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ELECTROCHEMISTRY OF 9,10-DICHLOROANTHRACENE AT LOW TEMPERATURES

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A preliminary electrochemical investigation of 9,10-dichloroanthracene in aprotic solvents was performed at low temperatures as low as -60°C. The generated anion was shown to be stabilized as the temperature decreased. The use of an optical transparent electrode enabled us to obtain a new relationship between absorbance of radical ion and electrode potential.

In order to elucidate the mechanisms of electrochemical reactions, it is desirable to simplify the electrochemical system as much as possible. For this purpose electrolysis at low temperatures which retards undesirable follow-up reactions of primary generated radical ions appears to be one of the most promising methods. Although Van Duyne and Reilley1) have recently reported detailed works, electrochemical studies in aprotic solvents at low temperatures are still few in number and it is valuable to perform electrochemical studies such as cyclic voltammetry and chronocoulometry on various compounds at low temperatures.

Because of our interest in electrochemiluminescence2) of aromatic hydrocarbons, we have investigated the electrochemical processes on 9,10-dichloroanthracene (9,10-di-Cl-A) at temperatures as low as -60°C using an optically transparent electrode (OTE)3). The use of OTE makes it possible to study spectroscopically the electrochemical reactions of ion radicals stabilized at low temperature.

Synthesized 9,10-di-Cl-A was purified by recrystallization and sublimation. Methylenedichloride, N,N-dimethylformamide and acetonitrile of guaranteed grade were used as solvents and sufficiently dehydrated before use. As a supporting electrolyte n-tetrabutylammonium perchlorate was used.

The electrolysis cell made of pyrex glass has a three-electrode configuration. The working electrode is the OTE, prepared by depositing a thin film of platinum on a clean quartz plate (3 mm x 30 mm) under high vacuum[3]. As a reference electrode, silver wire was used. The counter electrode is a platinum plate (15 mm x 20 mm). The applied potential to the working electrode was regulated with the aid of a potentiostat. The solution was degassed by repeating a freeze-pump-thaw cycle. The cell was then inserted into a transparent Dewar vessel made of pyrex glass and a constant low-temperature was maintained by circulating cold nitrogen gas into the Dewar vessel. The temperature was measured with a copper-constantan sensing thermocouple immersed in the solution. Spectroscopic mesurements were done in the usual way by using a tungsten lamp as a light source. The incident light path was vertical to the OTE surface, and the transmitted light was fed into a monochromator.

In Fig.1 the cyclic voltammograms of 9,10-di-Cl-A in methylenedichloride are shown. The cation is rather stable even at room temperature, whereas the anion is very unstable (the re-oxidation peak is not seen). As the temperature is decreased, the anion gradually becomes stable. Similar results were also obtained in acetonitrile. An oxidation current (arrow in Fig.1) due to a secondary product of electrolysis disappears at low temperatures.

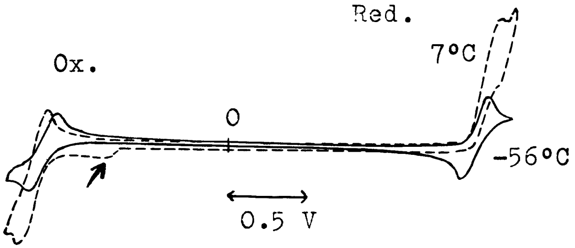

Fig.1 Cyclic voltammogram of 9,10-dichloroanthracene

Contrary to the above mentioned solvents, dimethylformamide has strong nucleophilic properties. Therefore, the cation was unstable in it even at the lowest temperature accessible. The anion become stable by lowering temperature as in methylenedichloride and in acetonitrile.

In Fig.2 the peak current ratio for the anion radical couple of 9,10-di-Cl-A is plotted against temperature. The ratio approaches unity as the temperature is decreased according to the increase in stability of the anion. Below -40°C the anion is considered to be stable.

As we employed OTE as a working electrode, spectroscopic studies of the ion radicals produced by electrolysis were also possible. By maintaining the OTE at a constant potential corresponding to the reduction peak current, the absorption spectrum of the generated anion was obtained as shown in Fig.3. The anion has an absorption maximum at 678 nm. The absorption at wavelengths shorter than 420 nm could not be measured because of the strong self-absorption of 9,10-di-Cl-A. Absorption spectra such as the one shown in Fig.3 were obtainable only at temperature where the anion was almost stable.

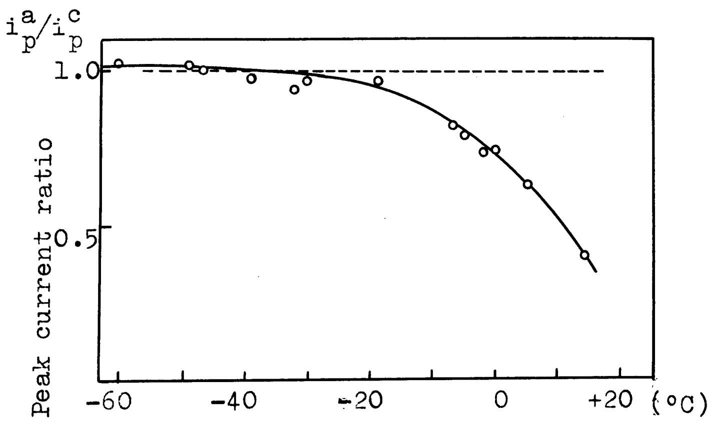

Fig.2 Temperature dependence of the peak

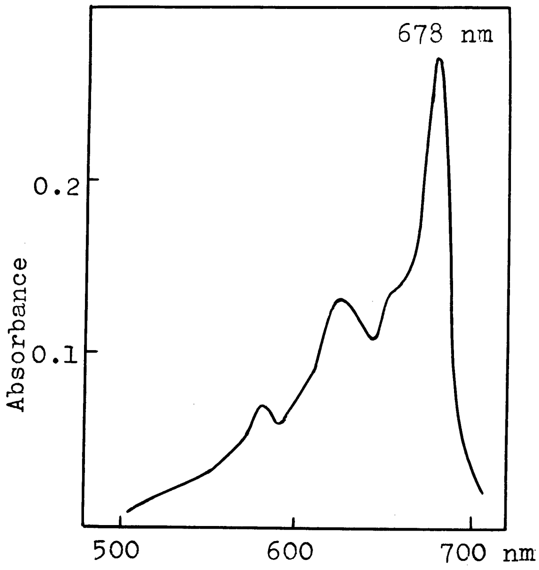

Fig.3 Absorption spectrum of the anion at -45°C

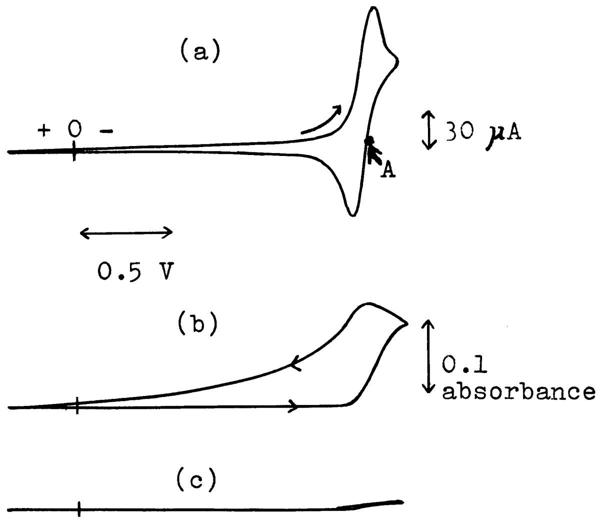

Fig.4 Absorbance vs. potential curves of the anion

(a) cyclic voltammogram(-56°C) (sweep rate: 42 mV/sec)
(b) absorbance at 678 nm (-56°C)
(c) absorbance at 678 nm (room temp.)

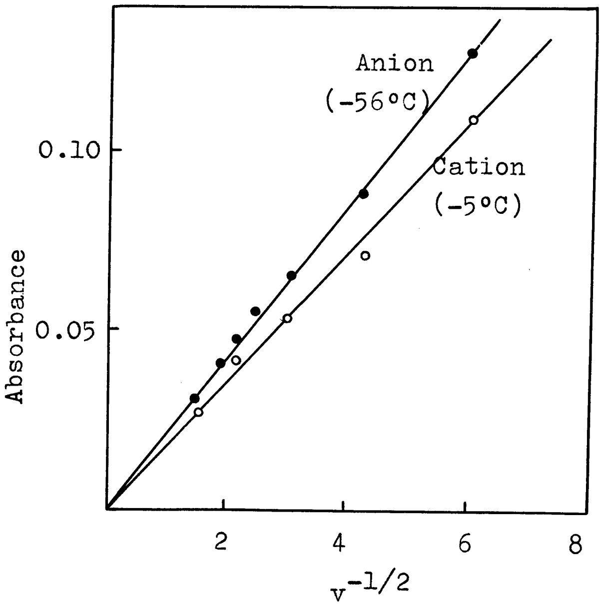

Fig.5 Sweep rate dependence of the maximum absorption

When triangular potential is applied to the OTE, the absorbance of the anion measured at the absorption maximum changes with the applied potential as shown in Fig.4. Recently Bard and Goldberg$^{4)}$ have reported similar curves, although they used the height of an ESR signal instead of absorbance as a measure of radical ion concentration. When the absorbance is measured by maintaining the incident light vertical to the OTE surface, the observed absorbance is proportional to the integrated value of the current. If the electrolysis is performed with a solid electrode under the condition of linear diffusion, the following equation is derived theoretically$^{4,5)}$,

$$\text{Absorbance} \propto \int i\,dt = \left(\frac{i_p}{v}\right)\int_{E_1}^{E_2}\left[X\left(\frac{nFE}{RT}\right)\Big/X_{max}\right]dE$$

where i_p, v and X_{max} are the peak current, the potential sweep rate and the maximum value of X, respectively. The above equation predicts that absorbance reaches a maximum value at point A in Fig.4(a) and that the maximum absorbance should be inversely proportional to the square root of the sweep rate of the potential. The former character was verified as shown in the absorbance vs. potential curve of Fig.(b). The latter was confirmed in Fig.5 where the maximum absorbance for the anion at -56°C and for the cation at -5°C are plotted against $v^{-1/2}$. It is seen that an approximately linear relationship holds both for the anion and the cation. These facts show that the theoretical treatments are applicable to the results obtained in this work at low temperature.

The detailed electrochemical studies and its interrelation to electrochemiluminescence of 9,10-di-Cl-A at low temperatures will be published separately.

References

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