(11) R. A. Olofson, J. M. Landesberg, K. N. Houk, and J. S. Michelman, J. Amer. Chem. Soc., **88**, 4265 (1966).
(12) P. Haake, L. P. Bauscher, and W. B. Miller, J. Amer. Chem. Soc., **91**, 1113 (1969).
(13) P. K. Glaskoe and F. A. Long, J. Phys. Chem., **64**, 188 (1960).

Figure 1. Cyclic voltammogram of a dichloromethane solution containing 1 mM RBr_2 and 0.1 M TBAP at a platinum electrode; the solvent background reduction occurs shortly beyond the span shown.

Electrogenerated Chemiluminescence. XIX. Preparation and Chemiluminescence of 5,12-Dibromo-5,12-dihydro-5,6,11,12-tetraphenylnaphthacene[1]

Csaba P. Keszthelyi and Allen J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received February 27, 1974

In recent years considerable interest has been centered on reactions that convert chemical energy directly to light, with the discovery of new chemiluminescor compounds comprising an important segment of the work. Two general types of electrogenerated chemiluminescence (ecl) have been investigated. The most widely studied is ecl occurring when reduced (A$^-$) and oxidized (D$^+$) species (frequently radical ions) generated at an electrode undergo an electron transfer reaction producing an electronically excited state (eq 1).[2] A second form of ecl involves the reduction of cer-

$$A^- + D^+ \longrightarrow D + A^*(\longrightarrow A + h\nu) \qquad (1)$$
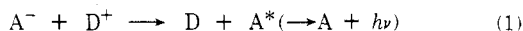
tain halogenated hydrocarbons [e.g., 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene (DPACl$_2$)] at an electrode without the electrogeneration of an oxidant;[3,4] chemical reduction of these same compounds, e.g., DPACl$_2$, by naphthalene or 9,10-diphenylanthracene (DPA) radical anions was shown to produce light in earlier studies.[5] The ecl studies of Siegel and Mark[3,4] demonstrated that the electrode potential must be such that reduction of the DPACl$_2$ and the generation of a radical anion occurs for emission to be observed. Thus reduction of DPACl$_2$ and 5,6,11,12-tetraphenylnaphthacene (rubrene) (I) produces emission characteristic of rubrene fluorescence[3,4] while reduction of DPACl$_2$ and $\alpha,\beta,\gamma,\delta$-tetraphenylporphin (TPP) produces emission from excited TPP.[6] We report here the preparation of 5,12-dibromo-5,12-dihydro-5,6,11,12-tetraphenylnaphthacene (RBr$_2$) (II) and the luminescence produced on its electroreduction. The preparation and chemiluminescent properties of this molecule have not previously been reported.

Results

When rubrene in dry dichloromethane solution is treated with bromine at room temperature, RBr$_2$ is produced (eq 2)
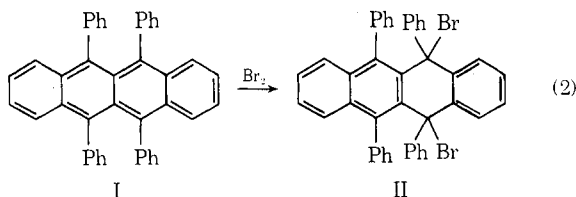
with the quantitative uptake of 1 mol of Br$_2$/mol of rubrene, without further bromination even in the presence of excess bromine. The solid RBr$_2$ decomposes at atmospheric pressure at temperatures above 120° to produce rubrene (identified by its fluorescent spectrum) and bromine; thermogravimetric studies of RBr$_2$ confirm the liberation of 1 mol of Br$_2$/mol of RBr$_2$ with the production of pure rubrene.[7] Uv irradiation of solutions of RBr$_2$ also causes decomposition with the production of rubrene. RBr$_2$ itself
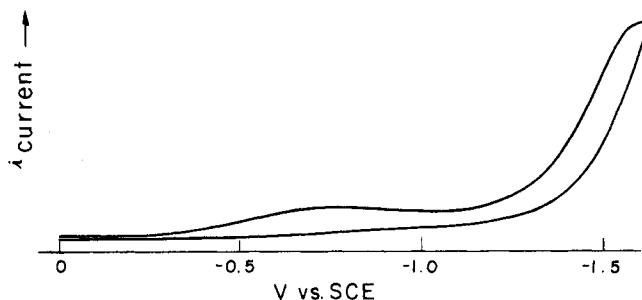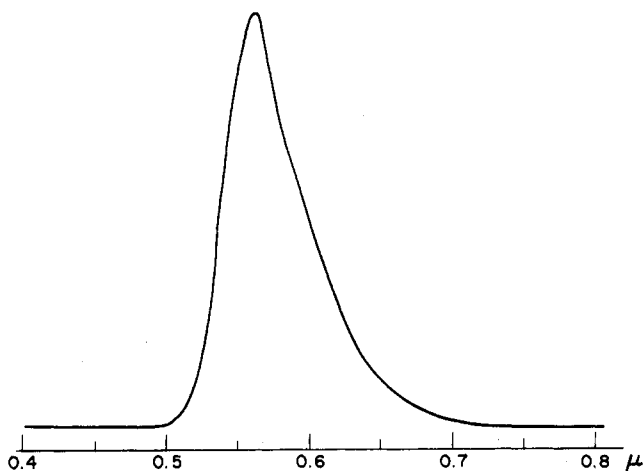
Figure 2. Electrogenerated chemiluminescence observed in the solution of Figure 1 upon application of a steady potential corresponding to the reduction peak.

shows weak fluorescence emission (λ_{max} 402 nm) and an excitation maximum at 320 nm; these results are consistent with absorption and emission from a molecule containing a conjugated diphenylnaphthalene chromophore.

A cyclic voltammogram for the reduction of RBr$_2$ in dichloromethane containing 0.1 M tetra-n-butylammonium perchlorate (TBAP) at a platinum electrode, shown in Figure 1, shows an irreversible reduction wave at about -1.5 V vs. sce. Since the reduction of rubrene (R) to its radical anion (R$\cdot^-$) occurs with an $E_{1/2}$ value of -1.39 V vs. sce, any rubrene produced in the reduction of RBr$_2$ is immediately reduced further. The electroreduction is accompanied by the emission of radiation characteristic of rubrene fluorescence (λ_{max} 560 nm) (Figure 2). Although a detailed mechanistic study of the mechanism of electroreduction of RBr$_2$ has not been carried out, the reaction probably follows a sequence of electron transfers and loss of bromide ions (an ecec reaction) leading to rubrene, as observed in the electrochemistry of other organic halides.[8] The overall electrode reaction is thus

$$RBr_2 + 3e \longrightarrow R\cdot^- + 2Br^- \qquad (3)$$
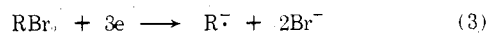
By analogy with previous systems of this type,[3–5] the production of excited state rubrene probably results from reaction of a strong oxidant intermediate (formed by reduction of the RBr$_2$ diffusing toward the electrode by R$\cdot^-$ diffusing away from it) with another molecule of R$\cdot^-$, for example

$$RBr_2 + R\cdot^- \longrightarrow RBr\cdot + Br^- + R \qquad (4)$$

$$RBr\cdot + R\cdot^- \longrightarrow R + Br^- + R^* \qquad (5)$$
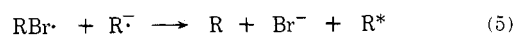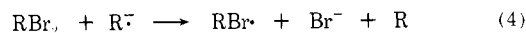
It is possible that reaction 4 produces an excited state, although it is unlikely that the free energy of this reaction is sufficient to produce excited rubrene directly. Following Siegel and Mark's[4] suggestion, there is also the possibility of dissociation of RBr· to R·[+] and Br^{−} followed by the familiar ecl reaction of R·[+] and R·[−] to produce an excited state.

Experimental Section

Rubrene, $C_{42}H_{28}$, puriss., mp >300°, from Aldrich Chemical Co., was recrystallized twice from a mixture of dichloromethane and hexane (both solvents are spectroscopic grade). A number of preparations of II were carried out under slightly different conditions, indicating that bromination proceeds readily and quantitatively. In a typical preparation, 50 mg of I was dissolved in 30 ml of dried dichloromethane under subdued light to reduce formation of rubrene photoperoxide, followed by stepwise addition of bromine until a 50% excess was present. The reaction between I and Br_2 is immediate at room temperature, and pure II was recovered by evaporation of solvent and excess bromine in a stream of purified nitrogen. The product II was recrystallized by dissolving it in dichloromethane, followed by addition of hexane to the solution which causes pale yellow crystals of II to separate out. *Anal.* Calcd for $C_{42}H_{28}Br_2$: C, 72.85; H, 4.08; Br, 23.08. Found: C, 72.70; H, 3.89; Br, 23.20. In separate experiments the quantitative uptake of 1 mol of Br_2/mol of I was verified by carrying out the initial preparation under gravimetric conditions, without transferring the product II prior to weighing.

The compound II does not exhibit a well-defined melting point; decomposition by the liberation of bromine gas commences above 100°, and continues past 150°, even at moderate heating rates. We have maintained room temperature conditions throughout our preparations; the possibility of additional bromination under strenuous conditions and a large excess of bromine cannot be ruled out. Moureu and Dufraisse[9] mention that in chloroform solutions under unspecified conditions rubrene adds four bromine atoms to yield products with exceptionally high melting points.

The ecl experiments generally followed previous practice.[2] Necessary precautions that have been adopted in this field over the years include the exclusion of air and moisture, hence the glassware housing the test solution and electrodes was evacuable and could be removed from the vacuum line in a hermetically sealed condition. In preparing the ecl solutions the solid supporting electrolyte, TBAP, was first dried in the ecl cell at 100° using a hot water bath, and the solute was added only subsequently with brief drying under reduced pressure at room temperature to remove any traces of solvent from the recrystallization procedure. Dried, freeze–pump–thawed CH_2Cl_2 is subsequently transferred under a temperature gradient into the ecl cell containing II and TBAP, followed by freeze–pump–thawing. The experimental procedure for generating and recording the ecl emission, as well as the cyclic voltammetric studies, were according to established methods.[10] Because of possible interference by oxygen, fluorescence studies were also conducted in a sealed cell containing freeze–pump–thawed CH_2Cl_2–II solutions. Fluorescence and ecl spectra were obtained with an Aminco-Bowman spectrophotofluorometer and are uncorrected for photomultiplier response (Hamamatsu TV Corp., R456, having uv improved S-20 characteristics).

References and Notes

(1) This was paper No. 226 presented at the 29th Southwest Regional Meeting of the American Chemical Society, Dec 5–7, 1973, El Paso, Texas; work was supported by the U.S. Army Research Office—Durham.

(2) A. J. Bard, C. P. Keszthelyi, H. Tachikawa, and N. E. Tokel in "Chemiluminescence and Bioluminescence," M. J. Cormier, D. M. Hercules, and J. Lee, Ed., Plenum Press, New York, N. Y., 1973, p 193, and references therein.

(3) T. M. Siegel and H. B. Mark, Jr., *J. Amer. Chem. Soc.*, **93**, 6281 (1971).

(4) T. M. Siegel and H. B. Mark, Jr., *J. Amer. Chem. Soc.*, **94**, 9020 (1972).

(5) E. A. Chandross and F. I. Sonntag, *J. Amer. Chem. Soc.*, **88**, 1089 (1966).

(6) N. E. Tokel, C. P. Keszthelyi, and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 4872 (1972).

(7) P. K. Dasgupta and C. P. Keszthelyi, unpublished results.

(8) M. R. Rifi in "Organic Electrochemistry," M. M. Baizer, Ed., M. Dekker, New York, N. Y., 1973, p 279.

(9) C. Moureu and C. Dufraisse, *Z. Phys. Chem.*, **130**, 472 (1927).

(10) C. P. Keszthelyi, H. Tachikawa, and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 1522 (1972).