Electrochemiluminescence of 9,10-Dichloroanthracene and 9,10-Dibromoanthracene

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Recent investigations on the electrochemiluminescence (ECL) of organic compounds have revealed that in most cases the emission spectra coincide with the fluorescence spectra of the corresponding compounds. However, in some compounds such as anthracene, the ECL spectra have components which cannot be assigned to fluorescence,[1] and their assignments are still in question. We recently found from an investigation of the ECL of 9,10-dichloroanthracene (9,10-di-Cl-A) and 9,10-dibromoanthracene (9,10-di-Br-A) that the ECL of the former was composed of two main components which were clearly distinguishable, while the ECL of the latter had only one component. In this communication we wish to elucidate the difference in ECL of these compounds.

Synthesized 9,10-di-Cl-A and 9,10-di-Br-A were purified by sublimation. In a *N,N*-dimethylformamide (DMF) solution containing potassium perchlorate as a supporting electrolyte, the ECL of both compounds was examined at a platinum wire electrode of 0.05 cm in diameter and 3 cm in length. A 40-Hz square-wave potential (less than 6V) was applied to the working electrode with a function generator. Dried nitrogen gas was passed through the solution during the measurements.

The results[2] obtained at room temperature are shown in Figs. 1 and 2 for 9,10-di-Cl-A (7×10^{-4}M) and 9,10-di-Br-A (5×10^{-4}M), respectively. Fluorescence spectra measured under the same conditions as those of ECL measurements are also given. Ordinate scales are arbitrary for ECL and fluorescence, hence their intensities cannot be compared with each other.

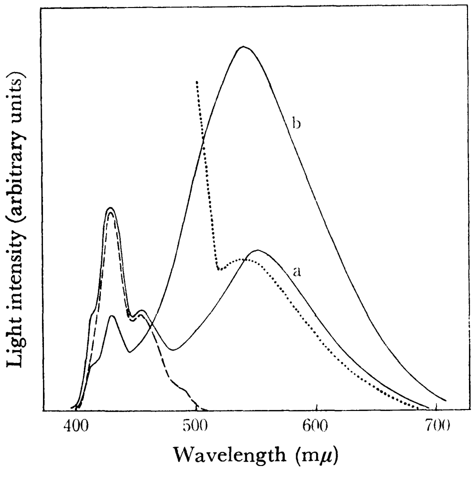

Fig. 1. Emission spectra of 9,10-di-Cl-A.
Solid line a: ECL (7×10^{-4} M)
b: ECL of 9,10-di-Cl-A (7×10^{-4} M) containing anthracene (10^{-3} M)
Broken line: Fluorescence (7×10^{-4} M)
Dotted line: Emission observed on the saturated DMF solution of 9,10-di-Cl-A (Irradiation at 366 mμ)

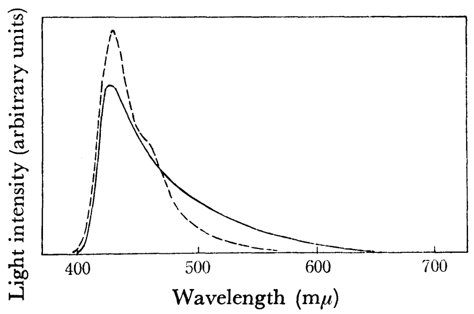

Fig. 2. Emission spectra of 9,10-di-Br-A.
Solid line: ECL (5×10^{-4} M)
Broken line: Fluorescence (5×10^{-4} M)

The ECL of 9,10-di-Br-A agrees with its fluorescence. However, the ECL of 9,10-di-Cl-A has a second component in the longer wavelength region, differing from its fluorescence component. The same ECL spectrum is also observed in methylene chloride instead of DMF. The long-wavelength component agrees with the excimer emission observed with a saturated DMF solution of 9,10-di-Cl-A (dotted line in Fig. 1).[3] When a small amount of anthracene (*ca.* 10^{-3}M) was added to the solution of 9,10-di-Cl-A, the long-wavelength ECL component was strongly enhanced as shown by curve b in Fig. 1. The observed spectral change was not due to the ECL of anthracene, because it had a maximum near 405 mμ.[1] Similar phenomena were also observed on addition of 9,10-dimethyl-A. However, the addition of 9,10-di-Br-A and 9,10-diphenyl-A, known to form an excimer or an exciplex with difficulty, caused no change in the ECL spectrum of 9,10-di-Cl-A.

On the other hand, the ECL spectrum of 9,10-di-Br-A did not change with the addition of anthracence and the observed emission was merely a superposition of each ECL spectrum.

To understand these behaviors the report by Chandross and Ferguson[3] that an excimer emission was observed on 9,10-di-Cl-A but no measurable one on 9,10-di-Br-A should be noted. They also found an exciplex emission of 9,10-di-Cl-A and anthracene.

Thus, the present results indicate conclusively that the long-wavelength component in 9,10-di-Cl-A ECL can be attributed to an excimer emission.

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[1] T. C. Werner, J. Chang, and D. M. Hercules, *J. Amer. Chem. Soc.*, **92**, 763 (1970).

[2] Photomultiplier used; EMI 9558QB.

[3] E. A. Chandross and J. G. Ferguson, *J. Chem. Phys.*, **45**, 3554 (1966).