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Electrochemistry and Electrogenerated Chemiluminescence of $Mo_2Cl_4(PMe_3)_4$

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The electrochemical behavior and electrogenerated chemiluminescence (ecl) of $Mo_2Cl_4(PMe_3)_4$ in tetrahydrofuran and acetonitrile solutions have been investigated. Oxidation to the +1 cation and reduction to the −1 anion occur in quasi-reversible and reversible cyclic voltammetric waves, respectively. The oxidation product undergoes a subsequent chemical reaction, while the reduction product is stable. Emission is produced by the electron-transfer reaction between the +1 and −1 species; this emission is characteristic of $^1(\delta\delta^*)$ $Mo_2Cl_4(PMe_3)_4$ with emission λ_{max} 680 nm. The ecl efficiency (photons produced per electron consumed) is 0.002. Electrogenerated chemiluminescence has been observed in acetonitrile solution by the reaction of electrogenerated $Mo_2Cl_4(PMe_3)_4^-$ with the strongly oxidizing intermediate, SO_4^-, generated by reduction of $S_2O_8^{2-}$.

Introduction

A number of electrogenerated chemiluminescence (ecl) reactions involving electron-transfer reactions between oxidized and reduced forms of a parent species (e.g., the radical cation and radical anion) have been investigated.[1] These include a number of studies of inorganic species such as $Ru(bpy)_3^{2+}$,[2] $Os(bpy)_3^{2+}$,[3] and related compounds.[4] Recently Nocera and Gray[5] described the ecl of $Mo_6Cl_{14}^{2-}$ produced by alternate oxidation and reduction at a Pt electrode in MeCN solution. Although the photoluminescence efficiency was quite high ($\phi_{em} = 0.19$), the measured ecl efficiency (photons emitted/electrons transferred), ϕ_{ecl}, was very low ($\leq 10^{-5}$). An alternative approach to the generation of ecl that avoids cycling of the electrode to regions where oxidation and reduction of the parent complex occur involves the use of a species (e.g., $S_2O_8^{2-}$ or $C_2O_4^{2-}$) that undergoes an irreversible decomposition reaction upon oxidation or reduction to generate a strongly oxidizing or reducing reactant capable of participating in an ecl reaction sequence.[6-8] For example, reduction of a mixture of $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$ results in emission from $Ru(bpy)_3^{2+*}$, because the SO_4^- species formed is a strong oxidant that can participate in the ecl reaction sequence.

In this paper we report the electrochemistry and ecl from the quadruply bonded $Mo_2Cl_4(PMe_3)_4$ complex.[9] A recent study of the spectroscopic and photophysical properties of this species demonstrated a high emission quantum yield upon photoexcitation (0.26) and a long lifetime of the $^1(\delta\delta^*)$ excited state (140 ns),[10] thereby suggesting a study of the electrochemistry and ecl of this compound. Here we discuss ecl resulting both from the anion–cation electron-transfer reaction as well as that from coreduction of $Mo_2Cl_4(PMe_3)_4$ and $S_2O_8^{2-}$.

Experimental Section

Materials. $Mo_2Cl_4(PMe_3)_4$ was synthesized as reported previously.[11] Reagent grade tetrahydrofuran (THF, MCB Manufacturing Chemists, Inc.) was purified and dried by distillation from potassium metal and benzophenone under dry nitrogen, collecting the center fraction. The solvent was then degassed under vacuum by three freeze–pump–thaw cycles. Fisher Scientific acetonitrile (MeCN, Certified ACS) was dried and degassed by three transfers from dry P_2O_5 under vacuum. Tetrabutylammonium fluoroborate ($TBABF_4$, electrometric grade), purchased from Southwestern Analytical Chemical Co., was recrystallized three times from ethyl acetate and then dried under vacuum at 85–100 °C for 24 h.

Apparatus. Electrochemical measurements were carried out in the controlled potential mode by using a Princeton Applied Research (PAR) Model 173 potentiostat and Model 175 programmer. The output of the PAR Model 179 digital coulometer

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TABLE I: Cyclic Voltammetry Results for $Mo_2Cl_4(PMe_3)_4$[a]

scan rate, v, mV/s	reduction			oxidation		
	$i_p/v^{1/2}C$	i_{pa}/i_{pc}	ΔE_p, mV	$i_p/v^{1/2}C$	i_{pc}/i_{pa}	ΔE_p, mV
20	0.60	0.93	100	0.79		
50	0.58	0.96	120	0.65	0.57	110
100	0.51	0.97	130	0.60	0.74	120
200	0.53	0.95	130	0.60	0.83	120
500	0.52	0.95	150	0.57	0.91	150
1000	0.49	0.93	190	0.55	0.93	170

[a] The solution was 1.62 mM $Mo_2Cl_4(PMe_3)_4$ and 0.5 M $TBABF_4$ in THF at 25 °C. i_{pc} = peak cathodic current (μA); i_{pa} = peak anodic current (μA). ΔE_p is peak potentials separation. C is the concentration of $Mo_2Cl_4(PMe_3)_4$ (mM).

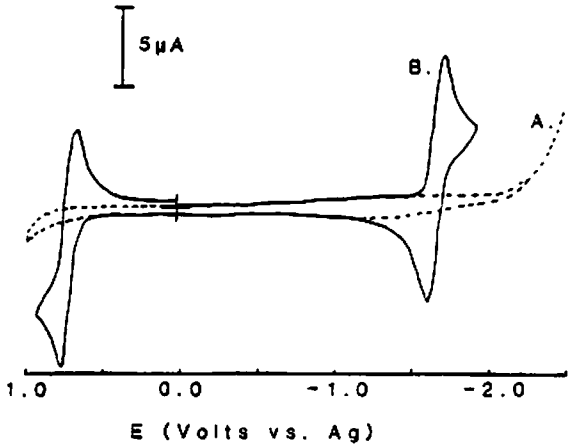

Figure 1. (a) Cyclic voltammogram of 0.5 M $TBABF_4$ in THF, scan rate = 100 mV/s; (b) cyclic voltammogram of 2 mM $Mo_2Cl_4(PMe_3)_4$, 0.5 M $TBABF_4$ in THF solution, scan rate = 100 mV/s.

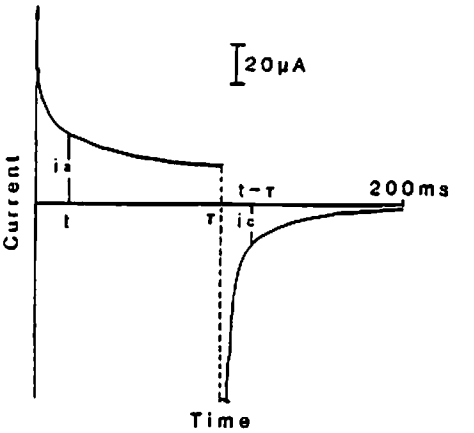

Figure 2. Chronoamperometry of $Mo_2Cl_4(PMe_3)_4$ (2 mM), 0.5 M $TBABF_4$ in THF solution, τ = 100 ms. Potential step from 0 to 0.75 V and then back to 0.0 V.

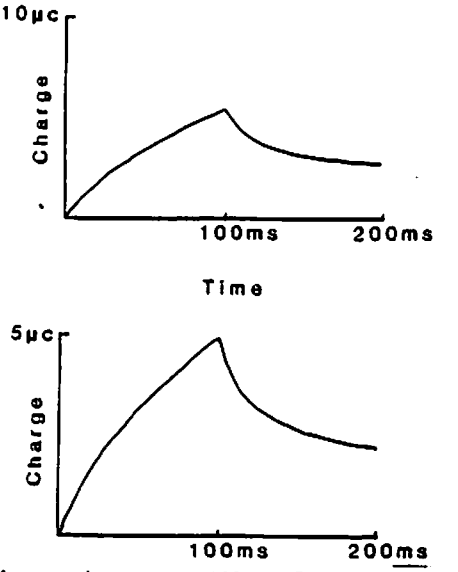

Figure 3. Chronocoulometry, τ = 100 ms. Same solution as in Figure 2. (a) Potential step from 500 to 800 mV. (b) Potential step from −1.55 to −1.90 V.

was either recorded directly with a Houston Instrument Model 2000 X-Y recorder or monitored and subsequently recorded with a Nicolet Model 1090 A digital oscilloscope. The three-electrode cell employed a Pt disk working electrode (area, 0.03 cm^2), a Pt wire auxiliary electrode, and a Ag wire quasi-reference electrode. Solutions were prepared by transferring 2–3 mL of the solvent under vacuum into the one-compartment cell (at liquid nitrogen temperature) containing predried supporting electrolyte and transition-metal complex.

Ecl spectra were taken by using an Aminco-Bowman spectrophotofluorometer (SPF) in conjunction with a Hamamatsu TVR 928 photomultiplier tube. An integrating sphere was used for the determination of ecl efficiencies. The intensity of emission was determined relative to $Ru(bpy)_3^{2+}$, the ecl efficiency of which has been determined in several studies.[2]

Results and Discussion

Electrochemical Measurements. The cyclic voltammogram of $Mo_2Cl_4(PMe_3)_4$ in THF solution containing 0.5 M $TBABF_4$ is shown in Figure 1. At a polished Pt disk electrode at a scan rate (v) of 100 mV/s, reversible waves corresponding to the oxidation and reduction of $Mo_2Cl_4(PMe_3)_4$ were observed at 0.60 and −1.78 V vs. the Ag wire quasi-reference electrode (Ag qre).[12] The potential of the qre was determined vs. the Cp_2Fe^+/Cp_2Fe couple (Cp_2Fe is ferrocene), which showed a reversible wave at 0.40 V vs. Ag qre in the same solution. The peak potential separation (ΔE_p) values for both waves were about 120 mV. This is mainly due to the uncompensated iR-drop in this resistive solution, since the ΔE_p value for the Cp_2Fe^+/Cp_2Fe wave was also 120 mV.

Cyclic voltammetric (CV) data for both oxidation and reduction waves are contained in Table I. The cyclic voltammetric peak current ratios of the anodic (i_{pa}) and cathodic (i_{pc}) waves provide information about the stability of the electrogenerated products. For the reduction wave, the values of i_{pa}/i_{pc} are all close to unity and are independent of scan rate (v), showing that the reduction product is stable on these time scales. The values of i_{pc}/i_{pa} for the oxidation wave are less than unity at scan rates below 200 mV/s and decrease with a decrease in v. This suggests that there is a chemical reaction following the oxidation of $Mo_2Cl_4(PMe_3)_4$, producing a substance that is neither oxidizable nor reducible at these potentials.[13] The $i_p/v^{1/2}C$ values for both oxidation and

(12) A report of the oxidation and reduction potentials of $Mo_2Cl_4(PMe_3)_4$ under similar conditions appeared following the completion of this work (Coffindaffer, T. W.; Niccolai, G. P.; Powell, D.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 3572). The reported $E_{1/2}(ox)$ = 0.65 V and $E_{1/2}(red)$ = −1.82 V (vs. Ag/AgCl) are in good agreement with the values we have found.

(13) Previous work has shown that one-electron-oxidized derivatives of $Mo_2Cl_4(PR_3)_4$ can be cleanly generated by bulk electrolysis of CH_2Cl_2 solutions at 0 °C; attempts to oxidize these species at room temperature resulted in decomposition of the molybdenum dimer, which is consistent with our findings: Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

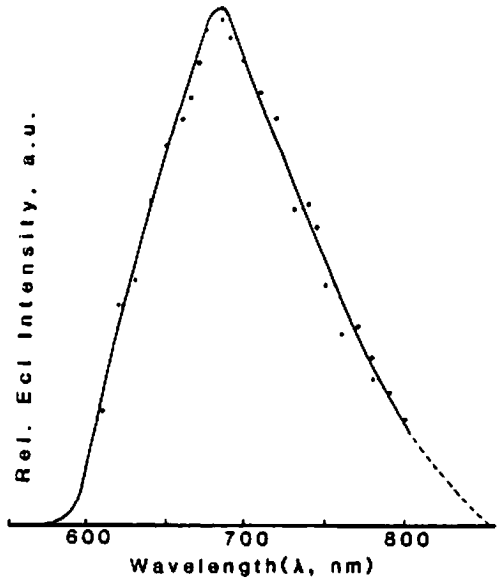

Figure 4. Spectrum (ecl) of $Mo_2Cl_4(PMe_3)_4$ in THF solution.

reduction waves of $Mo_2Cl_4(PMe_3)_4$ are the same and essentially equal to that of Cp_2Fe, suggesting they are both one-electron processes.

To study the oxidation reaction more quantitatively, a double-potential step experiment was carried out. Figures 2 and 3 are the chronoamperometric and chronocoulometric responses of $Mo_2Cl_4(PMe_3)_4$ in THF solution for the potential stepped from 0.0 to 0.74 V and then back to 0.0 V with a forward step duration of 100 ms. From the values of i_{pc}/i_{pa} and Q_c/Q_a (where Q is charge) at different times, the rate constant for disappearance of the oxidized species is about 4.0 s^{-1}.[14,15] From the slope of the plot of Q vs. $t^{1/2}$, the diffusion coefficient (D) of $Mo_2Cl_4(PMe_3)_4$ in THF was determined to be 2.4×10^{-6} cm^2/s, about the same as that estimated from the CV $i_p/v^{1/2}C$ value, 3.0×10^{-6} cm^2/s.

Electrogenerated Chemiluminescence. The ecl spectrum of $Mo_2Cl_4(PMe_3)_4$ in THF/$TBABF_4$ solution was obtained by pulsing the potential of the Pt electrode between −1.95 and 0.7 V vs. Ag qre. As shown in Figure 4, the ecl spectrum of $Mo_2Cl_4(PMe_3)_4$ shows an emission maximum at 680 nm; this is identical with that obtained on photoexcitation.[10] As is usual in ecl reactions, the emission results from the electron-transfer reaction between $Mo_2Cl_4(PMe_3)_4^-$ and $Mo_2Cl_4(PMe_3)_4^+$, i.e.,

$$Mo_2Cl_4(PMe_3)_4 + e \rightleftharpoons Mo_2Cl_4(PMe_3)_4^- \quad (1)$$

$$Mo_2Cl_4(PMe_3)_4 - e \rightleftharpoons Mo_2Cl_4(PMe_3)_4^+ \quad (2)$$

$$Mo_2Cl_4(PMe_3)_4^- + Mo_2Cl_4(PMe_3)_4^+ \rightarrow Mo_2Cl_4(PMe_3)_4^* + Mo_2Cl_4(PMe_3)_4 \quad (3)$$

$$Mo_2Cl_4(PMe_3)_4^* \rightarrow Mo_2Cl_4(PMe_3)_4 + h\nu \quad (4)$$

The redox reaction to the ground state has a ΔH° of about 2.28 eV as calculated from the E_p values of the 0/−1 and +1/0 waves, with the assumption of an entropic contribution of ca. 0.1 eV. This is greater than the energy of the emissive $^1(\delta\delta^*)$ state, (2.01 eV, $E_{0\text{-}0}$).[10] The electrochemical processes can be described in terms of the molecular orbital diagram for the system. A quadruple metal–metal bond possesses a $(\sigma^2\pi^4\delta^2)$ electronic configuration with a δ^* LUMO.[16] Oxidation and reduction of such a system involves removing an electron from the δ level and adding an electron to δ^*, respectively. Annihilation of the $Mo_2Cl_4(PMe_3)_4^{+/-}$ species results in formation of the excited $^1(\delta\delta^*)$ state.

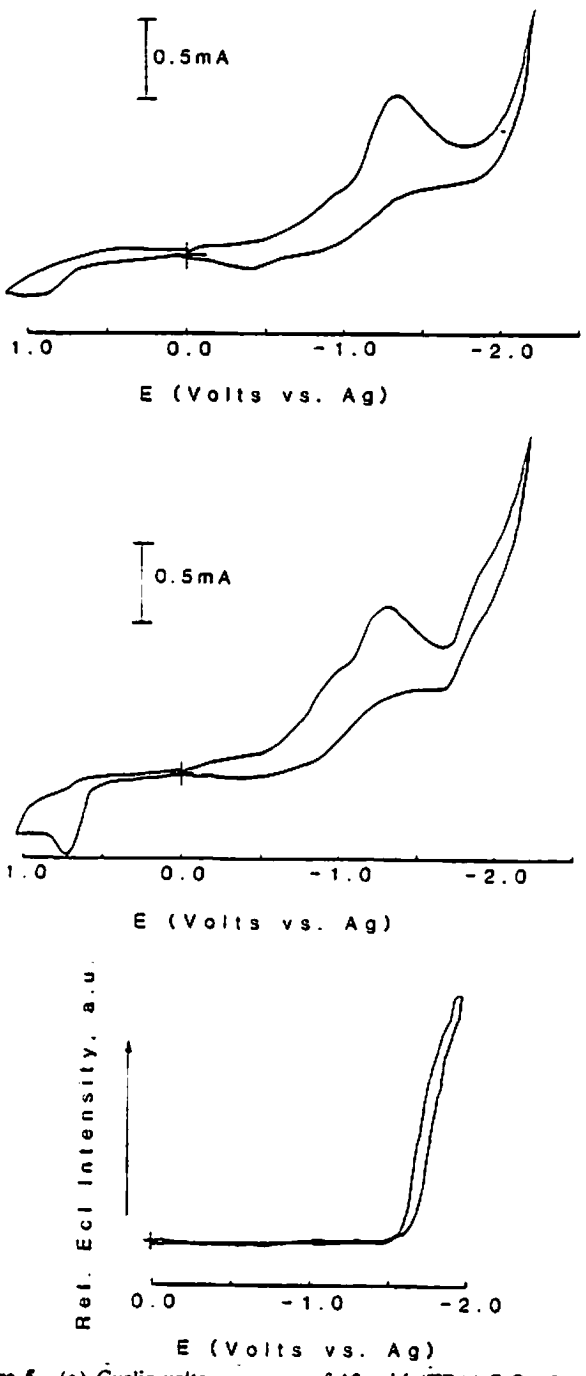

Figure 5. (a) Cyclic voltammogram of 10 mM $(TBA)_2S_2O_8$, 0.1 M $TBABF_4$ in MeCN. Scan rate = 200 mV/s. (b) Cyclic voltammogram of 2 mM $Mo_2Cl_4(PMe_3)_4$, 10 mM $(TBA)_2S_2O_8$, 0.1 M $TBABF_4$ in MeCN. Scan rate = 200 mV/s. (c) Ecl intensity as a function of applied potential for 2 mM $Mo_2Cl_4(PMe_3)_4$, 10 mM $(TBA)_2S_2O_8$, 0.1 M $TBABF_4$ in MeCN, 200 mV/s.

The ecl coulombic efficiency, ϕ_{ecl}, is defined as

$$\phi_{ecl} = \int_0^{t'} I\,dt/Q$$

in which the total ecl intensity, I (Einstein/s), integrated over a finite period of time, t', is divided by the integrated cathodic or anodic current (Faraday/s), which is the total cathodic or anodic charge. This coulombic efficiency is close to the number of photons produced per electron-transfer annihilation event. In this work, $Ru(bpy)_3^{2+}$ in MeCN solution was used as a relative standard to determine the ecl quantum yield of $Mo_2Cl_4(PMe_3)_4$, since $Mo_2Cl_4(PMe_3)_4$ did not show sufficient intensity to make a direct measurement of ecl efficiency. In this case, the relative ecl intensity was measured as the integrated photomultiplier tube re-

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(15) Christie, J. H. *Electroanal. Chem.* 1967, *13*, 79.
(16) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

sponse, J, which is proportional to $\int_0^r I\,dt$. The value of ϕ_{ecl} for $Mo_2Cl_4(PMe_3)_4$ was then obtained from the relation

$$\phi_{ecl} = \phi_{ecl}^{\circ}(JQ^{\circ}/J^{\circ}Q)$$

where ϕ_{ecl}° is the ecl efficiency of $Ru(bpy)_3^{2+}$ (1 mM and 0.1 M $TBABF_4$/MeCN), taken as 0.05.[2] J and J° are photomultiplier tube responses, and Q and Q° are the charges during the pulses for $Mo_2Cl_4(PMe_3)_4$ and $Ru(bpy)_3^{2+}$, respectively. The ecl efficiency of $Mo_2Cl_4(PMe_3)_4$ was found to be about 0.002 for a pulse width of 20 ms.

Compared to the photoluminescence efficiency (0.13),[17] the ecl efficiency of $Mo_2Cl_4(PMe_3)_4$ is very low. One reason for this low value may be the instability of the oxidation product. The emission signal was much larger when the potential was stepped in a negative direction ($Mo_2Cl_4(PMe_3)_4^-$ production) first, with a much smaller ecl signal obtained when the voltage was stepped first in the positive direction ($Mo_2Cl_4(PMe_3)_4^+$ production).

$Mo_2Cl_4(PMe_3)_4$–$S_2O_8^{2-}$ System. A cyclic voltammogram of a 10 mM $(TBA)_2S_2O_8$ 0.1 M $TBABF_4$/MeCN solution is shown in Figure 5a. At a Pt electrode reduction of $S_2O_8^{2-}$ occurs in a drawn-out wave with a peak at about −1.3 V vs. Ag qre. When $Mo_2Cl_4(PMe_3)_4$ (equivalent to 2 mM) was added to the $S_2O_8^{2-}$ solution, the waveshape of $Mo_2Cl_4(PMe_3)_4$ displayed in Figure 5b was very different from that displayed in Figure 1. The reduction wave of $Mo_2Cl_4(PMe_3)_4$ at −1.7 V exhibited only a small reversal peak in the presence of $S_2O_8^{2-}$, and the reduction potential was shifted to a more negative value near the solvent limit. The oxidation wave of $Mo_2Cl_4(PMe_3)_4$ became irreversible in the presence of $S_2O_8^{2-}$, probably because of film formation on the electrode surface. Such film formation has also been described in other $S_2O_8^{2-}$ systems.[8]

Electrogenerated chemiluminescence was observed with this solution upon electrochemical reduction of $Mo_2Cl_4(PMe_3)_4$ in the presence of $S_2O_8^{2-}$. The ecl spectrum was the same as the photoluminescence spectrum and the ecl spectrum of $Mo_2Cl_4(PMe_3)_4$ obtained by potential pulsing between −1.95 and 0.70 V in the absence of $S_2O_8^{2-}$. Studies of ecl intensity as a function of applied potential demonstrated that ecl is initiated by the electrochemical reduction of $Mo_2Cl_4(PMe_3)_4$. Luminescence was not observed at potentials where $S_2O_8^{2-}$, but not $Mo_2Cl_4(PMe_3)_4$, was reduced (Figure 5c). The ecl intensity increased as the reduction current of $Mo_2Cl_4(PMe_3)_4$ increased. This suggests that the ecl mechanism is associated with the electroreduction of $Mo_2Cl_4(PMe_3)_4$ and follows the basic mechanism proposed in previous studies.[7]

$$Mo_2Cl_4(PMe_3)_4 + e \rightarrow Mo_2Cl_4(PMe_3)_4^-$$

$$Mo_2Cl_4(PMe_3)_4^- + S_2O_8^{2-} \rightarrow Mo_2Cl_4(PMe_3)_4 + S_2O_8^{\cdot 3-}$$

$$S_2O_8^{\cdot 3-} \rightarrow SO_4^{\cdot -} + SO_4^{2-}$$

$$Mo_2Cl_4(PMe_3)_4^- + SO_4^{\cdot -} \rightarrow Mo_2Cl_4(PMe_3)_4^* + SO_4^{2-}$$

$$Mo_2Cl_4(PMe_3)_4 + SO_4^{\cdot -} \rightarrow Mo_2Cl_4(PMe_3)_4^+ + SO_4^{2-}$$

The ecl intensity–time profile in the presence of $S_2O_8^{2-}$ for a Pt electrode pulsed repetitively between −0.5 and −2.0 V at 10-ms intervals is given in Figure 6a. The ecl intensity at Pt was constant for at least 1 h, followed by a slow decay. This decay of the ecl signal was probably due to a depletion of reactants (e.g., $S_2O_8^{2-}$ or $Mo_2Cl_4(PMe_3)_4$).

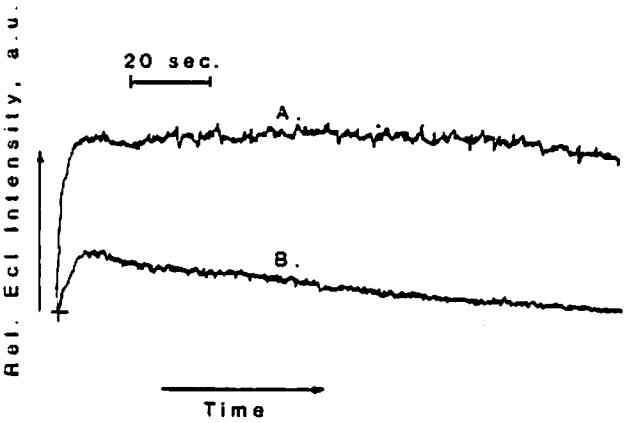

Figure 6. (a) Ecl intensity–time profile of 2 mM $Mo_2Cl_4(PMe_3)_4$, 10 mM $(TBA)_2S_2O_8$ in MeCN. Pulse potential: −0.5 to −2.0 V vs. Ag. Pulse interval = 10 ms. (b) Ecl intensity–time profile in 2 mM $Mo_2Cl_4(PMe_3)_4$, 10 mM $(NH_4)_2C_2O_4$ in MeCN. Pulse potential: 0.0–0.7 V vs. Ag. Pulse interval = 10 ms. Note: the intensity scale in A is at least 100 times larger than that in B.

Unlike $S_2O_8^{2-}$ systems, when $C_2O_4^{2-}$ was added to a $Mo_2Cl_4(PMe_3)_4$ solution, the ecl intensity was much weaker on a Pt electrode pulsed repetitively between 0.0 and 0.7 V at which $Mo_2Cl_4(PMe_3)_4$ was oxidized. The ecl intensity–time profile (Figure 6b) showed a rapid decay of the ecl signal. This confirms the instability of $Mo_2Cl_4(PMe_3)_4^+$, since $Mo_2Cl_4(PMe_3)_4^+$ is involved in the ecl mechanism in $C_2O_4^{2-}$ systems.

Conclusions

Electrochemical measurements show reversible one-electron oxidation and reduction reactions of $Mo_2Cl_4(PMe_3)_4$. The product of reduction is stable, but there is a chemical reaction following oxidation of the dimer. Ecl has been observed at a Pt electrode potential pulsed between −1.95 and 0.70 V. The ecl spectrum shows a peak at 680 nm with an ecl efficiency of 0.002. A more intense ecl emission can be obtained by the addition of $S_2O_8^{2-}$ into $Mo_2Cl_4(PMe_3)_4$ when the potential is pulsed between −0.5 and −2.0 V.

Acknowledgment. We thank Chi-Woo Lee for assistance with the preliminary cyclic voltammetry experiments. Graduate fellowships from the Sun Co. (T.C.Z. and M.D.H.) and the Standard Oil Co. (Ohio) (M.D.H.) are acknowledged. The support of this research by the Army Research Office (A.J.B.) and National Science Foundation (CHE84-19828) (H.B.G.) is gratefully acknowledged. This is paper no. 47 in the series Electrogenerated Chemiluminescence (A.J.B).

Registry No. $Mo_2Cl_4(PMe_3)_4$, 67619-17-4; $Mo_2Cl_4(PMe_3)_4^+$, 102682-49-5; $Mo_2Cl_4(PMe_3)_4^-$, 102682-50-8; $S_2O_8^{2-}$, 15092-81-6; $SO_4^{\cdot -}$, 12143-45-2; Mo, 7439-98-7.

(17) Emission quantum yield in THF solution: Zietlow, T. C., unpublished results. ϕ_{em} in 2-methylpentane solution[10] is even greater (0.26).