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CHEMILUMINESCENCE FROM ELECTRON TRANSFER REACTIONS OF TRANSITION METAL COMPLEXES*

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Summary

Chemiluminescence experiments were carried out with several transition metal complexes in fluid solution, using continuous and/or stop–flow techniques. The oxidation of Cr(II) polypyridine complexes by $S_2O_8^{2-}$ led to luminescence emission from the ^2E_g metal-centred excited state (^{2}MC) of the corresponding Cr(III) complexes. The reduction of Ru(III) polypyridine complexes (including the mixed ligand $Ru(bipy)_2(DMCH)^{3+}$ complex) by OH^- or $C_2O_4^{2-}$ led to luminescence emission from the triplet charge transfer excited state of the corresponding Ru(II) complexes. The mixing of Cr(II) and Ru(III) polypyridine complexes led to luminescence emission from the ^{2}MC of the corresponding Cr(III) complexes. The mechanistic and energetic aspects of these chemiluminescence processes are discussed.

1. Introduction

In the last few years electronically excited states of transition metal complexes have been widely used as reactants in electron transfer processes for both theoretical and practical purposes (for reviews see refs. 1 and 2):

$$A + h\nu \rightarrow {}^*A \qquad (1)$$

$$^*A + B \rightarrow A^+ + B^- \qquad (2)$$

Such investigations have led to considerable progress towards the understanding of electron transfer mechanisms [3] and, on the applications side, towards the design of artificial systems for the conversion of solar energy into chemical energy (among the most recent papers see ref. 4). Much less attention has been devoted

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to electron transfer processes leading to the formation of excited states of transition metal complexes [5 - 8]:

$$A^{+} + B^{-} \rightarrow {}^{*}A + B \qquad (3)$$

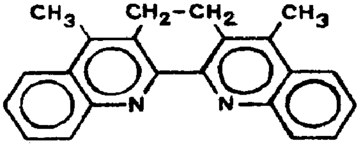
$$ {}^{*}A \rightarrow A + h\nu \qquad (4)$$

although such processes are also interesting for theoretical reasons and for the practical purpose of converting chemical energy into light. This type of energy conversion is, of course, less appealing than the conversion of light into chemical energy; nevertheless, it does have important applicative implications, *e.g.* in the production of "cold light" sources (lightsticks based on chemiluminescence reactions have already been commercialized by American Cyanamid (Cyalumen)) and in the design of electronic display devices [9] and lasers [10].

Polypyridine complexes of transition metal ions exhibit photophysical, photochemical and electrochemical properties [1, 2] that are particularly suitable for excited state electron transfer quenching processes. For the same reasons they are also suitable candidates for electron transfer chemiluminescent reactions. We thus began a systematic investigation of these processes with the dual aim of testing specific aspects of electron transfer theories and of finding systems which might be of some practical value.

2. Experimental details

Cr(II) complexes of 2,2′-bipyridine (bipy), 4,4′-dimethyl-2,2′-bipyridine (4,4′-Me_2bipy), 1,10-phenanthroline (phen), 5,6-dimethyl-1,10-phenanthroline (5,6-Me_2phen) and 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen) were obtained in a dry-box under nitrogen from chromium dichloride in 10^{-2} M $HClO_4$ and the free ligand dissolved in methanol. The final solution was 1:1 methanol: water by volume. The Ru(III) complexes of bipy, phen, 4,7-Me_2phen and 5-chloro-1,10-phenanthroline (5-Cl-phen) were obtained in 1 N H_2SO_4 solution by oxidizing the corresponding Ru(II) complexes, which were prepared according to published procedures, with lead dioxide. The $Ru(bipy)_2(DMCH)^{3+}$ complex, where DMCH stands for the 2,2′-biquinolyl derivative



was obtained by oxidation with lead dioxide in concentrated sulphuric acid solution of the corresponding Ru(II) complex which was kindly supplied by Belser and von Zelewsky [11]. The excess lead dioxide and the insoluble lead sulphate product were eliminated by filtration. All the other chemicals used were of the best grade commercially available.

The absorption spectra were measured by means of a Perkin–Elmer 323 spectrophotometer. Uncorrected photoluminescence and chemiluminescence spectra were recorded by using a Perkin–Elmer MPF 3 spectrofluorimeter equipped with an R 928 photomultiplier. For the chemiluminescence spectra, home-made continuous flow mixing cells were used which were placed into the cell compartment of the spectrofluorimeter. Pulsed chemiluminescence experiments were carried out by means of Durrum–Gibson stop–flow equipment. An evaluation of relative chemiluminescence intensities was obtained by comparing either the emission spectra in continuous flow experiments or the signals of the pulse experiments. In all cases freshly prepared solutions of the various reactants were used and the experiments were carried out at room temperature (about 20 °C).

3. Results

Chemiluminescence emission was obtained with all the Cr(II) and Ru(III) complexes used. A summary of the experimental results is given in Table 1 which shows for each complex the reaction partner, the free-energy change of the reaction leading to excited state formation, the emission maximum of the oxidized reductant and/or the reduced oxidant (obtained from independent photoluminescence experiments) and the maximum (maxima) of the chemiluminescence emis-

TABLE 1

Chemiluminescence from Cr(II) and Ru(III) complexes

Reductant A^-	*Oxidant* B^+	$-\Delta G$[a] (eV)	$\lambda(^*A)$[b] (nm)	$\lambda(^*B)$[c] (nm)	λ(chem)[d] (nm)
$Cr(bipy)_3^{2+}$	$S_2O_8^{2-}$	$\geqq 3.65$	727	—	≈ 730
$Cr(4,4'\text{-}Me_2bipy)_3^{2+}$	$S_2O_8^{2-}$	$\geqq 3.85$	731	—	[e]
$Cr(phen)_3^{2+}$	$S_2O_8^{2-}$	$\geqq 3.65$	727	—	≈ 730
$Cr(5,6\text{-}Me_2phen)_3^{2+}$	$S_2O_8^{2-}$	$\geqq 3.78$	—	—	≈ 730
$Cr(4,7\text{-}Me_2phen)_3^{2+}$	$S_2O_8^{2-}$	$\geqq 3.89$	734	—	≈ 730
OH^-	$Ru(bipy)_3^{3+}$	[f]	—	607	≈ 610
OH^-	$Ru(4,7\text{-}Me_2phen)_3^{3+}$	[f]	—	607	≈ 610
OH^-	$Ru(5\text{-}Cl\text{-}phen)_3^{3+}$	[f]	—	593	≈ 610
OH^-	$Ru(bipy)_2(DMCH)^{3+}$[g]	[f]	—	736	≈ 740
$C_2O_4^{2-}$	$Ru(bipy)_2(DMCH)^{3+}$[g]	2.46	—	736	≈ 740
$Cr(4,4'\text{-}Me_2bipy)_3^{2+}$	$Ru(bipy)_3^{3+}$	1.71	731	607	[e]
$Cr(4,4'\text{-}Me_2bipy)_3^{2+}$	$Ru(4,7\text{-}Me_2phen)_3^{3+}$	1.54	731	607	[e]
$Cr(phen)_3^{2+}$	$Ru(bipy)_3^{3+}$	1.51	727	607	≈ 610, ≈ 730
$Cr(5,6\text{-}Me_2phen)_3^{2+}$	$Ru(bipy)_3^{3+}$	1.64	—	607	≈ 610, ≈ 730
$Cr(4,7\text{-}Me_2phen)_3^{2+}$	$Ru(bipy)_3^{3+}$	1.75	734	607	≈ 610, ≈ 730

[a] Free-energy change available to the reaction that can lead to the excited state (see text): for the redox potentials of the Cr(II) and Ru(III) complexes see refs. 1 and 12 unless otherwise noted; for the reduction potentials of $S_2O_8^{2-}$ see ref. 13; for the oxidation potential of CO_2^- see ref. 14.

[b] Photoluminescence maximum of the oxidized reductant, see refs. 1 and 12.

[c] Photoluminescence maximum of the reduced oxidant, from ref. 15 unless otherwise noted.

[d] Maxima of the observed chemiluminescence.

[e] Only stop–flow experiments.

[f] Unknown (see text).

[g] For the reduction potential see ref. 11; for the luminescence spectrum see ref. 16.

sion. In all cases the chemiluminescence spectra were identical with the photoluminescence spectra of the reaction products.

For all the complexes the lifetime of the emitting state under the experimental conditions used was much shorter (see below) than the time needed for mixing the solutions in the stop–flow apparatus (about 2 ms). Thus, the intensity decay observed in the pulse experiments is a probe of the rate of excited state formation.

4. Discussion

4.1. *Chromium complexes*

The $Cr(LL)_3^{3+}$ complexes (where LL is a chelated polypyridine ligand) are known to emit luminescence in fluid solution at room temperature ($\varphi_{em} \approx 10^{-4}$) [12]. The emitting state is the lowest doublet metal-centred excited state, usually indicated as ^2MC. Such an excited state, which belongs to the ^3E_g representation in octahedral symmetry, derives from the same t_{2g}^3 electronic configuration as the $^4A_{2g}$ ground state. For this reason the emission wavelength is almost independent of the nature of the polypyridine ligands and the emission lifetime is relatively long (*i.e.* in the region of 100 μs) [12]. As previously discussed [7], the most probable reaction mechanism for the chemiluminescence emission observed on $S_2O_8^{2-}$ oxidation of the Cr(II) complexes is the following (the asterisk indicates ^2MC):

$$Cr(LL)_3^{2+} + S_2O_8^{2-} \rightarrow Cr(LL)_3^{3+} + SO_4^{2-} + SO_4^- \quad (5)$$

$$Cr(LL)_3^{2+} + SO_4^- \rightarrow {}^*Cr(LL)_3^{3+} + SO_4^{2-} \quad (6)$$

$${}^*Cr(LL)_3^{3+} \rightarrow Cr(LL)_3^{3+} + h\nu \quad (7)$$

The free-energy change of reaction (5) is of the order of –1 eV, its actual value depending on the particular chromium complex used. Thus, this reaction is not sufficiently exergonic to produce the lowest excited state of the Cr(III) complexes whose energy content is about 1.7 eV. The reaction between $Cr(LL)_3^{2+}$ and SO_4^- is much more exergonic so that ^2MC and also some higher excited states are accessible. Since it is known that any (spectroscopic) excited state of these complexes undergoes fast deactivation to the ^2MC [12], chemiluminescence is expected (and found) to occur only from the ^2MC. Interestingly, these seem to be the first examples of chemiluminescence arising from ^2MCs.

4.2. *Ruthenium complexes*

The $Ru(LL)_3^{2+}$ complexes are also known to emit luminescence in fluid solution at room temperature ($\varphi_{em} \approx 10^{-2}$) [1, 2]. Emission originates from the lowest, formally spin-forbidden, metal-to-ligand charge transfer excited state, usually indicated as ^3CT. The excited state lifetime is of the order of 1 μs and the excited state energy depends on the electronic affinity of the ligands involved. Thus, the emission maxima of the tris-bipy and tris-phen complexes are at almost the same wavelengths, but the $(^3CT)Ru(bipy)_2(DMCH)^{2+}$ emission occurs at much longer wavelengths because of the lower π^* orbital system introduced by the easily reducible DMCH ligand. The chemiluminescence emission on reduction with OH^- ions of Ru(III) complexes containing bipy, phen and some phen derivatives has previously been observed and discussed by various researchers [5, 8]. The reaction probably proceeds via intermediates in which OH^- has added to one of the ligands, but the exact reaction mechanism is unknown. $Ru(LL)_3^{3+}$ complexes are only stable in strongly acidic solution. In water or even in media of moderate acidity they undergo a fast reduction reaction. We found that the $Ru(bipy)_2(DMCH)^{3+}$ complex is only stable for a very short time even in 5 N H_2SO_4, so that it was difficult to prepare the complex and then to mix it with a sodium hydroxide solution. In preliminary experiments a much more intense chemiluminescence was obtained on electrochemical oxidation of an aqueous solution containing $Ru(bipy)_2(DMCH)^{2+}$ and potassium oxalate, as Rubinstein and Bard [17] have recently observed with $Ru(bipy)_3^{2+}$. In such experiments the chemiluminescence probably arises from the following reaction sequence (the asterisk indicates ^3CT):

$$Ru(bipy)_2(DMCH)^{2+} \xrightarrow{-e^-} Ru(bipy)_2(DMCH)^{3+} \qquad (8)$$

$$Ru(bipy)_2(DMCH)^{3+} + C_2O_4^{2-} \rightarrow Ru(bipy)_2(DMCH)^{2+} + CO_2 + CO_2^- \qquad (9)$$

$$Ru(bipy)_2(DMCH)^{3+} + CO_2^- \rightarrow {}^*Ru(bipy)_2(DMCH)^{2+} + CO_2 \qquad (10)$$

$$^*Ru(bipy)_2(DMCH)^{2+} \rightarrow Ru(bipy)_2(DMCH)^{2+} + h\nu \qquad (11)$$

The free-energy change available to the reactants in eqn. (10) is about −2.5 eV, *i.e.* much larger than the 0–0 excited state energy of $^*Ru(bipy)_2(DMCH)^{2+}$ (1.72 eV). Our results confirm the quite general ability of the Ru(III) polypyridine complexes to give chemiluminescent reactions and also provide additional opportunities for systematic studies because of the availability of complexes with various excited state energies and excited state redox potentials.

4.3. *Cr(II)–Ru(III) systems*

The very interesting photochemical behaviour of systems containing both $Cr(bipy)_3^{3+}$ and $Ru(bipy)_3^{2+}$ has already been discussed [18]. Although no permanent photoreaction was observed on excitation with visible light of an aqueous solution containing $Cr(bipy)_3^{3+}$ and $Ru(bipy)_3^{2+}$, flash experiments revealed the sequence of events that is schematized by the full arrows in Fig. 1: (i) light excitation of $Ru(bipy)_3^{2+}$ or $Cr(bipy)_3^{3+}$ ultimately leads to excited states which are strongly reducing ($^*Ru(bipy)_3^{2+}$) or strongly oxidizing ($^*Cr(bipy)_3^{3+}$) species; (ii) these species undergo fast electron transfer quenching reactions yielding $Ru(bipy)_3^{3+}$ and $Cr(bipy)_3^{2+}$; (iii) a back electron transfer reaction takes place which returns the system to its original state. The implications of this reaction sequence as far as the conversion of light into chemical energy is concerned have also been discussed [1, 18]. Vogler *et al.* [8] have recently observed some chemiluminescence on mixing $Ru(bipy)_3^{3+}$ and $Cr(bipy)_3^{2+}$, and by using interference filters they have shown that the emission is due to $^*Cr(bipy)_3^{3+}$. We have now begun to explore in a systematic way the possibility of going along the broken arrows in Fig. 1 in order to convert chemical

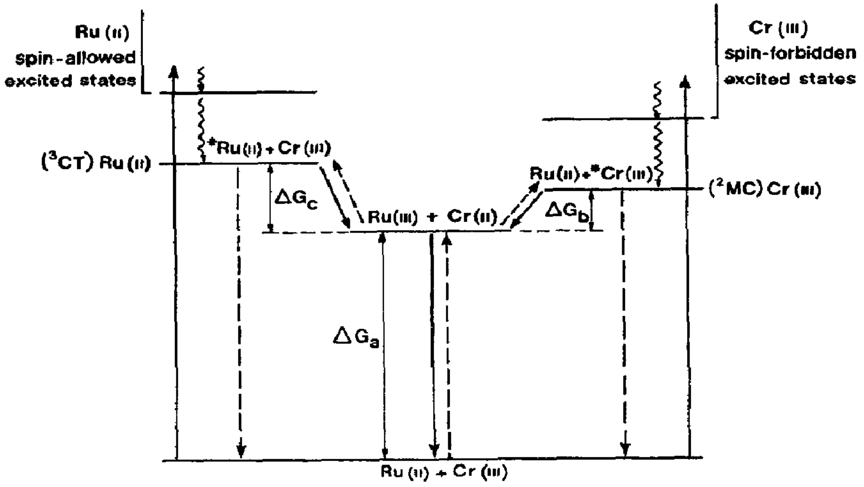


Fig. 1.

or electrical energy into light. In principle, three parallel electron transfer reactions are possible in these systems:

$$\mathrm{Ru(LL)_3^{3+} + Cr(LL)_3^{2+}} \longrightarrow \mathrm{Ru(LL)_3^{2+} + Cr(LL)_3^{3+}} \qquad (12a)$$

$$\mathrm{Ru(LL)_3^{3+} + Cr(LL)_3^{2+}} \longrightarrow \mathrm{Ru(LL)_3^{2+} + {}^*Cr(LL)_3^{3+}} \qquad (12b)$$

$$\mathrm{Ru(LL)_3^{3+} + Cr(LL)_3^{2+}} \longrightarrow \mathrm{{}^*Ru(LL)_3^{2+} + Cr(LL)_3^{3+}} \qquad (12c)$$

Reaction (12a) is very exergonic in all cases (see the values of ΔG in Table 1, which refer to ΔG_a in Fig. 1), whereas the free-energy changes of reactions (12b) and (12c) (ΔG_b and ΔG_c in Fig. 1) are markedly affected by the specific nature of the reaction partners. For the $\mathrm{Ru(bipy)_3^{3+}}$ – $\mathrm{Cr(phen)_3^{2+}}$ system (ΔG_a = –1.51 eV, ΔG_b = +0.20 eV and ΔG_c = +0.61 eV) we observed two weak emission bands of almost equal intensities corresponding to the $\mathrm{{}^*Ru(bipy)_3^{2+}}$ and $\mathrm{{}^*Cr(phen)_3^{3+}}$ emissions (Table 1). This is rather surprising even if we take into account that the emission quantum yield of the ruthenium complex is about two orders of magnitude higher than that of the chromium complex. If we replace $\mathrm{Cr(phen)_3^{2+}}$ with $\mathrm{Cr(5,6\text{-}Me_2phen)_3^{2+}}$ or $\mathrm{Cr(4,7\text{-}Me_2phen)_3^{2+}}$, ΔG_b and ΔG_c become less positive (ΔG_b = +0.05 eV and ΔG_b = –0.06 eV respectively, and ΔG_c = +0.48 eV and ΔG_c = +0.37 eV respectively) and, as expected, the emission intensity at about 730 nm is much stronger (about 10^3 times for $\mathrm{Cr(4,7\text{-}Me_2phen)_3^{2+}}$). The 610 nm emission, however, is almost the same as that observed with $\mathrm{Cr(phen)_3^{2+}}$. This suggests that the weak 610 nm emission originates not from reaction (12c) but probably from a reaction of $\mathrm{Ru(bipy)_3^{3+}}$ with the solvent or with an impurity. For the $\mathrm{Cr(4,4'\text{-}Me_2bipy)_3^{2+}}$–$\mathrm{Ru(bipy)_3^{3+}}$ and $\mathrm{Cr(4,4'\text{-}Me_2bipy)_3^{2+}}$–$\mathrm{Ru(4,7\text{-}Me_2phen)_3^{3+}}$ systems (ΔG_b = –0.02 eV and ΔG_b = +0.15 eV respectively) the chemiluminescence signals at $\lambda > 700$ nm obtained in stop–flow experiments were in a 3 : 1 ratio, showing again that the free-energy change affects the reaction rate in this endergonic or weakly exergonic region. Other experiments are now in progress in order to obtain more quantitative results and to understand the role played by free-energy changes, intrinsic barriers and frequency factors in determining the reaction rates.

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