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Electrochemiluminescence of Aromatics in *N,N*-Dimethylformamide

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Electrochemiluminescence (ECL) of aromatics was studied in dimethylformamide. The solutions were electrolyzed with square-wave voltage at various frequencies. For anthracene, emission from species produced by electrochemical reaction was observed together with anthracene fluorescence. These emissions were quenched when water was added to the solution. For rubrene and perylene, fluorescence from the molecules was observed. For phenanthrene, emission differing from phenanthrene fluorescence was observed at 515 mμ.

Many investigations have shown that alternating current electrolysis of aromatics hydrocarbons in conducting fluid media produces chemiluminescence.[1-6] The spectrum of this electrochemiluminescence (ECL) comprises, in most cases, normal or excimer fluorescences of the aromatics,[3] though spectra of different origin have sometimes been observed.[7]

The mechanism of the appearance of normal and excimer fluorescence in the ECL processes is generally recognized to be as follows.

Production of cation and anion

$$A - e^- \rightarrow A^+ \tag{1}$$

$$A + e^- \rightarrow A^- \tag*{(1)$'$}$$

Combination of the ions yielding singlet or triplet excited states

$$A^+ + A^- \rightarrow {}^1A^* \text{ (or } {}^3A^*) + A \tag{2}$$

Triplet annihilation process

$$2\,{}^3A^* \rightarrow {}^1A^* + A \tag{3}$$

Emission of fluorescence

$$^1A^* \rightarrow A + h\nu_F \tag{4}$$

Production of excimer

$$A^+ + A^- \rightarrow ({}^1A^*\cdots A) \tag{5}$$

Emission from excimer

$$({}^1A^*\cdots A) \rightarrow 2A + h\nu_{F'} \tag{6}$$

It has been suggested on the basis of energetics[2] that the fluorescent singlet state is generally formed rather from processes (3) and (4) via the triplet state than from the direct combination of cation and anion. To explain the ECL emission band at longer wavelengths than the normal fluorescence, the excimer fluorescence mechanisms (5) and (6) were proposed as well.[3] In some cases, the contribution from species electrochemically formed or from the impurities in the solution cannot be ignored.

In this paper, we report the studies on the ECL emission obtained for anthracence rubrene, perylene phenanthrene and pyrene in dimethylformamide (DMF), applying square-wave voltage at various frequencies.

Experimental

Anthracene and phenanthrene were recrystalized from benzene after passing through a column of silica gel and then sublimed in a vacuum. Commercially obtained rubrene and pyrene were sublimed in a vacuum. Perylene was recrystalized from toluene and then sublimed in a vacuum. Tetra-*n*-butylammonium perchlorate (TBAP) used as a supporting electrolyte was prepared from an aqueous solution of sodium perchlorate and tetra-*n*-butylammonium iodide and repeatedly recrystalized from aqueous solutions. DMF used as solvent was distilled at reduced pressure after standing for two days over potassium carbonate or magnesium sulfate. The distillate was stored in a vacuum desiccator. Acetonitrile was purified in the same way as described elsewhere.[8]

The cell used is made of quartz, 30 mm in diameter, and has two platinum electrodes shown in Fig. 1, namely, a slightly curved plate (20×20 mm) and a rod 3 mm in diameter. The electrodes were 5 mm apart.

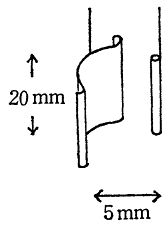

Fig. 1. The shape and arrangement of electrodes.

The solutions containing 10^{-3}—10^{-2} M aromatics and 5×10^{-1} M TBAP in DMF or acetonitrile were deaerated by bubbling with nitrogen gas before electrolysis. All solutions except for the cases of phenanthrene and pyrene were electrolyzed by applying voltage of the square-wave type generated from a transistor switching circuit shown in Fig. 2. Switching was controlled with a signal from a National VP-702B low frequency oscillator. The frequency was varied from 20 to 2×10^5 cps. ECL emission spectra were recorded in most cases using a Nalumi RM 23 monochrometer, an RCA 1P28 photomultiplier tube and a pen recorder. Response of the ECL emission was measured with a photomultiplier tube placed near the cell and a synchroscope (National VP 511B). Frequency dependence of the emission

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[1] D. M. Hercules, *Science*, **145**, 808 (1964); T. C. Werner, J. Chang, and D. M. Hercules, *J. Amer. Chem. Soc.*, **92**, 763 (1970).

[2] G. J. Hoytink, *Discuss. Faraday Soc.*, **45**, 14 (1968).

[3] E. A. Chandross, J. W. Longworth, and R. E. Visco, *J. Amer. Chem. Soc.*, **87**, 3259 (1965).

[4] A. Zweig, D. L. Maricle, J. S. Brinen, and A. H. Maurer, *ibid.*, **89**, 473 (1967).

[5] A. Weller and K. Zachariasse, *J. Chem. Phys.*, **46**, 4984 (1967).

[6] M. Sano and F. Egusa, This Bulletin, **41**, 1490 (1968).

[7] L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **90**, 6284 (1968).

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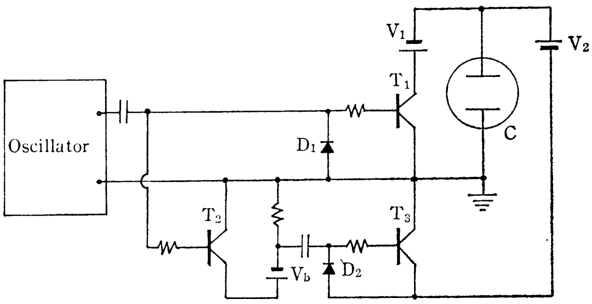

Fig. 2. Switching circuit for generating square-wave voltage.
V_1 and V_2; battery and resistance
V_b; 6—45 V
T_1, T_2 and T_3; 2SC525
D_1 and D_2; IN540
C; reaction cell

intensity was also recorded on the pen recorder through an AC-DC converter(Yokogawa 3142). During electrolysis, the ECL emission changed with time owing to irreversible electrochemical reactions. Measurements were, therefore, carried out immediately after the start of electrolysis. When acetonitrile was used as a solvent, the ECL intensity was found to be weaker than that for DMF. Detailed experiments were performed only for DMF solutions.

Results and Discussion

Anthracene. The ECL of anthracene was reported by two groups. Chandross *et al.* reported a broad spectrum with maximum at 450 mμ,[3,9] while Faulkner and Bard obtained a quite different spectrum having a rather sharp maximum at 400 mμ and another one at 460 mμ.[7] The ECL spectrum of anthracene in DMF we obtained is shown in Fig. 3, where the solution was electrolyzed at a frequency of 20 cps. The broken line shows an ECL spectrum for the applied voltage of 2.5 V.[10] The emission appearing at a wavelength shorter than 470 mμ has a shape similar to that of the normal fluorescence of anthracene and may be assigned to it. It is difficult to determine the species relevant to the 470—600 mμ emission from its spectral shape. The ECL emission spectra obtained at voltages lower than 3.0 V stayed essentially the same as the broken line in Fig. 3. Above 3.0 V, the spectrum changed very much. A typical example is shown by the solid line in Fig. 3 obtained at 3.6 V. The spectrum seems to consist of three components, (A) the fluorescence of anthracence, (B) a strong emission centered at 455 mμ, and (C) a shoulder at 500 mμ. The B band is similar to that previously obtained by Faulkner and Bard[7] who asigned it to the fluorescence of anthranol. When the applied voltage was varied in the range 3.0—6.0 V, the spectral feature did not change. It was found that the intensity ratio of the B band to the A band decreased with increase in the frequency of the applied voltage.

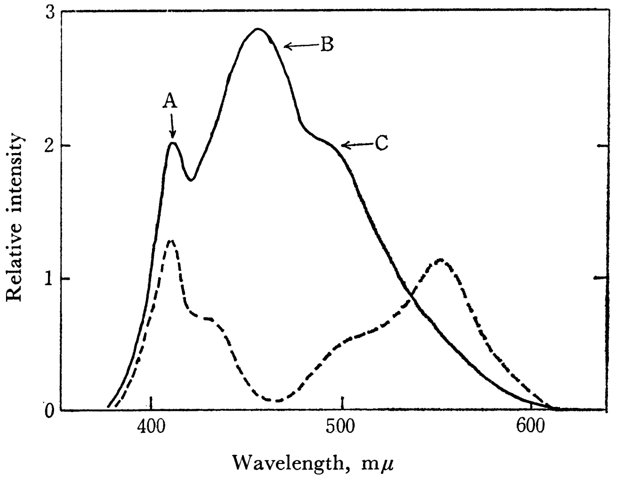

Fig. 3. Emission spectra of anthracence solution electrolyzed at 20 cps. --- at 2.5 V; —— at 3.6 V

The total ECL response on the photomultiplier was traced with a synchroscope, and is shown in Fig. 4 together with the wave form of the applied voltage. It was confirmed from visual observation that the emission near the earthed electrode was so weak that its contribution to the wave form is negligible. Figure 4a shows a wave form of the ECL intensity obtained at 2.5 V. There is a strong peak appearing immediately after the begining of each positive-half cycle, while the peak appearing at the negative-half cycle was very weak. It can be suggested that the emission results, for the most part, from an annihilation reaction of the cation and anion radicals of anthracence, and the marked difference between peak heights at positive- and negative-half cycles is explained by assuming that the cation radical is much more short-lived than the anion radical.[11] It is then expected that as the frequency is increased until its reciprocal is equal to the life-time of the cation radical or less,

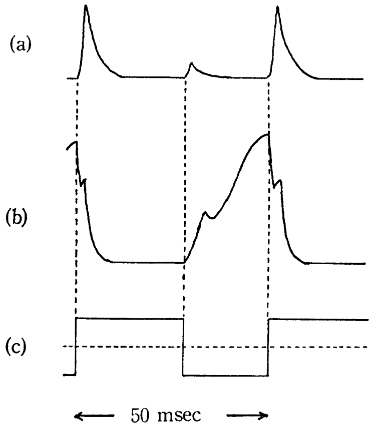

Fig. 4. Wave form of ECL intensity of anthracene solution,
(a) electrolyzed at 2.5 V.
(b) electrolyzed at 3.5 V.
(c) Wave form of the applied voltage.

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

10) In this paper, a rod-like electrode was earthed, and positive and negative voltages were alternately applied to the other electrode. The voltage given in the text indicates the absolute value of the voltage applied to the latter.

11) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, **13**, 93 (1967).

the magnitudes of the two peaks should become alike. It was, in fact, found that the two peaks were equal in magnitude at 100 cps. When the solution was electrolyzed at 3.0 V, the ECL intensity increased but the wave form was identical with that obtained at 2.5 V.

At a voltage higher than 3.0 V, the ECL emission had a wave form as shown in Fig. 4b. There is a new strong peak at the negative-half cycle in addition to the peak described before. It can be easily deduced that this peak corresponds to the B band shown in Fig. 3 which appears only at a higher voltage. Since the peak has a long rise time and appears only at the negative-half cycle, it may be concluded that the B band is due to a species formed secondarily from the ionic species. As mentioned before, the higher the frequency, the smaller the intensity of the B band. This tendency may be explained very well by the results obtained in Fig. 4.

Frequency dependence of the ECL intensity was measured at 6.0 V (Fig. 5). Curve a shows a typical result obtained at wavelengths shorter than 405 mμ corresponding to the normal fluorescence of anthracence. The curve is nearly flat in the region up to 150 cps and quickly drops at higher frequencies. The drop at high frequency might be explained by the change of bulk impedance. Curve b in Fig. 5 shows a typical curve for the emission at longer wavelengths than 440 mμ. The curve decreases rapidly with frequency even in the range where curve a is flat. The result confirms also that the slow-rising component in Fig. 4b corresponds to the B band. Addition of water to the same solution as used above was found to quench the ECL emission.

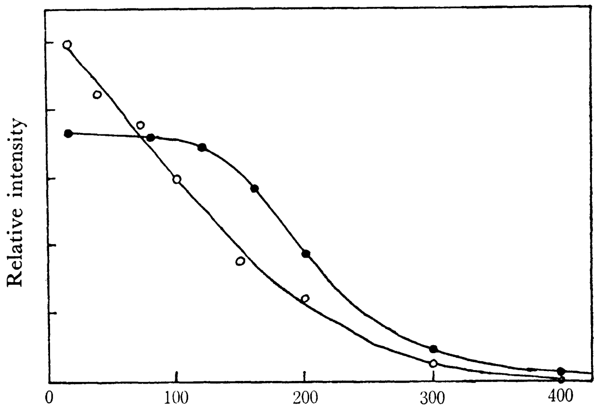

Fig. 5. Frequency dependence of ECL intensity of anthracene solution electrolyzed at 6.0 V. Curve a, emissions at wavelengths longer that 440 mμ (●), curve b, emissions in wavelengths shorter than 405 mμ (○).

From the position and shape of the spectrum, it seems reasonable to assign the B band at 455 mμ in Fig. 3 to the fluorescence of anthranol. As this band has a threshold voltage higher than that yielding the anthracene fluorescence and is observed as a slow-rising peak only at negative-half cycle (Fig. 5b), it may be suggested that anthracene dinegative ion participates in the mechanism yielding the anthranol fluorescence. At present, however, it is difficult to explain details of the anthranol emission process.

With the continuation of electrolysis, the ECL emission gradually changed its intensity as shown in Fig. 6. Here, the electrolysis was performed at an applied voltage below 3.0 V, and no emission band at 455 mμ appeared. From the curves shown in Fig. 8, the following relationships are derived.

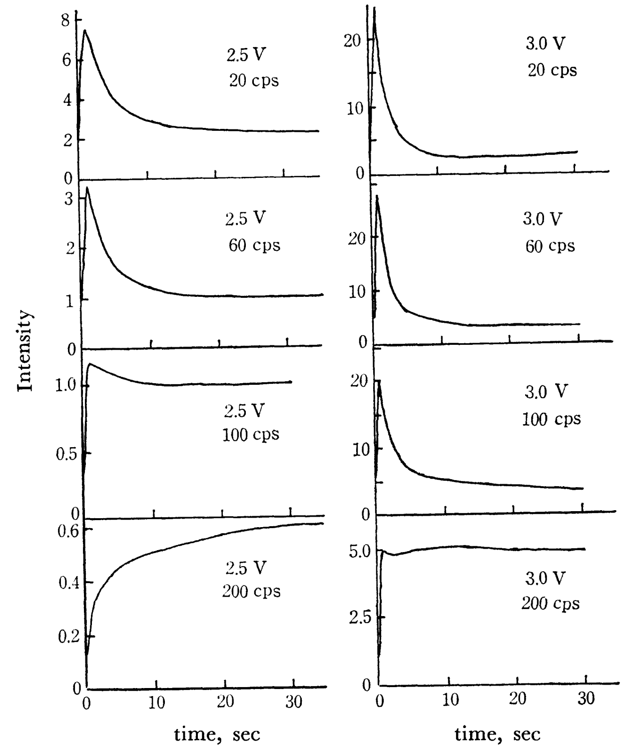

Fig. 6. Time dependence of ECL intensity of anthracene solution.

(1) At a given frequency, the higher the voltage, the quicker the decay of emission.

(2) At a constant voltage, the greater the frequency, the slower the decay of emission.

Since the electric current increases with the applied voltage, it is reasonable to consider that irreversible chemical change of anthracene is promoted by increasing the voltage. Relation (1) seems to be based on it. It is expected that if the frequency is high enough, the cation radical formed on a positive-half cycle reacts efficiently with the anion radical and disappears. The annihilation of the cation may decrease the decomposition rate of anthracene. Relation (2) seems to be due to this.

Rubrene. The intense ECL emission of rubrene has been assigned to the normal fluorescence of rubrene.[12,13] All the ECL spectra we obtained at 1.8, and 3.6 V at the frequency of 20 cps had a peak identical with that of the normal fluorescence of rubrene. The wave form was also measured at various voltages. By the electrolysis of solution at 2.0 V, a strong peak

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[12] D. M. Hercules, R. C. Lansbury, and D. K. Roe, *J. Amer. Chem. Soc.*, **88**, 4578 (1966).

[13] D. L. Maricle and A. H. Maurer, *ibid.*, **89**, 188 (1967).

appeared at the positive-half cycle and a weak peak at the negative-half cycle. Their average lifetimes were found to be about 2.5 msec. At 3.0 V, a slow-rising peak appeared at the positive-half cycle as well as sharp-rising peaks. The peak increased with time. It may be suggested that the sharp-rising peaks are the emission due to the annihilation between the cation and the anion radicals of rubrene, while the slow-rising peak is the emission originated from the reaction product from rubrene. In spite of the change of the wave form with the voltage, the spectrum did not change. It is possible that, even if the reaction product participates in the ECL emission, the excited singlet state of rubrene is finally formed by charge transfer process or by energy transfer process.

Perylene. The ECL-intensity of perylene was weak compared with that of anthracence and rubrene. The solution was electrolyzed at 2.5, 3.0, and 3.6 V at 50 cps. Concentration of TBAP was 5.6×10^{-2} M. The solid line in Fig. 7 shows a spectrum obtained at 3.0 V. The broken line shows the spectrum obtained by Chandross *et al.* who assigned it to the excimer fluorescence of perylene.[3] The spectrum we obtained is similar to that of the normal fluorescence of perylene. Wave form of the ECL intensity was also measured at various voltages (Fig. 8). It differs largely from that observed for anthracene or for rubrene. By increasing the voltage, the time lag for the sharp-rising on a negative-half cycle was found to become longer. In addition to the peak, there was a slow-rising peak in the positive-half cycle and even in the negative-half cycle at a higher voltage. Assuming that the ECL emssion is assigned only to the normal fluorescence, these results suggest that there is, in addition to the annihilation reaction, an other one producing the excited singlet state of perylene.

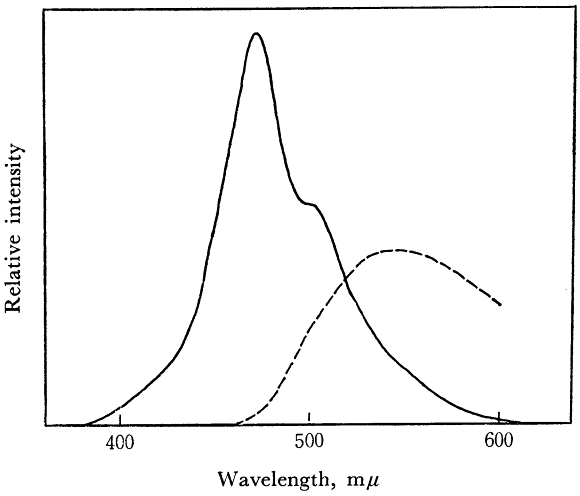

Fig. 7. Emission spectrum obtained from perylene solution electrolyzed at 3.0 V at 50 cps (solid line).
Broken line indicates ECL spectrum from a pyrene solution reported by Chandross *et al.*[3]

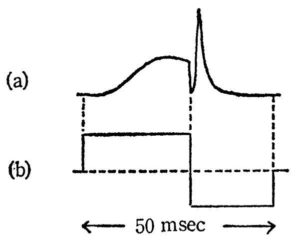

Fig. 8. Curve a, wave form of the ECL intensity of perylene solution electrolyzed at 2.5 V. Curve b, that of the applied voltage.

Frequency dependence of the ECL emission was measured at various voltages. Concentration of TBAP was 2.66×10^{-2} M. Curves (a) and (b) in Fig. 9 obtained at 3.0 and 4.0 V, respectively, decline monotonically with the frequency. Curves (c) and (d) at 5.0 and 6.0 V, respectively, have maxima. As the voltage increases, the maxima tend to shift toward the high frequency side. The shift seems to be related with the slow-rising peak.

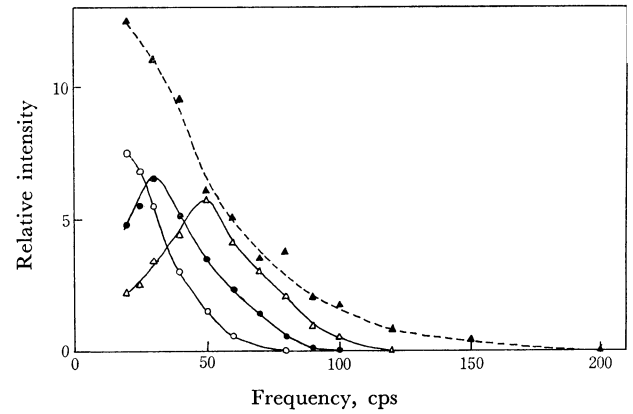

Fig. 9. Frequency dependence of the ECL emission from perylene solution, electrolyzed.
(a) ▲, at 3.0 V, 5.6×10^{-2} M TBAP;
(b) ○, at 4.0 V, 2.3×10^{-2} M TBAP;
(c) ●, at 5.0 V, 2.3×10^{-2} M TBAP;
(d) △, at 6.0 V, 2.3×10^{-2} M TBAP.

Phenanthrene. ECL emission spectrum from phenanthrene solution in DMF is shown in Fig. 10. Electrolysis was carried out with the sinusoidally alternating voltage of 60 cps. The spectrum obtained resembles that of the phosphorescence of phenanthrene. However, it seems unreasonable that the phosphorescence of phenanthrene should be observed so strongly in a solution at room temperature. Therefore, the

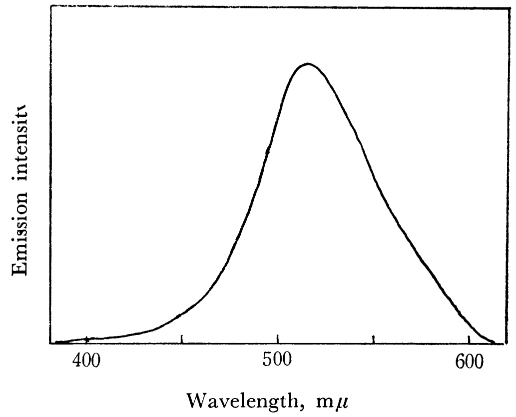

Fig. 10. Emission spectrum from phenanthrene solution.

possibility of an impurity luminescence cannot entirely be neglected.

Pyrene. When pyrene in DMF was electrolyzed with a DC voltage at 6.0 V, white-blue emission was observed at the anodic surface together with gas evolution. The emission intensity was so weak that we could not measure the spectrum.

Concluding Remark. There have been a few studies on the ECL imposing square wave voltage.[14] It may be emphasized that the observation of the wave form of the ECL-intensity as described in this paper is a useful method to study the mechanism of emission and the assignments of the emitting species. Measurement of the frequency dependence of the ECL emission bands may also give valuable information on the electrolytic reaction mechanisms.

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14) A. Zweig, G. Metzler, A. H. Maurer, and G. Roberts, *J. Amer. Chem. Soc.*, **88**, 2864 (1966).