

ELECTROGENERATED CHEMILUMINESCENCE.

XXIV. ELECTROCHEMISTRY AND ELECTROGENERATED CHEMILUMINESCENCE OF 9,10-DICHLORO-9,10-DIHYDRO-9,10-DIPHENYLANTHRACENE *

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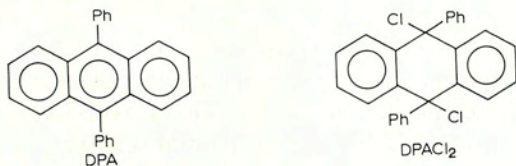
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ABSTRACT

A study of the electrochemistry and electrogenerated chemiluminescence (e.c.l.) of 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene (DPACl₂) in acetonitrile solutions using rotating ring-disk electrode and stationary electrode techniques is described. The measured e.c.l. efficiency was about 0.1 to 0.8%, smaller than that observed for the corresponding DPA radical ion annihilation e.c.l. The emission is independent of applied external magnetic field, supporting the mechanism involving direct formation of emitting singlet. The e.c.l. emission and the electroreduction of DPACl₂ depend on the chloride concentration in the solution; the results suggest that this dependence is an electrode surface effect.

INTRODUCTION

Chandross and Sonntag [1] described the intense chemiluminescence (c.l.) which occurs when the radical anion of 9,10-diphenylanthracene (DPA) is treated with 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene (DPACl₂)



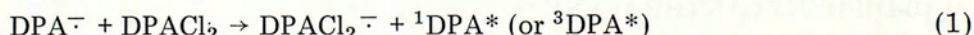
(or other oxidizing agents, e.g. benzoyl peroxide or oxalyl chloride). In all cases, the luminescence observed was identical with that of DPA fluorescence. Rauhut [2] also studied similar c.l. reactions, such as the reaction of DPACl₂ with sodium naphthalenide, and observed DPA emission. Later, Siegel and

* In honour of Academician A.N. Frumkin's 80th birthday.

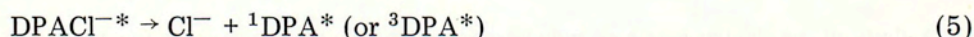
Mark [3] reported electrogenerated chemiluminescence (e.c.l.) during the reduction of DPACl₂ at a Pt electrode at potentials where DPA radical anion was formed. They described the e.c.l. emission in this case as being about two orders of magnitude greater than that obtained from the DPA⁻/DPA[†] annihilation e.c.l. obtained under similar conditions.

Several possible mechanisms for the process emerged from these studies:

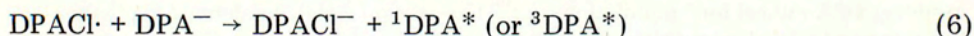
Mechanism A. Direct excitation of DPA⁻ on reaction with DPACl₂:



Mechanism B. Reaction of an intermediate in the DPACl₂ reduction to form an excited state:



Mechanism C. Formation of strong oxidant upon DPACl₂ reduction which reacts with DPA⁻: Eqns. (2) and (3), followed by

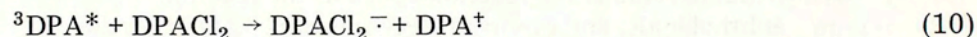


Mechanism D. Formation of DPA[†] from an intermediate DPACl₂ reduction, which undergoes an annihilation reaction with DPA⁻: Eqns. (2) and (3), followed by



Recently Akins and Birke [28] studied the e.c.l. which arises upon reduction of benzoyl peroxide and DPA and suggested a reaction mechanism based on the oxidation of a triplet intermediate to the radical cation. This possibility, when applied to the DPACl₂ case, yields the following additional reaction path:

Mechanism E. Formation of DPA[†] on oxidation of ³DPA*; eqns. (2), (3), and formation of ³DPA* by (6) [or possibly (1) or (5)], followed by



followed by the annihilation reaction, eqn. (9).

For the sake of simplicity the above reaction schemes are mainly concerned with the excitation step and secondary reactions (e.g. oxidation of Cl^- by an intermediate) and numerous quenching reactions are omitted. Siegel and Mark [3] showed that when the electroreduction of DPACl_2 is carried out in the presence of an added hydrocarbon, R, (e.g. rubrene), with reduction to form R^- but not DPA^- , the luminescence always corresponds to that of species R. Similar results were obtained for the reduction of tetraphenylporphyrin in the presence of DPACl_2 [4]. This appears to eliminate mechanism B [i.e. eqns. (4) and (5)] as the path to excited DPA. From a study of a similar system, involving reduction of fluoranthene, anthracene and 1,2-dibromo-1,2-diphenylethane (DPEBr_2), they postulated direct formation of the excited singlet state in the major excitation step. From studies of the annihilation reaction in the usual e.c.l. of DPA [5–8] this implies that, if a similar path is followed in the DPACl_2 path, then either DPA^\ddagger is formed in the reaction, or the intermediate formed (e.g. $\text{DPACl}\cdot$) is as strong an oxidant as DPA^\ddagger . Mechanism E, however, does not require $\text{DPACl}\cdot$ to be as strong an oxidant.

A reinvestigation of the e.c.l. of DPACl_2 was undertaken for several reasons. First, independent determinations of the efficiency of DPA annihilation e.c.l. ($\phi_{\text{e.c.l.}}$) yield values of at least 1% [5,6,8,9]. The reported efficiency of the DPACl_2 system would thus be surprisingly high. Second, magnetic field effects have been used in e.c.l. to probe the intermediacy of triplets in the light-production path [7,9–11]. A study of the effect of an external magnetic field on this type of e.c.l. system has not been reported previously. Finally, the electrochemistry of DPACl_2 has not been studied in any detail. The behavior appeared to be quite different on mercury and platinum electrodes, and was not very reproducible. A more complete study by cyclic voltammetry, controlled potential coulometry, and at the rotating ring-disk electrode (RRDE) seemed in order. We were particularly interested in trying to observe some of the proposed intermediates at the ring electrode of the RRDE following reduction of DPACl_2 at the disk.

EXPERIMENTAL

The purification of the solvents N,N-dimethylformamide (DMF) and acetonitrile (AN) has been described in previous publications in this series; in this work the AN was further purified by two or more distillations from P_2O_5 under vacuum. DPACl_2 was prepared and purified according to the method described by Chandross and Sonntag [1]. The product had a sharp melting point of 169–170°C (literature value [1] 174°C), although it appeared that some decomposition occurred during melting. Freshly prepared DPACl_2 solutions showed no fluorescence and no impurities could be observed on thin layer chromatograms run in a variety of solvent and support systems. The DPA Aldrich Analyzed grade (99+%) was used without further

purification. Mercury used in the hanging mercury drop electrode was purified by passing through 1 : 1 nitric acid followed by three distillations under vacuum. The supporting electrolyte used was tetrabutylammonium perchlorate (TBAP) (polarographic grade), obtained from Southwestern Analytical Chemicals, Inc., Austin, Texas and was dried for 48 h under high vacuum at 60–100°C before use. Tetramethylammonium chloride (TMACl), used as the source of added chloride ion, was also polarographic grade material from Southwestern Analytical Chemicals, Inc. All the materials were stored either in a desiccator over P₂O₅ or in a helium filled dry box. The DPACl₂ was protected from light during storage.

A cell design similar to that previously described [12] was used for all experiments involving the stationary Pt electrode. Experiments employing the Au or Hg electrodes were performed in the helium filled glove box (Model HE-43, Vacuum Atmospheres, Inc., Hawthorne, Calif.) using a small diameter open beaker as the cell. For accurate e.c.l. efficiency measurements, a cell employing a large area Pt disk electrode was employed. This cell also has been previously described [9]. Low temperature measurements were performed in a cell employing an evacuated double-walled glass vessel surrounding the solution. This vessel contained the cryogenic slush baths used to obtain the low temperatures. Incorporation of the bottom of the cell with the inner wall of the vessel permitted the disk electrode to be viewed from below.

The pulsed e.c.l. efficiency measurements of DPA were carried out using the technique previously described [8,9] for the DPA–thianthrene case. The DPACl₂ efficiency measurements were performed in a similar manner, however in this case the potential was not alternately pulsed between negative and positive potentials but only stepped to the DPA reduction potential and maintained there as long as is required for a particular experiment. The current flowing through the cell and the light intensity, measured with a calibrated PIN photodiode (UDT-500UV, United Detector Technology, Inc., Santa Monica, Calif.) were determined simultaneously as a function of time following the potential step. Integration of the current–time and intensity–time curves enabled [9] the calculation of $\phi_{e.c.l.}$, which in this case was defined as:

$$\phi_{e.c.l.} = \frac{\text{Total number of photons emitted per unit time}}{\text{Total amount of DPA anion produced per unit time}} \quad (12)$$

assuming (see below) the formation of DPA⁻ from DPACl₂ was a three-electron process. $\phi_{e.c.l.}$ was measured over times following the potential step of from 10 ms to 20 s.

RRDE experiments were performed using the cell and electrode described by Maloy and Bard [5]. The $\phi_{e.c.l.}$ measurements involved setting the disk potential to the required value and simultaneously measuring the steady state current and intensity parameters, $\phi_{e.c.l.}$ determined by eqn. (12).

For the experiments where the intensity–time curves were obtained for the initial few milliseconds following the potential step, a small (0.03 cm²)

Pt electrode was used. As rapid double layer charging is essential in this type of experiment, the positive feedback iR compensation of the potentiostat (Model 173, Princeton Applied Research Corp., Princeton, N.J.) was adjusted to the "critical" value following the procedure outlined by Lauer and Osteryoung [13]. The double layer charging time for this electrode was typically measured to be between 15 to 30 μs . The response time of the photodiode was calibrated using a light emitting diode with a rise time of 1 ns and was found to have a response time of approximately 15 μs when the feedback resistance in the amplification circuit was set at 401 Ω . In a typical experiment, the intensity—time curve was recorded on a cathode ray oscilloscope (Tektronix Model 564 with a Type 3AR differential amplifier and 3B3 time base), the time base being triggered as the potential step was applied to the cell.

Electrochemical studies were performed using vacuum line degassing (freeze-pump-thaw) procedures as much as possible. For experiments involving addition of chloride, it was found much more convenient to carry out the experiments in the glove box, using solvents previously vacuum degassed. Because the electrochemistry of DPACl_2 appeared to be highly dependent upon the state of the electrode surface (see below), the Pt and Au electrodes were pretreated in a standard manner before each use. The Pt electrode was polished with an alumina slurry (0.3 μm particle size), followed by cycling between the oxygen evolution and hydrogen evolution potential regions in 1 M H_2SO_4 for about 60 cycles. The Au electrode was only polished.

All potentials reported in this work are referred to the Ag wire pseudo-reference electrode, which was found to be much more convenient than the aqueous SCE for use in vacuum line and dry box experiments. A disadvantage of this electrode is that the $E_{1/2}$ and E_p values will vary somewhat from run to run, although within a given experiment, the electrode was usually quite stable if it was shielded from the test solution by a fine porosity sintered-glass disk. The known potential of the reversible $\text{DPA}-\text{DPA}^-$ system provided an internal calibration in most of the experiments.

RESULTS AND DISCUSSION

Efficiency measurements

The efficiency of photon production during DPACl_2 reduction (defined as photons emitted per DPA^- molecule generated) was determined at both the RRDE and at a stationary Pt electrode. A typical disk voltammogram of DPACl_2 in AN containing 0.1 M TBAP is shown in Fig. 1, along with the measured photodiode response as a function of disk potential. As has been reported previously, light emission only occurs when DPA^- is produced; both the light and the current reach steady state values when the plateau of the DPA reduction wave is reached. The $\phi_{\text{e.c.l.}}$ -values obtained at the RRDE as a function of rotation rate, ω , are listed in Table 1. Measurements made

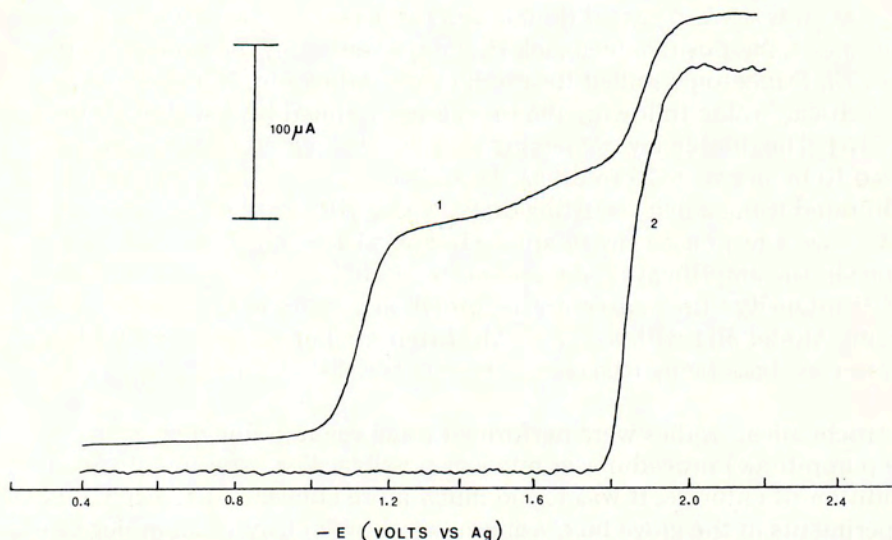


Fig. 1. (1) Voltammogram of a 1.2 mM DPACl_2 solution in AN/0.1 M TBAP obtained at the rotating Pt disk electrode ($\omega = 198 \text{ s}^{-1}$). (2) The light emission intensity (photodiode response) as a function of the disk potential.

at a stationary electrode (Table 2) in both DMF and AN upon pulsing to potentials where DPA reduction occurs and integrating the resulting intensity-time and current-time curves show somewhat lower efficiencies. The $\phi_{\text{e.c.l.}}$ values were independent, within experimental error, of pulse length, from 10 ms to 20 s, and essentially the same in DMF and AN. Addition of free DPA and lowering the solution temperature to -64°C also did not markedly affect $\phi_{\text{e.c.l.}}$. The lower values obtained at the stationary electrode compared

TABLE 1

$\phi_{\text{e.c.l.}}$ measured at the RRDE as a function of rotation rate ^a

ω/s^{-1}	$\phi_{\text{e.c.l.}}/\%$ ^b
66	0.76
132	0.79
198	0.59
264	0.43
330	0.32
396	0.27

^a The solution contained 1.2 mM DPACl_2 and 0.1 M TBAP in AN.

^b Determined from response of photodiode (calibrated in photons s^{-1}) and the current height of $\text{DPA} \rightarrow \text{DPA}^-$ wave.

TABLE 2

 $\phi_{e.c.l}$ for DPACl₂ at the stationary Pt electrode ^a

Solvent	Solution composition	$\bar{\phi}_{e.c.l.}/\%$
AN	0.5 mM DPACl ₂	0.14
	+ 0.1 M TBAP	0.17
AN	0.5 mM DPACl ₂	0.10
	+ 0.7 mM DPA	0.13
	+ 0.1 M TBAP	
DMF	0.5 mM DPACl ₂	0.08
	+ 0.1 M TBAP	0.11
DMF	0.35 mM DPACl ₂	0.09
	+ 0.1 M TBAP (-64°C)	0.12

^a The ϕ -values were measured at least twice for each solution composition shown (in completely separate experiments) and the upper and lower values are quoted here. Experiment was at room temperature, unless noted otherwise.

to the RRDE may partially result from a greater difficulty in determining the contribution of the DPA reduction to the current, but also probably reflect changes in the solution during current flow in the vicinity of the electrode.

For comparison, $\phi_{e.c.l.}$ was determined for the DPA radical anion—radical cation annihilation system in AN using the same electrode, cell, geometry, etc. The values obtained, 0.38 and 0.45% for pulse lengths of 2.5 s and 25 ms, respectively, are within the range of those reported by Bezman and Faulkner [6]. $\phi_{e.c.l.}$ -values obtained at the RRDE electrode for the DPA system in our laboratory [5,9] ranged from 1.5 to 3%. We conclude from these measurements that the actual efficiency of the DPACl₂ system is no greater, and probably a factor of 2 to 3 times smaller, than that of the DPA⁺/DPA⁻ system.

Magnetic field effects

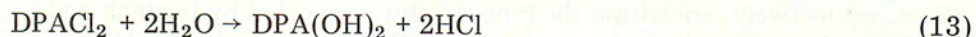
Previous studies [7,9–11] have demonstrated that a magnetic field affects the rate of the triplet—triplet annihilation (t.t.a.) reaction and the rate of the quenching of triplets by paramagnetic radical ions. Thus, the intensity of e.c.l. emission is changed (usually increased from 5 to 30% for annihilation e.c.l. occurring by t.t.a.) when triplet formation plays an important role in the light-emitting process in e.c.l., while systems which emit totally or predominantly through a direct excited singlet production route, show no field effect. The e.c.l. of the DPACl₂ system at a stationary electrode for various pulse widths showed no difference in intensity between experiments with no

applied magnetic field and those with fields of up to 7.5 kgauss. This finding suggests that t.t.a. does not play a major role in the light emission process, and direct excited singlet formation must occur either by (6) or (9). Furthermore, if the reaction proceeds by mechanism E, triplet quenching by the radical ions cannot be important. Reaction (11) may be field dependent, but it is an electron transfer reaction between paramagnetic species, as is the $R^{\cdot+}/R^{\cdot-}$ annihilation, which apparently is unaffected by magnetic field.

Electrochemical studies

In an attempt to find the intermediate oxidant which reacts with $DPA^{\cdot-}$ to form the excited singlet (i.e. $DPA^{\cdot+}$, $DPACl^{\cdot}$, or Cl^{\cdot} from dissociation of $DPACl^{\cdot}$), RRDE experiments were undertaken in which the disk was held at the potential of $DPACl_2$ or DPA reduction and the ring scanned to various potentials. Unfortunately no intermediates were detected in the whole available potential range, even when the disk was set at potentials where $DPA^{\cdot-}$ was formed so that intermediates would be generated in the gap region. The collection efficiency for $DPA^{\cdot-}$ (defined as the ring current for the ring held at potentials at the foot of the DPA reduction wave to disk current for DPA reduction) was smaller than 0.3% for ω -values up to 400 s^{-1} . Thus $DPA^{\cdot-}$ must undergo a very rapid electron transfer reaction with $DPACl_2$ and any intermediates in traversing the gap region from disk to ring.

The electrochemical behavior of $DPACl_2$ was also found to change from one scan to another at a rotating disk electrode (RDE) or stationary platinum electrode. For a freshly prepared solution of $DPACl_2$ in dry AN, the "decomposition product" wave at -0.4 V , attributed to H^+ formed by partial decomposition of the $DPACl_2$ [14] in wet solvent, eqn. (13),



was not observed. A first scan (Fig. 2) shows a small wave at $E_{1/2} = -1.15\text{ V}$ followed by a second wave with $E_{1/2}$ near -1.6 V and a final wave, which can be identified as the DPA reduction wave, at $E_{1/2} = -1.90\text{ V}$ (all potentials are quoted versus a Ag wire pseudo reference electrode; essentially, the same behavior was observed with an SCE, against which the DPA reduction wave $E_{1/2} = -1.86\text{ V}$). As the scans are repeated, the first wave increases rapidly with respect to the second wave until usually a point is reached where only the first wave and the DPA reduction waves are observed (Fig. 2). Essentially the same behavior was observed for cyclic voltammograms run in AN or DMF as solvents. In a typical experiment, three peaks could be observed on the first set of scan runs, whereas, after the potential was held at either of the first two waves, or at the DPA wave, for any length of time, the first wave was usually predominant. The DPA reduction wave remained unchanged throughout. The first scans for a given fresh solution and electrode were usually irreproducible with the relative height of the first two waves varying greatly from day to day for fresh solutions. Better reproducibility was ob-

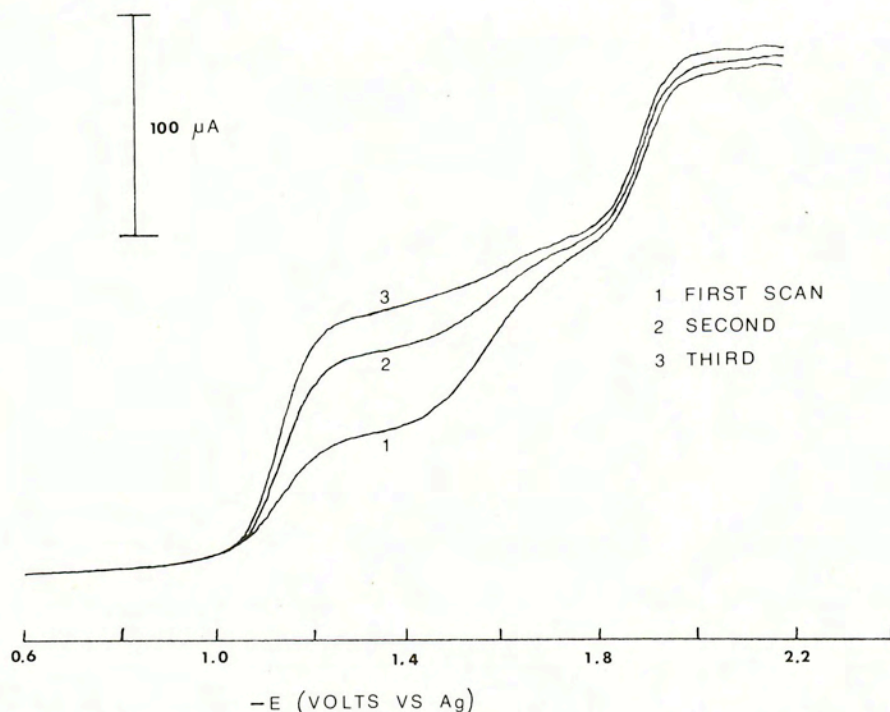


Fig. 2. Voltammograms obtained at the rotating Pt disk electrode for 1.2 mM DPACl_2 in AN/0.1 M TBAP solution, showing the change of the voltammogram with successive scans. The potential scan rate was 20 mV s^{-1} and $\omega = 198 \text{ s}^{-1}$.

tained when the electrodes were pretreated in a consistent manner before each run. Controlled potential coulometry of DPACl_2 at a Pt electrode in DMF gave the following results. When the potential was set at the reduction potential of the first wave, it was found that DPA was produced (easily detectable in solution by its intense fluorescence) and an n_{app} of 1.95 (where n_{app} is the number of electrons per molecule of DPACl_2) was obtained. The resulting solution contained only DPA and Cl^- in a 1 : 2 mole ratio as shown by cyclic voltammetry. Thus, the overall reaction was



with the complete reduction occurring at the potential of the first wave. The same results were obtained when the potential was held at the second reduction step. These results agreed with the observed voltammograms for DPACl_2 , i.e., that the first wave reaches an overall $2e^-$ height (by comparison to the DPA/ DPA^- wave) as electrolysis is carried out in solution.

Because Cl^- is a product of the electrolysis, we investigated the effect of adding small amounts of Cl^- (as TMACl) on the voltammetry of DPACl_2 . The results strongly suggest that Cl^- is responsible for the variation of behav-

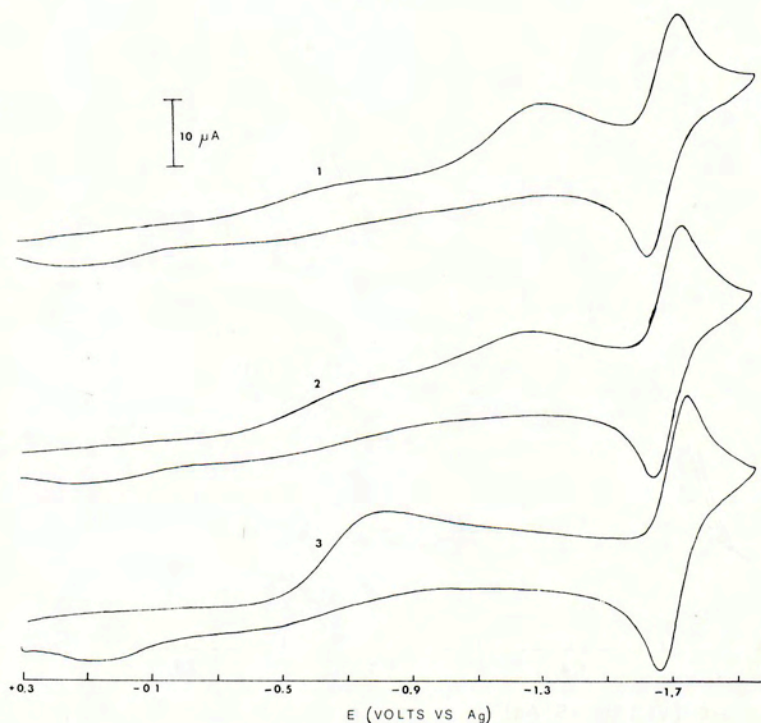


Fig. 3. Cyclic voltammograms at a Pt disk electrode for a 0.8 mM DPACl₂ in AN/0.1 M TBAP solution showing the effect of added chloride ion (as tetramethylammonium chloride). (1) Freshly prepared DPACl₂ solution with (2) 0.1 mM Cl⁻ added and (3) 3.0 mM Cl⁻ added. Scan rate = 200 mV s⁻¹.

ior of the first two reduction waves upon repeated scanning. Cyclic voltammograms obtained at the Pt disk electrode for a 0.8 mM DPACl₂ solution in AN/0.1 M TBAP, showing the effect of addition of 0.1 mM and 2 mM TMACl are shown in Fig. 3. The first scan shows a small first wave, with a large second wave just before the DPA reduction wave. With the addition of 0.1 mM Cl⁻, the first wave is significantly increased (i.e., much more than would be observed for a second scan in cyclic voltammetry). For 3 mM added Cl⁻, the first wave is the more predominant, with the second wave almost not detectable. When high Cl⁻ concentrations (e.g. 10 mM) are present only the first wave is observed and it is much more sharply defined. Note that a small anodic wave at 0.0 V appears as Cl⁻ is added. At high Cl⁻ concentrations, this wave is very large and has the appearance of a sharp adsorption wave. The effect of added Cl⁻ was at times even more pronounced than that shown in Fig. 3 and appeared to be related to the degree of electrode preconditioning before a given run. Since the effect is observed at an RDE where fresh solution is continually flowing to the electrode surface and the total amount of Cl⁻ generated during a scan would only produce a very small concentration

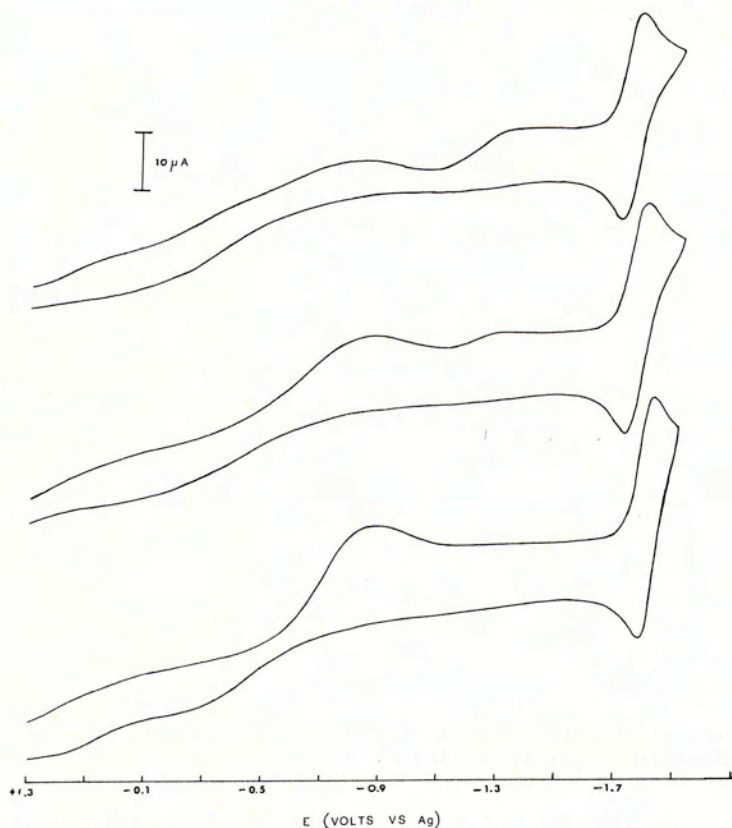


Fig. 4. Cyclic voltammograms at a Au disk electrode for a 0.8 mM DPACl₂ in AN/0.1 M TBAP solution showing the effect of added chloride ion. (1) Freshly prepared DPACl₂ solution with (2) 0.1 mM Cl⁻ added and (3) 1.0 mM Cl⁻ added. Scan rate = 200 mV s⁻¹.

of Cl⁻ in the bulk solution, and since the effect of added Cl⁻ is observed for ratios of Cl⁻ to DPACl₂ of 1/8, the effect cannot be attributable to a homogeneous reaction involving DPACl₂ and Cl⁻ and is more likely due to an effect of Cl⁻ on the electrode surface. To investigate the effect of the nature of the electrode surface more fully, cyclic voltammetry was carried out using Au disk electrodes (pre-treated as described in the Experimental section). The effect of Cl⁻ on the DPACl₂ reduction at a Au electrode is shown in Fig. 4. The first cyclic scan in the absence of Cl⁻ again shows three waves with the first wave growing rapidly as Cl⁻ is added. Note that the addition of 0.1 mM Cl⁻ appears to have a greater effect at the Au electrode than at the Pt electrode; otherwise, the behavior is essentially the same. The effect of added Br⁻ is similar, although much more Br⁻ is required to produce a given increase in the first wave than for Cl⁻.

In our early experiments with DPACl₂, we observed only the first peak in cyclic voltammetry. Concurrent with this observation was the fact that an

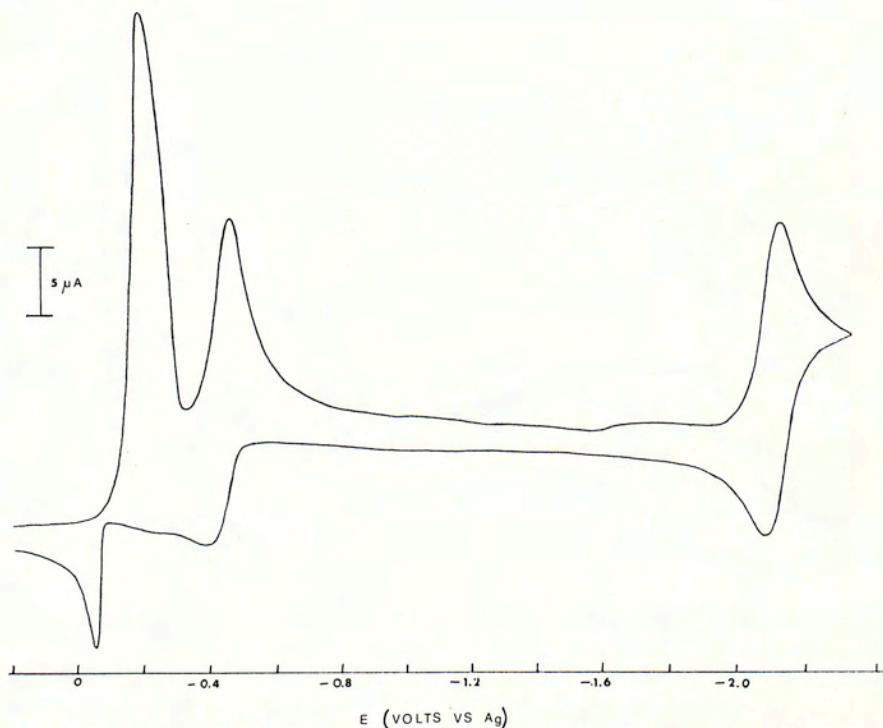


Fig. 5. Cyclic voltammogram obtained at a hanging mercury drop electrode at a scan rate of 200 mV s^{-1} for a 1.0 mM DPACl_2 in $\text{AN}/0.1 \text{ M TBAP}$ solution.

appreciable HCl reduction wave (at about -0.4 V) could often be observed. Thus Cl^- generated by reaction (13) (especially for solutions prepared by the slower vacuum line techniques) has a similar effect to that of the added chloride in the experiments described above. The use of carefully dried AN virtually eliminated this problem.

The addition of Cl^- to DPACl_2 solutions had no effect on the homogeneous bulk properties of DPACl_2 . No effect on the thin layer chromatographic R_F values in various solvent systems (using silica gel, alumina and cellulose plates), with and without Cl^- was seen. Furthermore there was no effect on the u.v. spectrum of DPACl_2 in AN when large quantities of TMACl were added. Thus, the observed effect is probably a surface effect involving adsorbed chloride ion. There are no data on chloride adsorption on Pt and Au electrodes in DMF and AN. Measurements in aqueous solutions suggest that Cl^- is adsorbed on Pt (-0.2 to $+1.2 \text{ V}$ vs. SCE) and Au (up to -0.7 V), although the results are not in very good agreement [15–17]. The specific adsorption of Cl^- at the fairly negative potentials of the DPACl_2 reduction wave is surprising and bears further investigation.

The behavior of DPACl_2 at a mercury electrode was very different, as is also evident from the results of Siegel and Mark [3]. A cyclic voltammogram of DPACl_2 at a hanging mercury drop electrode (HMDE) is shown in Fig. 5.

The two DPACl_2 reduction waves at ca. -1 and -1.6 V disappear and are replaced by the surface or adsorption waves at -0.2 and -0.45 V; the DPA reduction wave is unchanged. These results suggest, as is frequently observed with other organohalogen compounds [18,19], that there is a very strong interaction of the DPACl_2 and the Hg, probably with the formation of an organometallic mercury compound which remains on the electrode surface. Oxidation of mercury to form Hg_2Cl_2 probably also occurs during this reaction, with the reduction wave at -0.2 and the oxidation wave near 0 V probably involving the $\text{Hg}_2\text{Cl}_2/\text{Hg}, \text{Cl}^-$ (ads) system.

Potential step transients and simulation

The emission resulting from a potential step to a potential on the plateau of the DPA reduction wave at a stationary Pt electrode is shown in Fig. 6. The observed rise time for the emission (from step initiation to peak) was 1.3 ms, which is much longer than that observed for transients from annihilation

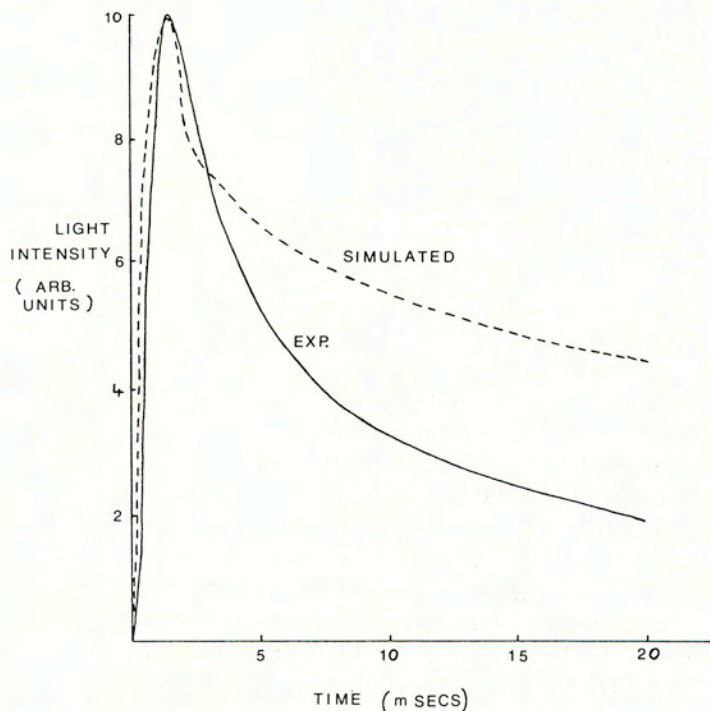
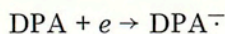
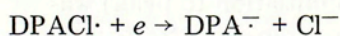
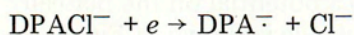
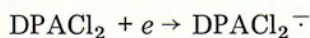


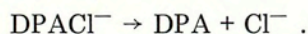
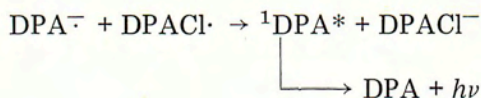
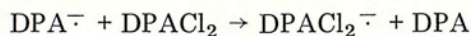
Fig. 6. Comparison of the simulated (dotted curve) and the experimental (solid line) light intensity vs. time curves for DPACl_2 emission at a stationary Pt electrode, both curves normalized to the same scale. The simulated curve was obtained assuming the mechanism discussed in the text with $k = 800 \text{ s}^{-1}$.

lation e.c.l. For example, for the same electrode, detector, and instrumentation, the $\text{DPA}^\ddagger/\text{DPA}^-$ system e.c.l. shows a rise time of $50 \mu\text{s}$, which is about the potentiostat-cell rise time and photodiode response time under these experimental conditions. Thus there appears to be a slow step preceding the light emitting process in DPACl_2 e.c.l. A preliminary attempt was made to simulate the e.c.l. transient using the familiar digital simulation techniques [20–23], and assuming that mechanism C, with direct formation of excited singlet, was the predominant path. The following reactions were all assumed to proceed at their diffusion controlled rates:

At electrode:



In solution:



The rate-determining step was assumed to be



The result of one such simulation, with $k = 800 \text{ s}^{-1}$, is shown in Fig. 6. Obviously these results can only be considered representative of a large number of possible simulated curves with adjustment of the rate constants of the different reactions. At our present level of understanding of the reaction mechanism, more extensive attempts at digital simulations appear unwarranted. The simulation does predict the slow rise time of the emission and also predicts that this rise time will be independent of DPACl_2 concentration (since the rate-determining step is first order with respect to DPACl_2^-), which is found to be the case experimentally. The simulation fails to predict the more rapid decay of the transient, perhaps suggesting the need to include other modes of decomposition of $\text{DPACl}\cdot$ (e.g. disproportionation to form DPACl_2 and DPA). Simulation of the direct excitation route (mechanism A) produces transients which do not show the observed slow rise time or emission peak.

In addition to its effect on the electrochemistry of DPACl_2 at Pt and Au, added Cl^- in relatively large quantities also affects the intensity of the e.c.l.

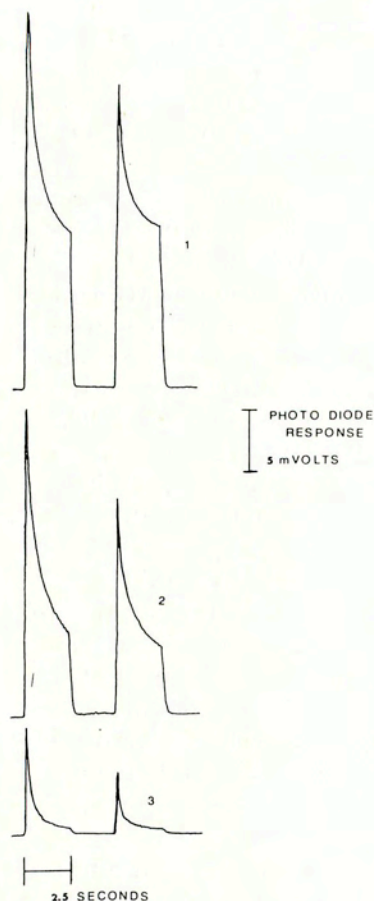


Fig. 7. Light intensity vs. time for two successive pulses at a stationary Pt electrode for a 0.8 mM DPACl₂ in AN/0.1 M TBAP solution. The potential was pulsed from 0.0 to -2.0 V in 2.5 s pulses. The effect of the addition of chloride ion is shown. All of the pulses are shown on the same intensity scale. (1) Freshly prepared DPACl₂ solution with (2) 3.0 mM Cl⁻ added and (3) 15.0 mM Cl⁻ added.

emission. The effect of the addition of 3.0 mM and 15 mM chloride on the intensity of the first two light pulses where the Pt electrode was pulsed between 0.0 and -2.0 V in 2.5 s pulses is shown in Fig. 7. The placement of the photodiode with respect to the cell was not altered during the experiment and the chloride was added as a solid to the DPACl₂ solution. At Cl⁻ concentrations above 15 mM, the light intensity was reduced almost to zero. Since relatively large concentrations of Cl⁻ are required to decrease the emission intensity as compared to the amounts which show the electrochemical (surface) effect, the emission effect could be attributed to a homogeneous solution reaction. An attempt was made to study this effect in the following non-electrochemical experiment: Approximately 5 ml each of equal concen-

tration DPACl_2 solutions were placed in test tubes inside the dry box. One of these solutions was then saturated with chloride (as TMACl). A solution of DPA anion was then prepared by addition of fine Na slices to a DPA solution in tetrahydrofuran (THF). When the DPA anion concentration appeared to have reached a steady state value (as seen by the intensity of the blue-colored solution produced), equal amounts of this solution ($250 \mu\text{l}$) were injected rapidly by micropipette into the two solutions. Both solutions appeared to produce equal intensity light for about six such injections in each. At this stage, the light emission from the chloride-containing solution decreased rapidly while the solution which began as chloride-free, lasted for a few more injections. Similar results were obtained when the experiment was repeated with fresh solutions; the chloride appeared to have no initial effect on the chemiluminescence intensity, whereas, after prolonged reaction with DPA anion, the emission from chloride-containing solution appeared to decrease rapidly. Although the results are essentially qualitative, they suggest that some light quenching product is formed on prolonged reaction in the solution which contained chloride, rather than Cl^- itself acting as a quencher. These very high Cl^- concentration results are probably consistent with the e.c.l. results in which the light intensity showed a large drop with the addition of only 5–10 mM chloride, because in e.c.l. the light-producing reaction takes place near the electrode surface where a relatively high local concentration of the quenching product may be produced. Examination of the final solutions from the chemiluminescence experiment by thin layer chromatography revealed no detectable difference in the products from each, so that any quencher may be present in relatively small amounts or was not separated under the conditions used in the chromatographic analysis.

Chloride ion is capable of decreasing the emission by an electron transfer reaction with the intermediate oxidant. Thus either $\text{DPACl}\cdot$ or DPA^\ddagger should be capable of oxidizing Cl^- to $\text{Cl}\cdot$ (or Cl_2 or Cl_3^-), since $E_p(\text{DPA}^\ddagger/\text{DPA}) > E_p(\text{Cl}^-/\text{Cl}\cdot)$. Honda and coworkers [24] found, however, that reaction of DPA^- with the product of the oxidation of Cl^- at an electrode produced e.c.l. Although they favored a reaction between DPA^- and Cl_3^- to produce $\text{DPACl}\cdot$ which then caused emission by mechanism B [reactions (4) and (5)], an energy deficient route involving $\text{Cl}\cdot$ and DPA^- and occurring via t.t.a., seems possible. Furthermore, it is known that Cl_2 reacts with DPA to form DPACl_2 [1], so that production of that species followed by reaction with DPA^- through the paths discussed here is also a possible path.

CONCLUSIONS

The efficiency of DPACl_2 e.c.l. is reasonably high, but less than that of the $\text{DPA}(-)/\text{DPA}(+)$ system. This seems reasonable, since several of the mechanisms depend upon the annihilation reaction as the excitation step, and it is difficult to see why an intermediate oxidant would be more efficient or less of a quencher than DPA^\ddagger . The lack of a magnetic field effect points to

the direct generation of singlet excited state as the dominant path in light emission, as has been suggested by several previous studies. The simulation result suggests some slow step preceding emission, so that mechanism A, which also seems unlikely from an energetic standpoint, is improbable. Mechanism B, which appears to be the only one in which some excitation energy can be obtained through bond cleavage, has been eliminated by the mixed DPACl₂—hydrocarbon experiments, especially for those hydrocarbons (e.g. rubrene, tetraphenylporphin) where energy transfer from singlet excited DPA to hydrocarbon is unlikely. Mechanisms C and D require that DPACl· be as strong an oxidant as DPA⁺, so that the standard potential of the DPACl·/DPACl⁻ couple would be near +1.4 V vs. SCE. This seems unreasonably high for such a species. The triphenylmethyl radical and many of the hydrocarbon RH·/RH⁻ couples have standard potentials near -1.0 V vs. SCE [19,25]. While substitution of an electronegative chlorine atom onto the molecule would shift the potential to more positive values, a shift of over 2 V seems unlikely. Mechanism E has the virtue of accumulating energy for DPA⁺ production in two steps, and, when DPACl₂ is the major oxidant, as in (10), it could be fairly efficient (although no more so than the annihilation route, since two DPA⁻ molecules must be generated for each annihilation to occur). However the back reaction of (10) to produce DPACl₂ and ground state DPA upon electron transfer would seriously decrease the efficiency, unless decomposition of DPACl₂⁻ was very rapid. Note that this kind of reaction sequence is possible in most energy deficient e.c.l. schemes, for example DPA(-)/TMPD(+) (where TMPD is N,N,N',N'-tetramethyl-*p*-phenylenediamine), in which TMPD⁺ could oxidize ³DPA to DPA⁺. Yet these reactions are characterized by magnetic field effects and other evidence of triplets capable of being intercepted [26], so that in these cases the triplet-oxidant reaction represents a quenching route. The very fast decomposition of DPACl₂⁻ however, eqn. (3), may make the situation in the DPACl₂ case somewhat different. The effect of chloride ion on the electroreduction of DPACl₂ bears further investigation. The results suggest that it is a surface effect, probably involving adsorbed chloride. Possible mechanisms include a "ligand bridge" effect, as is often observed in aqueous solution studies of transition metal complexes, or a surface rearrangement or reaction of the DPACl₂ (which can exist in *cis*- and *trans*-forms [27]).

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