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Electrogenerated Chemiluminescence. 30. Electrochemical Oxidation of Oxalate Ion in the Presence of Luminescers in Acetonitrile Solutions

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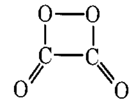
Abstract: The electrochemical oxidation of oxalate at a platinum electrode in acetonitrile solutions as studied by cyclic and rotating-ring disk voltammetry and controlled potential coulometry shows an irreversible two-electron oxidation at ca. 0.3 V vs. SCE to CO_2 with no intermediates detectable by these techniques. The oxidation of oxalate in the presence of several fluorescers (such as rubrene, 9,10-diphenylanthracene, and the bipyridyl chelates of ruthenium(II) and osmium(II)) does not produce light, but emission characteristic of the fluorescer occurs during the simultaneous oxidation of the additive and oxalate. Studies of the conditions for emission in the presence of thianthrene and naphthalene lead to a mechanism for the oxidation of oxalate and the excitation process based on oxidation of oxalate to $C_2O_4^{-}\cdot$, which undergoes rapid decomposition to CO_2 and $CO_2^{-}\cdot$. The $CO_2^{-}\cdot$ can transfer an electron to the additive molecule to produce a radical anion, which can then undergo an ecl annihilation reaction with the electrogenerated radical cation.

There has been much interest in the intense chemiluminescence which results from the reaction of oxalyl chloride or oxalate esters and hydrogen peroxide in the presence of fluorescent compounds in nonaqueous solvents.[1-3] In the proposed mechanism for these processes, the reaction between the oxalate ester and H_2O_2 produces the dioxetanedione (**1**) as an intermediate. This forms a complex with the fluorescer which decomposes to two molecules of CO_2 and the fluorescer in the excited state. Attempts at isolating and observing this intermediate have generally not been successful. Thus, Heller et al.[4] identified the dioxetanedione in the mass spectrum of the products of the reaction of an oxalate ester and H_2O_2. However, the studies of DeCorpo et al.[5] on the relative concentrations of the positive ions of C_2O_4 and CO_2 as a function of ion residence time suggest that the $C_2O_4^+$ was not formed in the chemiluminescent reaction. Indeed in a recent review Hastings and Wilson[6] state: "In the reaction of oxalic esters, the mythical intermediate dioxetanedione remains as seductive and elusive as ever. The chemiluminescence community should offer a reward for its capture." In an attempt to find this intermediate we studied the electrochemical oxidation of oxalate ion, $C_2O_4^{2-}$, in acetonitrile (ACN).



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The electrochemical oxidation of oxalate in aqueous solutions leads to CO_2; the mechanism of this reaction has not been established. The only previous study of the oxidation of oxalate in an aprotic solvent was that of Jacobsen and Sawyer.[7] These authors studied the oxidation at a gold electrode in dimethyl sulfoxide solutions. They found an overall oxidation to CO_2 and proposed that an unstable intermediate was formed during the oxidation. However, the low solubility of the oxalate salts (Na^+, Li^+, NH_4^+, tetraethylammonium) and the difficulty of excluding water from the solutions led to experimental problems and prevented the establishment of the reaction mechanism. We report here a study of the oxidation of oxalate in ACN in the presence of several fluorescers. While no evidence of the dioxetanedione as an intermediate was found in these studies, a new chemiluminescent reaction was discovered when oxalate and a fluorescent compound were oxidized at the same time at a platinum electrode. The nature of this reaction was investigated. The results provide some insight into the mechanism of oxalate oxidation at an electrode and demonstrate the interesting phenomenon of the production of a strong reductant upon oxidation.

Experimental Section

The apparatus and general techniques in the ecl and electrochemical measurements have been reported previously.[8] The simple three-electrode ecl cell incorporating a silver pseudo-reference electrode was employed for ecl measurements[9] and a three-compartment coulometry cell for electrochemical measurements.[10] The rotating ring-disk electrode (RRDE) and associated apparatus have also been described.[11,12] Tetra-*n*-butylammonium oxalate (TBAOX) was prepared by mixing oxalic acid (Baker Analyzed) and tetra-*n*-butylammonium hydroxide (Southwestern Analytical Chemicals, Inc.) in a mole ratio of 1:2 followed by evaporation and drying in a rotary evaporator. The CO_2 gas (Big Three Industries, Inc.) was used as

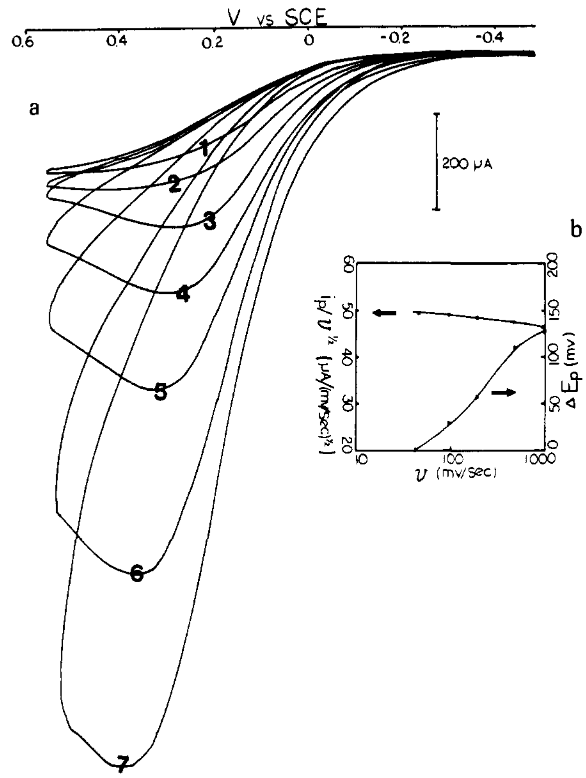


Figure 1. Cyclic voltammograms for the oxidation of 4.0 mM TBAOX in 0.1 M TBAP-ACN at scan rates of (1) 10; (2) 20; (3) 50; (4) 100; (5) 200; (6) 500; (7) 1000 mV s^{-1}.

received. Solvents were purified and solutions prepared on a vacuum line and experiments were carried out in an inert atmosphere (He) glove box (Vacuum Atmospheres, Inc. Hawthorne, Calif.).

Results

Electrochemical Studies. Cyclic voltammetric investigations of oxalate oxidation at a platinum electrode in ACN in solutions containing millimolar amounts of TBAOX and 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) show an irreversible oxidation peak at about 0.3 V vs. a saturated calomel electrode (SCE) (Figure 1). No cathodic reversal peak was observed for scan rates up to 10 V/s. The value of $i_p/v^{1/2}$ (where i_p is the peak current and v the scan rate) changed only slightly with v, and E_{pa}, the anodic peak potential, shifted to more positive potentials with increasing scan rate (about 75 mV per tenfold change in v). Similarly, a rotating disk voltammogram showed a single oxidation wave with a limiting disk current proportional to concentration and $\omega^{1/2}$ (where ω is the angular rotation rate) for concentrations of 0.49-4.2 mM and rotation rates up to 4000 revolutions/min, following the Levich equation.[13] No ring current was observed when the disk of the RRDE was maintained at a potential on the limiting current plateau of the anodic wave and the ring held at more negative potentials, up to −2.0 V vs. sce, indicating that no electroactive intermediate or product generated at the disk is sufficiently long-lived to reach the ring electrode at these rotation rates. Controlled potential coulometric oxidation of 56.7-61.9 μmol of oxalate contained in 30 mL of 0.1 M TBAP-ACN at a platinum gauze electrode showed 1.97 ± 0.02 faradays passed per mole of oxalate (three trials). Bubbles were evolved at the working electrode surface during the coulometric oxidation and no new cyclic voltammetry peaks were observed at an indicator electrode immersed in the electrolysis solution either during or after the coulometric oxidation.

The electrochemical results suggest an overall two-electron oxidation of oxalate to form CO_2; the same reaction is observed in aqueous solutions. A possible sequence for the oxidation can be written as follows:

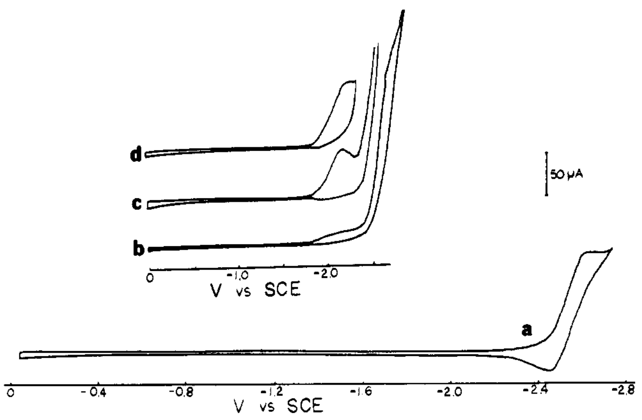


Figure 2. Cyclic voltammograms of solution containing 1.5 mM naphthalene in 0.1 M TBAP-ACN equilibrated with CO_2 gas at the following pressures (Torr): (a) 0; (b) 500; (c) 710; (d) 760.

$$C_2O_4^{2-} - e \rightarrow C_2O_4^{-}\cdot \quad (1)$$

$$C_2O_4^{-}\cdot \rightarrow CO_2 + CO_2^{-}\cdot \quad (2)$$

$$C_2O_4^{-}\cdot - e \rightarrow C_2O_4 \rightarrow 2CO_2 \quad (3)$$

$$CO_2^{-}\cdot - e \rightarrow CO_2 \quad (4)$$

The proposed intermediates $C_2O_4^{-}\cdot$, C_2O_4, and $CO_2^{-}\cdot$, if they exist, are too short-lived to be detected by the electrochemical methods at the time scales employed. The reduction of CO_2 in aprotic solvents has been reported previously,[14-18] with halfwave potentials of −2.795 V vs. $Ag/AgClO_4$ in *N,N*-dimethylformamide (DMF)[15] and −2.11 V vs. SCE in dimethyl sulfoxide[17] being reported. A study of CO_2 reduction in ACN suggested $CO_2^{-}\cdot$ as an intermediate, but no reduction potential was given.[18] When a solution of 0.1 M TBAP in ACN prepared and degassed on a vacuum line was saturated with CO_2 and the cyclic voltammetry examined at a platinum electrode, a cathodic peak at −2.2 V vs. SCE, showing no reversal peak, was observed (Figure 2). This peak occurs about 0.4 V before the reduction of naphthalene occurs in this solvent. The peak is observed following oxidation of oxalate, and was observed previously in studies in Me_2SO solutions.[7] No reversal peak is observed for $CO_2^{-}\cdot$ oxidation and all previous studies suggest that this species is very unstable and undergoes following reactions to produce oxalate, carbonate, and carbon monoxide.

Oxidation in the Presence of Fluorescent Compounds. To test if the dioxetanedione was an intermediate, the oxidation of oxalate was carried out in the presence of a number of fluorescent compounds and emission was sought. Although no emission was observed when only oxalate was oxidized, chemiluminescence resulted when both the additive and oxalate were oxidized for most of the compounds added. A typical experiment involves rubrene as an additive. A cyclic voltammogram for a solution containing 0.94 mM rubrene and 4.36 mM TBAOX in 0.1 M TBAP-ACN (Figure 3) shows the irreversible oxalate oxidation wave followed by that for the oxidation of rubrene to the radical cation ($R^{+}\cdot$) at 0.97 vs. SCE. This latter wave is reversible in ACN in the absence of oxalate; the lack of a reverse wave here indicates a rapid reaction of $R^{+}\cdot$ with oxalate or an intermediate. No emission was observed when the electrode potential was stepped or pulsed to potentials beyond the oxalate oxidation wave. However, when the potential was pulsed between 0 and 1.0 V vs. SCE, emission characteristic of rubrene fluorescence resulted (Figure 3b). The intensity of this emission was about an order of magnitude smaller than that observed for the radical ion annihilation ecl

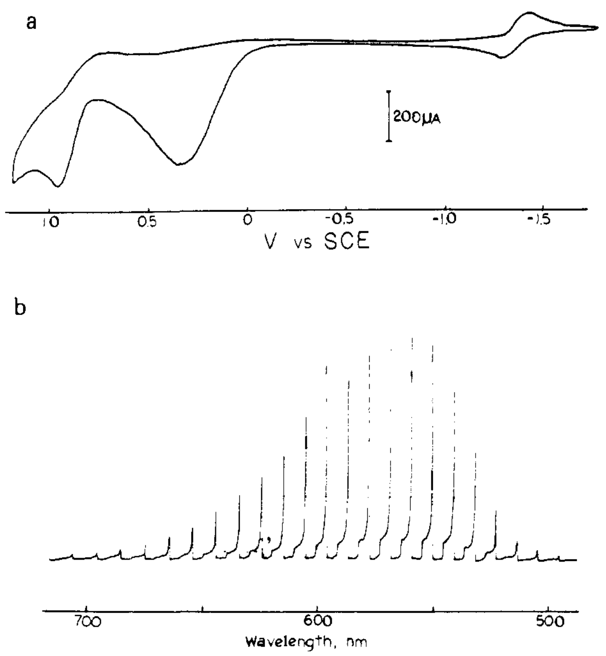


Figure 3. (a) Cyclic voltammogram of solution containing 0.94 mM rubrene and 4.36 mM TBAOX in 0.1 M TBAP-ACN; (b) ecl spectrum with 5-s pulses between 0 and 1.0 V vs. SCE.

Table I. Summary of Results of Experiments Involving Oxidation of Oxalate and Additives[a]

Solution components[b]	Solvent	Species oxidized	Ecl
Rubrene	DMF	Rubrene	Very weak
	ACN	Rubrene	No
Rubrene, oxalate	DMF	Oxalate	No
		Oxalate, rubrene	Yes
	ACN-BZ	Oxalate	No
		Oxalate, rubrene	Yes
DPA	ACN	DPA	No
DPA, oxalate		Oxalate	No
		Oxalate, DPA	Yes
TPP	DMF	TPP	No
TPP, oxalate	DMF	Oxalate	No
		Oxalate, TPP	Yes
TH, oxalate	ACN	TH, oxalate	No
TH, PPD, oxalate	ACN	Oxalate	No
		TH, oxalate	Yes
$Ru(bpy)_3(ClO_4)_2$, oxalate	ACN	Oxalate	No
		Oxalate, chelate	Yes
	H_2O	Oxalate, chelate	No
$Os(bpy)_3(ClO_4)_2$, oxalate	ACN	Oxalate	No
		Oxalate, chelate	Yes
TMTH, NAP, oxalate	ACN	Oxalate	No
		Oxalate, TMTH	No

[a] All solutions contained 0.1 M TBAP. Oxidations performed by pulsing Pt electrode from 0 V to potential where indicated reaction occurred. [b] Abbreviations: DPA, 9,10-diphenylanthracene; TPP, 1,3,6,8-tetraphenylpyrene; TH, thianthrene; TMTH, 1,4,6,9-tetramethylthianthrene; NAP, naphthalene; PPD, 2,5-diphenyl-1,3,4-oxadiazole.

reaction of rubrene observed by pulsing the electrode between 1.1 and −1.5 V under similar conditions in the absence of oxalate. When the annihilation reaction was carried out in the solution containing oxalate, the intensity of the ecl was lower and was about the same as that obtained by oxidizing oxalate and rubrene simultaneously. During annihilation ecl in the presence of oxalate, the emission peaks for the cathodic pulses were smaller than those of the corresponding anodic ones. Rubrene is known to produce emission simply on oxidation (so-called "preannihilation ecl") in certain solvents, such as DMF.[19] However, no emission was observed during the oxidation of rubrene in 0.1 M TBAP-ACN in the absence of oxalate. The behavior in a 1:1 benzene-ACN mixture containing 0.1 M TBAP, 1.0 mM TBAOX, and 1.3 mM rubrene was similar to that in ACN alone, i.e., no emission when only oxalate was oxidized and emission during simultaneous oxidation of oxalate and rubrene, with no observable preannihilation ecl of rubrene alone. Similar results were obtained with 9,10-diphenylanthracene (DPA), tetraphenylpyrene (TPP), and the tris(bipyridyl) complexes of ruthenium(II) and osmium(II) as additives in ACN (see Table I and Figure 4). In all cases the reversal peak for the oxidation of the additive disappeared upon addition of oxalate and emission characteristic of the additive appeared upon oxidation of additive and oxalate.

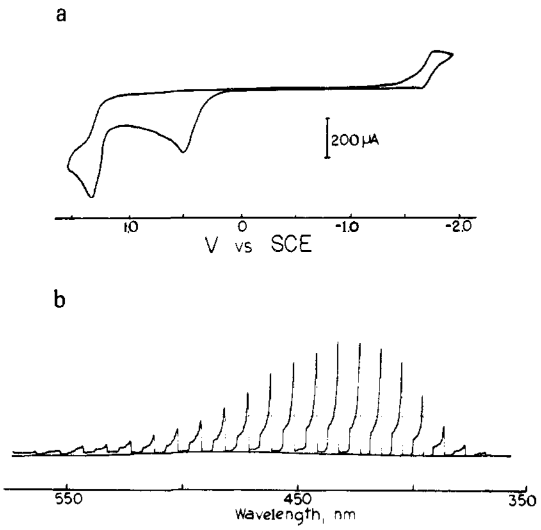


Figure 4. (a) Cyclic voltammogram of solution containing 1.0 mM DPA and 2.5 mM TBAOX in 0.1 M TBAP-ACN; (b) ecl spectrum with 5-s pulses between 0 and 1.4 V vs. SCE.

Thianthrene (TH) forms a stable radical cation upon oxidation in ACN at about 1.25 V vs. SCE, is not reducible up to at least −2.4 V, and fluoresces. However, a mixture of TBAOX and TH shows no emission during the simultaneous oxidation of both species. The annihilation ecl during reaction of TH$^{+\cdot}$ and the anion radical of 2,5-diphenyl-1,3,4-oxadiazole (PPD) formed at −2.17 V vs. SCE has been previously reported.[20] When a platinum electrode immersed in a solution containing 2 mM each TBAOX, TH, and PPD in 0.1 M TBAP-ACN is pulsed between 0 and 1.3 V, emission characteristic of TH fluorescence is observed (Figure 5). To test the ecl behavior in the presence of additives which reduce at potentials more negative than that for CO_2 reduction, systems containing naphthalene (NAP) were investigated. NAP is reduced to a stable radical anion at −2.66 V vs. SCE in ACN (Figure 2) and shows ecl emission during reaction with suitable electrogenerated radical cations.[21] Thus annihilation ecl is observed for a solution containing 1.2 mM NAP, 1.0 mM TMTH (1,4,6,9-tetramethylthianthrene), and 0.1 M TBAP in ACN when the potential is cycled between −2.7 (NAP$^{-\cdot}$ formation) and 1.3 V (TMTH$^{+\cdot}$ formation). Annihilation ecl is also observed in the presence of 1.0 mM oxalate. However, no emission is observed with this system by pulsing from 0 V to potentials where oxalate alone or both oxalate and TMTH are oxidized, even in the presence of NAP.

Intensity-Time Curves. The rate of growth and decay of the emission intensity during oxidation of oxalate and fluorescer differs markedly from that of the usual annihilation ecl. For

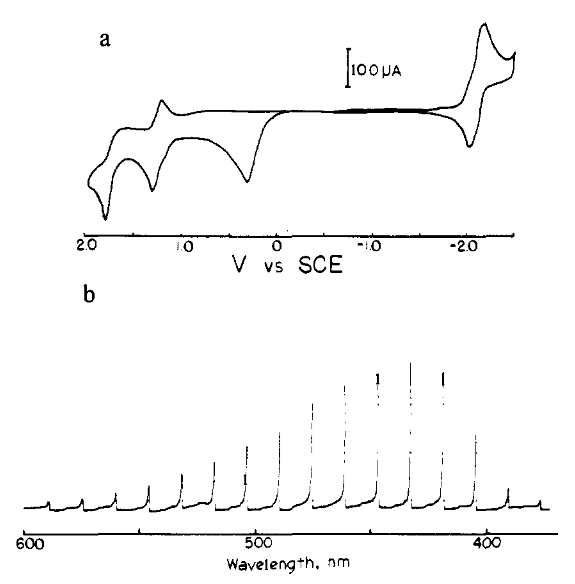


Figure 5. (a) Cyclic voltammogram of solution containing 2 mM each TH, PPD, and TBAOX in 0.1 M TBAP-ACN; (b) ecl spectrum with 5-s pulses between 0 and 1.3 V vs. SCE. No emission is observed under similar pulsing conditions in a solution lacking the PPD.

annihilation ecl the intensity rises upon pulsing in a time essentially determined by the time-constant characteristics of the potentiostat and cell, usually about 50 μs, and then decays in a generally exponential manner.[22,23] For 5-s pulses alternately producing $R^{-}\cdot$ and $R^{+}\cdot$ the intensity has decayed essentially to zero after about 2.5 s (Figure 6a). In the oxalate-additive oxidation ecl the rise time is much longer, typically of the order of 10-50 ms. Moreover, the intensity decays more slowly and reaches a fairly constant value, which is maintained to the end of the pulse (Figure 6b). When the potential is returned to zero the emission intensity then decays, at a measurable rate, to zero. The addition of oxalate also affects the annihilation intensity-time behavior. The ecl intensity is decreased, as noted before, the transient shape during $R^{+}\cdot$ generation is intermediate between the usual annihilation ecl and the oxalate oxidation behavior, and the intensity peak during the cathodic step ($R^{-}\cdot$ generation) is greatly decreased, signalling loss of $R^{+}\cdot$ in the vicinity of the electrode.

Discussion

The fact that ecl occurs only upon oxidation of both the additive (D) and oxalate and not with oxalate alone eliminates the production of a high energy intermediate, such as the dioxetanedione, as the source of luminescence. The production of light during the simultaneous oxidation of $C_2O_4^{2-}$ and such diverse substances as rubrene, DPA, and the ruthenium and osmium chelates eliminates some addition reaction (e.g., between the oxidized form of the additive and oxalate or an intermediate) followed by further oxidation and elimination of CO_2 to form an excited species as a plausible mechanism. Similarly, the lack of emission during the oxidation of thianthrene and oxalate in the absence of PPD, but formation of excited thianthrene in the presence of PPD, makes this addition-type mechanism unlikely, and also dictates against a mechanism involving direct reaction of D^{+} with an intermediate in the oxalate oxidation (e.g., $C_2O_4^{-}\cdot$) to form D*. Moreover, the added substance (A) must be capable of being reduced at potentials more positive than ca. −2.2 V vs. SCE for emission to be observed, as is illustrated by the experiments with TH alone and with PPD, and with naphthalene. A reasonable hypothesis is that an intermediate in the oxidation of oxalate is capable of reducing A to $A^{-}\cdot$ and that emission results from the annihilation reaction between $A^{-}\cdot$ and $D^{+}\cdot$.

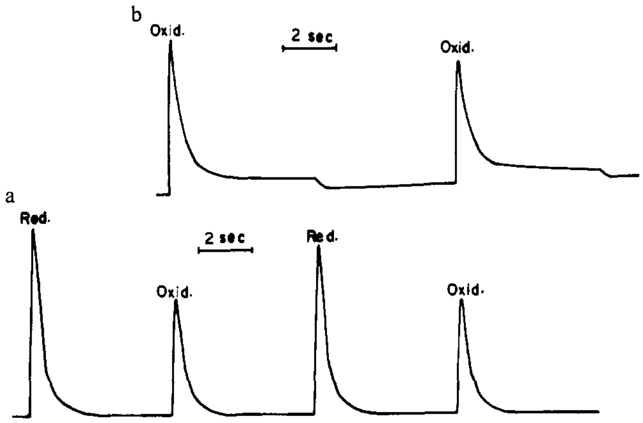


Figure 6. Comparison of ecl intensity-time transient for (a) annihilation ecl in solution containing 1.0 mM rubrene in 0.1 M TBAP-DMF pulsed between 1.1 and −1.5 V vs. SCE, and (b) oxidation ecl for a solution as in (a) containing 1.8 mM TBAOX and pulsed between 0 and 1.1 V vs. SCE.

Finally, $CO_2^{-}\cdot$ appears to be a good choice for this intermediate, based on the potential of the $CO_2/CO_2^{-}\cdot$ couple. Thus the following mechanism can be proposed. During the simultaneous oxidation of oxalate and D (D = rubrene, DPA, TH, TPP, or chelate) the oxidized form of D diffuses toward the bulk solution, where it reacts with oxalate diffusing toward the electrode.

$$D - e \rightarrow D^{+}\cdot \qquad (5)$$

$$D^{+}\cdot + C_2O_4^{2-} \rightarrow D + C_2O_4^{-}\cdot \qquad (6)$$

$$C_2O_4^{-}\cdot \rightarrow CO_2 + CO_2^{-}\cdot \qquad (7)$$

The $CO_2^{-}\cdot$ can transfer an electron to A (A = rubrene, DPA, TPP, chelate, PPD)

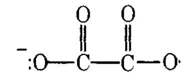
$$CO_2^{-}\cdot + A \rightarrow CO_2 + A^{-}\cdot \qquad (8)$$

in addition to decomposing by a number of other paths, such as reaction with $D^{+}\cdot$, oxidation at the electrode, and dimerization to form oxalate. The annihilation reaction then results in emission.

$$A^{-}\cdot + D^{+}\cdot \rightarrow A + D^{*} \qquad (9)$$

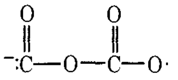
It is unlikely that $CO_2^{-}\cdot$ resulting from the direct oxidation of the oxalate at the electrode participates in the ecl process, since this species would be oxidized rapidly at the electrode surface and does not survive long enough to be detected at the ring electrode of the RRDE. This mechanism suggests that the reaction between $D^{+}\cdot$ and $CO_2^{-}\cdot$ does not produce an excited state of D, although the energy of the reaction should be large enough. For example, for the $TH^{+}\cdot/CO_2^{-}\cdot$ reaction $|\Delta H| >$ 3.3 eV, which is greater than the excited singlet energy of TH (ca. 2.8 eV). A possible explanation is that because $CO_2^{-}\cdot$ is a relatively small molecule, the solvation energy difference between it and CO_2 is large. This results in large solvation work terms in the Marcus electron transfer kinetics formalism[24] with a slower electron transfer rate. Such a slow electron transfer would be less likely to produce an excited product. An alternate explanation is that in the absence of an acceptor molecule the lifetime of $CO_2^{-}\cdot$ is too small to allow a significant amount of reaction with $D^{+}\cdot$.

Studies of the electroreduction of CO_2 in nonaqueous solvents have shown the production of oxalate, carbonate, and CO with $CO_2^{-}\cdot$ assumed as the intermediate species.[14-18] Two mechanisms have been proposed for formation of oxalate: (1) direct coupling of two $CO_2^{-}\cdot$ molecules;[25] and (2) reaction of $CO_2^{-}\cdot$ to form $C_2O_4^{-}\cdot$, which undergoes further reduction at the electrode.[18] Although formally this second pathway appears to be the reverse of reaction 7, the forms of $C_2O_4^{-}\cdot$ may be very different. Thus the species resulting from the oxidation of oxalate would have structure I, while that formed by the reaction of CO_2 and $CO_2^{-}\cdot$ could have structure II, thus accounting for the formation of CO and CO_3^{2-} as other reduction products.[26] Thus, conversion of I to II might require dissociation, rearrangement, and recombination, with $CO_2^{-}\cdot$ having a sufficiently long lifetime as an intermediate to transfer an electron to an acceptor.



$^{-}{:}O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O\cdot$

I



$^{-}{:}\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-O\cdot$

II

The ecl which results on *oxidation* of oxalate and a suitable additive resembles the ecl which is produced by the *reduction* of a substance undergoing a dissociative decomposition [e.g., 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene ($DPACl_2$) and benzoyl peroxide] and a reducible additive.[12,27,28] For this latter case the production of a strong oxidant upon reduction was invoked as a necessary step to emission. The formation of a strong reductant ($CO_2^{-}\cdot$) upon oxidation, as proposed here, is an interesting parallel. The ecl intensity-time behavior found in this study resembles that observed during reduction of $DPACl_2$[12] and can be justified by the mechanism presented, i.e., a relatively slow rise time necessitated by the diffusion of $D^{+}\cdot$ away from the electrode and a buildup of sufficient concentrations of the needed intermediates and a decay to a steady state because of continual diffusion of oxalate toward the electrode and regeneration of D via reaction 6. Finally these results point to the usefulness and sensitivity of ecl in detecting short-lived electrogenerated reaction intermediates. Thus intermediates in the oxidation of oxalate and reduction of $DPACl_2$ give rise to easily observed emission, although they could not be detected by the sensitive RRDE method.

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Dioxetane Chemiluminescence. The Effect of Deuterium Substitution on the Thermal Decomposition of *trans*-3,4-Diphenyl-1,2-dioxetane

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Abstract: *trans*-Diphenyl-1,2-dioxetane was prepared by cyclization of the corresponding β-bromohydroperoxide. Thermal decomposition of this compound proceeds with an activation energy of 23.6 ± 1.6 kcal/mol to yield benzaldehyde, 10 ± 2% of which was in an excited triplet state. The effects of replacement of a dioxetane ring proton with a deuterium were investigated. No detectable partitioning between electronically excited protio- and deuteriobenzaldehyde was detected. The secondary deuterium isotope effect on the rate of thermal decomposition of this dioxetane was found to be 1.01 ± 0.02. We suggest that the absence of an isotope effect is consistent with a stepwise decomposition for 1,2-dioxetanes.

The discovery that 1,2-dioxetanes are isolable molecules that thermally decompose to produce high yields of electronically excited carbonyl compounds ushered in a new era of research into chemiluminescent processes.[1,2] Since the initial observations, investigators have probed the structural dependency of this remarkable reaction in an attempt to elucidate, in intimate detail, the conversion of ground state starting material to electronically excited states of the products.

Two fundamental mechanistic schemes have emerged for dioxetane decomposition. The first, originally considered by McCapra[3] and Kearns,[4] postulates simultaneous cleavage of both the oxygen to oxygen and the carbon to carbon bonds of