$$T(\rho) = \exp(-0.675k_0\rho)$$

is a reasonable approximation. Hence, $k\rho$ in (5) is equal to $0.675k_0\rho$. The absorption coefficient at the center of the line is

$$k_0 = {}^1/_5(g_2/g_1)(n\lambda_0{}^3/8\pi^{3/2}\nu_0\tau_0)$$

where g_1 and g_2 are the statistical weights of the ground and excited states, λ_0 is the wavelength at the center of the line, and n is the number of mercury atoms per cc.[5] Hence, k_0 (cm^{-1}) = 0.420×10^4p (p in mm) at 25°. Thus the present diffusion model gives

$$\tau = \tau_0(1 + 0.284 \times 10^4p\rho)$$

In the present experiment, the distance from the slab of irradiated mercury to the emerging surface of the cell facing the photomultiplier tube is 1.27 cm. With this ρ, and using (4), the experimental relation becomes

$$\tau = \tau_0(1 + 0.25 \times 10^4p\rho)$$

which agrees well with the above estimation.

At a higher opacity, various complications arise. First $T(\rho)$ fails to decrease exponentially with opacity, and the mean absorption coefficient loses its significance. In addition, not only the mercury slab in the exciting beam (and facing the photomultiplier tube) but also the slabs in other volume elements contribute to photocurrents; hence the value of ρ to be used in the estimation of opacity becomes uncertain. In spite of these complications, the qualitative behavior of τ at a higher opacity can be deduced from Milne's treatment of radiation transport.[12] Since τ is a mean life, the decay of excited atoms in the absence of a quencher after the exciting beam is cut off should follow the first-order law

$$n^*(t) = n^*(0) \exp(-t/\tau) \qquad (8)$$

Milne's one-dimension diffusion model gives τ in (8) in the form

$$\tau = \tau_0[1 + (k_0\rho)^2/\delta^2]$$

where δ is the positive root of $\tan x = k_0\rho/x$ which lies between 0 and $\pi/2$. At a low opacity $\delta \simeq k_0\rho$, and eq 5 results. At a high opacity, $\delta \simeq \pi/2$ and

$$\tau = \tau_0[1 + 4(k_0\rho)^2/\pi^2]$$

Since k_0 is proportional to p, τ now increases with the second power of p. This is in qualitative agreement with the present result (Figure 3) where τ is found to increase more rapidly than the first power of p at higher opacities.

Acknowledgment. Dr. W. H. Harwood and Mr. C. L. Hassell offered valuable discussion, and Mr. J. D. Reedy helped with experimental work. The author gratefully acknowledges this assistance.

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Chemiluminescence from the Reduction of Rubrene Radical Cations

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Abstract: It has been demonstrated that reduction of aromatic hydrocarbon cation radicals can produce chemiluminescence when electron donors other than the corresponding anion radical are used. Such reactions have been studied in detail for rubrene radical cations, using dimethylformamide, water, *n*-butylamine, and triethylamine as electron donors. Spectral studies showed that the chemiluminescence emission was identical with hydrocarbon fluorescence. Studies of a number of experimental variables are reported including the effects of concentration, water, oxygen, and repetitive scans on the chemiluminescence emission. Also, it was observed that solvent oxidation products quenched chemiluminescence emission when dimethylformamide was used as solvent, and that products of the reaction between rubrene cation and water-quenched light emission.

Recently a number of reports have appeared describing production of chemiluminescence in aromatic hydrocarbon systems. Chemiluminescence has been observed by alternating current electrolysis of hydrocarbons in nonaqueous solvents[1-3] and by chemical oxidation of hydrocarbon anions,[4] and a report has described excimer formation in the electrochemically produced chemiluminescence.[5]

The chemiluminescence observed during alternating current electrolysis has been interpreted as resulting from an annihilation reaction between positive and negative hydrocarbon radical ions produced during electrolysis. The mechanism for this reaction has been postulated to be an electron transfer from the negative to the positive radical ion to produce an excited singlet state. The observation of excimer emission[5] in such systems tends to support this point of view. Observation of chemiluminescence by chemical oxidation of

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(2) R. E. Visco and E. A. Chandross, *J. Am. Chem. Soc.*, **86**, 5350 (1964).

(3) K. S. V. Santhanam and A. J. Bard, *ibid.*, **87**, 139 (1965).

(4) E. A. Chandross and F. I. Sonntag, *ibid.*, **86**, 3179 (1964).

(5) E. A. Chandross, J. W. Longworth, and R. E. Visco, *ibid.*, **87**, 3259 (1965).

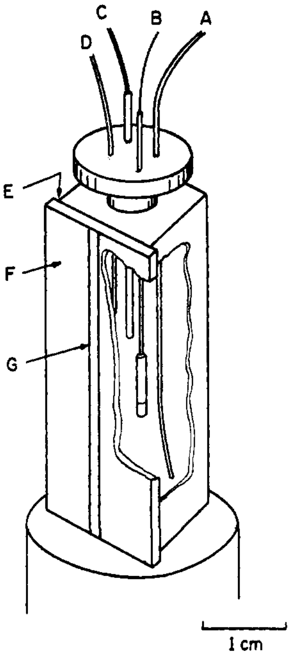

Figure 1. Cell used to obtain chemiluminescence spectra: A, nitrogen-inlet tube; B, counter electrode; C, connection to salt bridge; D, nitrogen-outlet tube; E, silicone rubber gasket; F, area of glass having SnO_2 removed; G, SnO_2 strip electrode.

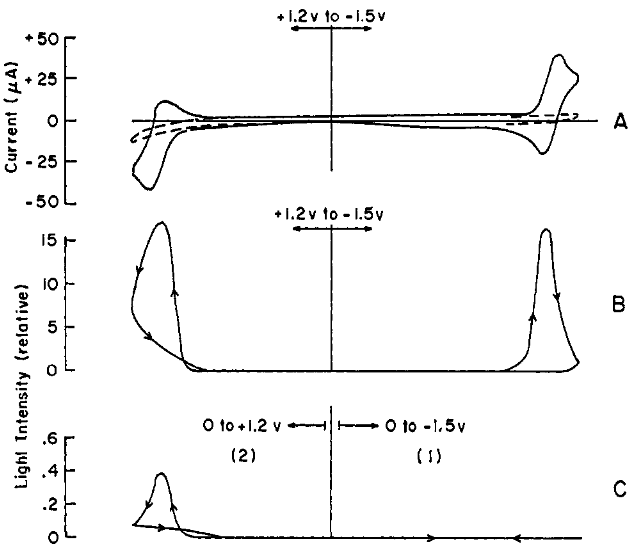

Figure 2. Current–voltage and light intensity–voltage curves for rubrene in dimethylformamide: 1.0×10^{-3} M rubrene, 1.0×10^{-2} M tetrabutylammonium perchlorate; reference electrode, Ag|AgBr in 10^{-2} M tetraethylammonium bromide; sweep rate, 0.1 cps. (A) Current–voltage curve: solid line, solution with rubrene; dashed line, solution without rubrene. (B) Light intensity–voltage curve: scan range from +1.2 to −1.5 v; light emission on both anodic and cathodic cycles. (C) Light intensity–voltage curve: (1) scan range from 0 to −1.5 v (cathodic cycle only), no light emission observed; (2) scan range from 0 to +1.2 v (anodic cycle only), light emission observed.

hydrocarbon anions implies abstraction of an electron from a lower π level, leaving an electron in a higher energy π^* orbital, although the exact mechanism is probably somewhat more complicated.[6] Also it should be possible to produce an excited state by electron addition to a π^* orbital of an aromatic positive ion, with chemiluminescence resulting from such a reaction.

We wish to report the observation of chemiluminescence produced by reaction of electrochemically generated hydrocarbon radical cations of rubrene, 9,10-diphenylanthracene, perylene, and 3,5,8,10-tetraphenylpyrene with amines, water, and dimethylformamide. The chemiluminescence spectrum recorded for rubrene cation reduction was found to be identical with the rubrene fluorescence spectrum. The intensity of chemiluminescence emission, however, was found to be about two orders of magnitude below that observed from the cation–anion combination reaction for the same hydrocarbon.[1,2]

Experimental Section

The aromatic hydrocarbons used were obtained from Aldrich Chemical Co. and were vacuumed sublimed before use. Rubrene was vacuum sublimed several times, and its purity was checked by absorption and fluorescence spectrometry, and by thin layer chromatography. Dimethylformamide and acetonitrile were either Matheson Coleman and Bell or Eastman Kodak Spectrograde. Acetonitrile was dried over calcium hydride and distilled. Dimethylformamide was dried over anhydrous potassium carbonate and vacuum distilled. Tetra-*n*-butylammonium perchlorate was Southwestern Analytical Reagents polarographic grade and was used without further purification. A conventional three-electrode cell was used for all measurements except those where spectra were recorded. The resistance between indicator electrode and the tip of the reference probe was about 25 ohms. The reference electrode was AgBr|Ag in 0.01 M $(C_2H_5)_4NBr$; its potential *vs.* aqueous sce was −0.075 v. A porous Vycor rod in Teflon tubing provided connection between the reference electrode and the cell. The apparatus used to record potential–current–light emission curves will be described elsewhere.[7]

Chemiluminescence spectra were recorded on a spectrofluorometer constructed from Aminco Building Block Components. Spectra are uncorrected; an RCA 1P21 photomultiplier tube was used. A cut-away diagram of the cell used to obtain chemiluminescence spectra is shown in Figure 1. It was constructed from a 1-cm² fluorescence cell by cutting off one face of the cell and replacing it with a piece of Corning tin oxide coated glass. General Electric RTV-102 silicone rubber sealant was used to fabricate a gasket to seal the tin oxide glass to the fluorescence cell. This procedure allowed the glass face of the cell to be used as the working electrode. In order to maintain a reasonable electrode area, all of the tin oxide was removed from the glass except for a vertical strip, 40 × 1 mm. The counter electrode was a platinum wire in a Teflon tube which had been plugged with a porous Vycor rod in order that the counter electrode was both chemically and optically isolated from the solution. A reference electrode of AgBr|Ag in 0.01 M $(C_2H_5)_4NBr$ was located in a separate compartment connected to the cell *via* a Teflon salt bridge. Nitrogen inlet and outlet tubes were available so a solution in the cell could be purged with nitrogen either before or during electrolysis.

Results and Discussion

Figure 2 shows typical examples of the three types of curves obtained during triangular-wave cyclic voltammetry of rubrene in DMF. Curve A is a current–voltage plot for 10^{-3} M rubrene in DMF using 10^{-2} M tetrabutylammonium perchlorate as the supporting electrolyte. The dashed line is the curve obtained when the same scan was run on a solution containing only supporting electrolyte and no rubrene. On the anodic sweep one generates the radical cation of rubrene by one-electron oxidation of the hydrocarbon, and on the cathodic sweep one generates the radical anion as indicated below.

$$R \longrightarrow R^+ + e^- \text{ (anodic sweep)} \tag{1a}$$

$$R + e \longrightarrow R^- \text{ (cathodic sweep)} \tag{1b}$$

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[6] E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **88**, 1089 (1966).

[7] R. C. Lansbury, D. M. Hercules, and D. K. Roe, to be published.

The peak potential for the one-electron oxidation of rubrene was found to be +1.07 v, and the peak potential for the one-electron reduction was found to be −1.37 v, both *vs.* the silver–silver bromide reference electrode. For a diffusion-controlled process, the corresponding half-wave potentials would then be +1.04 and −1.34 v, respectively. Both the oxidation and reduction waves appear to be diffusion controlled at sweep rates of <0.2 v/sec. The negative ion radical is quite stable, while the positive radical ion is quite unstable, having a half-life in DMF of about 3 sec. That radicals were produced on both anodic and cathodic cycles was indicated by the signals observed when cyclic voltammograms were run in an electron spin resonance cavity. An esr signal was observed only in the voltage range where either oxidation or reduction of the hydrocarbon occurred; however, the signal was too weak to observe fine structure for either the positive or negative radical ion. Recently other workers have observed clearly defined esr signals for radical cations of substituted anthracenes under similar conditions.[8,9]

Curve B is a light intensity *vs.* voltage curve obtained when the rubrene system is scanned from +1.1 to −1.5 v. It should be noticed that a peak is observed on both the anodic and cathodic cycles of the scan, which is consistent with the interpretation that the chemiluminescence results from an annihilation reaction between the plus and minus radical ions. The ratio of the peak heights of the light emission curves for anodic and cathodic scans (A/C) varies as a function of sweep rate owing to the instability of the radical cation. The following data, obtained for 10^{-3} *M* rubrene in DMF using a triangular wave form sweeping between +1.4 and −1.4 v, bear this out. At a sweep rate of 0.02 cps, A/C = 6.5; at 0.04 cps, 4.0; at 0.06 cps, 2.1; at 0.08 cps, 1.2; and at 0.01 cps, 1.06. This effect arises because, when scanning into the positive region, there are always sufficient radical anions in the vicinity of the electrode from the previous half-cycle to react with the radical cation produced; when scanning into the negative region, however, because of the instability of the cations, the amount available to react with the anions produced will vary depending upon the time elapsed between the two halves of the cycle.

Curve C shows the light intensity–voltage curve observed when a solution of rubrene in DMF was scanned only between the limits of 0 to +1.1 v. On the 0- to +1.1-v sweep, light emission was observed over the voltage range where the radical cation is produced. Although the intensity of this light was *ca.* 5% of that produced by the cation–anion annihilation reaction, it clearly arose from a reaction of the rubrene cation. This behavior was observed for rubrene solutions in DMF that had been vacuum degassed as well as those which had been bubbled with nitrogen, indicating that the effect was not due to traces of oxygen. Also light emission was observed for solutions in which no radical anion had ever been produced, indicating that it was not due to reaction with residual amounts of the stable radical anion. Light emission in the 0- to +1.5-v range was not observed when acetonitrile was used as a solvent. Therefore, the DMF used was extensively purified and different batches of DMF from different sources were used; light emission in the 0- to +1.5-v range was still observed in all DMF solutions tried. These results indicated quite strongly that the rubrene cation radical was reacting with the dimethylformamide to produce chemiluminescence.

In order to verify further that light emission in DMF did not arise from reaction with an impurity, the rubrene radical cation was shown to produce light by reacting with several electron donors added to acetonitrile solutions. Table I summarizes the data obtained for reaction of rubrene radical cation with dimethylformamide, water, *n*-butylamine, and triethylamine in acetonitrile. The relative intensity calculated in Table I is the photocurrent divided by concentration of the electron donor. It must be stressed that these intensities indicate only the order of magnitude of the light emission because of difficulties in reproducing exact geometries, varying shape of light emission–potential curves, and the possible presence of traces of oxygen, which have been shown to drastically affect chemiluminescence in acetonitrile.[7] It was also observed that a potential–intensity scan of butylamine solutions with no rubrene present showed lower intensity light emission, but this did not occur at potentials where rubrene emission was observed, but only at potentials more positive, corresponding to a point well into the oxidation wave of the amine (*ca.* +2 v). Generally, the light-producing reactions for the cation alone were less intense than for the cation–anion annihilation reaction, although in the case of triethylamine in acetonitrile the intensity was about 50% of that observed from the annihilation reaction.

Table I. Relative Intensities of Chemiluminescence Produced by Reduction of Rubrene Radical Cation

Donor to R^+	Solvent	Rel intensity[a]
Rubrene radical anion	DMF	4×10^4
Rubrene radical anion	CH_3CN	10^4
Dimethylformamide	DMF	10^3
Dimethylformamide	CH_3CN	300
Triethylamine	CH_3CN	4×10^3
n-Butylamine	CH_3CN	10^3
Water	CH_3CN	50
n-Butylamine with no rubrene present	CH_3CN	5[b]

[a] Relative intensity is corrected for concentration of donor. [b] Light emission from *n*-butylamine with no rubrene present was observed only in the vicinity of +2 v, while emission when rubrene was present occurred around +1 v.

Light production from cation-radical reduction was found not to be a unique property of rubrene. Perylene, 9,10-diphenylanthracene, and 2,5,8,10-tetraphenylpyrene also produced light emission when only the cation radical was generated in DMF.

Figure 3 shows a comparison of the fluorescence spectrum of rubrene, the chemiluminescence spectrum for the cation–anion annihilation reaction, and the chemiluminescence spectrum for the cation–solvent reaction for rubrene in DMF. The fluorescence spectrum of rubrene was obtained using front-surface excitation. The chemiluminescence spectra were obtained using the cell shown in Figure 1. A square wave

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(8) E. A. Chandros and R. E. Visco, private communication.

(9) R. E. Sioda and W. S. Koski, *J. Am. Chem. Soc.*, **87**, 5573 (1965).

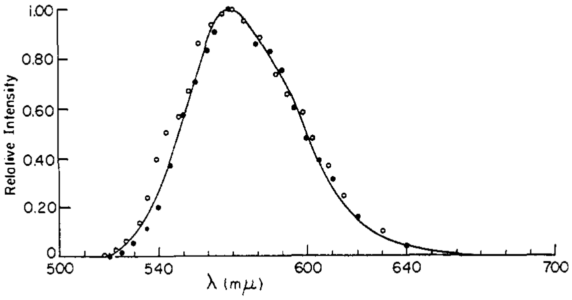

Figure 3. Comparison of chemiluminescence spectra with the fluorescence spectra of rubrene: ———, fluorescence spectrum of rubrene (front surface excitation); ●, points taken from smoothed chemiluminescence spectrum for cation–anion annihilation reaction; ○, points taken from smoothed chemiluminescence spectrum for cation–solvent reaction (all curves: 1.0 × 10^{-3} *M* rubrene, 1.0 × 10^{-2} *M* tetra-*n*-butylammonium perchlorate; solvent, dimethylformamide).

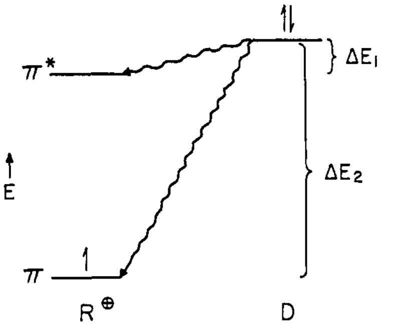

Figure 4. Comparison of possible pathways for chemiluminescence electron-transfer reactions.

was applied to the cell while slowly scanning the wavelength drive on the monochromator. This procedure gave an emission spectrum consisting of a series of light spikes as a function of wavelength. The peak readings for the spikes were treated with a smoothing program to estimate the continuous spectrum.[10] The points shown in Figure 3 are points taken from the smoothed curve calculated by the computer.[11] It is evident from Figure 3 that both light-emission reactions of rubrene give spectra which are identical with the spectrum of rubrene under the same conditions. This is consistent with the report that the rubrene cation–anion annihilation does not produce excimer spectra.[5]

That light emission is observed from reactions between rubrene radical cation and a variety of electron donors is consistent with the interpretation that any reaction which is sufficiently energetic to provide the rubrene cation with an electron *via* the π^*-orbital system should produce light emission. If there is an energy barrier to electron-transfer reactions requiring loss of a large amount of vibrational energy simultaneous with electron transfer, then transfer will be forbidden. Figure 4 shows the energy levels of the orbitals of rubrene and a potential electron donor. If we consider electron transfer from the donor to rubrene *via* the pathway $R^+ + D \rightarrow R^* + D^+$, loss of a small amount of energy (ΔE_1) is required, whereas the pathway $R^+ + D \rightarrow R + D^+$ requires a much greater energy loss (ΔE_2) and hence will be slower. This is consistent with the widely observed fact that internal conversion between excited singlet states of aromatic hydrocarbons occurs rapidly ($k_{ic} = 10^{13}$–10^{11} sec^{-1}), whereas internal conversion between the lowest excited singlet state and the ground state of a hydrocarbon occurs much more slowly ($k_{ic} < 10^5$ sec^{-1}). This interpretation is consistent with the recent discussion of Marcus[12] on the theory of chemiluminescence from electron-transfer reactions. The above interpretation implies that the light emission reaction observed between radical cations and radical anions is only one example of a more general type of chemiluminescence reaction involving electron transfer to a potentially fluorescent acceptor species.[13]

Although in reactions of the rubrene cation with species other than the anion one is tempted to assume a simple one-electron transfer from the donor, energy considerations are generally inconsistent with this interpretation. Light emission from rubrene requires approximately 2.2 ev (for the 0 → 0 transition) and in CH_3CN electrochemical oxidation of the hydrocarbon occurs at about +1.1 ev relative to the Ag|AgBr reference electrode. This implies that the oxidation wave for a potential electron donor to R^+ should be more negative than *ca.* −1.1 ev *vs.* the same reference electrode. Generally, the oxidation waves for the amines used in this study occur at potentials more *positive* than the rubrene oxidation wave. However, the amine oxidation waves are very irreversible[14] indicating that the observed $E_{1/2}$ value is not a valid measure of the thermodynamic oxidation potential of the amine. However, to produce sufficient energy for light emission the amine wave would have to be irreversible by 2.5 v or more, which is deemed rather unlikely. It is more likely that the actual light-producing step involves reaction of R^+ with an intermediate in the amine oxidation. Another possibility also exists. Since the amine oxidation is irreversible, the rising portion of the amine wave will overlap slightly with the rubrene wave and some amine will be oxidized at the electrode surface. However, studies on light emission as a function of potential scan range (reported later in this paper) indicate that intermediates produced by amine oxidation at the electrode surface make a minor contribution to the over-all light production.

On the basis of studies of electrochemical oxidation of triethylamine in nonaqueous solvents[15] we propose the following as a possible mechanism for light production by the rubrene cation (R^+).

$$R^+ + Et_3N \longrightarrow R + Et_3N^+ \text{ (in the diffusion layer)}$$
$$Et_3N \longrightarrow Et_3N^+ + e^- \text{ (at the electrode surface)}$$
$$Et_3N^+ + CH_3CN \longrightarrow Et_3NH^+ + \cdot CH_2CN$$
$$\cdot CH_2CN + R^+ \longrightarrow R^* + CH_2CN^+$$
$$R^* \longrightarrow R + h\nu$$
$$CH_2CN^+ \longrightarrow \text{products}$$

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[10] Computer program developed by A. Gordon and F. E. Lytle, MIT, 1966.

[11] It is important in comparisons such as that shown in Figure 3 that identical conditions of concentration be used because of the severe self-absorption effects observed at the concentration level used, about 10^{-3} *M*. It is also important that identical slit widths be used in the spectrometer for the same reason. These effects probably account for the larger spread of the data in the 540-mμ region.

[12] R. A. Marcus, *J. Chem. Phys.*, **43**, 2654 (1965).

[13] Other examples have been observed: F. E. Lytle and D. M. Hercules, to be published.

[14] C. K. Mann, *Anal. Chem.*, **36**, 2424 (1964).

[15] (a) R. F. Dapo and C. K. Mann, *ibid.*, **35**, 677 (1963); (b) C. D. Russell, *ibid.*, **35**, 1291 (1963).

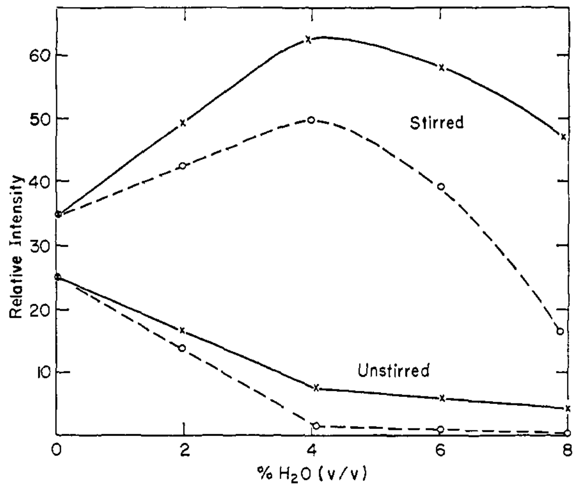

Figure 5. Effect of water on the chemiluminescence reaction of rubrene: top curves, stirred solutions; bottom curves, unstirred solutions; ×, scan range 0 to +1.2 v; ○, scan range −15 tc +1.2 v (all curves normalized).

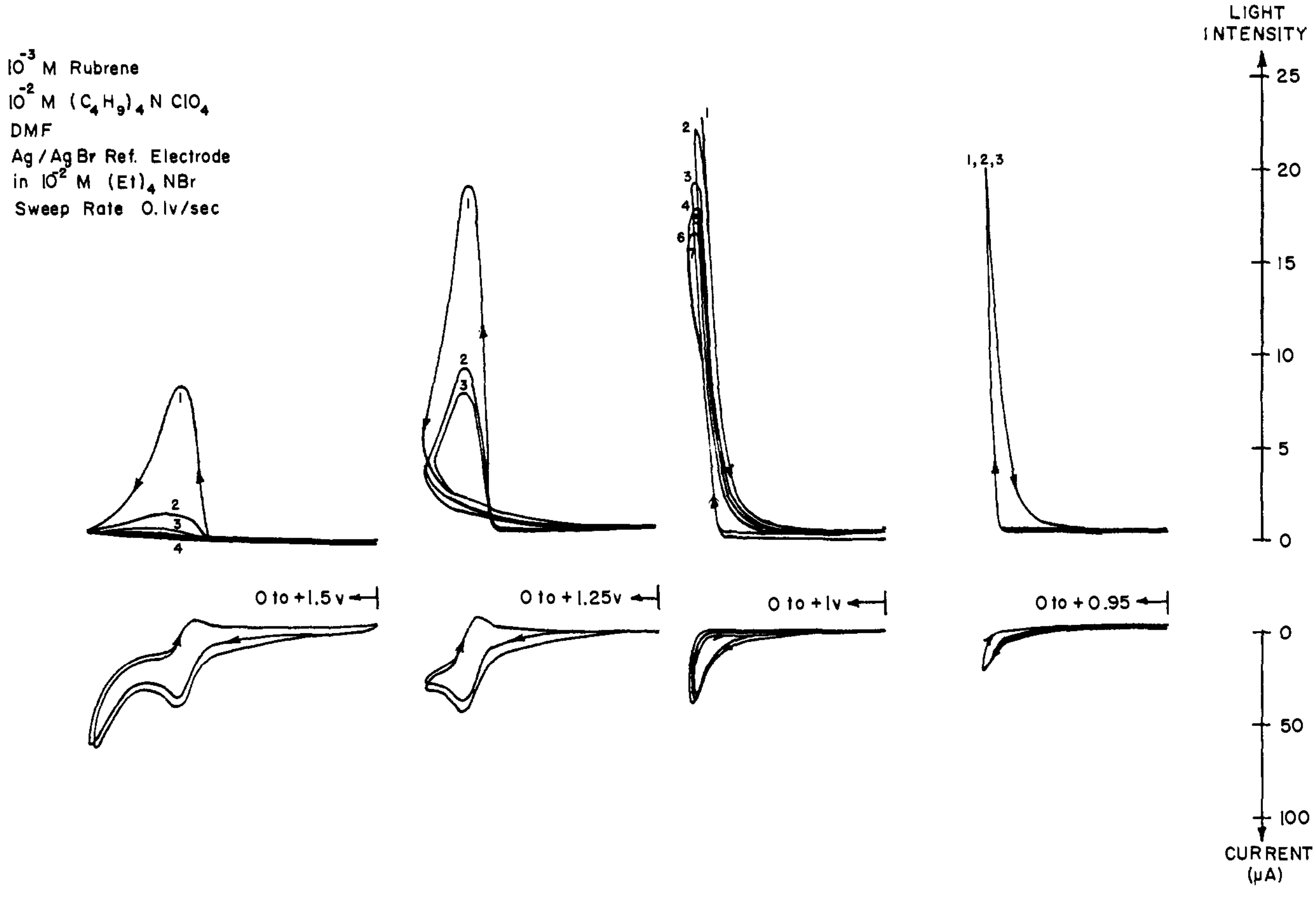

Figure 6. Effect of subsequent scans on the intensity potential curves for rubrene.

This mechanism is consistent with the fact that electron-transfer reactions involving amines are less efficient than the cation–anion reaction. Oxygen was found to quench chemiluminescence both of the annihilation reaction and of the cation–solvent reaction. This is consistent with observations of earlier workers[1,2] that equilibration with atmospheric oxygen completely quenched emission from a number of aromatic hydrocarbons. The quenching effect of oxygen on the chemiluminescence of rubrene cannot be accounted for by the effect of oxygen on the excited state of rubrene. It was observed that in dimethylformamide and acetonitrile the fluorescence efficiency of the rubrene was reduced only by *ca.* 10% on equilibration with atmospheric oxygen, whereas in the case of the annihilation reaction in acetonitrile 5×10^{-5} *M* oxygen reduced the apparent quantum efficiency of rubrene from 0.14 in a degassed solution to 0.01.[7] The effect of oxygen is not surprising as it is known that oxygen reacts rapidly with radical anions.

Some workers have reported that water has no effect on the cation–anion annihilation reaction[1,3] while others observed that water decreased light emission from this reaction.[2] We have studied the effect of water on the chemiluminescence from both the cation–anion reaction and from the cation–solvent reaction; the actual effect observed depends upon the amount of water added and the conditions of the solution, as indicated in Figure 5. In stirred solutions of rubrene in DMF it was observed that light intensity increased with water concentration to a level of 4% and then decreased. In unstirred solutions the light intensity decreased until 4% water was added and then continued to decrease, showing a change in slope. The change in slope observed at 4% is caused by precipitation of rubrene from solution. The similarity of the two curves suggests strongly that the effect of water on chemiluminescence is due to the effect of water on the cation radical since the forms of the curve appear to be independent of the electron donor. The difference in the sign of the slopes between stirred and unstirred solutions is puzzling. The most reasonable interpretation seems to be that water and the rubrene cation react in the Nernst diffusion layer, yielding products which quench the chemiluminescent reaction between them. In stirred solutions, these products are swept away from the face of the electrode surface so that reaction always occurs at a clean surface whereas in unstirred solutions these products accumulate in the diffusion layer and interfere with the chemiluminescent reactions of the cation.

The effect of repetitively scanning into the positive potential region was studied for rubrene in dimethylformamide and a varying effect on light emission behavior was observed as shown in Figure 6. When scanning over the potential range 0 to +1.5 v, after four successive scans no light emission could be observed on subsequent scans. As the potential scan range was decreased, the light emission behavior depended less on the number of previous scans, until scanning over the potential range 0 to +0.95 v the light intensity–voltage curves of successive scans were virtually superimposable. This behavior can be explained by the fact that, in DMF, oxidation of rubrene to the cation occurs just on the edge of the solvent oxidation wave. At positive potentials of *ca.* +1.5 v, significant solvent oxidation accompanies oxidation of the hydrocarbon, and the products of the solvent oxidation are accumulated in the vicinity of the electrode. This was demonstrated by the observation of a large reduction peak when the electrode was made cathodic after several successive scans into the anodic range. This peak was found to correspond to one observed when solvent containing no rubrene was oxidized. The solvent oxidation products quench the luminescent reaction of the radical cation, and therefore as they accumulate on subsequent sweeps into the oxidation region, light emission vanishes. However, when one sweeps onto just the foot of the rubrene wave, solvent oxidation does not occur to a significant extent, and the effect of solvent oxidation products on the light emission reaction is not observed.

Acknowledgments. We wish to acknowledge the assistance of Professor K. Bowers in the esr work. Dr. Donald Maricle suggested the tetraphenylpyrene as a possible chemiluminescent hydrocarbon. We wish to thank Dr. Jack Chang for repeating some of our measurements. This work is supported in part through funds provided by the U. S. Atomic Energy Commission under Contract AT(30-1)-905.

The X-Ray Structure Determination of Thujic Acid (7,7-Dimethylcycloheptatriene-3-carboxylic Acid)

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Abstract: The structure of the *p*-bromophenacyl ester of thujic acid (7,7-dimethylcycloheptatriene-3-carboxylic acid) has been determined employing three-dimensional X-ray crystallographic techniques. The structure was solved by the heavy atom method and then refined through successive electron and difference density syntheses and by the method of least squares. All the hydrogen atoms except three (one methyl group) have been located. The bond distances in the cycloheptatriene alternate, the 1,6 distance is 2.42 A, and the ring assumes a boat conformation. These facts preclude a norcaradiene arrangement and the planar, pseudo-aromatic structure previously proposed for the ring. The C7 atom is undergoing a large thermal vibration which is compatible with the observation that, in solution, the molecule is inverting between conformers. The geometry of the molecule implies a small twist in the 1,2 and 5,6 double bonds. Some relevant $2p_z$–$2p_z$ overlap integrals of the ring have been calculated and they are discussed in terms of a novel π-bonding system. The X-ray results are very similar to those obtained for tropilidene by electron diffraction.

At the time this work was initiated there was still some controversy concerning the nature of the tropilidene ring. Although it seemed clear that the system was a monocyclic triene, the question of its planarity remained unsettled.[3] A preliminary communication of this structure determination indicated that in thujic acid (7,7-dimethylcycloheptatriene-3-carboxylic acid): (1) the cycloheptatriene ring is in a boat conformation, (2) the bond lengths alternate, and (3) the molecule is probably inverting between boat conformers in solution.[4] Subsequent studies have supported the boat feature of the molecule[5–8] and have

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(3) For a concise review of the problem and some pertinent references, see J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3896 (1965).

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