

Reports

Chemiluminescence Resulting from Electrochemically Generated Species

Abstract. *Chemiluminescence is reported from chemical species produced during electrolysis of aromatic hydrocarbons in deoxygenated nonaqueous solvents. Emission occurs in the solution near the cathode, and the emitting species is the excited singlet state of the hydrocarbon. Oxygen exerts a severe quenching effect on the chemiluminescence. Possible mechanisms are discussed.*

Although a number of workers have studied a variety of chemiluminescent systems, relatively little attention has been focused on light emission caused by electrolysis. In 1929 Harvey observed that chemiluminescence of luminol could be produced by electrolysis in solution (1), and a few other investigators followed up this work (2). Kuwana and co-workers using modern electrochemical techniques have studied the luminol system in detail (3).

This report describes the production of chemiluminescence by the reaction of species produced during electrolysis of aromatic hydrocarbons dissolved in deoxygenated nonaqueous solvents. The emission observed appears to be from an excited singlet state of the hydrocarbon and the light reaction occurs in solution, not at the electrode surface.

Three different arrangements of electrodes were used: a single platinum

working electrode with an external counter electrode separated from the solution by a fritted glass disc of fine porosity; two platinum-foil electrodes separated from each other by about 1 cm; and two concentric cylindrical electrodes, the interior one a platinum rod (2.5 mm in diameter) and the exterior one constructed from 52-mesh platinum gauze (6 mm in diameter). Studies were carried out (i) by passing a current through the cell (without stirring the solution) for a given period of time and then quickly reversing the direction of current flow; (ii) by applying a constant direct-current voltage, both with or without stirring; and (iii) by applying an alternating-current square wave, both with or without stirring. The solvents used were dimethylformamide and acetonitrile, purified according to described procedures (4, 5). The supporting electrolytes were tetra-

ethylammonium bromide and tetraethylammonium perchlorate (both polarographic grade); they were dried in a vacuum oven for several hours at 60°C before being used.

The current-reversal technique with a single electrode was used. A current of 3 to 10 ma was passed through the cell for about 10 seconds and then the direction of current flow was reversed. By this procedure the cathodically produced species was generated in the vicinity of the anodically produced species and vice versa. Under these conditions emission occurred as a glow covering the electrode and extending about 0.5 to 1.0 mm into solution above the electrode surface. There was a delay of about 1 to 2 seconds between switching the direction of current flow and observing the emission. The emission rose to a maximum intensity in about 3 seconds and then fell quickly. When the solution was stirred, streaming of luminescence from the electrode into solution (about 1 cm) was observed. Generally, emission was more intense on switching the electrode from plus to minus than on going from minus to plus.

When two square platinum electrodes were used and the solution was vigorously stirred, the emission observed continuously in the vicinity of the cathode, and was sufficiently bright for some compounds (notably rubrene) that it was visible in dim room light. The square-wave alternating current produced a flashing effect alternately at the two electrodes and could excite luminescence up to a frequency of 10 cy/sec for rubrene. When the concentric cylindrical electrodes were used with 3 to 4 volts of direct current, a continuous emission was observed even when the solution was not stirred, diffusion being sufficient to mix the reacting species.

Figure 1 shows a photograph of a cell taken by light from the chemiluminescent reaction. Table 1 lists some of the hydrocarbons studied, the solvents and electrolytes used, and the color of chemiluminescence compared with the color of solution fluorescence.

Some characteristics of the chemiluminescent reaction have been deduced from simple experiments. The hydrocarbon is essential for chemiluminescence because no emission was observed at the same current densities when only supporting electrolyte and solvent were used. The correlation between the color of chemiluminescence

Table 1. Aromatic hydrocarbons showing chemiluminescence produced by electrochemically generated species. The hydrocarbon concentrations were $10^{-3}M$. The supporting electrolyte concentrations were 0.1 or 0.01M.

Aromatic hydrocarbon	Solvent*	Electrolyte†	Color‡	
			Chemiluminescence	Solution fluorescence
Anthracene	CH ₃ CN	TEAB	Blue-white (w)	Blue-violet
Chrysene	CH ₃ CN	TEAB	Blue-white (m)	Blue-violet
Chrysene	DMF	TEAP	Blue-white (m)	Blue-violet
Pyrene	DMF	TEAB	Blue-white (s)	Blue
Naphthacene	DMF	TEAB	Green (s)	Green
Perylene	DMF	TEAP	Blue (s)	Blue
Perylene	CH ₃ CN	TEAB	Blue (s)	Blue
Perylene	DMF	TEAB	Blue (s)	Blue
Coronene	DMF	TEAB	Blue (m)	Blue
Rubrene	DMF	TEAB	Orange-red (vs)	Orange-red
Decacyclene	DMF	TEAB	Green (w)	Green
1,2,5,6-Dibenzanthracene	DMF	TEAB	Blue-violet (m)	Violet

* DMF, dimethylformamide. † TEAB, Tetraethylammonium bromide. TEAP, tetraethylammonium perchlorate. ‡ w, weak emission; m, moderate intensity; s, strong emission; and vs, very strong emission.

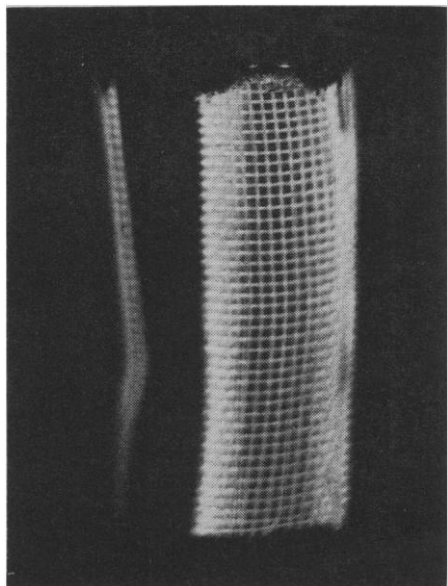


Fig. 1. Electrochemically generated luminescence; emission from the electrode is the only source of light (60 seconds; f , 4.5; Royal-X-pan film). The solution was $10^{-3}M$ rubrene in dimethylformamide with $0.01M$ tetraethylammonium bromide as supporting electrolyte. Concentric electrodes with nitrogen continuously bubbling through the solution. The clear definition of the electrode grids when viewed head-on, and the diffuse glow at the sides indicate that the glow occurs in solution near the inside electrode surface.

and normal fluorescence indicates that the lowest excited singlet state of the aromatic hydrocarbon is the emitting species. Because chemiluminescence was observed with both perchlorate and bromide as supporting electrolytes, anodically produced bromine does not participate in the light-producing reaction. Also, allowing a dilute bromine solution to flow over the cathode during electrolysis produced no emission. Because of the delayed response encountered in the current-reversal experiments and the observation of streams of luminescence in stirred solutions, chemiluminescence is not produced by a reaction at the electrode surface. In stirred solutions, emission was observed only in the vicinity of the cathode, and this indicates that the more stable of the two species is generated at the anode. This observation may be correlated with the emission observed at the electrode when the current was reversed from plus to minus—although sometimes a weaker emission could be seen at the other electrode, particularly in the case of chrysene. Also, in the current-reversal experiments, if the circuit was broken while chemiluminescence was being emitted, the emission dropped

off quickly, but was resumed at a reduced intensity upon connecting the circuit again. This process could be repeated several times, the emission becoming less intense each time, until finally no emission was observed upon connecting the circuit. Oxygen showed a pronounced quenching effect on the emission, indicating the participation of free radicals, since all of the hydrocarbons studied are fluorescent in air-saturated solutions at room temperature. Water had no effect on the emission, a result that was surprising but consistent with observations on the electrochemical behavior of the biphenyl negative radical ion (4).

One is tempted to interpret the chemiluminescence as arising from the reaction of hydrocarbon radical ions (Ar^+ and Ar^-) to produce an excited singlet state (Ar^*):



which then emits its characteristic fluorescence. However, this interpretation is not consistent with all the data presented. Because emission in stirred solutions occurs mainly in the vicinity of the cathode and because the positive aromatic hydrocarbon ions are less stable under the conditions of the experiments than the negative radical ions (6), it seems unlikely that Ar^+ would be transported from the anode to the cathode while the more stable Ar^- is not transported from the cathode to the anode.

The species produced at the cathode seems to be Ar^- as judged by colors observed with the naked eye at the cathode when electrolyses were performed in room light. This would suggest the possibility of oxidation of Ar^- by an anodically generated species to produce chemiluminescence. Energy considerations argue against such a mechanism because, to produce an excited singlet state of the hydrocarbon by oxidation of Ar^- , one must remove an electron from a π -bonding orbital while leaving an electron in a higher-energy π -antibonding orbital. This also leaves the nature of the species produced at the anode in question, because the experiments described indicate that luminescence cannot be produced by oxidation of Ar^- by molecular bromine. The possibility of having a complexed bromine radical (such as Br_2^-) react with Ar^- is unlikely because chemiluminescence is observed in perchlorate media.

One possible way out of the dilemma is to postulate production of a com-

plexed aromatic positive radical ion (such as Ar_2^+) at the anode which is stable enough to be transported to the cathode. Although no such species has been reported, Ar^+ is a good electron acceptor and aromatic hydrocarbons are good electron donors, forming molecular complexes readily. This idea receives some support from the fact that molecular complex formation has been reported with the tropylium ion (7) and the pyrylium ion (8) as acceptors, and that the concentration of hydrocarbon in these studies ($10^{-3}M$) is in the range where complex formation is known to occur.

DAVID M. HERCULES

Department of Chemistry and
Laboratory for Nuclear Science,
Massachusetts Institute of Technology,
Cambridge

References and Notes

1. N. Harvey, *J. Phys. Chem.* **33**, 1456 (1929).
2. V. Vojtík, *Collection Czech. Chem. Commun.* **19**, 862 (1954); A. Bernanose, T. Bremer, P. Goldfinger, *Bull. soc. chim. Belges* **56**, 269 (1947).
3. T. Kuwana, *J. Electroanal. Chem.* **6**, 164 (1963); —, B. Epstein, E. T. Seo, *J. Phys. Chem.* **67**, 2243 (1963).
4. D. Maricle, *Anal. Chem.* **35**, 683 (1963).
5. J. F. Coetzee, G. P. Cunningham, D. K. McGuire, G. R. Padmanabhan, *Anal. Chem.* **34**, 1139 (1962).
6. J. P. Paris, W. Prichard, D. M. Hercules, unpublished studies, Juniata College, 1962.
7. M. Feldman and S. Winstein, *J. Am. Chem. Soc.* **83**, 3338 (1961).
8. —, *Tetrahedron Letters*, **1962**, 853 (1962).
9. Supported in part by the U.S. Atomic Energy Commission under contract AT(30-1)-905 and by USPHS grant GM 11766-01 from the National Institutes of Health. I thank J. P. Paris for his contribution to this work.

1 July 1964

Late Eocene Multituberculates and Other Mammals from Wyoming

Abstract. *Isolated teeth of multituberculates have been found in association with late Eocene fossil mammals. Previous studies reported that multituberculates were not found in deposits younger than early Eocene age (Graybull provincial substage or equivalents). This newly found occurrence indicates that these animals are more likely to be late Eocene in age than reworked early Eocene materials.*

Joint field parties of Carnegie Museum and the University of Colorado Museum have been collecting fossil vertebrates from upper Eocene deposits (Tepee Trail formation, Hendry Ranch member) of the Badwater area, Natrona County, Wyoming (1, 2). In the course of collecting small fossils by washing techniques, remains of a multi-