Electrochemiluminescence of 9,10-Dichloroanthracene at Low Temperatures

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The electrochemiluminescence (ECL) of 9,10-dichloroanthracene in methylene chloride was investigated at temperatures as low as −60°C. The cation was quite stable and the anion was unstable at room temperature. The anion, however, increased its stability as the temperature decreased and below *ca.* −40°C it was essentially stable. Temperature was also found to have great influence on the relative intensity of the two spectral components of the ECL of 9,10-dichloroanthracene. By lowering the temperature the components at the longer wavelength increased strongly compared with the other component. When the ECL was observed by applying a rectangular potential, the intensities of the two components decayed exponentially with the same decay constant. Therefore, it was concluded that the emission at the longer wavelength originated not from the products of electrolysis but from the excimer and that the primary process to produce these two emissions was the same.

It is well known that in aprotic solvents numerous aromatic compounds often show luminescence at the surface of an electrode to which an alternating potential is applied. This phenomenon, electrochemiluminescence (ECL), is mainly attributed to the annihilation of generated cations and anions. The first observation on ECL of many aromatic compounds was reported by Hercules.[1] Since then, detailed investigations on ECL have been carried out chiefly by Chandross *et al.*,[2,3] Zweig[4], Bard *et al.*[5,6] and Hercules *et al.*[7] and the various mechanisms of ECL have been postulated.

It is recognized that the observed ECL spectra sometimes contain longer wavelength emission which is not assignable to the corresponding fluorescence. The longer wavelength emission is often attributed to i) excimer fluorescence, ii) phosphorescence, or iii) fluorescence of the electrolytic products excited by energy transfer from excited molecules of the parent compound.

The following reaction scheme (A=aromatic) is considered to be appropriate to explain the phenomenon cited above, although a preannihilation mechanism[8] is not included.

$$\left.\begin{aligned} &A + e \longrightarrow A^-, \text{ cathodic process} \\ &A - e \longrightarrow A^+, \text{ anodic process} \end{aligned}\right\} \quad (1)$$

$$A^- + A^+ \rightleftharpoons {}^1(A\cdots A)^* \rightleftharpoons {}^1A^* + A, \quad (2)$$

$$A^- + A^+ \rightleftharpoons {}^3(A\cdots A) \longrightarrow {}^3A + A, \quad (3)$$

$${}^3A + {}^3A \rightleftharpoons {}^1(A\cdots A)^* \quad (4)$$

$${}^1A^* \longrightarrow A + h\nu_1, \text{ fluorescence} \quad (5)$$

$${}^1(A\cdots A)^* \longrightarrow 2A + h\nu_2, \text{ excimer fluorescence} \quad (6)$$

$${}^3A \longrightarrow A + h\nu_3, \text{ phosphorescence} \quad (7)$$

$${}^1A^* + B \longrightarrow A + {}^1B^*, \text{ B: electrolytic product} \quad (8)$$

$${}^1B^* \longrightarrow B + h\nu_4, \text{ fluorescence} \quad (9)$$

We consider here two mechanisms to produce an excimer, one of which is due to the triplet-triplet annihilation and the other involving direct formation through cation-anion annihilation. To reveal the emitting species of the observed ECL and to elucidate in detail the mechanism to produce them are of great value both in the study of emission spectroscopy and in the study of electron transfer reactions associated with a large change in enthalpy of reaction.

For the mechanism of ECL to be established, it is necessary to re-examine rigorously the electrochemical systems. For example, the character of the solvents has great influence on the electrochemical reactions. We have observed that dimethylformamide (DMF), frequently used for the study of ECL, is not suitable, because in this solvent most cations of aromatic molecules are not stable on account of DMF's strong nucleophilic property. For that reason the ECL processes (8) and (9) in which electrolytic products take part cannot be excluded from the plausible mechanisms of ECL. This has made the detailed discussion on the mechanism of ECL more complicated.

Therefore, it is essential to observe ECL spectra under the conditions where both anions and cations can exist stably. One of the best ways is to observe ECL spectra at low temperatures where undesirable reactions of ion radicals with solvent or impurities are greatly or completely retarded.

For rigorously quantitative treatment, electrochemical studies of aromatic compounds in aprotic solvents at low temperatures often involve difficulties in the choice of solvents, supporting electrolytes and a reference electrode, and through investigations have not been made until Van Duyne and Reilly's recent studies[9]. Only two investigations of ECL were done at low temperatures, one by Parker and Short[10] and the other by Weller and Zachariasse[11]. Although interest-

1) D. M. Hercules, *Science*, **145**, 808 (1964).
2) E. A. Chandross, J. W. Longworth, and R. E. Visco, *J. Amer. Chem. Soc.*, **87**, 3259 (1965).
3) E. A. Chandross and F. I. Sonntag, *ibid.*, **88**, 1089 (1966).
4) A. Zweig, "Advances in Photochemistry," Vol. 6, ed. by W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Interscience Publishers, New York, (1968) p. 425.
5) J. M. Malog, K. B. Prater, and A. J. Bard, *J. Phys. Chem.*, **72**, 4348 (1968).
6) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **90**, 6284 (1968).
7) T. C. Werner, J. Cheng, and D. M. Hercules, *ibid.*, **92**, 763, 5560 (1970).
8) D. L. Maricle and A. Maurer, *ibid.*, **89**, 188 (1967).
9) R. P. Van Duyne and C. N. Reilly, *Anal. Chem.*, **44**, 142, 153, 158 (1972).
10) C. A. Parker and G. D. Short, *Trans. Faraday Soc.*, **63**, 2618 (1967).
11) A. Weller and K. Zachariasse, *Chem. Phys. Lett.*, **10**, 197 (1971).

ing results were obtained by Parker and Short, they did not examine precisely their electrochemical system. On the other hand the latter authors' work concerned only with ECL spectra produced by the annihilation between the ion radicals of the two different molecules. By lowering the temperature not only the anion and the cation but also excimers will increase their stability, so that the observation of ECL spectra at low temperatures will become a useful means to study the mechanism of ECL involving excimer formation.

In order to elucidate the mechanism of the ECL of 9,10-dichloroanthracene (9,10-di-Cl-A), whose ECL spectrum had already been reported to be composed of the two components[12], electrochemical examinations of the ECL of this compound were performed at low temperatures. Large temperature effect was found not only on the ion radical stability but also on the ECL spectrum of 9,10-di-Cl-A. From the results obtained we will discuss the primary process of the observed ECL of 9,10-di-Cl-A.

Experimental

Materials. 9,10-di-Cl-A was synthesized by the method reported earlier[12] and purified by sublimation after recrystallization from carbon tetrachloride. Methylene chloride of guaranteed grade was further purified by distillation, dried over Molecular Sieve Linde 5A, and transferred to an electrolysis cell *in vacuo*. Dry tetrabutylammonium perchlorate (TBAP) or potassium perchlorate was used as a supporting electrolyte. Its concentration was *ca.* 0.05 M throughout the experiments.

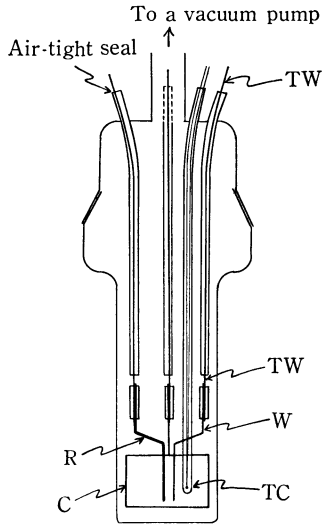

Fig. 1. Electrolysis cell.
W: working electrode, R: reference electrode, C: counter electrode, TC: thermocouple, TW: tungsten wire.

Apparatus. A Pyrex glass electrolysis cell is shown in in Fig. 1. The working electrode, W, is of Pt wire (0.05—0.08 cm diameter, 3 cm length); R is a reference electrode of Ag wire (0.1 cm diameter); and C is a counter electrode of Pt plate (1.5 cm×2.0 cm and 0.02 cm in thickness). These electrodes are connected to the outside leads through tungsten wires.

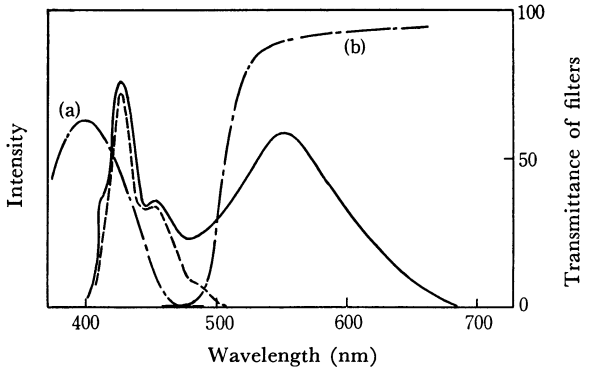

Fig. 2. Emission spectra of 9,10-di-Cl-A in DMF.
——: ECL (7×10^{-4} M), ----: fluorescence (7×10^{-4} M), ——: filters: (a) V-VIA, (b) V-051 (Similar ECL spectra were also observed in methylene chloride and acetonitrile.)

Aliquot amounts of 9,10-di-Cl-A and a supporting electrolyte were weighed into the electrolysis cell which was then evacuated by using an oil diffusion pump. The solvent was transferred into the cell *in vacuo* and the solution was degassed by repeating a freeze-pump-thaw cycle. The cell was then sealed off from the vacuum line and its cylindrical part was inserted into a transparent Dewar vessel made of Pyrex glass. By circulating cold nitrogen gas into the Dewar vessel, constant low-temperature was maintained. Temperatures were measured with a copper-constantan thermocouple.

Controlled potential electrolysis using a three-electrode configuration was performed by employing a potentiostat. Cyclic voltammograms were recorded on a Yokogawa *X–Y* Recorder Type 3077 at various temperatures. For the separate measurements of the intensities of two components of the ECL of 9,10-di-Cl-A (Fig. 2), Toshiba glass filters V-VIA and V-051 were used. Transmittance curves of these filters are also shown in Fig. 2. The light transmitted through each filter was measured with a Hamamatsu R136 photomultiplier and recorded on the *X–Y* recorder or on a Matsushita VP-541A oscilloscope. The observed light intensities should be proportional to the intensities of the corresponding emissions, so that the change in the ratio of these two intensities with temperature was thought to give us informations about the spectral change with temperature.

Results

Cyclic Voltammogram. The cyclic voltammograms of 9,10-di-Cl-A are presented in Figs. 3 and 4. In DMF both the anion and the cation are unstable at the room temperature. As the temperature decreases the re-oxidation current of the anion comes to be observed, corresponding to an increase of the stability of the anion radical. The cation, however, was still unstable at low temperature on account of the strong nucleophilic property of DMF.[9] In methylene chloride, known as a good solvent for cation radicals, the cation of 9,10-di-Cl-A was stable[14] but the anion was unstable. When the potential was reversed after producing the anion, near +0.9 V *vs.* Ag the oxidation current (probably due to secondary products

12) T. Matsumoto, M. Sato, S. Hirayama, and S. Uemura, This Bulletin, **44**, 1450 (1971).

14) The cation chemically produced in concentrated sulfuric acid also persists for several days without any change.

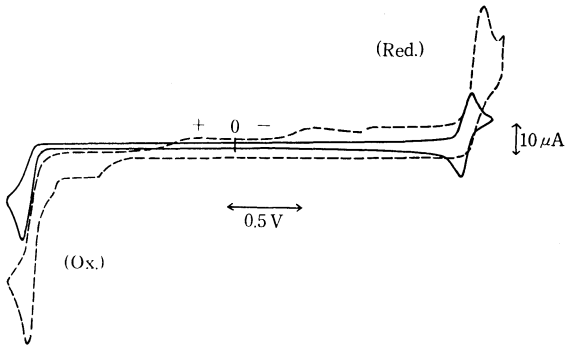

Fig. 3. Cyclic voltammogram of 9,10-di-Cl-A (10^{-3} M).
Solvent: DMF, Supporting electrolyte: $KClO_4$, Potential sweep rate: 132 mV/s ——: −41°C, ----: room temperature

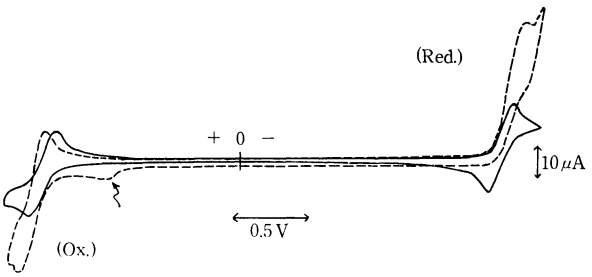

Fig. 4. Cyclic voltammogram of 9,10-di-Cl-A (10^{-3} M).
Solvent: methylene chloride, Supporting electrolyte: TBAP
Potential sweep rate: 144 mV/s
——: −56°C, ----: 7°C

of electrolysis) was observed (arrow in Fig. 4). Upon lowering the temperature this current finally disappears. In both cyclic voltammograms in Figs. 3 and 4 the difference between the anodic and cathodic peak potentials are larger than that of an ideal reversible wave. The peak current ratio for the anion radical couple was, however, close to unity even at a slow sweep rate of potential of 32 mV/s if the temperature was lower than *ca.* −40°C.[15] This shows almost complete stability of the anion at low temperatures. Similar results were obtained in acetonitrile.

In Fig. 5 the relationship between the applied potential and the observed emission intensity is shown. Light intensities were measured by using the photomultiplier without glass filters. This figure shows that as temperature decreases, the emission intensity becomes stronger and the emission lasts longer. Curiously the emission was observed only in the negative potential region even at low temperatures where both radical ions were considered to be stable. This phenomenon was independent of the direction of the potential sweep. From the results it is clear that the preannihilation mechanism is not suitable for the ECL of 9,10-di-Cl-A. In order to simulate the ECL-potential relationship, preliminary computer calculation was carried out by assuming that both ion radicals are completely stable and that the emission is observable only when the annihilation occurs between an anion and a cation.[16] The theoretical emission-potential curve differs from the observed curves in that the emission is observable both in the negative and positive potential regions.

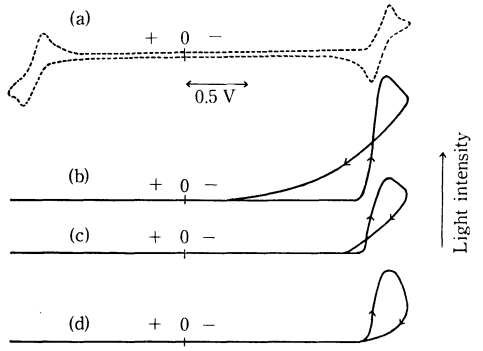

Fig. 5. Relationship between emission intensity and applied triangular potential.
[9,10-di-Cl-A] 10^{-3} M
Potential sweep rate: 580 mV/s
(a): Cyclic voltammogram (−48°C), (b): emission (−48°C), (c): emission (−5°C), (d): emission (+8°C)

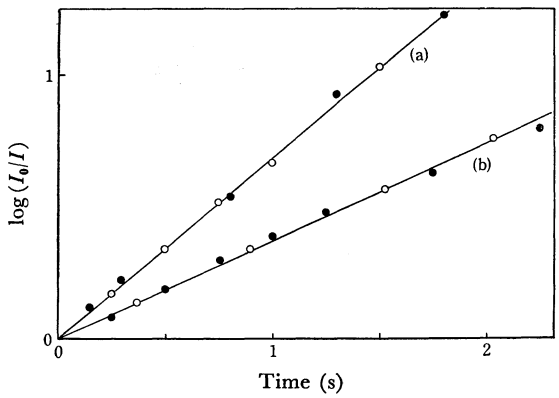

Fig. 6. $\log(I_0/I)$ *vs.* time plots for the two components of the ECL when a rectangular potential was applied.
I_0: maximum emission intensity
Curves: (a): 0°C, (b): −44°C
●: excimer, ○: fluorescence

Temperature Effect on ECL. When a rectangular potential having an amplitude a little larger than the difference between the reduction and the oxidation potentials shown in Fig. 4 was applied to the working electrode, an emission, whose intensity decays with time, was observed every time when the sign of the potential changed. This differs from the situation found in the case of a triangular potential. For the decay curves observed when the potential changed from positive (cation) to negative (anion), a $\log I_0/I$ *vs.* time plot was carried out as illustrated in Fig. 6, where I_0 corresponds to the maximum light intensity and the time corresponding to this point was put equal to zero. The results were shown for the two cases, one for the decay observed through the glass filter V–VIA and the other through the glass filter V–051. Both decay curves are seen to follow approximately exponential decay. The apparent decay

15) T. Matsumoto, M. Sato and S. Hirayama, *Chem. Lett.*, **1972**, 603.

16) T. Matsumoto, M. Sato, S. Hirayama, and S. Uemura, unpublished results.

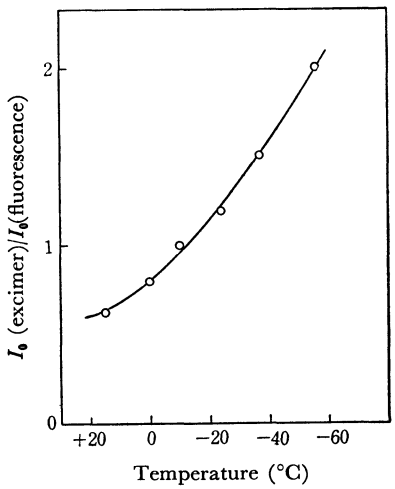

Fig. 7. Temperature dependence of the relative emission intensity of the two ECL components.
[9,10-di-Cl-A] 10^{-3} M

constants for both curves are the same at the same temperature and diminish with a decrease in temperature. This is probably because the diffusion coefficients of molecules become smaller and stabilities of ion radicals increase as the temperature decreases.

The ratio of the peak heights of the two decay curves corresponding to the two emission components, designated by (I_0(excimer)/I_0(fluorescence)), is plotted against temperature in Fig. 7. The ratio continuously increases as the temperature decreases.

The emission from the excimer of 9,10-di-Cl-A by photo-excitation was observed by Chandross[17] in softened methylcyclohexane at low temperatures. In the same concentration region of 9,10-di-Cl-A, where its ECL was observed and at temperature as low as −60°C, no excimer emission was detected in either methylene chloride or DMF by photo-excitation.

In order to know the effect of concentration on the ECL spectra of 9,10-di-Cl-A, the ratio of the ECL intensity at 550 nm (excimer) to that at 450 nm (fluorescence) was measured in the concentration range of 10^{-3} to 10^{-4} M. As a measure of the fluorescence intensity, the light intensity at 450 nm was chosen in order to get rid of the effect of re-absorption of the fluorescent component at the shorter wavelength. The ratio showed a little increase as concentration increases, but its effect on ECL did not seem to have such a large effect as temperature had.

Discussion

Concerning the mechanism of the ECL of 9,10-di-Cl-A, it appears that the anion-cation annihilation process is indispensable and that this process occurs mostly in the bulk solution away from the working electrode. This is because we could not observe ECL when the electrolysis was carried out by applying triangular or rectangular potential in the region where only one type of ion was produced.

When we compare the emission *vs.* potential curve with the current *vs.* potential curve shown in Fig. 5, it is easily seen that the potential where ECL becomes observable almost coincides with the potential where the cathodic current begins to flow and that the potential where the ECL intensity reaches a maximum nearly corresponds with the cathodic peak potential. These results are compatible with the results of computer simulation.[16] ECL is still observable in the small negative potential region where a faradaic current is almost zero. This trend becomes more remarkable with the decrease of temperature as shown in Fig. 5. We can explain this in terms of the increased viscosity and stability of ion radicals at low temperatures. These facts indicate that ECL originates from the annihilation of ion radicals which have diffused away from the electrode.

There remains, however, an important question why the ECL could not be observed near the peak current potential where the cation was produced with a triagular potential. The results of computer simulation of the ECL based on the annihilation of the stable anion and cation radicals indicate that the ECL should be observed strongly in the two separate regions which correspond to the peak current potentials for reduction and oxidation. As far as the cyclic voltammetry concerns, both ion radicals are quite stable below −40°C,[15] so that we cannot find an pertinent explanation for the finding.

From the experiments at low temperatures it has also been assured that, of the two components of the ECL spectra of 9,10-di-Cl-A, the one at the longer wavelength corresponds to the emission from the excimer. The other possibility that the longer wavelength component is due to the secondary products of electrolysis is easily excluded,[6] because the emission intensity of this component increases as the anion increases its stability. The fact that an excimer is stabilized at low temperatures should also be noted. Combined with other experimental facts previously reported,[12] these new findings are thought to confirm our previous interpretation.

The primary process to produce two components of the ECL of 9,10-di-Cl-A is considered to be the same because the emission decay curves for the two components are the same at any temperature. However, it is not clear from the present work alone whether the mechanism to form the excimer is produced from reaction (2) or from reactions (3) and (4). The latter possibility, *i. e.*, the participation of the triplet state, has been pointed out by Weller and Zachariasse[11], and Freed and Faulkner[19] in an "energy deficient" ECL system. In our case, if we estimate roughly the enthalpy change in the anion-cation annihilation by the equation $\Delta H = E^{ox} - E^{red}$, where E^{ox} and E^{red} are the peak current potentials[20] for oxidation and reduction, respectively, the value of ΔH is of the same order as the energy of the lowest excited signlet state

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

19) D. J. Freed and L. R. Faulkner, *J. Amer. Chem. Soc.*, **93**, 2097 (1971).

20) G. J. Hoytink, *Discuss. Faraday Soc.*, **45**, 14 (1968),

of 9,10-di-Cl-A[21]. In addition the energy required to form the excimer is smaller than that of the excited singlet state. Therefore, we cannot eliminate the the possibility of the direct excimer formation by the simple consideration of energy balance alone. The simplest and most reliable way to ascertain experimentally the participation of the triplet state in ECL would be to observe the T–T′ absorption of the molecule in the triplet state, using an optically transparent electrode (OTE) as a working electrode.[22] With the aid of OTE, the transient absorption due to the anion or the cation generated near OTE has been measured.[15] If the mechanism of ECL is primarily based on the reaction Schemes (3) and (4), the local concentration of the triplet state molecules is expected to be as high as that of the ion radicals, which will permit us to measure its absorption with OTE.

As has been discussed hitherto, no conclusion can be drawn as to the mechanism of ECL except that the primary process of the ECL of 9,10-di-Cl-A is the annihilation of the anion and cation. It should be noted, however, that the excimer emission observed in the ECL is much stronger than that observed by photo-excitation. In fact at a concentration as low as 5×10^{-4} M, no excimer emission was observed by photo-excitation even at *ca.* −60°C. Change in concentration did not have large effect on ECL. These results are considered to indicate either (i) the excimer is directly formed by the anion-cation annihilation, or (ii) the local concentration in the neighbourhood of the excited molecule (singlet or triplet) is quite high because the excited molecule which has been produced as a result of the electron transfer reaction between two ions — anion and cation — will always have its counterpart in its close vicinity. If the mechanism (i) is working in our case, it is quite interesting since it entails an efficient energy dissipation process in electron transfer reactions which are accompanied by a large change in reaction enthalpy.

21) I. B. Berlman "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York (1965), p. 127.

22) To ascertain the participation of a triplet molecule the effect of magnetic field on the intensity of ECL has been investigated by L. R. Faulkner and A. J. Bard (*J. Amer. Chem. Soc.*, **91**, 6495 (1969)) and K. S. V. Santhanam (*Can. J. Chem.*, **49**, 3577 (1971)).