

Chemiluminescence and electrochemiluminescence of coordination compounds

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Abstract - Chemiluminescence and electrochemiluminescence reactions involving coordination compounds represent an interesting class of reactions which may offer useful information on the mechanism of outer-sphere electron transfer processes. Most studies have concentrated on the Ru-polypyridine complexes but examples of different complexes, including binuclear species and clusters, have also been reported. Some important examples of such processes are briefly discussed and some general theoretical and experimental considerations on comproportionation reactions leading to the formation of metal-to-ligand charge transfer excited states are presented.

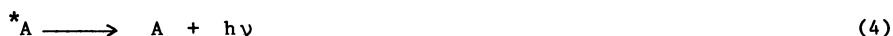
INTRODUCTION

Electron transfer reactions play a fundamental role in chemistry and are very important in the connections between chemistry and light (refs. 1-5). The formulation of the Marcus theory (ref. 6) has strongly stimulated the experiments in this field. Electron transfer reactions in which light is used as a reactant (photochemical reactions, eqs. 1-2)



have been the object of extensive investigations in the last few years. These studies have been designed to provide a better understanding of the mechanism of electron transfer processes and to test theoretical models. This type of reaction is also the basis of almost all types of natural and artificial photosynthetic process.

Electron transfer processes in which excited states (and thus light) are generated as a product (chemiluminescence reaction, eq. 3-4)



have received much less attention, although they are certainly not less interesting. This paper discusses various aspects of such processes with particular emphasis on systems involving coordination compounds.

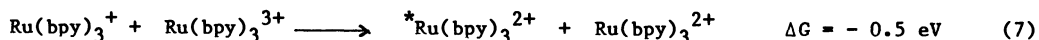
Chemiluminescence can be easily obtained upon mixing redox partners. This method cannot be employed, however, when the two redox partners are not stable for at least the time of the experiment. To obviate such a restriction, the reacting partners can be prepared in situ and then mixed as soon as they are formed. This can be done by either redox catalysis or electrolysis. The first method applies to high exoergonic redox reactions limited by large activation energy. In the second, the redox partners can be prepared by alternating cathodic reduction and anodic oxidation. The latter technique is called electrochemiluminescence (Ecl) (ref. 1).

Most investigations have been restricted to $\text{Ru}(\text{bpy})_3^{2+}$ or its derivatives (refs. 7-16). This is due, of course, to the intrinsic properties of such complexes (ref. 2) which can emit luminescence at room temperature in solution and undergo reversible one-electron transfer processes leading to sufficiently stable reduced or oxidized species. Recently, other families of complexes have been involved in Ecl experiments in order to obtain more complete information on the occurrence of this process.

ELECTROCHEMILUMINESCENCE ON COMPROPORTIONAL REACTION

The most noticeable and studied example is that described by Bard and co-workers (refs. 9, 11) concerning $\text{Ru}(\text{bpy})_3^{2+}$ in acetonitrile solution. When cyclic square waves between the reduction and oxidation potential of $\text{Ru}(\text{bpy})_3^{2+}$ are applied to a Pt electrode in solution, the typical orange emission, which continues indefinitely if the potential stepping is maintained, is observed.

The reaction mechanism is as follows:



The Ecl efficiency, ϕ_{Ecl} , defined as the number of photons produced per redox event, was estimated to be 0.05 in MeCN at 25 C (ref. 11). Since ϕ_{Ecl} strictly approaches the luminescence efficiency, Bard *et al.* concluded that the production efficiency of ${}^*\text{Ru}(\text{bpy})_3^{2+}$ upon the $1^+/3^+$ annihilation reaction is near to unity.

It should be noted that, in Ecl experiments involving organic aromatic compounds in aprotic media, the luminescence emission obtained by the annihilation reaction of electrogenerated radical ions is usually fluorescence, i.e. the emitting excited state is a singlet. The most simple Ecl mechanism implies the direct formation of the singlet excited state in the redox reaction step, if possible on energetic ground (energy sufficient systems, S-route). However, fluorescence emission has also been noted in "energy deficient systems", that is, those for which the emitted photon contains far more energy than that released by a single electron transfer event. In such a case, the proposed mechanism involves the formation of the triplet excited state from the redox process and then the formation of the excited singlet via triplet-triplet annihilation (T-route).

In coordination compounds, the spin-allowed excited states undergo fast deactivation because of spin-orbit coupling. Thus only the lowest excited state generally emits, and its lifetime is usually too short to be involved in annihilation processes. In these compounds, the luminescence emission observed in Ecl experiments is a phosphorescence and the emitting spin-forbidden excited states are generated via an energy sufficient route. Very good agreement between theoretical energy sufficient behaviour and experimental results was reported by Glass and Faulkner (ref. 17) for the $\text{Ru}(\text{bpy})_3^{2+}$ system.

Although most of the reported observations involve transition metal complexes containing bipyridine or related ligands, other types of complexes having different ligands and/or excited states have also been studied. Palladium and platinum porphyrines are Ecl active (ref. 18) and emit from intraligand excited states. Ecl was also observed under suitable experimental conditions for $\text{Cr}(\text{bpy})_3^{3+}$ (ref. 15), whose emitting excited state is metal-centered. More recently Ecl has been observed with $\text{Pt}(\text{thpy})_2$ (ref. 19), binuclear complexes and clusters. Molybdenum (II) halide cluster ions, $(\text{Mo}_6\text{Cl}_{14})^{2-}$ (ref. 20), and $\text{Mo}_7\text{Cl}_4(\text{PMe}_3)_4$ (ref. 21) are examples of this type. In the Ecl emission obtained by oxidizing and reducing $\text{Pt}_2(\text{POP})_4^{4-}$ in MeCN (ref. 22), the creation of the emitting excited state is associated with changes in the metal-metal bond order of the complex.

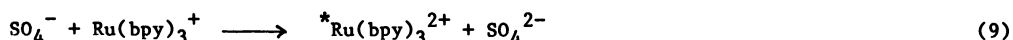
Ecl appears to be a common phenomenon for luminescent coordination compounds as long as energy requirements are satisfied. Few data have been reported for Ecl efficiency; except for $\text{Ru}(\text{bpy})_3^{2+}$, ϕ_{Ecl} is generally lower than the photoluminescence efficiency. This can be attributed to at least two reasons: (i) the instability of the oxidation and/or reduction products which participate in the comproportionation reaction, as is often proved by the decrease of the parent complex concentration after consecutive current pulses (refs. 20, 21); and (ii) the competition between the reaction leading to the excited state product and that leading directly to the ground state product. Some remarks on the relative importance of these two reactions will be made below.

OTHER ELECTROCHEMILUMINESCENCE REACTIONS

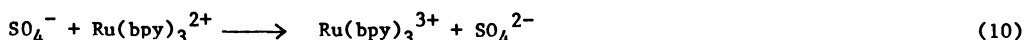
An alternative Ecl generation approach, which eliminates the necessity to cyclicly reduce and oxidize the parent species, involves the presence of strongly oxidizing or reducing reactants in the solution. This is done by using species ($\text{S}_2\text{O}_8^{2-}$, $\text{C}_2\text{O}_4^{2-}$) that can undergo an irreversible one-electron oxidation or reduction process leading to strongly oxidizing (SO_4^-) (refs. 15, 16) or reducing (CO_2^-) (ref. 8) radicals. For example, the electrochemical reduction of $\text{Ru}(\text{bpy})_3^{2+}$ - $\text{S}_2\text{O}_8^{2-}$ mixtures leads to bright Ecl emission (refs. 15, 16). The reaction proceeds as follows:



the SO_4^- species thus obtained can either oxidize the reduced complex to produce the excited state



or oxidize a $\text{Ru}(\text{bpy})_3^{2+}$ molecule

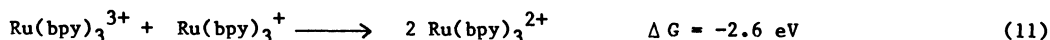


followed by reaction 7.

Intense E_{cl} signals were obtained in this type of experiment with different complexes, including Ru-polypyridyne and $\text{Cr}(\text{bpy})_3^{3+}$ (ref. 15), $\text{Mo}_2\text{Cl}_4(\text{PME}_3)_4$ (ref. 21) and $\text{Pt}(\text{thpy})_2$ (ref. 19). The complexity of the reaction mechanism for such systems generally precludes quantitative measurements. An evaluation of $\Phi_{\text{E}_{\text{cl}}}$ was given by Bard for the $\text{Ru}(\text{bpy})_3^{2+}-\text{S}_2\text{O}_8^{2-}$ system and led to a $\Phi_{\text{E}_{\text{cl}}}$ value of about half that of the annihilation system (ref. 16).

MECHANISTIC IMPLICATIONS OF THE COMPROPORTIONAL REACTION

As mentioned in the introduction, chemiluminescent reactions may represent an interesting tool in investigating theoretical aspects of the outer-sphere electron transfer reaction. If a chemiluminescence electron transfer reaction occurs, the process that leading to the formation of the excited state of a product should compete with the much more exoergic process leading to the direct formation of the ground state of the same product. According to the Marcus theory (ref. 6), the activation energy of a strongly exoergic electron transfer process should increase with increasing exoergicity (Marcus inverted region); thus the more exoergic reaction leading to the ground state should be lower than the chemiluminescent reaction. In the comproportionation reaction of $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^+$, the almost unitary efficiency of reaction 7 with respect to reaction 11



was taken as evidence for the "Marcus inverted region".

As recently outlined by Balzani *et al.* (ref. 21), reactions 7 and 11 differ from each other not only for the free energy change but also for another important factor. It is known that the Ru-polypyridine reduced species is reduced on the ligand (ML^-) while the oxidized species is oxidized on the metal (M^+L). By taking into account that the excited state of the complex, which is a MLCT, formally corresponds to a M^+L^- distribution, the electron transfer path in the comproportionation reaction is different, depending on whether the excited state is generated by the reduced or oxidized complex. Simple orbital overlap arguments suggest (ref. 21) that in the comproportionation reaction the excited state should derive from the oxidized parent. Unfortunately, there is no simple way to identify the parent of such an excited state.

We are currently engaged in collecting information on this topic by using Ru-polypyridyne complexes in which spectroscopic and electrochemical properties can be tuned by an appropriate choice of ligands (ref. 23). In these complexes the nature of the ligand can influence the energy of the lowest MLCT excited state, which is the emitting excited state, with substantial differences in the 0-0 energy and in the redox properties. By the appropriate choice of a pair of such complexes, it should be possible in an E_{cl} experiment to reduce or oxidize selectively one of the species and distinguish the emitting one.

For example, by stepping the potential between +1.11 V and -0.91 V in a solution containing $\text{Ru}(\text{DTB-bpy})_3^{2+}$ (DTB-bpy = diterbutylbipyridine) and $\text{Ru}(\text{bpy})_2(\text{biq})^{2+}$ (biq = 2,2'-biquinoline) it is only possible to reduce $\text{Ru}(\text{bpy})_2(\text{biq})^{2+}$ and to oxidize $\text{Ru}(\text{DTB-bpy})_3^{2+}$. This clearly appears from fig. 1, where the redox potentials of the two complexes are shown. Moreover, these complexes emit at different wavelenghts ($E_{0-0} = 2.16 \text{ eV}$ and 1.70 eV for $\text{Ru}(\text{DTB-bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_2(\text{biq})^{2+}$, respectively). E_{cl} experiments carried out on this couple have shown (ref. 24) that, under the above experimental conditions, only the $\text{Ru}(\text{bpy})_2(\text{biq})^{2+}$ is formed. This is due to the fact that the energy released in the reaction between $\text{Ru}(\text{DTB-bpy})_3^+$ and $\text{Ru}(\text{bpy})_2(\text{biq})^+$ ($\Delta G = 2.02 \text{ eV}$) is enough to create the emitting excited state of the $\text{Ru}(\text{bpy})_2(\text{biq})^{2+}$ species but not to create the ${}^* \text{Ru}(\text{DTB-bpy})_3^{2+}$.

On the contrary, if the E_{cl} experiments are carried out in a solution containing $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_2(\text{DMCH})^{2+}$ (DMCH = 6,7-dihydro-5,8-dimethylbenzo[b,i][1,10]phenanthroline) by stepping the potential between -1.00 V and +1.26 V, two strong emissions appear, one centred at about 620 nm and the other centred at about 725 nm (ref. 24).

At the potential values, while only $\text{Ru}(\text{bpy})_2(\text{DMCH})^{2+}$ can be reduced, both $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_2(\text{DMCH})^{2+}$ can be oxidized (see fig 1). The comproportionation reaction has now enough energy ($\Delta G = 2.26 \text{ eV}$) to create the excited state of either $\text{Ru}(\text{bpy})_3^{2+}$ ($E_{0-0} = 2.13 \text{ eV}$) or $\text{Ru}(\text{bpy})_2(\text{DMCH})^{2+}$ ($E_{0-0} = 1.72 \text{ eV}$).

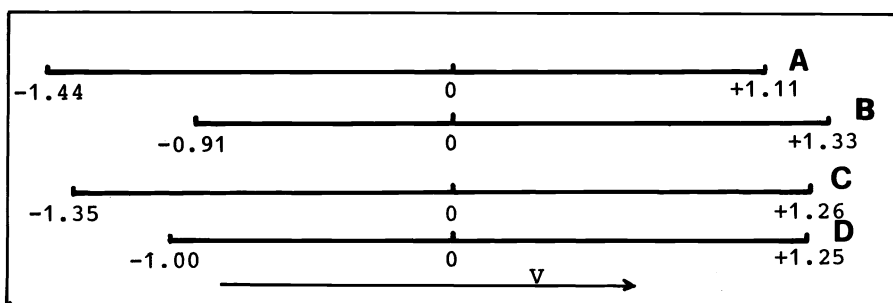


Fig. 1 - Oxidation and reduction potentials of: A = $\text{Ru}(\text{DTB-bpy})_3^{2+}$; B = $\text{Ru}(\text{bpy})_2(\text{biq})^{2+}$; C = $\text{Ru}(\text{bpy})_3^{2+}$; D = $\text{Ru}(\text{bpy})_2(\text{DMCH})^{2+}$. Data from ref. 23.

Energy restrictions and the occurrence of other phenomena such as energy transfer reduce the possibility of extending these experiments and of gathering quantitative data. They do, however, offer an interesting opportunity to compare electron transfer reactions involving similar (but not identical) compounds.

CONCLUSIONS

Chemiluminescent and electrochemiluminescent reactions represent a useful approach to the study of outer-sphere electron transfer reactions involving coordination compounds. Examples so far reported have mainly concentrated on Ru-polypyridine and related complexes, but other families having different ligands and different nature of excited states have also been studied. More recently, Ecl experiments have been carried out on binuclear complexes and clusters. Ecl may also be obtained by using strongly oxidizing or reducing species capable of reacting with the products of the electrochemical reduction or oxidation step.

Finally, a chemiluminescent comproportionation process leading to a charge transfer excited state offers the unique opportunity to compare the rate of electron transfer reactions involving similar compounds.

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