

together with 5% of volatile material. The bulk of this is  $C_6Cl_6$ , but about 20% has been identified as 1,1-dimethoxytetrachlorocyclopentadiene, by comparison of v.p.c. retention time, n.m.r. spectrum, and mass spectrum with those of an authentic sample.<sup>10</sup> Thus only 1% of the product seemingly derived from II can be found; the major reaction of  $C_6Cl_6$  is Lewis acid catalyzed dimerization<sup>11</sup> and subsequent changes. With  $AlCl_3$ ,  $BF_3$ ,  $SbCl_5$ , or  $SbF_5$  in  $SO_2$ ,  $C_6Cl_6$  gives no detectable triplet signal,<sup>12</sup> although all give the strong doublet radical signal at  $g = 2$ .

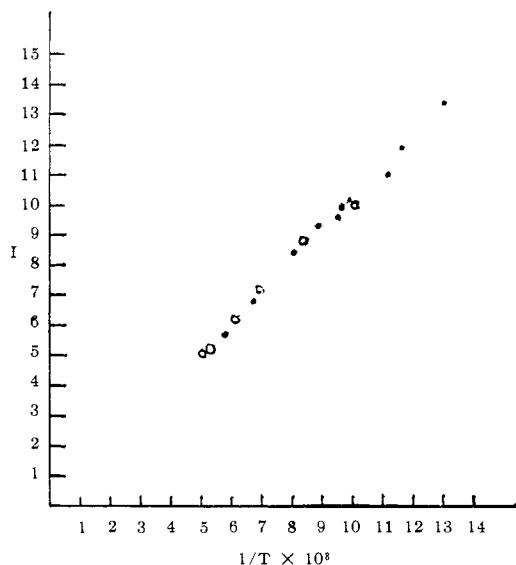


Fig. 2.—Amplitude of  $\Delta m = 2$  signal vs. reciprocal temperature: O, run A (Columbia); ●, run B (Bell Labs).

The e.s.r. spectrum of the  $\Delta m = 2$  transition was observed as a function of temperature (Fig. 2). For a triplet excited state lying  $E_a$  above the ground singlet state the intensity of the signal should be related to the temperature by

$$\text{intensity } (I) = k/T \left( \frac{3e^{-E_a/(RT)}}{1 + 3e^{-E_a/(RT)}} \right)$$

As Fig. 2 shows, experimentally we see essentially no variation from the Curie Law ( $I = k/T$ ) down to 77°K. With an  $E_a$  of 30 cal./mole the lowest temperature point would deviate from the straight line, because of the exponential term, by 5%, while an 8% deviation would result from  $E_a = 46$  cal./mole. From the plot in Fig. 2 the triplet is thus either the ground state or very close to it. Additional evidence on this point is found in the fact that the corrected intensity of the  $\Delta m = 2$  signal at 4.2°K. is 22 times that of the same sample at 77°K., as expected if  $E_a$  is zero. The observed ratio of 22 has an uncertainty of perhaps 30–40%.<sup>13</sup> We conclude that the triplet is either the

(10) J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, **71**, 948 (1949).

(11) J. S. Newcomer and E. T. McBee, *ibid.*, **71**, 952 (1949); E. T. McBee, J. D. Idol, and C. W. Roberts, *ibid.*, **77**, 4375 (1955).

(12) See also H. P. Fritz and L. Schäfer, *J. Organometallic Chem.*, **1**, 318 (1964).

(13) Variations in  $Q$  and in the filling factor and some residual saturation at liquid helium are expected to be significant contributors to this uncertainty.

ground state of the system or at most 6–8 cal./mole from it.<sup>14</sup>

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### Electroluminescence in Solutions of Aromatic Hydrocarbons

Sir:

We have studied an unusual type of electroluminescent cell which operates on alternating current (a.c.) at applied voltages  $\geq 3.5$  v. and produces bright chemiluminescence from the reaction between positive and negative radical ions derived from aromatic hydrocarbons.

Hoijsink has observed chemiluminescence upon mixing solutions of electrogenerated anthracene positive and negative ions.<sup>1</sup> We were able to perform a similar experiment in a single vessel but decomposition occurs rapidly. We hoped to improve the efficiency of this experiment by using a.c. electrolysis and by choosing compounds having greater chemical stability and higher fluorescence efficiency than anthracene. A.c. electrolysis provides a means of generating both radical ions at the same electrode by diffusion-controlled electrochemical reactions on alternate half-cycles. It is then possible for these species to undergo the chemiluminescent reaction in the Nernst diffusion layer rather than to require mechanical transport of the reactants with concomitant opportunity for side reactions. The surface concentration of R is virtually zero during the entire voltage cycle, and a continued diffusion of starting material is ensured. The disadvantages that the highly colored radical ions ( $R^+$  and  $R^-$ ) react readily with traces of oxygen and water and that these ions in general undergo other undesirable side reactions, leading to discoloration of the solution, appear to be greatly reduced by the use of a.c.

The electrochemical processes associated with anthracene and its derivatives have been studied previously.<sup>2–5</sup> Reduction yields the stable anion radical. It has been reported that electrochemical oxidation of anthracene gives the dipositive cation  $R^{2+}$ , but some substituted anthracenes appear to give  $R^+$  and/or  $R^{2+}$ . We have investigated the behavior of 9,10-diphenylanthracene (DPA) as a model system. Solutions (DMF) of anthracene, perylene, rubrene, quaterphenyl, and 1,1,4,4-tetra-phenylbutadiene were also found to luminesce under our conditions.<sup>6</sup> The working electrodes

(1) Professor G. J. Hoijsink (Amsterdam) mentioned these results during a visit in the summer of 1963.

(2) P. H. Given, *J. Chem. Soc.*, 2684 (1958).

(3) G. J. Hoijsink, J. von Schooten, E. de Boer, and W. Aalbersberg, *Rec. trav. chim.*, **73**, 355 (1954).

(4) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).

(5) J. D. Voorhies and N. H. Furman, *Anal. Chem.*, **31**, 381 (1959).

(6) The solvents employed were Spectrograde N,N-dimethylformamide (DMF), Spectrograde acetonitrile (AN), N-methylpyrrolidone, acetone, or glyme. Solvents used for detailed electrochemical studies were further purified by commonly used procedures: J. F. Coetzee, *et al.*, *Anal. Chem.*, **34**, 1139 (1964); S. Wawzonek, *et al.*, *J. Electrochem. Soc.*, **102**, 235 (1955). Tetraalkylammonium perchlorates were supporting electrolytes; alkali perchlorates or chlorides can also be used. Oxygen was excluded by passing dry  $N_2$  through or over the solution.

were platinum coaxial helices or parallel pairs of platinum or gold foils. Isolated aqueous saturated calomel electrodes were used as reference electrodes. Qualitative experiments were done with 60 c.p.s. sine-wave alternating current, but measurements were made with square-wave alternating current.

In stirred solutions operating in the potentiodynamic mode with a.c. voltage of sufficient magnitude, bright DPA fluorescence is observed in the vicinity of the working electrode. In quiet solutions (electrodes separated by several centimeters), where the products of one electrode cannot be transported to the other electrode, luminescence originates within a few millimeters of the electrode surfaces. The intentional addition of water or molecular oxygen decreases the light intensity but does not entirely quench the process.

The variation of electroluminescence intensity with applied voltage and frequency was measured at  $\lambda_{\max}$  (identical with that of the normal fluorescence) with a monochromator and photometer. Intensity increased linearly with voltage up to a point<sup>7</sup> but leveled off thereafter. At frequencies below 100 c.p.s. more than 95% of the light is modulated, while at 2 kc.p.s. at least 80% is modulated. The output frequency is *twice* that of the square-wave input, peaking on each half-cycle. Intensity decreases as the frequency is raised, and the upper limit ( $\geq 10$  kc.) appears to be determined by the  $RC$  (resistance  $\times$  capacitance) time constant of the electrochemical cell. At a few cycles per second, discrete light pulses can be seen.

Cyclic voltammetry<sup>8</sup> was used to study the anodic and cathodic processes of DPA in both DMF and AN. In agreement with earlier steady-state measurements,<sup>2-5</sup> reduction in DMF yields a stable blue radical at a peak potential of  $-1.95$  v. *vs.* s.c.e. without evidence of irreversibility up to sweep rates of 0.3 v./sec. Oxidation in DMF, with a peak potential of  $+1.25$  v. *vs.* s.c.e., appears to be complicated by the simultaneous oxidation of the solvent (or possible impurities). There is an oxidation process proportional to the concentration of DPA, but repeated cycling also produces electroactive species identical with those observed when the solvent alone is electrolyzed. The products of oxidation in DMF are colorless, and no cathodic current corresponding to the reduction of an oxidized DPA species is observed on reversing the sweep. Potentiostatic experiments in both stirred and quiet solutions with separated, but not isolated, electrodes indicate that the colorless product of DPA oxidation in DMF is a relatively long-lived and sufficiently strong oxidizing agent to react with  $R^-$  in the chemiluminescent process.

In AN the blue anion radical can be observed visually at  $-1.8$  to  $-2.0$  v., but reduction occurs too close to solvent reduction for quantitative measurements. There are two well-defined one-electron oxidations in AN. The peak potential of  $+1.22$  v. for the first process, invariant with sweep rate up to 1.4 v./sec., has a peak current proportional to the square root of the sweep rate. A cathodic process with current equal to that of the first anodic process is observed when the sweep direction is reversed. The electrochemical data<sup>8</sup> and the observation of a blue product at the anode

(7) In the particular cell used, luminescence was observed at *ca.* 3.5 v. and tapered off above *ca.* 15 v.

(8) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

demonstrate that the electrochemical process is associated with the reversible  $R^+ - R$  couple. The second anodic process at  $+1.6$  v., of magnitude comparable to the first, is a further irreversible one-electron oxidation since the peak potential becomes more anodic with increasing sweep rate. The cyclic voltammograms in AN indicate that  $R^+$  has a chemical lifetime of at least 10 sec.

By varying the midpoint of the triangular voltage program, it could be demonstrated (in AN) that  $R^+$  and  $R^-$  are the reactants in the chemiluminescent reaction coupled with the electrochemical charge-transfer reactions. A discussion of the basis for chemiluminescence in the reactions



for this and other related systems is given elsewhere.<sup>9</sup> The reaction of  $R^-$  with various oxidizing agents to form the excited singlet of  $R$  is compatible with our observation of luminescence in DMF even though these solutions do not appear to have any appreciable concentration of  $R^+$ . The general requirement for chemiluminescence in these systems appears to be the reaction of a nonquenching oxidizing agent with  $R^-$ , which provides sufficient energy. For DPA this is 2.9-3.0 e.v., corresponding to the fluorescence peaks at 435 and 410 m $\mu$ . The chemiluminescent reaction of  $R^-$  with the oxidized form of DPA (which is *not* the radical cation) seems to satisfy these conditions. The difference in the standard potentials of the  $R - R^-$  and  $R^+ - R$  couples in AN is sufficient to provide the required energy.<sup>10</sup>

**Acknowledgment.**—We wish to thank Dr. J. W. Longworth for his assistance in making some of the photometric measurements.

(9) E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964).

(10) NOTE ADDED IN PROOF.—Qualitative observations of electroluminescence have recently been reported by D. M. Hercules, *Science*, **145**, 808 (1964). Low-frequency alternating current (up to 10 c.p.s.) was utilized in some of the experiments.

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### Visible Absorption Spectra of Sodium in Molten Sodium Iodide

Sir:

In order to establish a possible correlation between the visible absorption of alkali metals in molten alkali halides and F center formation as observed in the solid, the visible absorption spectra of Na in molten NaI were obtained.

Quartz cuvettes, 1 cm. in diameter (i.d.), were used as containers. Although heated alkali metal vapors react with silicates, it was found that if the salts were anhydrous, the alkali metal would dissolve in the salt without discoloring that portion of the cell containing the melt. The cells were wrapped with inconel heating strips and placed in an insulating container. The steady-state temperatures were controlled by means of a Variac to within  $\pm 5^\circ$ . The temperature of the system was measured by means of a platinum-platinum-13% rhodium thermocouple.