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# Chemiluminescent Reactions of Ru(2,2′-bipyridine)$_3{}^{1+,3+}$ and $Mo_6Cl_{14}{}^{1-,3-}$

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## Abstract

A number of new chemiluminescent reactions are reported. These include the reaction of $Mo_6Cl_{14}{}^{1-}$ and $Mo_6Cl_{14}{}^{3-}$ with solvent acetonitrile, of the latter species with Ru(bipyr)$_3{}^{3+}$ (bipyr = 2,2′-bipyridine) and of Ru(bipyr)$_3{}^{+}$ and Ru(bipyr)$_3{}^{3+}$ with solvent acetonitrile and with various oxidants and reductants. Approximate chemiluminescence yields and kinetics are also reported for the reduction of acidic aqueous solutions of Ru(bipyr)$_3{}^{3+}$ by luminol, $SnCl_2$, $SO_3{}^{2-}$, $H_2O_2$, ethylenediaminetetracetic acid, $N_3{}^-$, ethanol, $Pt(CN)_4{}^{2-}$, $Fe(CN)_6{}^{4-}$ and $W(CN)_8{}^{4-}$.

## Introduction

Chemiluminescent (CL) reactions of coordination compounds have been relatively uncommon [1, 2] until recently. Most of the now reported examples, however, involve reduction of Ru(bipyr)$_3{}^{3+}$ (bipyr = 2,2′-bipyridine [3–8], although several cases of oxidations of Cr(bipyr)$_3{}^{3+}$ are also known [6, 8, 9]. We have reported some oxidative addition reactions of certain Ir and Re complexes as being chemiluminescent [6].

The above cases are ones in which essentially stable reactant solutions are mixed; in favorable circumstances ordinary kinetic studies can be made both of the stoichiometric or analytical reaction and of the chemiluminescence (CL) intensity**. Closely related, however, are electrogenerated CL reactions (ECL) in which one or both reactants are produced electrochemically and then react away from the electrodes. Examples now include ruthenium polypyridine complexes [10–14], Ru(I) [15] and Os(II) diimine species [16], Pt(II) and Pd(II) complexes [17–19], $MoCl_4(PMe_3)_4$ [19], and cluster complexes of the type $Mo_6Cl_{14}{}^{n-}$ [21].

We report here on some additional CL reactions. Although the emission is weak in many cases (not visible to the unaided eye), the findings can have mechanistic significance and may encourage wider research.

## Experimental

### *Procedures*

The CL measurements were carried out with the use of equipment which consisted of a reaction compartment positioned on top of a red-sensitive photomultiplier (PM) tube (RCA 30314C) cooled to −30 °C, which in turn was connected to a quantum counter (SSR Instrument Co., Model 1140A) and a chart recorder. The apparatus was equipped with a slide holder such that filters could be interposed between the sample and the PM tube. In most cases, the samples consisted of *ca.* 10 $cm^3$ of recently mixed solution placed in a scintillation vial. In the case of rapid reactions, one component of the system was placed in the vial and the second reactant solution was injected by means of a light-shielded syringe delivery arrangement. An *in situ* estimation of the strength of the CL could thus be made. The reaction cell was held in a light-tight jacket, thermostatted to 25 ± 0.1 °C. Background was about 30 counts per second.

Chemiluminescence was not noted unless the count rate was well above background. For example, in the case of the systems shown in Table I, typical data were (reductant, background count rate ($s^{-1}$), observed initial count rate with reaction vial present ($s^{-1}$)): $Na_2SO_3$, 3000, 30 000; $H_2O_2$, 3000, 13 500; NaBr, 2800, 4400; EDTA, 2500, 22 000; 5% ethanol, 9000, 30 000; $NaN_3$, 2500, 10 000. In the case of $SnCl_2$ as reductant and of the luminol system, the background rate was 3000 and 3500 $s^{-1}$, respectively; since the chemiluminescence was visible to the eye, this background was far below the chemiluminescent emission.

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**We will use CL to denote either the noun or the adjective.

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TABLE I. Reaction of $Ru(bipyr)_3{}^{3+}$ in 0.08 M $HClO_4$ at 25 °C with Various Reductants

| Reductant (concentration M) | $[Ru(bipyr)_3{}^{3+}]$ (M) | $\eta_{CL}$ | Observations |
|---|---|---|---|
| Luminol<br>$(1 \times 10^{-5})$ | $1 \times 10^{-4}$ [a] | visible[b] | Multiphasic CL was visible for about 3 s. |
| $SnCl_2$<br>$(8.86 \times 10^{-4})$ | $7.5 \times 10^{-5}$ [a] | visible[b] | CL was present for about 3 s, the period of the analytical reaction. |
| | $1.8 \times 10^{-6}$ | CL[c] | The analytical and most of the CL was fast; a residual CL was second-order [1/(intensity) linear with time]. |
| $Na_2SO_3$<br>$(4.9 \times 10^{-5})$ | $5.3 \times 10^{-5}$ | $4.4 \times 10^{-6}$ | Biphasic decay of CL with half-lives of 7 and 400 s. The analytical reaction was first-order with a half-life of 800 s, or twice that of the CL. |
| $H_2O_2$<br>$(3.1 \times 10^{-4})$ | $2.2 \times 10^{-5}$ | $3.2 \times 10^{-7}$ | Both the CL and the analytical reaction showed first-order behavior. The respective half-lives were 50 and 100 s. The temperature dependence of the analytical reaction gave an apparent activation energy of 8 kcal $mol^{-1}$. |
| $Br^-$<br>$(1.3 \times 10^{-2})$ | $6.5 \times 10^{-5}$ | $1 \times 10^{-7}$ | Both the CL and the analytical reaction showed first-order behavior. The respective half-lives were 65 and 140 s at 17.5 °C. |
| EDTA[d]<br>$(6.5 \times 10^{-5})$ | $3.3 \times 10^{-5}$ | $3.1 \times 10^{-7}$ | Both the CL decay and the analytical reaction were initially first-order with a half-life of 12 s. After the first half-life, the CL decayed more slowly than did the analytical rate of reaction. |
| $NaN_3$<br>$(2.6 \times 10^{-4})$ | $3.1 \times 10^{-5}$ | CL[c] | Both the CL decay and the analytical reaction were first-order initially with a half-life of 20 s. Successive CL half-lives increased steadily. The CL intensity was greatly enhanced if added $Ru(bipyr)_3{}^{2+}$ was present. |
| Ethanol<br>(5%) | $5.4 \times 10^{-5}$ | CL[c] | Both the CL decay and the analytical reaction were first-order with a half-life of 8 s. |
| $K_2Pt(CN)_4$<br>$(1 \times 10^{-4})$ | $1 \times 10^{-4}$ | CL[c] | Both the analytical reaction and the CL decay were too fast to measure. |
| $K_4Fe(CN)_6$ | $1 \times 10^{-4}$ | | Rapid chemical reaction; no observable CL. |
| $K_4W(CN)_8$ | $1 \times 10^{-4}$ | | Rapid chemical reaction; no observable CL. |

[a] In 0.1 M $H_2SO_4$. [b] Chemiluminescence visible to the unaided eye (and too intense for the quantum counter). [c] CL detected on the quantum counter but no estimate made of the yield. [d] Ethylenediaminetetracetic acid.

The detection efficiency, essentially the 'geometry' of the set-up, was determined by calibration with a known luminol system [22], whose CL efficiency ($\eta_{CL}$) was 0.0124 einstein per mole of reaction. A neutral density filter was used to attenuate the light in this case to avoid saturation of the PM tube. The general procedure was to record the emission *versus* time for the luminol system, obtain the integrated counts on the quantum counter, and to compare this with the number of einsteins calculated to have been emitted. For our equipment in its usual configuration, 1 count $\simeq 1 \times 10^4$ light quanta. The analogous procedure was then followed for a solution of unknown $\eta_{CL}$. The total was again obtained from the trace of the CL intensity *versus* time, corrected for the moles of reaction that occurred, and then scaled according to the luminol-determined geometry factor. The systems studied emitted at somewhat different wavelengths than does the luminol one, but the PM tube response was sufficiently flat over the regions spanned that no correction was considered to be necessary.

The progress of an overall or analytical reaction was followed spectrophotometrically, by means either of a Cary Model 14 or an HP Model 8450A spectrophotometer. Emission spectra were obtained with a Perkin-Elmer LS-5 spectrofluorimeter equipped with a Hamatsu R928-10S PM tube.

### *Preparation of Materials*

$[Ru(bipyr)_3](ClO_4)_2$ was prepared by metathesis of the chloride salt (Strem Chemicals). The UV–Vis absorption spectrum of solutions agreed with the literature values [23] to within a few percent. $(Bu_4N)_2[Mo_6Cl_{14}]$ (Bu = butyl) was prepared by a literature procedure [24]; the UV–Vis absorption spectrum in 6 M HCl and in acetonitrile (AN) agreed to within a few percent with the reported peak positions and extinction coefficients (as did the peak positions of the photoexcited emission in AN [25]).

Acidic aqueous solutions of $Ru(bipyr)_3{}^{3+}$ were prepared by $PbO_2$ oxidation, followed by filtration through a 0.22 Millipore filter. The filtration was necessary both to remove excess $PbO_2$ as an impurity and because finely divided $PbO_2$ would otherwise settle on the bottom of the scintillation vial and obscure any emission. Solutions of $Ru(bipyr)_3{}^{+}$, $Ru(bipyr)_3{}^{3+}$, $Mo_6Cl_{14}{}^{-}$ and $Mo_6Cl_{14}{}^{3-}$ in AN were prepared by electrolysis, using $(Bu_4N)ClO_4$ as the supporting electrolyte and Pt gauze electrodes, the cathode and anode compartments being connected through a fritted glass diaphragm. Where the object was to prepare the reduced species, the initial solution was deaerated by means of several freeze-thaw cycles under vacuum. All of the electrolyses were carried out in an atmosphere of dry argon.

Commercial distilled water was redistilled from sodium persulfate in the presence of oxygen as a carrier gas. The vapor was passed through a tubular furnace at 800 °C before condensation. Aldrich Gold label (>99% purity Spectrograde) AN was refluxed in the presence of calcium hydride for 8 h and then fractionally distilled under dry nitrogen. All of the glassware and Teflon sleeves were cleaned with Nochromic and/or boiled in a basic permanganate solution prior to using the distillation apparatus. Other reagents used were of Reagent grade.

## Results

### *(1) Reactions of $Mo_6Cl_{14}{}^{-}$ and $Mo_6Cl_{14}{}^{3-}$ in AN*

#### *(a) Solvent only*

Acetonitrile solutions of both $Mo_6Cl_{14}{}^{-}$ and $Mo_6Cl_{14}{}^{3-}$ showed a prolonged, weak CL. Use of suitable interference filters placed the peak intensity of the CL emission in the 760 nm region, which is that of photoexcited $Mo_6Cl_{14}{}^{2-}$ [25]. Acetonitrile is not readily oxidized or reduced, and the reaction may have been with impurities, such as traces of water or secondary electrolysis products (the solutions were used as prepared in the electrolysis cell).

#### *(b) Oxidation of $Mo_6Cl_{14}{}^{3-}$ by $Ru(bipyr)_3{}^{3+}$*

The reaction

$$Mo_6Cl_{14}{}^{3-} + Ru(bipyr)_3{}^{3+} \longrightarrow \begin{Bmatrix} [Mo_6Cl_{14}{}^{2-}]^* \\ Mo_6Cl_{14}{}^{2-} \end{Bmatrix} + Ru(bipyr)_3{}^{2+} \qquad (1)$$

was fast, occurring as the solutions of $Mo_6Cl_{14}{}^{3-}$ and $Ru(bipyr)_3{}^{3+}$ were mixed. There was a moderately strong CL, and the use of interference filters again placed the CL emission peak intensity in the 760 nm region, indicating that the excited stated product was $[Mo_6Cl_{14}{}^{2-}]^*$ rather than $[Ru(bipyr)_3{}^{3+}]^*$; the latter shows a peak emission at 620 nm.

### *(2) Oxidation of $Ru(bipyr)_3^+$ in AN*

#### *(a) Solvent only*

A *ca.* $5 \times 10^{-5}$ M solution of $Ru(bipyr)_3^+$ in AN showed a weak CL with a 1–2 min half-life and an initial intensity of 250 counts per second (cps). Interestingly, the $Ru(bipyr)_3^+$ solution was light sensitive. A brief exposure to room fluorescence lights led to an immediate two-and-a-half fold increase in the CL intensity. The emission decayed rapidly to the level expected had the solution remained in the dark.

#### *(b) Added oxidants*

Several oxidants were tested with AN solutions of $Ru(bipyr)_3^+$. A slow bubbling of oxygen through the solution greatly increased the emisson intensity as well as the rate of the analytical oxidation reaction. Addition of $10^{-3}$ M $Na_2S_2O_8$ in a 1:50 $H_2O$:AN solvent mixture produced a CL with an initial intensity of 1500 cps, which decayed with a *ca.* 3 s half-life. Addition of a *ca.* $10^{-4}$ M solution either of $UO_2(NO_3)_2$ or of $Cu(ClO_4)_2$ in AN produced a small increase in emission intensity, which decayed with half-lives of 10 and 2 min, respectively. The stoichiometry of the analytical reaction was not determined in the above cases.

### *(3) Reduction of $Ru(bipyr)_3{}^{3+}$ in AN*

#### *(a) Solvent only*

The initial CL intensity of $5 \times 10^{-5}$ M solution of $Ru(bipyr)_3^{3+}$ in AN was 2500 cps, and both the emission intensity and the analytical amount of the complex decayed non-exponentially with time. Both rates were relatively and absolutely irreproducible. That is, if a given solution was divided into one portion for the CL measurement and the other used to follow the analytical rate, the relative rates of decay would vary from one experiment to another. In addition, the rates would vary as much as several fold from one experiment to another. This irreproducibility suggests that the solvent reduction as well as the CL arises from impurities which plague even strenuously purified AN [26, 27]. One likely impurity is again trace water. Separate tests on the effect of added small amounts of water showed a marked acceleration of the rate of disappearance of the $Ru(bipyr)_3{}^{3+}$, and an increase both in the intensity and in the rate of decay of the CL.

#### *(b) Added reductants*

Only qualitative tests were made with various reductants because of the variabilities of the behavior of solutions of the complex only in AN. Solutions *ca.* $10^{-5}$ M in NaBr, $Na_2SO_3$ and $SnCl_2$ showed some enhancement of the decay rate both of the CL and of the total concentration of the complex, as well as a small enhancement of the CL intensity. The low solubility of these salts in AN precluded the use of higher concentrations.

### *(4) Reduction of Ru(bipyr)$_3^{3+}$ in Acidic Aqueous Solution*

#### *(a) Solvent only*

Solutions $3.35 \times 10^{-5}$ M in $Ru(bipyr)_3^{3+}$ and 0.08 M in $HClO_4$ showed an initial CL intensity of 2500 cps and a total emission corresponding to about $7 \times 10^{-7}$ einstein per mole of complex reduced. The emission efficiency from the thexi state $[Ru(bipyr)_3^{2+}]^*$ is 0.042 [28, 29], and we found this to be reduced to 0.024 due to the presence of dissolved air. With this correction, the efficiency with which solvent reduction of $Ru(bipyr)_3^{3+}$ produces excited states is $\eta_{CE} = 2.9 \times 10^{-5}$.

The reaction was studied in some detail; it is biphasic and the many complexities present are the subject of a separate paper. We are concerned here primarily with a survey of CL behavior. One qualitative observation to be noted, however, is that, as in AN solution, brief exposure of a solution of $Ru(bipyr)_3^{3+}$ to room fluorescent lights increased the initial CL intensity several fold. This excess intensity decayed rapidly, and the eventual intensity *versus* time plot was essentially that to be expected had there been no exposure to light. Sutin [30] has reported a comparable finding.

#### *(b) Other reductants*

A variety of reductants were tested semi qualitatively, with results as summarized in Table I. A detailed study was made of the case of $Br^-$ as reductant, both of the kinetics of the analytical reaction and of that of the CL intensity. These results are to be reported elsewhere; very qualitatively, they resemble the case of $H_2O_2$ as reductant.

## Discussion

Chemiluminescent reactions involving coordination compounds may be categorized in various ways. The emitting species may be produced, for example, by (a) a one-electron reduction, (b) a one-electron oxidation, or (c) oxidative addition. Case (a) is the most common one at present, and appears to be the only one containing examples of strong CL, easily visible to the eye. The reason for such high potential efficiency may be that the intimate mechanism can be the very simple one of injection by the reductant of an electron into an unoccupied orbital of the complex. In case (b), the electron removed from the reactant complex cannot be from the HOMO since this would lead to a ground-state product. Either a lower-lying electron is lost, or some concerted rearrangement in electronic configuration occurs. Cr(II) complexes may be an exception since the emitting state of the Cr(III) product has the ground-state orbital population except for spin pairing [31]. Category (c) reactions may prove to be very interesting, but have been little studied. Nor has there been much variation in the type of ligand system tested. Our results and the ECL reported for $Mo_6Cl_{14}^{n-}$ complexes appear to be the first for complexes not having an aromatic nitrogen-to-metal bond.

The cases of reaction (1) and of the previously reported reaction

$$Cr(bipyr)_3^{2+} + Ru(bipyr)_3^{3+} \longrightarrow \left\{\begin{array}{l} [Cr(bipyr)_3^{3+}]^* \\ Cr(bipyr)_3^{3+} \end{array}\right\} + Ru(bipyr)_3^{2+} \qquad \begin{array}{r} (2^*) \\ (2) \end{array}$$

suggest the rule that if both products can show photoexcited emission, the observed CL will be from the one with the lower-lying excited state. Note that for both reactions (1) and (2) the emitting state seemingly is produced by a category (b) reaction, that is, by a one-electron oxidation. This has so far appeared to be a less efficient process than a category (a) reaction, however, judging from the rarity of its observation. An unresolved question is whether the emitting state is indeed directly produced or whether in cases such as the above, $[Ru(bipyr)_3^{2+}]^*$ is the direct product, but then undergoes geminal pair energy transfer to give the observed excited state process. A corresponding question arises in the case of ECL reaction of the type

$$M^{n-1} + M^{n+1} = [M^n]^* + M^n \qquad (3)$$

where $M^{n-1}$ and $M^{n+1}$ have been produced electrochemically. That is, does the elementary reaction place the excitation on the originally reduced or on the originally oxidized form of the complex?

Another type of categorization is into complementary *versus* non-complementary reactions. In the former case, both redox couples are one-electron in type, and the elementary and stoichiometry reactions may be the same. That is, the process may be one of electron transfer with no mechanistic complexities. Reactions (1) and (2), the reaction of $Ru(bipyr)_3^{+}$ with Cu(II), and the reactions of $Ru(bipyr)_3^{3+}$ with one-electron reductants all appear to be complementary reactions and all are fast. By contrast, reactions involving a two-electron oxidant or reductant are often slow, and the CL probably stems from the reaction of the starting complex with some intermediate. The solvent oxidations of $Mo_6Cl_{14}^{3-}$ and of $Ru(bipyr)_3^{+}$, the solvent reduction of $Mo_6Cl_{14}^{-}$ and most of the reductions of Table I belong to this class. Furthermore, in such cases, the overall free energy change may not be sufficient to make production of an excited state product appear to be possible energetically, yet CL is observed. This difficulty can, in principle, be circumvented if high-energy intermediates are present. Also, it seems typical of non-complementary reactions that the CL yield is small. A corollary is that the kinetics of the CL process may be different from that of the analytical reaction – there are several evidences of this in the observation of Table I. Note the cases of $Na_2SO_3$, $H_2O_2$ and $Br^-$ as reductants, for which the half-life of the CL decay is about half of that for the analytical reaction. With $SnCl_2$, EDTA and $NaN_3$, the initial decay of the CL was concordant with the analytical reaction, but at longer times the CL intensity decayed progressively more and more slowly.

Even complementary reactions may prove to be complicated mechanistically with respect to the CL step. Thus $E^\circ$ for reaction (2) is 1.52 V, and is *ca.* −0.6 V to give excited state product, reaction (2*). Chemiluminescent reactions are not studied under standard state conditions, of course, and the $\Delta H$ of the reaction may be more relevant in determining whether there is sufficient energy available to produce an excited state when electron transfer occurs within the encounter complex of the two reactants. If $\Delta H$ for reaction (2*) is as unfavorable as is the $E^\circ$, the actual reaction mechanism for CL may not be the same as that for the analytical reaction. There may, for example, be some change in the bipyridine ligands. The answer to this type of question will require some study.

The cases of enhanced CL following exposure to room fluorescent lights (or to conventional photochemical arc lamps) may be due to photoproduction of $[Mo_6Cl_{14}^{2-}]^*$ or $[Ru(bipyr)_3^{2+}]^*$, which then reacts with solution constituents to produce reactive intermediates. Photoproduction of $Ru(bipyr)_3^{3+}$ occurs, for example, on irradiation of acidic aqueous $Ru(bipyr)_2^{2+}$ [32].

The present study serves to illustrate both the scope and some of the complexities of CL reactions. Some of the questions raised above are under study in our laboratory.

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