

# Ruthenium(II) tris(2,2'-bipyridine) chelate as a chemiluminophore in extrinsic lyoluminescences of aluminium and magnesium in aqueous solution

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Received 1 July 2004; received in revised form 20 January 2005; accepted 20 January 2005

Available online 16 February 2005

## Abstract

Ruthenium(II) tris(2,2'-bipyridine) chelate shows chemiluminescence (CL) both during dissolution of metallic aluminium in alkaline conditions, and during dissolution of magnesium metal in acidic conditions. The presence of peroxodisulfate ions strongly enhances the CL. Magnesium system provides considerably better detectability of the present chelate giving linear calibration plot spanning over many orders of magnitude of concentration down to subnanomolar concentration levels. The possible primary species generated and luminescence mechanisms are shortly discussed.

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**Keywords:** Chemiluminescence; Generation of free radicals; Al(I); Al(II); Hydrated electron; Sulfate radical; Mg(I); Hydrogen atom; Oxyradicals

## 1. Introduction

We have previously studied chemiluminescence (CL) of luminol induced by dissolution of aluminium metal in alkaline aqueous solution in the presence of peroxodisulfate and some other peroxides as coreactants [1]. This chemiluminescence can also be classified as extrinsic lyoluminescence (ELL) of aluminium [2], but in this paper the use of the former more common term CL is preferred. In the above-mentioned system, dissolution of aluminium can result in action of metallic aluminium as a reductant, but also short-lived Al(I) and Al(II) species, hydrogen atom and its conjugated base, hydrated electron, can act as strong reductants [1]. Typical for most of these species is that they can behave as efficient one-electron reductants which naturally often results in generation of other

radicals in the solution in addition to the primarily generated radicals [1].

Ruthenium(II) tris(2,2'-bipyridine) ( $\text{Ru}(\text{bpy})_3^{2+}$ ) is a well studied luminescent chelate [3], the derivatives of which are in use as electrochemiluminescent labels in bioaffinity assays [4].  $\text{Ru}(\text{bpy})_3^{2+}$  is also known to produce strong chemiluminescence in the presence of hydrated electrons and sulfate radicals [5,6]. Thus, it should also produce chemiluminescence during dissolution of aluminium in alkaline aqueous solution in the presence of suitable oxidizing radical-producing coreactants, if suitable one-electron reductants are available.

Aluminium metal is a strong reductant for which the potentials for one-electron oxidation steps are unknown. It is known that  $E^0(\text{Al}^{3+}/\text{Al}) = -1.68 \text{ V}$  (versus SHE), and in alkaline solutions,  $E^0(\text{Al}(\text{OH})_4^-/\text{Al}, 4\text{OH}^-) = -2.31 \text{ V}$  [7]. The outer shell electrons of aluminium metal have different energies (outer electronic configuration  $3s^2 3p^1$ ) and therefore it is reasonable that the oxidation

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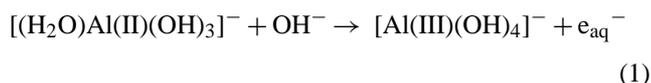
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can proceed stepwise and low-valent intermediates can exist.

Some one-electron reduction potentials for the other elements in group 13 are known with some certainty, but only thallium potentials are relatively reliable, i.e.,  $E^0(\text{Tl}^+/\text{Tl}) = -2.00 \text{ V}$ ,  $E^0(\text{Tl}^{2+}/\text{Tl}^+) = 2.22 \text{ V}$  and  $E^0(\text{Tl}^{3+}/\text{Tl}^{2+}) = 0.33 \text{ V}$  [8].  $\text{Ga}^{2+}$  is also reported to be an oxidant and for indium the following estimations of reduction potentials are given:  $E^0(\text{In}^+/\text{In}) = -2.4 \text{ V}$ ,  $E^0(\text{In}^{2+}/\text{In}^+) < 0.4 \text{ V}$  and  $E^0(\text{In}^{3+}/\text{In}^{2+}) = < -0.5 \text{ V}$  [8]. In general, the knowledge of one-electron reduction potentials of metal ions in homogeneous solution phases is still in its infancy, and unfortunately, most of the one-electron reduction potentials of metal ions given in *Standard Potentials* [7] are unreliable for one reason or another as discussed by Stanbury [8].

The first ionization potential of aluminium is very low, 6.0 eV, just slightly higher than that of lithium or sodium (5.3 and 5.1 eV, respectively) [9] and lower than those of calcium and magnesium (6.1 and 7.6 eV) [9]. The compilation *Standard Potentials* gives standard potential values of  $-3.04$ ,  $-2.71$ ,  $-2.84$ ,  $-2.05$  and  $-2.66 \text{ V}$  for couples  $\text{Li}^+/\text{Li}$ ,  $\text{Na}^+/\text{Na}$ ,  $\text{Ca}^{2+}/\text{Ca}$ ,  $\text{Mg}^{2+}/\text{Mg}^+$  and  $\text{Mg}^+/\text{Mg}$ , respectively [7]. One could assume on this basis that  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^+$  and  $\text{Mg}^{2+}$  could be reduced by the hydrated electron ( $E^0 = -2.9 \text{ V}$ ) [10]. However, as pointed out by Stanbury [8], the tabulated values in *Standard Potentials* refer to the bulk metal and correction to atomic species in water results in reduction potentials more negative than  $-3.5 \text{ V}$  for all of the alkali metal ions, and about  $-4.8 \text{ V}$  for the couple  $\text{Mg}^{2+}/\text{Mg}^+$ . Therefore, it is not surprising that all alkali and alkaline earth metal ions fail to react with the hydrated electron [11].

It is interesting to note that aquated six-coordinated  $\text{Al}^{3+}$  is rapidly reduced by the hydrated electron ( $k(e_{\text{aq}}^- + \text{Al}(\text{OH})_3) = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) [12], but on the contrary, tetra-hydroxyaluminate(III) ion ( $\text{Al}^{3+}$  is four-coordinated) is not reduced by  $e_{\text{aq}}^-$  ( $k(e_{\text{aq}}^- + \text{Al}(\text{OH})_4^-) = 5.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) [12] which implies that aluminate(II) ion is a stronger reductant than the hydrated electron. In fact, in the older literature it has been proposed that the following reaction has a negative free energy [11,13]:



According to Jørgensen [14], an approximation of one-electron reduction potentials of metal ions in aqueous solutions within each group can be calculated by the equation:

$$E_{M(z/z-1)}^0 = I_z - (2z - 1)\kappa - 4.5 \text{ eV} \quad (2)$$

where  $z$  is the oxidation state,  $I_z$  the  $z$ th ionization energy of the element [14] and  $\kappa$  a parameter of hydration energy difference, which is 5.3 eV for 3d series, and reported values for Al, Ga, In, and Mg are 5.37, 5.39, 4.73 and 4.98 eV, respectively [14]. Table 1 shows reduction potentials calculated according

Table 1

Estimated one-electron reduction potentials of unstable ions of some of the elements of group 13 and 2 in aqueous solution, and the estimates provided by Stanbury [8]

Metal	$I_z$ (eV) [9]	$E_{\text{calc}}^0$ (V) vs. SHE	$E^0$ (V) vs. SHE [8]
Aluminium			
Step III/II	28.45	-2.9	?
Step II/I	18.83	-1.8	?
Step I/0	5.98	-3.9	?
Gallium			
Step III/II	30.71	-0.74	?
Step II/I	20.51	-0.16	An oxidant
Step I/0	6.00	-3.9	?
Indium			
Step III/II	28.03	-0.12	< -0.5
Step II/I	18.87	0.18	< 0.4
Step I/0	5.79	-3.4	-2.4
Magnesium			
Step II/I	15.03	-4.41	-4.9
Step I/0	7.64	-1.84	

to Eq. (15) using ionization energies adopted from Ref. [9] and, for comparison, the values given by Stanbury [8]. Thus, e.g., for the couple  $\text{Al}(\text{III})/\text{Al}(\text{II})$  the approximation for  $E^0$  is calculated to be:

$$\begin{aligned} E_{\text{Al(III/II)}}^0 &= I_3 - (2 \times 3 - 1)\kappa - 4.5 \text{ eV} \\ &= 28.45 \text{ eV} - 5 \times 5.37 \text{ eV} - 4.5 \text{ eV} \\ &= -2.9 \text{ eV (relative to SHE)} \end{aligned} \quad (3)$$

The calculated values and values suggested by Stanbury are in reasonable agreement for Ga and In, therefore it is accepted that at least  $\text{Al}^0$  and  $\text{Al}^{2+}$ , as solvated species in water, are one-electron reductants comparable to  $e_{\text{aq}}^-$ , alkali metal colloids and  $\text{Mg}^+$ .  $\text{In}^{2+}$  and  $\text{Tl}^{2+}$  are reported to disproportionate [8] in aqueous solutions to oxidation states (I) and (III) which is a fate well possible also for  $\text{Al}^{2+}$ , if the solution is free from other reactive components. The stability of  $\text{Al}^+$  in aqueous solutions must also be very limited, as it has never been reliably demonstrated.

Extrinsic lyoluminescence of aluminium induced by  $\text{Ru}(\text{bpy})_3^{2+}$  was first studied, and later, it was also investigated, if magnesium could induce analogous extrinsic lyoluminescence in the presence of peroxodisulfate ions. When peroxodisulfate ion is reduced by a concerted two-electron transfer, the sulfate radicals can not be harnessed with luminophores to produce CL. Thus, the existence of extrinsic lyoluminescence of magnesium induced by  $\text{Ru}(\text{bpy})_3^{2+}$  would also suggest that dissolution of magnesium metal into aqueous solution could be used in efficiently producing one-electron reductions. This however, would need acidic conditions because magnesium is always covered with a naturally formed oxide film, as is also aluminium, but  $\text{MgO}$  is known to be insoluble in alkaline solutions. For this second system, hydrochloric acid was selected as a simple strong acid used as a medium of experiments in strongly and moderately acidic conditions studied.

## 2. Experimental

Aluminium lyoluminescence experiments were carried out using photon counting lyoluminescence apparatus [15] and Al cups as described previously [1]. The spectra were measured either using an apparatus constructed by Pihlajamaki and Kankare [16] or with Perkin-Elmer LS 50B luminometer. Preliminary experiments of magnesium lyoluminescence were carried out in disposable polystyrene test tubes using Perkin-Elmer LS 50B luminometer emission monochromator set to 600 nm. A 25 mm long piece of magnesium band (Merck Art. 5812) was put in the middle of the test tube containing CL-inducing solution so that the band front surface was in 180° angle against the light path leading to the emission monochromator. Later the final measurements were carried out using the above-mentioned lyoluminescence apparatus, but the magnesium band used was cut to 20.0 mm long pieces and pressed by a Teflon rod to the bottom of disposable lyoluminescence test tubes [15] where they stayed in an U-shaped position by the spring force of the magnesium piece itself.

Ruthenium(II) tris(2,2'-bipyridine) chloride hexahydrate was purchased from Aldrich. All these reagents were used without further purification. Sodium hydroxide and hydrochloric acid solutions were made from Merck ampulles. Quartz-distilled water was used for the preparation of all solutions.

## 3. Results and discussion

### 3.1. Extrinsic lyoluminescence of aluminium

A dotted line in Fig. 1 displays an Al-induced chemiluminescence response of a 1.0 M NaOH solution containing  $1.0 \times 10^{-3}$  M potassium peroxodisulfate but no deliberately added luminophore. This Al-induced background chemiluminescence is, however, too weak for a detailed spectral analysis but in more concentrated potassium peroxodisulfate solutions, a small emission peak at the wavelength around 600 nm is observed, the origin of which is not yet clear for us.

A solid line in Fig. 1 displays an Al-induced chemiluminescence spectrum of the afore mentioned highly alkaline solution containing additionally  $5.0 \times 10^{-5}$  M tris(2,2'-bipyridine) ruthenium(II) chloride, where the 620 nm emission peak can be assigned to the well known relaxation of the metal-to-ligand charge transfer excited triplet state ( $^3\text{MLCT}$ ) of tris(2,2'-bipyridine) ruthenium(II) denoted subsequently by  $^3\text{Ru}(\text{bpy})_3^{2+}$ . This figure also shows that aromatic Tb(III) chelates can be excited in the same conditions which led to another more detailed CL study which is in progression in our laboratory. Fig. 2 points out that the intensity of the Al-induced chemiluminescence depends linearly on the concentrations of  $\text{Ru}(\text{bpy})_3^{2+}$  and potassium peroxodisulfate in the sample solutions as well as on the concentration of hydrox-

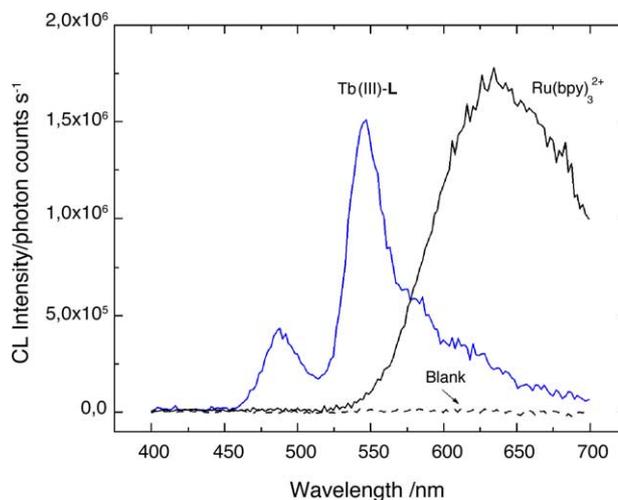


Fig. 1. CL emission spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Tb}(\text{III})\text{-L}$  induced by dissolution of aluminium in alkaline peroxydisulfate solutions. Conditions: 1.0 M NaOH, peroxydisulfate concentration  $1.0 \times 10^{-3}$  M, luminophore concentrations  $5 \times 10^{-5}$  M.  $\text{Tb}(\text{III})\text{-L}$  = Terbium(III)-{2,6-bis[*N,N*-bis(carboxymethyl)aminomethyl]-4-benzoylphenol}. Spectra measured using apparatus described elsewhere [16].

ide ions up to concentration of about 0.1 M. The deviation from linear dependence in the case of  $\text{Ru}(\text{bpy})_3^{2+}$  chelate under highly alkaline conditions was obviously due to a relatively rapid decomposition of  $\text{Ru}(\text{bpy})_3^{2+}$  and possibly reduction to metallic ruthenium. A brownish precipitation was clearly visible as small particles after the experiments with relatively concentrated hydroxide and  $\text{Ru}(\text{bpy})_3^{2+}$  chelate solutions, and also the color of the chelate had disappeared. However, the chemical nature of the precipitate was not examined.

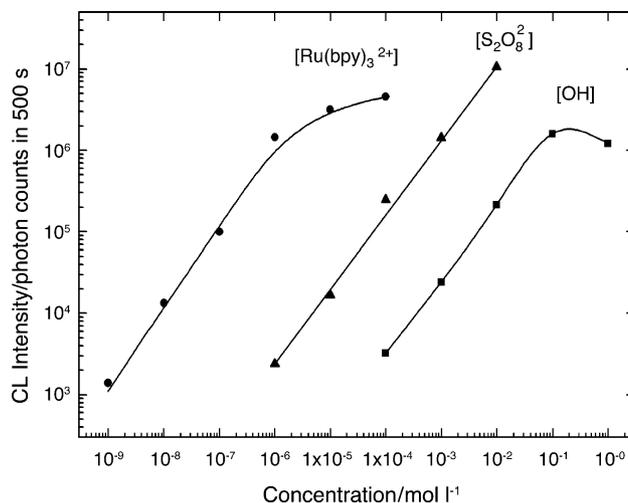


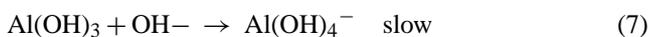
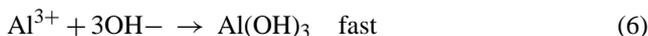
Fig. 2. Effect of hydroxide ion concentration (a), peroxydisulfate concentration (b), and chelate concentration (c) on extrinsic LL of aluminium induced by  $\text{Ru}(\text{bpy})_3^{2+}$ . Conditions: (a)  $1.0 \times 10^{-5}$  M  $\text{Ru}(\text{bpy})_3^{2+}$ ,  $1.0 \times 10^{-3}$  M  $\text{K}_2\text{S}_2\text{O}_8$  (■); (b) 1.0 M NaOH,  $1.0 \times 10^{-4}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  (▲); (c)  $2.0 \times 10^{-3}$  M  $\text{K}_2\text{S}_2\text{O}_8$ , 0.10 M NaOH (●). The 630 nm interference filter was used.

### 3.2. Mechanism of extrinsic lyoluminescence of aluminium induced by Ru(bpy)<sub>3</sub><sup>2+</sup>

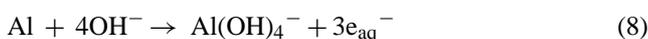
As discussed previously [1], the dissolution of aluminium in concentrated alkali hydroxides is usually described by the following overall reaction [17]:



which is generally thought to contain the following steps [18]:



An alternative overall reaction for the dissolution of aluminium in aqueous alkali hydroxides has been proposed by Walker [13]:



which has later been supported by Kalecinsky [19] and our previous work [1]. In this process the observed hydrogen evolution is attributed at least partly to a fast bimolecular reaction with the solvent after pair formation of hydrated electrons:

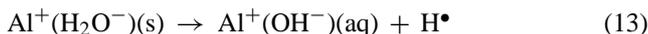
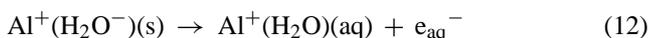
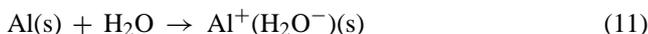


with a reported second-order rate constant of  $k_9 = 5.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$  [10]. This mechanism results in exactly the same overall reaction as the one presented above in connection with the direct discharge of water as a proton donor (4).

However, before the metallic aluminium can get into contact with alkaline solution the hydroxylated natural oxide film must first be dissolved:



This may then be followed by the reactions [1]:



If a hydrogen atom is formed, it is converted to its conjugate base, hydrated electron, in highly alkaline conditions:

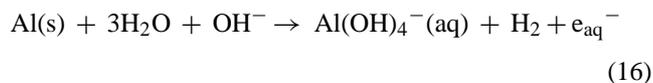


with a second order reaction rate constant of  $k_{14} = 2.2 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ , or hydrogen is evolved with a second order reaction rate constant  $k_{15} = 7.8 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$  [10].



The higher the pH is the more favourable reaction (14) is.

Hydrated electron is known to react slowly with water,  $k(\text{e}_{\text{aq}}^- + \text{H}_2\text{O}) = 19 \text{ l mol}^{-1} \text{ s}^{-1}$  [10] and additionally, the aluminate ion is known to be quite unreactive towards hydrated electrons as mentioned above, hence, the following reaction:



was suggested to be a source for hydrated electron usable in generating chemiluminescence from luminophores tolerating highly alkaline conditions [1].

When dissolved oxygen is present in the solutions and the above-mentioned  $\text{e}_{\text{aq}}^-$  generation is accepted, oxyradicals can be expected to be generated and consumed according to the following equations under highly alkaline conditions:



The above reactions have the following rate constants:  $k_{17} = 2 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $k_{18} = 1.3 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$  and  $k_{20} = 3.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$  [10]. However, the same species are also formed with unknown rates, if the one-electron reductions proceed without a hydrated electron as a mediating intermediate due to the presence of other suitable reductants.

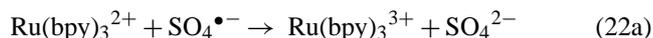
If peroxodisulfate ions are added to the solution, highly oxidizing  $\text{SO}_4^{\bullet-}$  radicals are formed by a one-electron reduction:



which is characterized by the rate constant  $k_{21} = 1.2 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$  [10]. The bimolecular self-recombination reaction rate for the production of peroxodisulfate ions is  $5 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$  [20]. The standard reduction potential for couple  $\text{SO}_4^{\bullet-}/\text{SO}_4^{2-}$  is 3.4 V versus SHE [21].

Fig. 3 displays the energy diagram of presently studied CL system using formal reduction potentials of oxygen and oxyradicals at pH 14 [22].

The aluminium/(Al<sub>2</sub>O<sub>3</sub>, Al(OH)<sub>3</sub>, OH<sup>-</sup>, Al(OH)<sub>4</sub><sup>-</sup>, Al<sup>+</sup>, Al<sup>2+</sup>, H<sup>•</sup>, e<sub>aq</sub><sup>-</sup>, SO<sub>4</sub><sup>•-</sup>)-interface provides various routes to generate the observed 2.1 eV <sup>3</sup>MLCT excited state. These include the previously studied oxidation-initiated reductive (ox-red) pathway [5]:

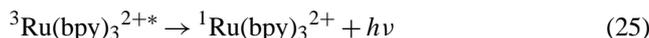
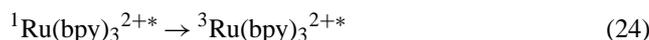


with the second-order rate constant of  $k_{22\text{b}} = 5.2 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$  [10]; the value of  $k_{22\text{a}}$  is presently unknown to us but it is probably also close to  $10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ . Alternatively, the excitation can occur by reduction-initiated

oxidative pathway (red-ox) [5]:



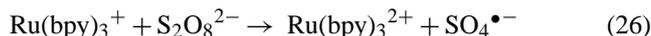
with the second-order rate constant of  $k_{23a} = 8.2 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$  but the value of  $k_{23b}$  is presently unknown to us. Taking into consideration that the standard reduction potentials of  $\text{SO}_4^-/\text{SO}_4^{2-}$ ,  $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}$ ,  $\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^+$  redox couples and hydrated electron (or atomic hydrogen) are 3.4, 1.3,  $-1.3$  and  $-2.9$  V (or  $-2.1$  V) versus SHE, respectively, the enthalpies of the excited state-producing reactions (22b) and (23b) are  $-4.0$  and  $-4.5$  eV. These reactions are sufficiently energetic to leave the resulting ruthenium(II) tris(2,2'-bipyridine) even in its lowest excited singlet  $^1\text{MLCT}$  state denoted by  $^1\text{Ru}(\text{bpy})_3^{2+*}$  which lies 2.7 eV above the  $^1\text{A}_1$  ground state [3,5]. This step is immediately followed by an exceptionally fast intersystem crossing to the lowest excited triplet state  $^3\text{Ru}(\text{bpy})_3^{2+*}$  which is relaxed to the  $^1\text{A}_1$  ground state inducing the 620 nm peaked emission [3]:



Alternatively, excited triplet state can be directly formed by analogous reactions to reactions (22b) and (23b) in which other species may replace  $e_{\text{aq}}^-$  or sulfate radical.

In principle, all the reducing species in the diagram having their lines above the line of couple  $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$ ,  $\text{SO}_4^{\bullet-}$  (Fig. 3) are able to one-electron reduce peroxodisulfate ions and, thus, replace hydrated electron in Eq. (21) and produce sulfate radical. However, practically nothing is known about the reaction rate constants of these thermodynamically highly allowed reductions. If these reductions follow Marcus elec-

tron transfer theory, most of the reactions have their free energy change in the Marcus inverted region and thus the reductions can be assumed to occur at slower rate than that of reaction (21) which occurs near diffusion controlled rate. In addition,  $\text{Ru}(\text{bpy})_3^+$  formed by one-electron reduction (see below) is also able to produce sulfate radical which may occur at much higher distances from the metal/solution interface than the reductions induced by bulk metal or low-valent metal ions:



Because all the solutions were air-equilibrated, an unknown amount of  $\text{O}_2^{\bullet-}$ ,  $\text{HO}_2^-$ , and  $\text{HO}_2^{\bullet}$  were formed either by reactions (17)–(20) or by analogous reactions in which hydrated electron is replaced by some other sufficiently strong one-electron reductant present in this system. Amongst these oxidizing species, only oxygen radical ion,  $\text{O}^{\bullet-}$ , [22] is sufficiently strong oxidant to raise  $\text{Ru}(\text{bpy})_3^+$  into its excited states upon one-electron oxidation by analogous reaction to reaction (23b) (Fig. 3).

All of the species having their lines in the diagram above the line  $\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^+$  are thermodynamically able to reduce  $\text{Ru}(\text{bpy})_3^{2+}$  and, thus, initiate the red-ox excitation pathway (Fig. 3). Thus, this is energetically possible in addition to hydrated electron, for bulk aluminium,  $\text{Al}^{2+}$ ,  $\text{Al}^+$ , and atomic hydrogen.

On the other hand, ox-red excitation pathway can only be initiated by oxidants having their line below the line of couple  $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}$ . Thus, again only  $\text{SO}_4^{\bullet-}$  and  $\text{O}^{\bullet-}$  are energetically capable of this. However, hydroxyl radical and oxide radical ion have a strong tendency for addition reaction to pyridine rings rather than the preferable one-electron oxidation [24], and thus, it is highly likely that only sulfate radical can efficiently initiate ox-red excitation pathway. When peroxodisulfate ions are present with a sufficiently high concentration, ox-red excitation pathway is almost certainly more favourable in the present system than red-ox excitation pathway due to the much longer lifetime of  $\text{Ru}(\text{bpy})_3^{3+}$  in comparison to  $\text{Ru}(\text{bpy})_3^+$  in aqueous medium [4,25].

According to the older literature [26]  $\text{Ru}(\text{bpy})_3^{3+}$  should yield CL in reaction with alkaline water solution. However, there seems to be no theoretical basis for this CL to occur. First, the reaction (27) should not be possible on thermodynamic grounds even if it would result in ground state  $\text{Ru}(\text{bpy})_3^{2+}$ , because the formal reduction potential of couple  $\cdot\text{OH}/\text{OH}^-$  at pH 13–14 is about 1.8–2 V versus SHE [10,22] (see also Fig. 3).



Second, the reaction (27) should have an enthalpy more negative than  $-1.3$  eV to result in  $^3\text{MLCT}$  excited state (Fig. 3). However, there seems to be no obvious source for this missing amount of energy. Thus, if there is an additional light generating route by a reaction of  $\text{Ru}(\text{bpy})_3^{3+}$  with hydroxide ions,

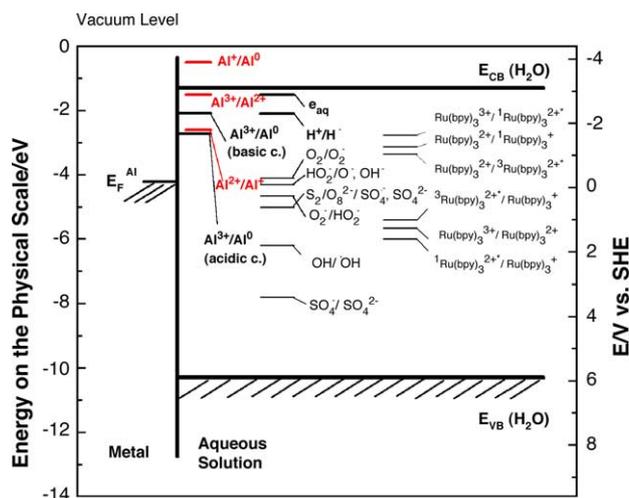
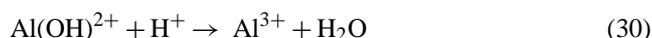
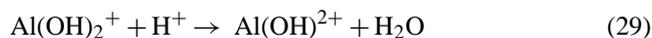


Fig. 3. Energy diagram of  $\text{Al}/\text{OH}^- - \text{S}_2\text{O}_8^{2-} - \text{Ru}(\text{bpy})_3^{2+}$ -system. The diagram is sketched on the grounds discussed previously in detail [23] and using values for oxyradicals given by Koppenol [22] and calculated one-electron reduction potentials of Al-species according to Jørgensen [14].

it proceeds via unknown pathways which we cannot explain at the moment.

### 3.3. Dissolution of oxide-covered aluminium in acids

For comparison, the possibility of producing CL in acid solutions was also studied. Aluminium oxides are dissolved in acidic solutions by hydrogen ions according to the reaction sequence [17]:



Aquated  $\text{Al}^{3+}$  is six-coordinated and therefore should preferably be presented as a complex  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  which has its  $\text{p}K_{\text{a}1}$  close to 5.0 [17]. In addition to protolysis, the behaviour of  $\text{Al}(\text{III})$  in acidic solutions is also complicated by the tendency of formation of polynuclear complexes such as  $[\text{Al}_2(\text{OH})_2]^{4+}$  and  $[\text{Al}_4(\text{OH})_{10}]^{2+}$  [17].

On contact of metallic aluminium with pure water, the following overall oxidation reaction occurs extremely rapidly, if the natural oxide film is successfully removed by some means [17]:



Thus, it seems highly likely that the oxide film must be dissolved extremely rapidly, if a direct contact between metallic aluminium and species dissolved in an aqueous solution are hoped for.

First, the behaviour of present aluminium brand (99.9%) was studied at open circuit conditions in acids. The aluminium used by us shows steady state open circuit potentials  $-0.46$ ,  $-0.56$  and  $-0.84$  V versus SHE during dissolution in 0.1, 1.0 and 11.6 M HCl, respectively, as measured using saturated calomel reference electrode and 20 G $\Omega$  input impedance of the volt meter. The open circuit potential of aluminium has been reported to be  $-1.50$  V versus SHE immediately after a contact of a fresh aluminium metal surface to neutral phosphate buffer denuded mechanically in situ [27]. As the open circuit potentials measured by us during the dissolution of Al electrode in hydrochloric acid is far more anodic than this, it seems reasonable to assume that the electrode originally covered with passive oxide layer never loses its passivity during dissolution in hydrochloric acid, i.e., aluminium is all the time covered with a thin (but possibly partly hydrous) aluminium oxide film even in concentrated HCl.

The oxide film is dissolved by protons via the reaction sequence presented above, and the electron transfer from metal occurs partially by tunneling through the dissolution-thinned oxide layer and possibly also inside the oxide layer. In our opinion, one reason why the dissolution of the oxide does not result in an active aluminium surface is that atomic hydrogen can also act as an oxidant in acidic solutions although it generally behaves as a strong reductant; it is known that

atomic hydrogen can oxidize e.g.,  $\text{Fe}^{2+}$ ,  $\text{I}^-$  and HSCN at pH 1 but not  $\text{Br}^-$  or  $\text{Cl}^-$  [28]. Thus, it is concluded on this basis [8,20] that the formal reduction potential of couple  $\text{H}^+/\text{H}^-$  is about 1.6 V versus SHE under strongly acidic conditions and, therefore, it can be assumed that a hydrogen atom is also able to oxidize aluminium metal and low-valent aluminium species.

After several experiments in hydrochloric and sulfuric acid media it became evident that no extrinsic lyoluminescence of aluminium induced by  $\text{Ru}(\text{bpy})_3^{2+}$  chelate or  $\text{Tb}(\text{III})$  ion could be produced in acidic conditions, nor in the absence or in the presence of peroxydisulfate ions. This implies that the oxidation of aluminium occurs in the metal/oxide interface mainly by indiffused protons and that the dissolution of aluminium is almost solely based on the dissolution of aluminium oxide in acids and the dissolution liberated trapped charges [2,5] seem to be unable to generate any observable luminescence from the studied luminophores under acidic conditions.

### 3.4. Extrinsic lyoluminescence of magnesium

The  $\text{Mg}/\text{H}^+ - \text{S}_2\text{O}_8^{2-} - \text{Ru}(\text{bpy})_3^{2+}$ -system was first studied using an ordinary Perkin-Elmer LS 50B luminometer in bioluminescence mode as a light detector. CL intensity was linearly proportional on the peroxydisulfate concentration in 0.1 M HCl solution, but some intensity was also obtained in the absence of peroxydisulfate ions in air-equilibrated solution (Fig. 4). It was revealed that with a fixed peroxydisulfate and  $\text{Ru}(\text{bpy})_3^{2+}$  chelate concentration, CL intensity was very steeply proportional on the hydrogen ion concentration when pH was below 2 (Fig. 4). When the emission slit was 20 nm,

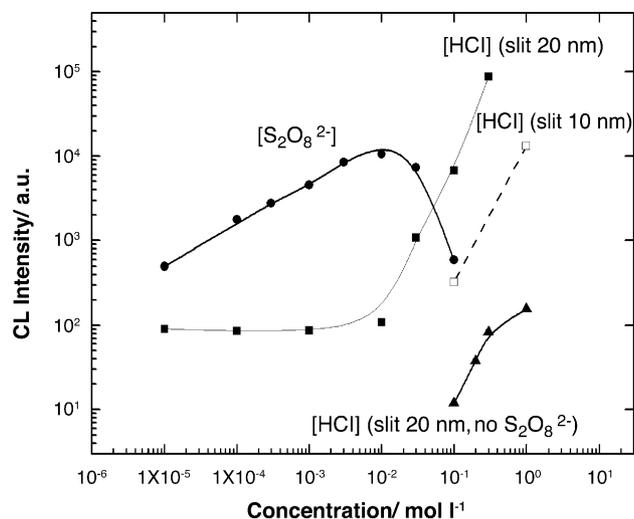


Fig. 4. Dependence of CL intensity on the concentrations of (a) peroxydisulfate, (b–d) hydrochloric acid. (a)  $1 \times 10^{-4}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  and 0.1 M HCl ( $\bullet$ ); (b)  $1 \times 10^{-4}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  and 0.01 M  $\text{K}_2\text{S}_2\text{O}_8$  ( $\blacksquare$ ); (c)  $1 \times 10^{-4}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  and 0.01 M  $\text{K}_2\text{S}_2\text{O}_8$ ; (d)  $1 \times 10^{-4}$  M  $\text{Ru}(\text{bpy})_3^{2+}$ , no peroxydisulfate ( $\blacktriangle$ ). Measured with Perkin-Elmer LS 50B in bioluminescence mode, emission monochromator set to 600 nm, integral of time drive over 180 s, slit 20 nm, except in case of (c) 10 nm ( $\square$ ).

the intensity was over scale at pH 0, thus HCl concentrations 0.1 and 1 M were remeasured with 10 nm emission slit (open squares, Fig. 4). Finally, calibration plots for  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{K}_2\text{S}_2\text{O}_8$  were remeasured with photon counting lyoluminometer at pH 0 (Fig. 5). Both of these species can be detected down to very low concentration levels and this system seems to be much better than  $\text{Al}/\text{OH}^- - \text{S}_2\text{O}_8^{2-} - \text{Ru}(\text{bpy})_3^{2+}$ -system discussed above.

### 3.5. Mechanism of extrinsic lyoluminescence of magnesium

Magnesium is more electropositive element than aluminium and its two-electron standard reduction potential is  $-2.356$  V versus SHE in acidic conditions and  $-2.687$  V versus SHE in basic conditions [7]. Fig. 6 displays the energy diagram of the present system using formal reduction potentials at pH 0 for oxygen species. In principle, the present system is quite similar to the  $\text{Al}/\text{OH}^- - \text{S}_2\text{O}_8^{2-}$ -system discussed above. Also the Al-species are added in the diagram for comparison, but actually, this diagram should contain an aluminium oxide film upon aluminium to be valid for aluminium under neutral and acidic conditions.

When metallic magnesium is in direct contact of strongly acidic aqueous solution magnesium is dissolved in reaction with protons:



It is probable that all of the atomic hydrogen generated is not lost in evolution of molecular hydrogen according to Eq. (15) but part of hydrogen atoms can act as a reductant or as an oxidant.

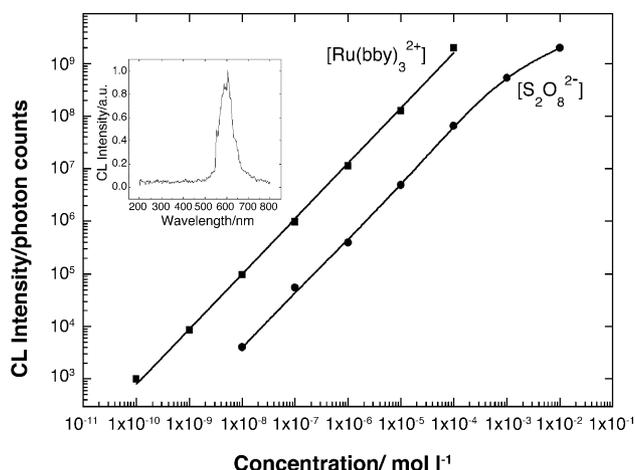


Fig. 5. Calibration curves for  $\text{Ru}(\text{bpy})_3^{2+} - \text{K}_2\text{S}_2\text{O}_8$  using  $\text{Mg}/\text{H}^+ - \text{S}_2\text{O}_8^{2-}$ -system for generation of CL. (■)  $1 \times 10^{-4}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  and (●) 0.01 M  $\text{K}_2\text{S}_2\text{O}_8$ . Photon counting lyoluminometer, 620 nm interference filter. Integration time 500 s. Inset displays an uncorrected emission spectrum of the present CL system as measured by LS 50B equipped with blue sensitive PMT ( $1 \times 10^{-4}$  M  $\text{Ru}(\text{bpy})_3^{2+}$ , 0.01 M  $\text{K}_2\text{S}_2\text{O}_8$ , 0.1 M HCl, emission slit 15 nm).

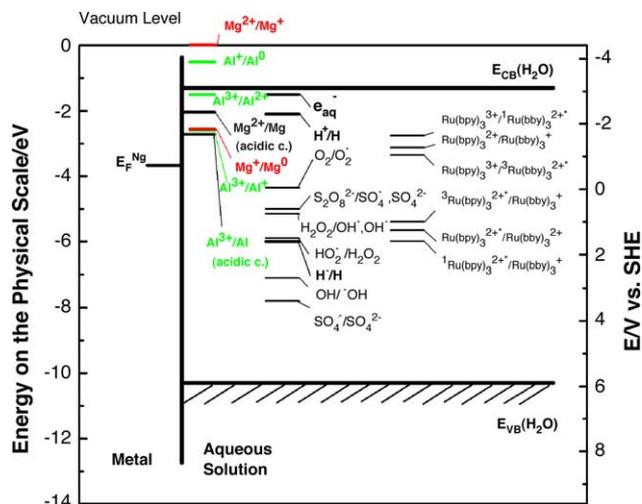
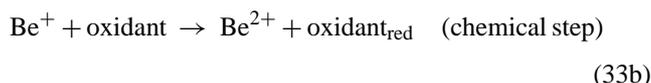


Fig. 6. Energy diagram of  $\text{Mg}/\text{H}^+ - \text{S}_2\text{O}_8^{2-} - \text{Ru}(\text{bpy})_3^{2+}$ -system. The diagram is sketched on the same grounds as Fig. 3.

Beryllium belongs to the same group as magnesium but is having a similar electronegativity to that of aluminium. Also for beryllium, the short-lived low-valent  $\text{Be}^+$  has been observed. Aida et al. have reported that anodic dissolution of beryllium, in the presence of lower concentration than 5 mM of water in ethanol solutions of lithium perchlorate electrolyte, clearly occurs in two steps [29]:



Thus, we believe, that also the present system includes  $\text{Mg}^+$  as an extremely strong one-electron reductant, but its lifetime must be very short.

The most significant differences between the studied two systems are that here under highly acidic conditions. (i) There is no mechanism for generation hydrated electron, and even if, it would be somehow generated it would be rapidly converted to its conjugated acid ( $k(\text{e}_{\text{aq}}^- + \text{H}^+) = 2.3 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ ) [10]. (ii) Atomic hydrogen and also (iii)  $\text{HO}_2^-$  are able to initiate the ox-red excitation pathway in addition to  $\bullet\text{OH}$  and  $\text{SO}_4^{\bullet-}$  radicals, and also successfully end up the red-ox excitation pathway, at least on thermodynamic basis (Fig. 6). Therefore, part of atomic hydrogen may also act as a moderately strong oxidant as discussed above. However, as can be seen from Fig. 4, CL is quite weak in the absence of sulfate radicals.  $\text{Mg}^+/\text{Mg}$  and  $\text{Mg}^{2+}/\text{Mg}^+$  couples can easily replace corresponding Al-species as reductants in the previously studied system.

We believe that ox-red pathway is again the prevailing excitation route due to the very long lifetime of  $\text{Ru}(\text{bpy})_3^{3+}$  in which the electron has been donated from a metal centered orbital (a true Ru(III) oxidation state), and fast decomposition of the ligand centered radical of  $\text{Ru}(\text{bpy})_3^+$  (i.e. central ion

is actually in oxidation state II) in aqueous solution although support for red-ox excitation route has also been presented [3,4,24]. Further studies on this system are needed, before we can say anything more definite about the present CL generation mechanisms. We believe that EPR measurements might give further knowledge about the present system although aqueous solutions are problematic, but perhaps at least spin trapping would give some useful information.

#### 4. Conclusions

Dissolution of aluminium in alkaline aqueous solution, as well as, dissolution of magnesium in acidic aqueous solution seem to create quite interesting metal/aqueous solution interfaces which provide possibilities to carry out extremely difficult reductions in aqueous solution. In addition, using appropriate coreactants capable of producing highly oxidizing radicals upon one-electron reduction, these interfaces allow generation of CL from quite a wide variety of luminophores excitable by redox reactions. Amongst the presently studied CL systems, especially,  $\text{Mg}/\text{H}^+-\text{S}_2\text{O}_8^{2-}$ -system gives quite nice analytical performance for detection of  $\text{Ru}(\text{bpy})_3^{2+}$ -based labels well-known to be usable in bioaffinity assays [4]. Thus, it is proposed that immunoassays and other bioaffinity assays can be carried out on the surface of oxide-covered magnesium slides or miniature vessels in basic conditions, and then the detection step of the label is carried out in a very simple way in acidic  $\text{S}_2\text{O}_8^{2-}$  solution.  $\text{Al}/\text{OH}^--\text{S}_2\text{O}_8^{2-}$ -system is more usable with derivatives of luminol and probably also with aromatic Tb(III) chelates as labels than with  $\text{Ru}(\text{bpy})_3^{2+}$ -based labels.

We believe that the presently studied reactive interfaces will also be useful for other researchers not interested in luminescence methods. Usually, but not always, chemists easily realize that difficult oxidations using hydrogen peroxide or peroxodisulfate as an oxidant, are most often induced by hydroxyl or sulfate radical generated from these precursors, and not by the actual two-electron oxidants themselves. On the contrary, reducing metals are normally always considered only on the basis of their multielectron reduction potentials found from various compilations, and the use of short-lived unusual valency states of metal ions in reductions and oxidations typically occurs normally only unintentionally, e.g. in some organic electrosyntheses using magnesium anodes and in applying different variants of Fenton reagents.

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