NOTES

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Anodic Oxidation of Anthracene in Acetonitrile at a Rotating Ring-disk Electrode

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Although many works have been reported on anodic oxidation of anthracene, there still remains some uncertainty as to its detailed mechanism.

Bard and his coworkers,[1] who studied the reaction in methylene chloride with linear potential sweep technique, reported that the oxidation product undergoes a rapid follow-up chemical reaction. Oxidation in pyridine media[2] gives rise to the formation of 9,10-dihydroanthranyl dipyridinium perchlorate indicating the reaction intermediate to be anthracene dication. The product obtained by the controlled potential electrolysis in acetonitrile was bianthrone.[3]

Anodic oxidation of anthracene has also been studied in relation to electro-chemiluminescence.[4–9] Although many of these studies suggest that it proceeds through two successive one-electron transfer, no definite proof for the formation of one-electron intermediate, anthracene monocation, has been reported. As an only exception, Peover and White,[10] who studied the oxidation of several polycyclic hydrocarbons by means of cyclic voltammetry, stated that a poorly developed cathodic current due to the reduction of anthracene monocation was detectable at high scan-rates. Application of cyclic potential sweep technique is, however, limited by the rate of charge transfer step. If the rate is not rapid enough the current-potential curve observed at high scan-rates becomes deformed and allows no quantitative analysis.

A rotating ring-disk electrode is receiving growing attention[11–14] as a powerful tool for studies of labile intermediates of an electrode reaction. We have attempted to apply this new technique to the reaction concerned.

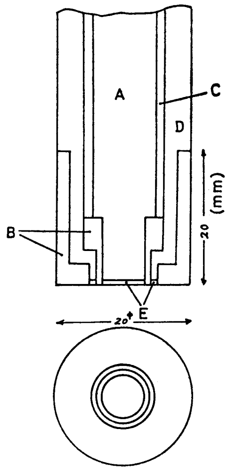

Fig. 1. Cross section of rotating ring-disk electrode. A, shaft (SS45C); B, teflon; C, bakelite; D, copper; E, platinum.

The shape and size to the ring-disk electrode used is schematically shown in Fig. 1. Platinum was used for both ring and disk electrodes. The maximum eccentricity of the electrode caused by rotation was found within 0.01 mm at a periphery of bottom surface. Potentials of both the ring and disk electrodes were independently controlled using a couple of electronic potentiostats. Currents flowing through the electrodes were respectively recorded by two X-Y recorders. The collection efficiency which is defined as the ratio of ring current to disk current was determined experimentally by measuring two representative redox reactions of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ and Cu(I)/Cu(II) couples. The values determined from the two reactions were exactly in agreement with 0.36. These values can be compared to the theoretical one, 0.40, calculated according to the Albery-Bruckenstein's equation.[11] Acetonitrile was used as a solvent and was purified carefully according to the directions of O'Donnell *et al.*[15] 0.1 M tetrabutylammonium perchlorate was used as a supporting electrolyte.

Prior to measuring anthracene, the reaction of 9,10-diphenylanthracene (DPA) known to give a stable monocation was studied. Curves A and B in Fig. 2 represent currents flowing through disk and ring elec-

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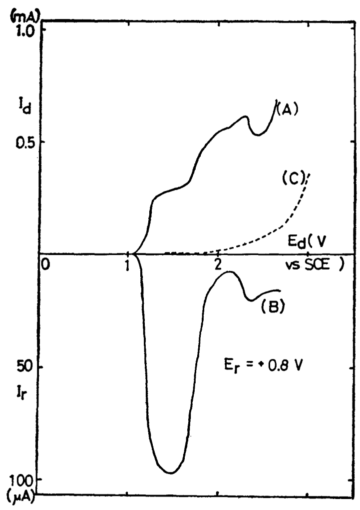

Fig. 2. I-E curves of 9,10-diphenylanthracene.
(A) disk current, (B) ring current with ring potential set at 0.8 V, (C) base current of disk. Solution, 10^{-3}M 9,10-DPA in acetonitril. Supporting electrolytes, 0.1M tetrabutylammonium perchlorate. Rotation speed, 940 rpm. Sweep rate of disk potential, 480 sec/V.

trodes, respectively, as a function of linearly changing potential of the disk electrode. It should be noted that these curves were obtained by changing the disk potential linearly and fixing the ring potential constant at 0.8 V. Curve C is a background disk current observed in a solution containing no DPA.

The results with DPA can be summarized as follows.

1) DPA is anodically oxidized through two one-electron steps since curve A consists of two waves of approximately equal height.

2) Product at the first wave, DPA monocation, is quite stable and gives rise to a hump-like strong cathodic current at the ring electrode (curve B). The collection efficiency for this species was 0.36.

3) Product at the second anodic wave, DPA dication formed at the potential range of 1.7 to 2.4 V, is labile and undergoes rapid chemical reaction with surroundings. As a result, the ring current diminishes markedly at this potential range.

A small but definite deflection of the disk current appears before the final rise and a corresponding deflection appears also in the ring current. The species responsible for this is uncertain.

Similar curves for unsubstituted anthracene (ANT) are shown in Fig. 3. Disk current exhibits a single wave with the same height as that found in the second wave of DPA. This seems to indicate that the oxidation of ANT proceeds in one step with two electron transfer, ANT→ANT^{2+}+2e. However, a sharp rise of cathodic current appearing in the ring current suggests that the electroactive species for this ring current is the monocation of anthracene, ANT^+, rather than its dication. In the case of DPA, the two-electron product was inactive to the ring current. It was reported[16] that the cathodic counterpart of DPA^{2+} appears at a much more negative potential than that of DPA^+. This may be also the case in the oxidation of ANT. A close resemblance in the behavior of ring currents shown in Figs. 2 and 3 strongly suggests that ANT is also oxidized through a consecutive two one-electron steps.

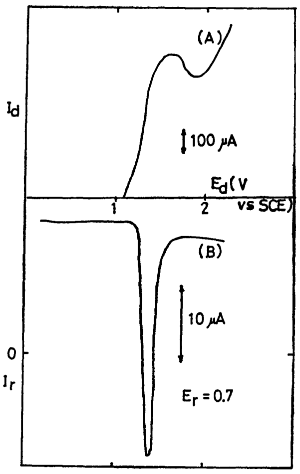

Fig. 3. I-E curves of anthracene.
(A) disk current, (B) ring current with ring potential set at 0.7 V. Solution, 10^{-3}M ANT in acetonitril. Supporting electrolytes, 0.1M tetrabutylammonium perchlorate. Rotation speed, 940 rpm. Sweep rate of disk potential, 40 sec/V.

The collection efficiency for the ring-active species, ANT^+, was as low as 0.052 indicating that the species is quite labile. If anthracene monocation undergoes a pseudo-first order reaction during the movement from disk to ring electrode, the fraction f which is collected by the ring electrode can be estimated by the equation

$$f = Ncal\, 2^{-\Delta t/\tau}$$

Transformation of this equation gives

$$\tau = -\Delta t \log 2/\log (f/Ncal),$$

where $Ncal$ is the calculated collection efficiency, τ the half-life time of anthracene monocation and Δt the mean transit time from disk to ring. Under normal conditions, Δt was estimated to be 0.02—0.1 sec. Corresponding half-life time of ANT^+ is in the range 0.7—3.4×10^{-2} sec. This figure is in agreement with the value estimated roughly as "a few millisecond" by Peover.[10]

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