTRODUCTION

Chemiluminescence accompanying certain reactions almost always occurs in the presence of oxygen or oxygen-rich compounds, e.g. hydrogen peroxide. In water solutions containing metal ions the kinetics of catalytic decomposition of H_2O_2 is complex and strongly depends on the reaction conditions [1]. This reaction leads to formation of a transient peroxo-metal complex decomposing with liberation of oxygen often accompanied by weak emission of light [2]. As these reactions most often take place in oxidised solutions, the emission from these systems is often accompanied by emission from dimers of singlet oxygen [3]. The aim of the study was to analyse the kinetic CL curves and determination of the mechanism of the processes taking place in the systems studied. We have also proposed two new systems, which can be used in analytical applications of the lanthanide ions ($Eu^{3+}\backslash N_3^-\backslash H_2O_2$) and d—electron cations ($Co^{2+}\backslash$propylene carbonate$\backslash H_2O_2$).

2. EXPERIMENTAL

The study was performed for the following metal salts: $FeCl_2$, $CoCl_2$, CuCl, $EuCl_2$ and $EuCl_3$, Aldrich, (analytical grade), NaN_3, H_2O_2, Na_2CO_3 and propylene carbonate (PC), Fluka (analytical grade). The reagents were used to study the following systems:

(**I**) $Fe^{2+}\backslash H_2O_2$,
(**II**) $Co^{2+}\backslash H_2O_2$,
(**III**) $Cu^{+}\backslash H_2O_2$,
(**IV**) $Eu^{2+}\backslash H_2O_2$,
(**V**) $Eu^{3+}\backslash N_3^-\backslash H_2O_2$,
(**VI**) $Co^{2+}\backslash PC\backslash H_2O_2$.

The CL spectra were obtained with the use of a flow measurement system shown in Figure 1 applying the cut-off filters method.

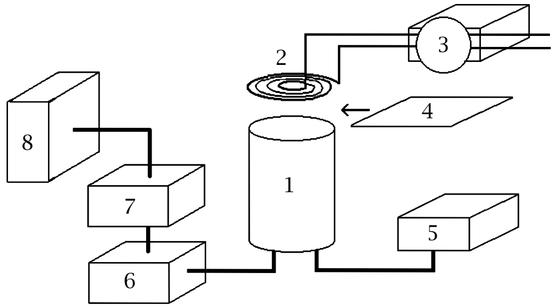


Figure 1. *Chemiluminescence flow measurement system:* 1- *photomultiplier tube Hamamatsu* R 636P *with cooler* C659-72, 2- *flow cell,* 3- *peristaltic pump Ismatec* MS 2/8-160, 4- *cut-off filters,* 5- *high voltage power supply unit Hamamatsu* C4710, 6- *high speed amplifier Hamamatsu* C5594-34, 7- *automatic signal counter* C570, 8- *computer.*

The flow rate of the reagents was set in the range 1.6–15 ml/min so that to ensure the maximum signal to noise ratio. The decay of CL in time was recorded using the measuring system for stationary measurements with an injection cell. The reaction was initiated by a solution of hydrogen peroxide injected to the solution containing the other reagents at a given pH. The concentrations of substrates in the systems studied were optimised in order to obtain the maximum efficiency of chemiluminescence. The following concentrations were used: Co^{2+}—10^{-5}-10^{-8} mol/l, Fe^{2+}, Cu^{+}, Eu^{2+}—0.05 mol/l, Eu^{3+}—10^{-4} mol/l, N_3^-—10^{-3} mol/l,

ClO^-—0.2 mol/l, CO_3^{2-}—0.1–0.5 mol/l, propylene carbonate—2 ml/8 ml ethanol/water solution at v/v = 1 : 1. In order to obtain a homogeneous (single phase) system ethyl alcohol was added to a solution containing Co^{2+} ions and propylene carbonate. All solutions were made using redistilled water.

3. RESULTS

The kinetic curves of chemiluminescence recorded for systems **I**–**VI** are shown in Figure 2.

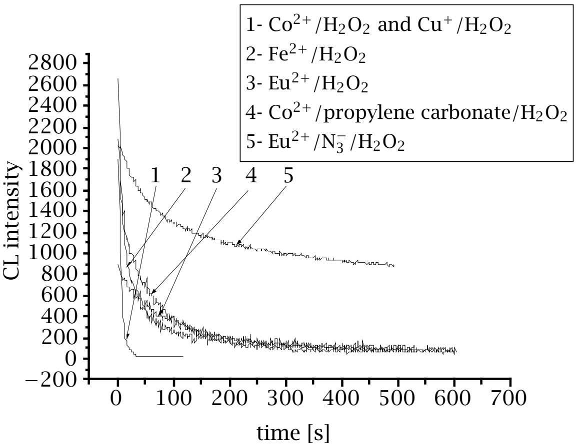


Figure 2. *Kinetic curves of systems **I**–**VI**.*

The curves obtained for systems **I**–**V** (curves 1–4 in Figure 2), indicate a similar exponential decay of CL emission. The duration of CL in these systems varies from a few tens to a few hundred seconds. The emission observed from the system **VI** (curve 5 in Figure 2) was different and characterised by long duration and high intensity of CL. As indicated by earlier results [4–6], the responsibility for the increase in the emission duration and intensity rests with the complex $(EuN_3)^{2+}$, forming in the system containing Eu^{3+} and N_3^- ions in the pH range 5.0–8.5. The final excited products of the reaction are identified on the basis of the CL spectrum. The CL spectra for systems **I**–**VI** are shown in Figure 3.

In the spectra of systems **IV** and **V** (spectrum 1, Figure 3) the dominant band with a maximum at ∼ 600 nm is a result of the radiative transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ in the Eu^{3+} ion. It means that in these systems the energy coming from decomposition of hydrogen peroxide is accepted by the europium ions being simultaneously emitters [7, 8]. The azide ions present in system **V** effectively (by about three orders of magnitude) increase both the duration and yield of CL of the system.

The emission spectrum of system **I**—the so-called Fenton system (spectrum 2, Figure 3) shows the emission bands at about 520, 580 and 630 nm. Results of the hitherto studies of the system have shown the occurrence of the radical processes of hydrogen peroxide decomposition leading to the formation of singlet oxygen dimols [9, 10]. The spectrum 3 in Figure 3, characteristic of systems **II** and **III**, containing the cations Cu^+ and Co^{2+} is similar to that system **I** (Fenton), however, the maximum emission in these systems is at ∼ 630 nm, which indicates a different dominant emitter than in system **I**.

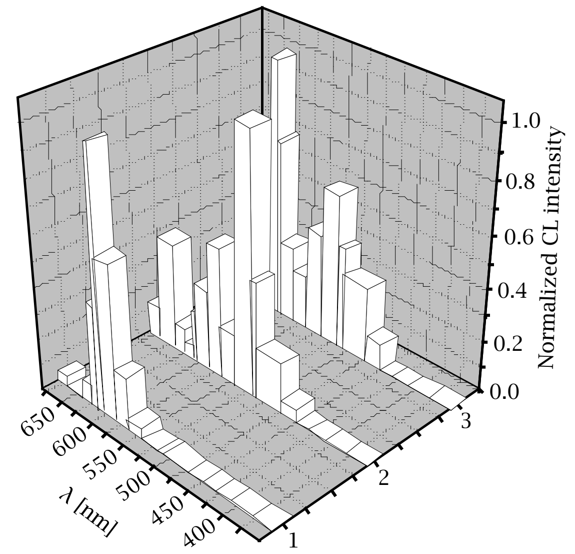


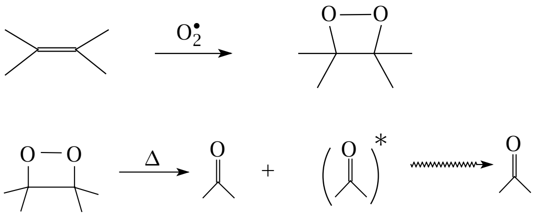
Figure 3. *Spectral distribution of systems:* 1- $Eu^{2+}\backslash H_2O_2$ *and* $Eu^{3+}\backslash N_3^-\backslash H_2O_2$, 2- $Fe^{2+}\backslash H_2O_2$, 3- $Co^{2+}\backslash H_2O_2$ *and* $Cu^+\backslash H_2O_2$.

In the inorganic systems containing metal ions and hydrogen peroxide CL is usually of very low intensity. Components very often added to such inorganic systems are sodium or potassium carbonates or hydrocarbonates [11, 12]. Their addition implies the adequate adjustment of pH of the reaction environment: neutral or basic. In this study we report the effect of addition of sodium carbonate on the CL of systems **I**–**V**. For systems **I**–**IV** the emission intensity increased as a result of sodium carbonate addition and the CL decay kinetics was similar as in the system without this addition. In system **V** a decrease in the emission intensity was observed with increasing concentration of carbonates.

A characteristic feature of the systems containing carbonates is the emission band with a maximum at ∼ 420 nm (spectrum 1, Figure 4). The hitherto obtained results [12] indicate that the radical processes taking place in this system lead to decomposition of carbonates and the energetic effect of such reactions (∼ 305 kJ/mol) is high enough to generate radiation with a maximum at 420 nm (spectrum 2, Figure 4).

It has been established that addition of propylene carbonate instead of sodium or potassium carbonate to systems **I**–**IV**, also effectively increases the yield of their CL. Particularly efficient has proven system **VI** containing cobalt ions, hydrogen peroxide and propylene

Table 1. *Chemiluminescence radical processes in studied systems containing hydrogen peroxide.*

System	Processes
$Fe^{2+}\backslash H_2O_2$ $Co^{2+}\backslash H_2O_2$ $Cu^{+}\backslash H_2O_2$	$M^{n+} + H_2O_2 \to M^{n+1} + HO^\bullet + HO^-$ Where M = Fe^{2+}, Co^{2+}, Cu^+ $HO^\bullet + H_2O_2 \to HO_2^\bullet + H_2O$ $HO_2^\bullet + HO_2^\bullet \to H_2O_2 + {}^1O_2$ $HO^\bullet + HO_2^\bullet \to H_2O + {}^1O_2$ ${}^1O_2\,{}^1O_2 \to {}^3O_2\,{}^3O_2 + h\nu$ ${}^1\Delta_g^+\,{}^1\Delta_g^+(2,0) \to {}^3\Sigma_g^-{}^3\Sigma_g^-(0,0)$ (λ = 520 nm) ${}^1\Delta_g^+\,{}^1\Delta_g^+(1,0) \to {}^3\Sigma_g^-{}^3\Sigma_g^-(0,0)$ (λ = 580 nm) ${}^1\Delta_g^+\,{}^1\Delta_g^+(0,0) \to {}^3\Sigma_g^-{}^3\Sigma_g^-(0,0)$ (λ = 630 nm)
$Eu^{2+}\backslash H_2O_2$	$Eu^{2+} + H_2O_2 \to Eu^{3+} + HO^\bullet + HO^-$ $Eu^{2+} + HO^\bullet \to (Eu^{3+})^* + HO^-$ $(Eu^{3+})^* \to Eu^{3+} + h\nu$ ${}^5D_0 \to {}^7F_1$ (λ = 594 nm) ${}^5D_0 \to {}^7F_2$ (λ = 615 nm)
$Eu^{3+}\backslash N_3^-\backslash H_2O_2$	${}^1O_2 + (Eu^{3+} - N_3^-) \to [Eu^{2+} \cdots N_3^\bullet \cdots O_2^{-\bullet}] \to ((Eu^{3+})^* - N_3^-) + {}^3O_2$ $((Eu^{3+})^* - N_3^-) \to (Eu^{3+} - N_3^-) + h\nu$ λ = 594 and 615 nm
$Co^{2+}\backslash PC\backslash H_2O_2$	 (λ = 550 nm)

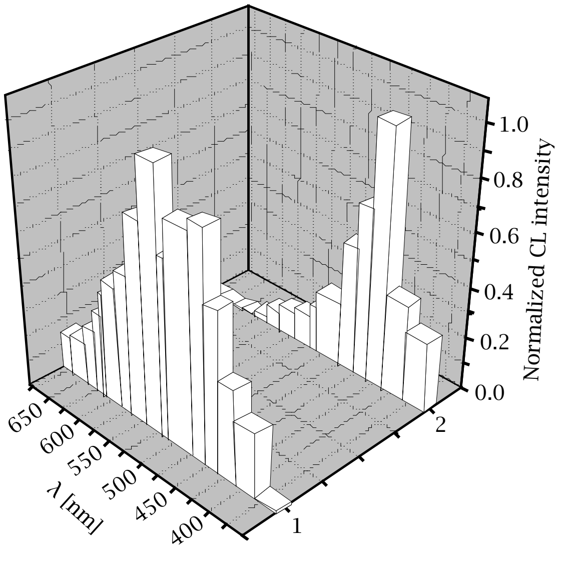


Figure 4. *Spectral distribution of systems:* 1- $Co^{2+}\backslash$*propylene carbonate*$\backslash H_2O_2$, 2- $Co^{2+}\backslash HCO_3^-\backslash H_2O_2$.

carbonate. The kinetics of CL decay in this system is the same as in system **II**, but the intensity of emission is by one order of magnitude higher. For this reason the system can be of potential use for quantitative determination of Co^{2+} ions (below 10^{-9} mol/l), analogously to the system $Co^{2+}\backslash HCO_3{}^-\backslash H_2O_2$. The emission spectrum of system **VI** is shown in Figure 4, spectrum 1.

The spectrum reveals a broad band with a maximum at ~ 550 nm, which indicates that system **VI** generates a different type emitter than the system $Co^{2+}\backslash HCO_3{}^-\backslash H_2O_2$, and this different emitter is formed in a process whose yield is similar to that of a radical decomposition of carbonates. The double bond in the propylene carbonate molecule and the presence of oxygen radicals in the systems with hydrogen peroxide suggests that the process of CL in system **VI** occurs according to the McCapra mechanism [13] (Table 1).

The system that deserves particular attention is system **V** ($Eu^{3+}\backslash N_3^-\backslash H_2O_2$). From among the members of the lanthanide series only europium together with azide ions and hydrogen peroxide forms a CL emitting system. No effect of the other f-electron ions on the kinetics and yield of CL in this system was found. The high yield of CL and the characteristic emission band of this system make it also attractive from the point of view of analytical applications. A characteristic feature of system **V** is that with the progress of the reaction it undergoes gelation. This phenomenon is observed for the reagents concentrations (Eu^{3+}, N_3^- and H_2O_2)

higher than 0.15 mol/l. The gel forming in the system is colourless, water soluble and stable at 100 °C. Most probably the phenomenon of gelation occurs as a results of the radical reactions leading to the formation of the N – OH bonds in the reaction products and then condensation of the reaction products. In the systems type metal ion$\backslash N_3^-\backslash H_2O_2$, the process of gelation has been noted only in the presence of europium ions.

4. Conclusions

The processes of emission accompanying the decomposition of hydrogen peroxide in the systems containing the ions catalysing this decomposition such as ($Fe^{2+\backslash 3+}$, $Co^{2+\backslash 3+}$, $Cu^{+\backslash 2+}$) take place with the involvement of singlet oxygen. The low yield of CL in these systems implies the need to use activators. One of a few inorganic activators is the complex $(Eu - N_3)^{2+}$, which effectively increases the yield of CL in solutions containing active oxygen species. A similar effect has been observed in the systems with propylene carbonate. In the latter systems the energy from H_2O_2 decomposition is captured by the excited carbonyl reaction products, according to the mechanism proposed by Mc Capra [13] (Table 1). The yield of CL in the systems type: metal ion$\backslash PC\backslash H_2O_2$ is additionally enhanced by addition of ethanol.

ACKNOWLEDGMENT

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

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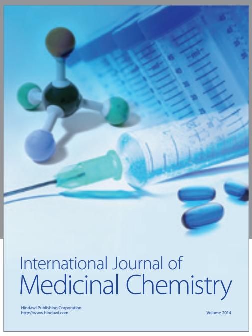
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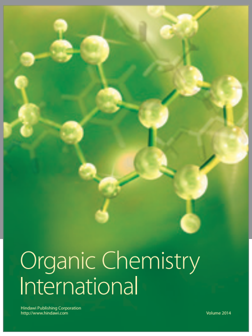
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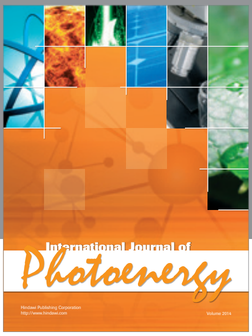
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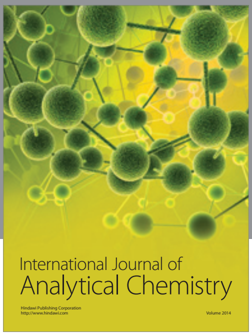
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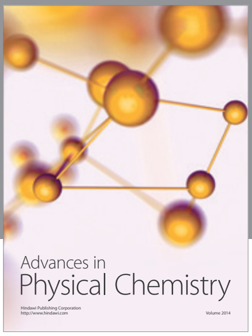
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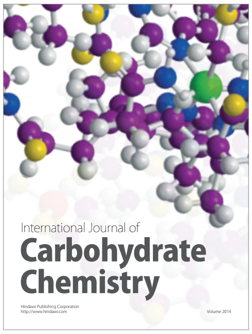
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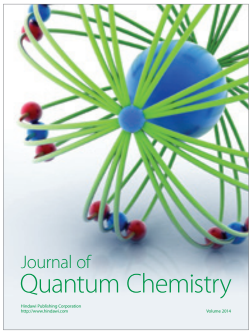
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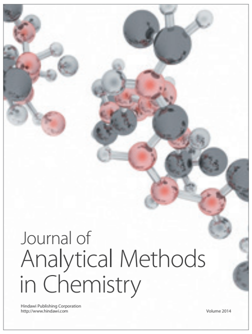
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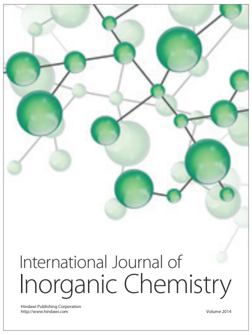
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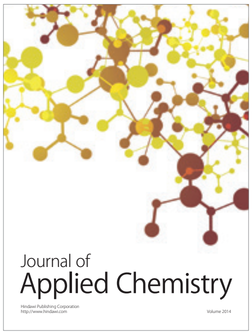
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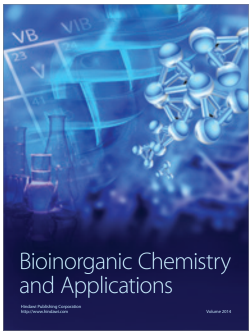
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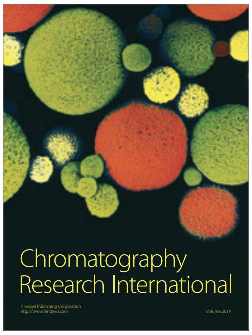
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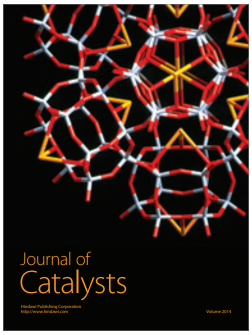
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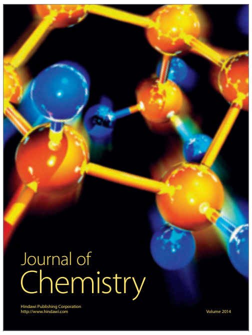
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