

SHORT COMMUNICATION

Chronocoulometric study of adsorption of 9,10-diphenylanthracene and its radical anion in dimethylformamide solutions at a platinum electrode

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Although numerous measurements of adsorption of organic compounds have been carried out in aqueous solutions, relatively few such studies in aprotic solvents have been made¹. Since the electrochemistry of aromatic hydrocarbons and other organic species in aprotic solvents has become a field of much interest and many electrochemical studies of the rates of the heterogeneous charge transfer reaction and associated homogeneous reactions of the reactants, products or intermediates have been carried out^{2,3}, the extent of adsorption of these species is of interest.

We report here the results of high precision chronocoulometric measurements of 9,10-diphenylanthracene (DPA) and its anion radical (DPA⁻) in N,N-dimethylformamide (DMF) solutions. DPA was chosen because its electrochemical reduction has been investigated quite extensively, DPA⁻ is stable at least for several hours in purified, vacuum degassed DMF, and it has been used in electrogenerated chemiluminescence studies^{4,5}.

Experimental

The DPA was obtained from Aldrich Chemicals and was vacuum sublimed before use. The DMF was purified by a previously published procedure⁶. The supporting electrolyte was polarographic grade tetra-n-butylammonium iodide (TBAI) obtained from Southwestern Analytical Chemicals.

The cell was similar to that previously described⁷, and comprised four chambers: a solution preparation chamber for freeze-pump-thaw degassing on a vacuum line, the working electrode chamber, separated from an intermediate chamber by a sintered glass disk, which in turn was separated from the auxiliary electrode chamber by a sintered glass disk. The working electrode chamber housed a large platinum gauze electrode and a platinum disk microelectrode (0.036 cm²). The gauze electrode served as a counter electrode in chronocoulometric experiments and as the generator electrode for producing DPA⁻. The reference electrode was a silver wire quasi-reference electrode contained in a tube isolated from the working electrode compartment by a medium porosity sintered glass disk. The potential of this electrode was quite stable and reproducible in the 0.10 M TBAI-DMF solution⁷. The platinum microelectrode was pretreated by washing with conc. nitric acid, followed by a 24 h soaking in ferrous ammonium sulfate,

and finally rinsed with water, dried and soaked in DMF for 1 h.

All solutions were prepared on a vacuum line and degassed by several freeze-pump-thaw cycles⁷. Solutions of DPA⁺ were produced by controlled potential coulometric reduction⁴. Coulometric and preliminary voltammetric experiments were performed with a Princeton Applied Research Model 170 instrument. The chronocoulometric experiments were performed on an instrument similar to that of Anson and Payne⁸ programmed with a Wavetek Model 114 function generator. Optimal *iR*-compensation using positive feedback techniques is critically important for successful chronocoulometric experiments in aprotic solvents. Current-time traces were monitored with a Tektronix Model 564 oscilloscope and *iR* compensation was adjusted to the maximum value not leading to oscillation. The instrument was interfaced to a PDP-12A (Digital Equipment Corp.) digital computer equipped with a real time clock and a ten bit AD converter. The acquired integrated current data were analyzed in the computer using an assembly language least-squares routine. The basic principles and methods of chronocoulometry with digital data acquisition have been described elsewhere^{9,10}.

Results and discussion

Cyclic voltammetry of both the reduction of DPA and the oxidation of DPA⁺ in DMF solutions for scan rates, *v*, of 0.021 to 0.511 V s⁻¹, showed reversible behavior with the ratio of forward to reverse peak currents of 1.00 ± 0.02. For reduction of DPA the cathodic peak potential, *E*_{pc}, was -1.327 ± 0.005 V vs. Ag reference electrode, and *E*_{pa} - *E*_{pc} was 61 mV (where *E*_{pa} is the anodic peak potential); *E*_{pa} - *E*_{pc} for DPA⁻ solutions was 64 mV. From the value of *i*_p/*v*^{1/2} (where *i*_p is the peak current), which was 0.67 ± 0.01 μA s^{1/2} V⁻¹ for 0.85 mM solutions of both DPA and DPA⁺, a diffusion coefficient, *D*, of 6.4 × 10⁻⁶ cm² s⁻¹ was calculated.

Chronocoulometric data were analyzed according to the equation of Christie *et al.*¹¹:

$$Q = Q_{dl} + nF A \Gamma + 2nF A c (D_0 t / \pi)^{1/2} \quad (1)$$

where *Q*_{dl} is the amount of electricity to charge the double layer, *Γ* is the amount of electroactive species adsorbed, *Q* the total charge passed at time *t*, and *A* is the electrode area. A plot of *Q* vs. *t*^{1/2} yields a line with an intercept (*Q*_{dl} + *nF A Γ*) and a slope dependent on concentration (*c*) and diffusion coefficient. In the absence of adsorption, the intercept is identical to that of the background solution in the absence of the electroactive compound, assuming *Q*_{dl} is unchanged.

A plot of *Q* - *t*^{1/2} data for a solution of 0.85 mM DPA in DMF containing 0.1 M TBAI with the potential stepped from -0.500 to -1.500 V vs. Ag ref. is shown in Fig. 1. The result of the same potential step in 0.10 M TBAI in DMF is also shown in Fig. 1. The slope of the line for the DPA solution, corrected for background, is 0.29 μC ms^{-1/2}; the intercept is 0.17 μC, identical to that of the background solution. A *Q* - *t*^{1/2} plot for a solution of 0.10 M TBAI in DMF and one containing 0.85 mM DPA⁺ for a potential step of -1.500 to -0.500 V vs. Ag ref. is shown in Fig. 2. The corrected slope of the DPA⁺ oxidation line is 0.29 μC ms^{-1/2} and the intercept is 0.18 μC, compared to the blank solution intercept of 0.17 μC. These values lead to a diffusion coefficient of 7.2 × 10⁻⁶ cm² s⁻¹ for

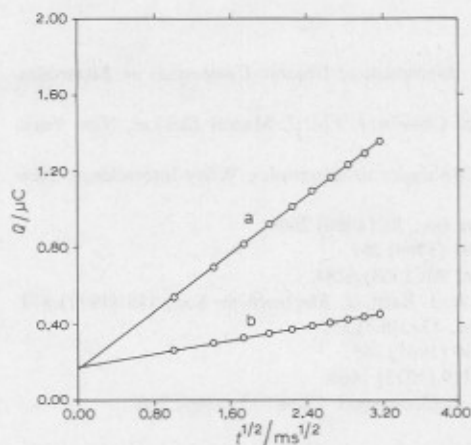


Fig. 1. Q vs. $t^{1/2}$ plots for a 0.10 M TBAI-DMF solution (a) containing 0.85 mM DPA and (b) without DPA. The potential step was from -0.500 to -1.500 V vs. Ag wire.

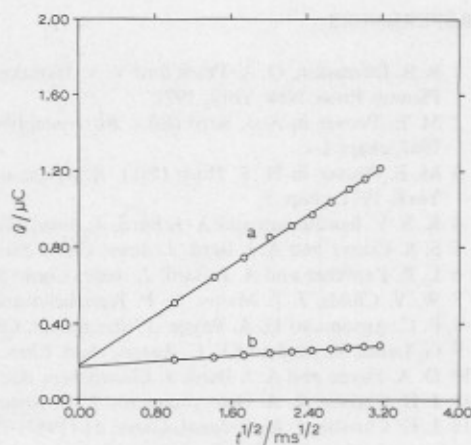


Fig. 2. Q vs. $t^{1/2}$ plots for a 0.1 M TBAI-DMF solution (a) containing 0.85 mM DPA $^{\bullet}$ and (b) without DPA $^{\bullet}$. The potential step was from -1.500 to -0.500 V vs. Ag wire.

both DPA and DPA $^{\bullet}$ and show that neither species is adsorbed appreciably. Assuming an experimental uncertainty of $\pm 0.01 \mu\text{C}$, the amount of adsorbed species is below $3 \times 10^{-12} \text{ mol cm}^{-2}$ under these conditions. Similar results were obtained for solutions containing 1.35 mM DPA and DPA $^{\bullet}$, yielding identical intercepts, but D calculated from these slopes was about 8% smaller. Double potential step experiments in both solutions for the charge accumulated to time τ , Q_{τ} , for a potential step -0.500 to -1.500 V, followed by a potential step back to -0.500 V and determination of $Q_{2\tau}$, yielded a $Q_{2\tau}/Q_{\tau}$ ratio of 0.57 ± 0.03 , compared to a theoretical value of 0.586 for a double potential step experiment for a system with no adsorption or kinetic perturbations¹².

These results, in agreement with those of Peover³, show that adsorption of aromatic hydrocarbons and their radical anions does not occur to an appreciable extent for low concentrations in aprotic solvents*. Thus, studies of reaction mechanisms and determinations of heterogeneous rate constants of these substances need not invoke adsorbed parents or intermediates. Finally, in studies of electro-generated chemiluminescence^{5,6}, the models neglecting adsorption are valid, and the light producing reactions do occur in the bulk solution and not at the electrode surface.

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* We have recently investigated, by this technique, the possibility of adsorption of dialkyl fumarates, cinnamionitrile, and ethyl cinnamate in DMF solutions in the presence of quaternary ammonium and alkali metal salts. At low concentrations of the electroactive substances, no appreciable adsorption of any of these species was observed.

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