

# Reactions of Aromatic Anion Radicals and Dianions. II.<sup>1</sup> Reversible Reduction of Anion Radicals to Dianions

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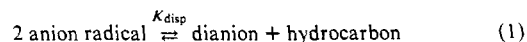
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**Abstract:** The aromatic hydrocarbons—anthracene, 9,10-diphenylanthracene, 1,2-benzanthracene, chrysene, coronene, and perylene—were observed to undergo two consecutive reversible one-electron transfers in several common electrolytic solvents to produce the anion radicals and the dianions, stable during the time scale of slow sweep cyclic voltammetry. The technique which allowed for the observation of the reversible reduction of the anion radicals involved carrying out voltammetric measurements in the presence of suspended neutral alumina which has the effect of keeping the solvents free of proton donors or other electrophilic impurities. Disproportionation equilibrium constants were found to be exceedingly small for all of the aromatic anion radicals in all of the solvents investigated. The values of the disproportionation equilibrium constants were found to be dependent on both the solvent and the nature of the counterion; however, both of these effects were small. On the other hand, the disproportionation constants for perylene and anthracene anion radicals were found to vary by a factor of 300 and 600, respectively, for a 100-fold change in supporting electrolyte concentration.

In solvents such as tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME), alkali metal reduction of polycyclic aromatic hydrocarbons leads to the formation of stable solutions of the corresponding anion radicals and, in some cases, the dianions. On the other hand, anion radicals produced by cathodic reduction of the hydrocarbons in dimethylformamide or acetonitrile containing tetraalkylammonium ions have much shorter lifetimes. For example, the anion radicals of anthracene (AN) and 9,10-diphenylanthracene (DPA) produced electrochemically in dimethylformamide (DMF) are only stable at low temperature under vacuum.<sup>2</sup> The lifetime of most polycyclic aromatic anion radicals is long enough in common electrolytic solvents for reversible cyclic voltammograms for the reduction of the aromatic hydrocarbons to be observed.<sup>3</sup> On the other hand, reversible reduction of the corresponding anion radicals has only been observed in very special cases. In general, reduction of aromatic anion radicals is accompanied by rapid irreversible protonation reactions, and little or no current for oxidation of the dianions can be detected during cyclic voltammetry. In a recent review, Dietz stated: "Spontaneous protonation of electrogenerated dianions of polycyclic aromatic hydrocarbons is so rapid that no other reactions are known".<sup>3</sup>

The first reversible reduction of the benzophenone anion radical was recently observed in liquid ammonia at  $-50^\circ$ .<sup>4</sup> We have observed the same process as well as the reversible reduction of several other simple anion radicals such as the nitrobenzene anion radical in more common electrolytic solvents such as DMF at room temperature when the voltammetric measurements were conducted in the presence of neutral alumina.<sup>5</sup> It should be mentioned that dianions of the acidic hydroquinones can readily be observed in aprotic solvents.<sup>6</sup>

Disproportionation mechanisms for the reactions of aromatic anion radicals are currently believed to be common.<sup>7</sup> For example, the mechanisms of protonation of perylene anion radical by water and alcohols and of anthracene anion radical by *tert*-butyl alcohol have been proposed to involve disproportionation of the anion radicals to the respective dianions which undergo rate-determining protonation.<sup>8,9</sup> In order to evaluate data for proposed disproportionation reactions, it is necessary to know the value of the disproportionation equilibrium constants (eq 1). In the past,



the most common method for determining the equilibrium constants has been by potentiometric titration.<sup>10</sup> In cases where the dianions are not stable under the experimental conditions,<sup>11</sup> the apparent equilibrium constants may be too large because of upset of the anion radical–dianion equilibrium by the rapid kinetic step involving the dianion. The latter effect has been commented on regarding the use of polarographic half-wave potentials for determining  $E^\circ$  values<sup>12</sup> from polarographic data. The possibility of error in apparent  $E^\circ$  is dependent upon the time gate of measurements, being greatest for slow measurements and minimal for rapid electrochemical techniques. Errors in calculated equilibrium constants for the disproportionation of the DPA<sup>13</sup> and the thianthrene cation radicals<sup>14</sup> have recently been emphasized. The magnitude of possible error is evident from the following. Under conditions where the thianthrene cation radical is oxidized irreversibly in acetonitrile, a  $\Delta E$  of 320 mV for the difference in peak potentials of the substrate and cation radical was found<sup>15</sup> which corresponds to a disproportionation equilibrium constant of about  $4 \times 10^{-6}$ . In the same solvent, under conditions where the cation radical is reversibly oxidized to the dication, a  $\Delta E$  of 510 mV was found<sup>16</sup> which corresponds to an equilibrium constant of  $2.3 \times 10^{-9}$ . Thus, the equilibrium constant calculated from the original data was in error by a factor of  $10^3$ . Obviously, in cases where the disproportionation mechanism requires that the doubly charged intermediate react in a nearly diffusion-controlled rate step, an error of the magnitude of  $10^3$  in the disproportionation equilibrium constant might allow the latter mechanism to be considered acceptable, while the true value would rule out the disproportionation.

The present investigation was stimulated by the recent success in observing reversible redox equilibria for cation radical–dication couples<sup>16</sup> and the strong current interest in disproportionation mechanisms for aromatic anion radicals.<sup>7–10,12</sup> In this paper, we describe reversible voltammetry for the reduction of several anion radicals of polycyclic aromatic compounds. Disproportionation equilibrium constants are calculated, and the feasibility of such reactions in these systems is discussed.

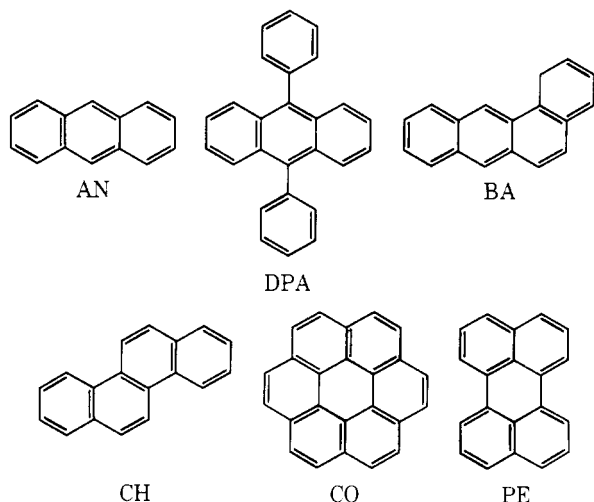
Table I. Voltammetric Data for the Reduction of Aromatic Hydrocarbons in Dimethylformamide at +11°

Compd	$E_1^{\circ a}$	$E_2^{\circ a}$	$\Delta E^{\circ b}$	$K_{\text{disp}}$
Anthracene	1915	2655	740	$1.0 \times 10^{-13}$
9,10-Diphenylanthracene	1830	2505	675	$1.5 \times 10^{-12}$
1,2-Benzanthracene	1960	2625	665	$2.0 \times 10^{-12}$
Chrysene	2225	2730	505	$1.5 \times 10^{-9}$
Coronene	2030	2670	640	$6.0 \times 10^{-12}$
Perylene	1640	2255	615	$1.5 \times 10^{-11}$

<sup>a</sup>Potential in mV vs. SCE. <sup>b</sup> $\Delta E^{\circ} = E_2^{\circ} - E_1^{\circ}$  in mV. Supporting electrolyte, (Me<sub>4</sub>NBr) = 0.2 M.

## Results

The structures of the compounds investigated are summarized below. The selection of compounds was determined by the amount of interest previously shown with regard to voltammetric behavior and reactions of the corresponding radical anions formed by alkali metal reduction.



**Reversible Reductions in Aprotic Solvents.** Voltammetric data for the six hydrocarbons in DMF at +11° in the presence of Me<sub>4</sub>NBr are summarized in Table I. Both the first and second charge transfers for all the substrates were reversible under the experimental conditions. Disproportionation equilibrium constants were calculated from the  $\Delta E^{\circ}$  values (the difference between the potentials of the first and second charge transfers). The voltammetric behavior of the most difficultly reduced compound, chrysene (CH), is illustrated in Figure 1. Even with the most carefully purified

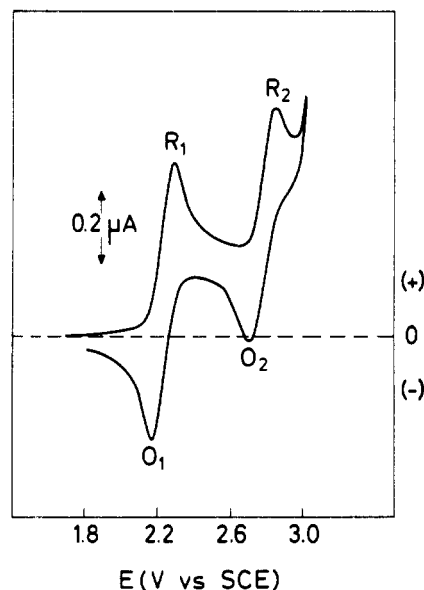


Figure 1. Voltammogram of CH (1.9 mM) in DMF saturated with Me<sub>4</sub>NBr at +12°. Sweep rate = 153 mV/sec.

solvent, the second reduction step is obscured by the background current in the absence of suspended neutral alumina.

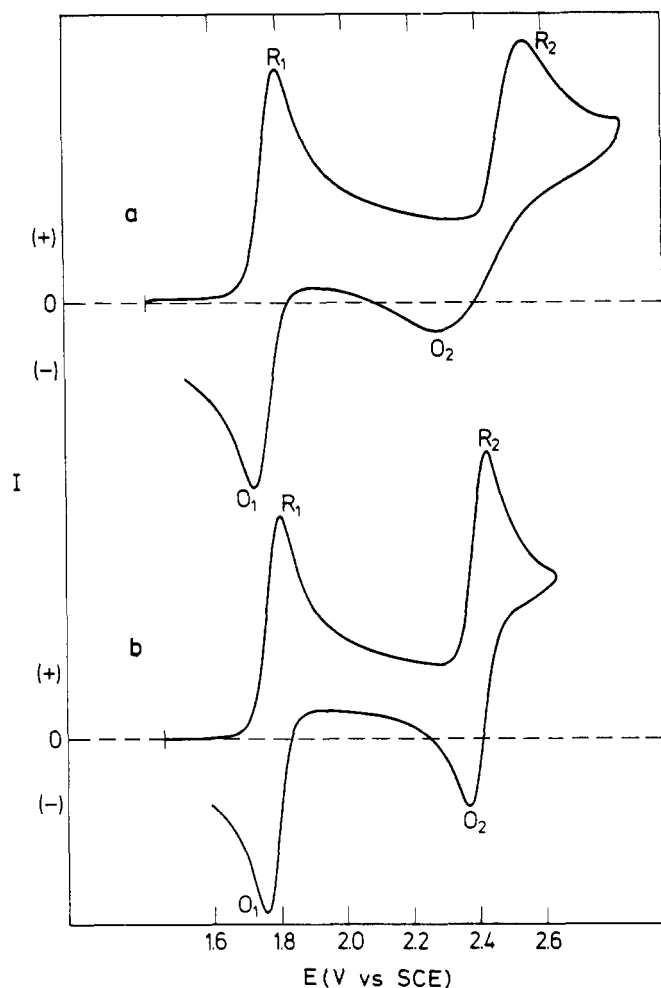
The electrochemical reversibility of the two consecutive charge transfers to the aromatic compounds in DMF in the presence of neutral alumina is demonstrated by the voltammetry of PE in the presence of *n*-Bu<sub>4</sub>NBF<sub>4</sub> (0.4 M) at two platinum electrodes varying greatly in area (Table II). The electron transfers are reversible, i.e., fast compared with diffusion, potential sweep and any reaction in the system, and the reduced forms are stable during the time scale of the experiment.<sup>17</sup> The voltammetric data (Table II) are in agreement with that predicted for mainly linear diffusion with a small uncompensated resistance. Peak separations are only slightly greater than the theoretical value (55 mV at +12°), and the slight increase in  $i_p/(\nu)^{1/2}$  values with decreasing sweep rate is probably due to spherical diffusion at the lower sweep rates since the effect is most noticeable at the smallest electrode. The ions were completely stable during the time scale of the experiments since the peak current ratios were found to be equal to 1.0 at all sweep rates.

Although chemically reversible, the second charge transfer to DPA in DMF in the presence of only *n*-Bu<sub>4</sub>N<sup>+</sup> ion is decidedly electrochemically irreversible (Figure 2a). When

Table II. Peak Current and Peak Potential Data for the Reduction of Perylene as a Function of Voltage Sweep Rate<sup>a</sup>

$\nu$ , mV/sec	$\Delta E_{p^1}$ , mV	$\Delta E_{p^2}$ , mV	$i_{pR^1}$ , $\mu A$	$i_{pO^1}$ , $\mu A$	$i_{pR^2}$ , $\mu A$	$i_{pO^2}$ , $\mu A$	$i_{pR^1}/(\nu)^{1/2}$	$i_{pO^1}/(\nu)^{1/2}$	$i_{pR^2}/(\nu)^{1/2}$	$i_{pO^2}/(\nu)^{1/2}$	$i_{pO^1}/i_{pR^1}$	$i_{pO^2}/i_{pR^2}$
Beckmann Electrode (Area $\approx 20 \text{ mm}^2$ )												
16	58	58	15.5	16.2	16.5	16.2	3.88	4.05	4.12	4.05	1.05	1.02
32	59	60	21.8	22.2	23.0	21.5	3.85	3.92	4.07	3.80	1.02	0.94
65	60	60	30.5	30.5	32.0	30.0	3.78	3.78	3.97	3.72	1.00	0.94
128	62	64	42.5	41.5	44.0	40.5	3.76	3.67	3.89	3.58	0.98	0.92
242	67	70	57.0	57.0	59.0	56.0	3.68	3.68	3.79	3.60	1.00	0.95
306	70	70	64.0	63.0	65.0	63.0	3.68	3.60	3.72	3.68	0.98	0.97
Small Pt Electrode (Area $\approx 0.3 \text{ mm}^2$ )												
16	62	64	0.18	0.18	0.19	0.18	0.045	0.045	0.047	0.045	1.00	0.95
32	61	64	0.24	0.25	0.25	0.25	0.042	0.044	0.044	0.044	1.05	1.00
65	61	63	0.32	0.34	0.34	0.34	0.039	0.042	0.042	0.042	1.07	1.00
128	62	65	0.44	0.46	0.47	0.46	0.039	0.041	0.042	0.041	1.05	0.98
153	64	66	0.50	0.50	0.49	0.50	0.040	0.040	0.040	0.050	1.00	1.02
242	65	68	0.58	0.61	0.60	0.61	0.037	0.039	0.038	0.039	1.05	1.03
306	66	70	0.65	0.65	0.65	0.68	0.037	0.037	0.037	0.038	1.00	1.02

<sup>a</sup>Supporting electrolyte, *n*-Bu<sub>4</sub>NBF<sub>4</sub> (0.4 M). Temperature +12°. Solvent DMF.

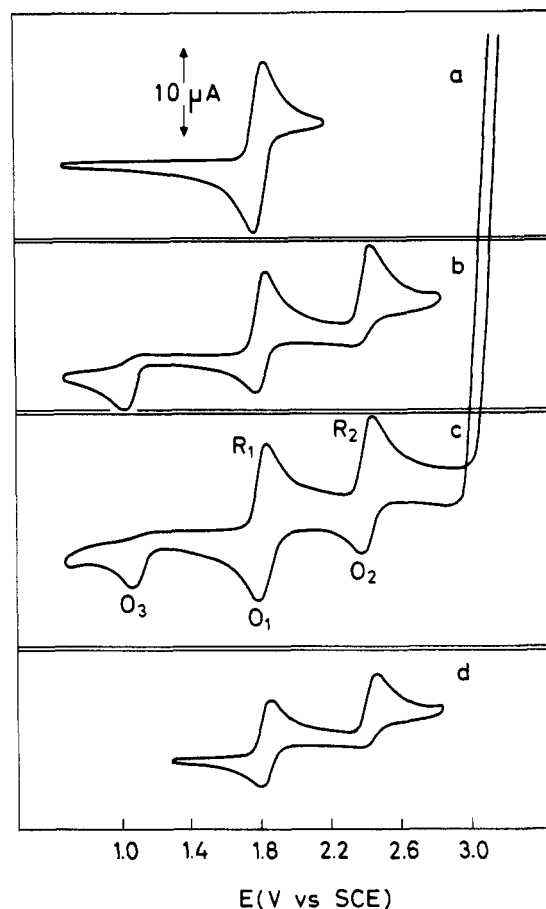


**Figure 2.** Voltammograms of DPA (2.2 mM) in DMF at  $-36^\circ$ : (a)  $n\text{-Bu}_4\text{NBF}_4$  (0.2 M); (b)  $n\text{-Bu}_4\text{NBF}_4$  (0.2 M) +  $\text{Et}_4\text{NClO}_4$  (0.02 M). Sweep rate: 153 mV/sec (a) and 65 mV/sec (b).

much lower concentrations of  $\text{Et}_4\text{N}^+$  ions were added to the same solution, the second charge transfer became reversible (Figure 2b).

The voltammetry for the reduction of DPA in DMF in the presence of a small amount of alumina at low temperature is illustrated in Figure 3. When the direction of potential sweep was changed after the first reduction step, reoxidation of the anion radical was observed (Figure 3a). Extending the sweep beyond the second reduction peak and then initiating the anodic scan showed that the dianion had been consumed in a rapid chemical step, and a new oxidation peak ( $O_3$ ) was observed (Figure 3b) which has previously been assigned to the oxidation of a protonation product of the dianion.<sup>18</sup> When the cathodic sweep was extended into the region of the background current and held for 15 sec before initiating the anodic scan, a peak ( $O_2$ ) for oxidation of the dianion was observed (Figure 3c). Figure 3d is the second cycle of the voltammogram in which the reoxidation of the protonated product ( $O_3$ ) was not included. In the latter case, the peak height for reduction of DPA was reduced to about half the value as on the first cycle showing that substrate was indeed consumed at  $R_2$  and regenerated at  $O_3$ .

**The Effect of the Solvent on the Voltammetry of Perylene.** Reversible reduction of  $\text{PE}^\cdot$  to  $\text{PE}^{2-}$  was observed in several common aprotic electrochemical solvents. The effect of the solvent upon the redox potentials of PE is shown by the data in Table III. Both charge transfers were found to be



**Figure 3.** Voltammograms of DPA in DMF at  $-30^\circ$ .  $\text{Et}_4\text{NClO}_4$ , 0.4 M. Sweep rate = 600 mV/sec.

**Table III.** Data for the Voltammetric Reduction of Perylene in Aprotic Solvents

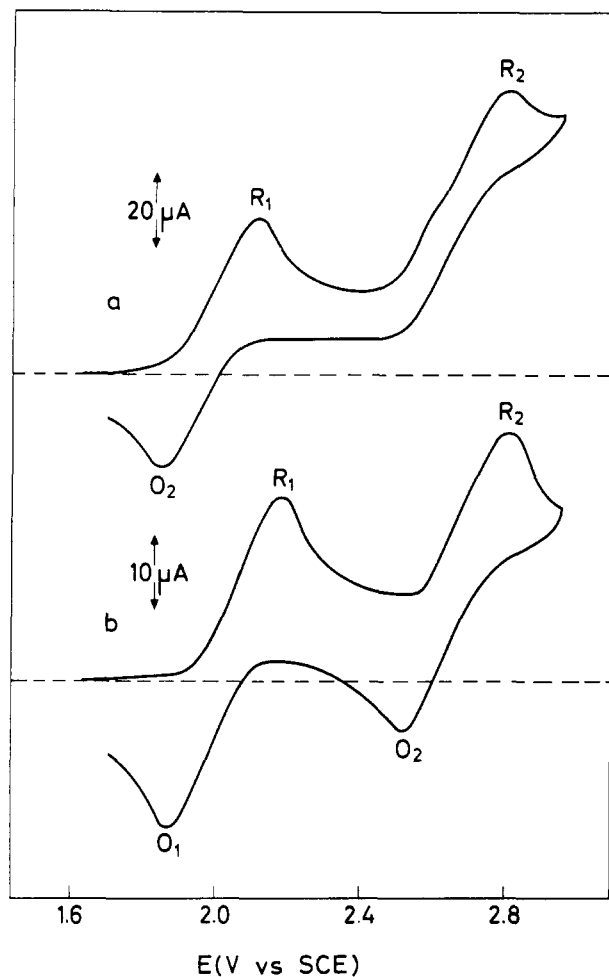
Solvent <sup>a</sup>	$D^d$	$E_1^\circ$ <sup>b</sup>	$E_2^\circ$ <sup>b</sup>	$\Delta E^\circ$ <sup>c</sup>	$K_{\text{disp}}$	$(K_{\text{disp}})_{\text{rel}}$
DMF	37	1610	2205	595	$3.5 \times 10^{-11}$	3.5
HMPT	30	1515	2135	620	$1.0 \times 10^{-11}$	1.0
Pyridine	13	1600	2155	555	$2.0 \times 10^{-10}$	20.0
MeCN	37	1610	2155	545	$3.0 \times 10^{-10}$	30.0
THF	7.4	1630	2170	540	$3.5 \times 10^{-10}$	35.0

<sup>a</sup> Supporting electrolyte:  $n\text{-Bu}_4\text{NBF}_4$  (0.2 M), temperature  $11^\circ$ .

<sup>b</sup> Potential in mV vs. SCE. <sup>c</sup>  $\Delta E^\circ = E_2^\circ - E_1^\circ$  in mV. <sup>d</sup> Dielectric constant from ref 19.

reversible for this compound in DMF, THF, pyridine, hexamethylphosphortriamide (HMPT), and acetonitrile.

**Voltammetry in Poorly Conducting Media.** The dielectric constant of THF is quite low (7.4 at  $25^\circ$ ),<sup>19</sup> and the redox couples measured without  $i_R$  compensation appear drawn out and irreversible. The latter is the case for the reduction of coronene (CO) in THF containing  $n\text{-Bu}_4\text{NBF}_4$  (0.2 M) and suspended alumina (Figure 4). No current for the oxidation of the dianion was observed at  $+22^\circ$  (Figure 4a); at  $-22^\circ$  (Figure 4b), the peak current ratio  $i_{O_2}/i_{R_2}$  was very close to 1.0. The latter illustrates the dramatic effect of temperature upon the rate of the protonation of the coronene dianion under the voltammetric conditions. Potential measurements on voltammograms measured in solutions of high resistance as shown in Figure 4 are not meaningful unless corrected for the  $i_R$  drop. Instead of compensating for the solution resistance electronically (by positive feedback), we have instead recorded uncompensated voltammograms over a range of sweep rates (and hence, currents) and



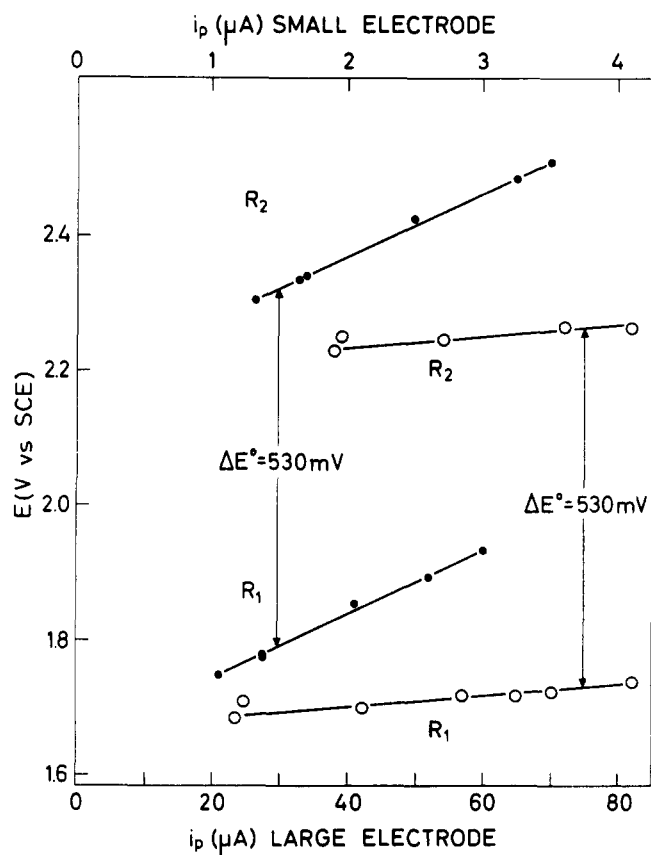
**Figure 4.** Voltammograms of CO in THF containing  $n\text{-Bu}_4\text{NBF}_4$  (0.2 M): (a) sweep rate = 153 mV/sec at +21.6°; (b) sweep rate = 128 mV/sec at -22°. Electrode area  $\sim 20 \text{ mm}^2$ .

**Table IV.** The Effect of the Electrolyte on Reversible Reduction Potentials in DMF

Compd	Electrolyte	$E_1^\circ$ <sup>a</sup>	$E_2^\circ$ <sup>a</sup>	$\Delta E^\circ$ <sup>b</sup>	$K_{\text{disp}}$	$(K_{\text{disp}})_{\text{rel}}$
PE	$\text{Me}_4\text{NI}$	1620	2230	610	$2.0 \times 10^{-11}$	1.0
	$\text{Et}_4\text{NI}$	1635	2180	545	$3.0 \times 10^{-10}$	15
	$n\text{-Pr}_4\text{NI}$	1625	2205	580	$6.5 \times 10^{-11}$	3.3
	$n\text{-Bu}_4\text{NI}$	1610	2205	595	$3.5 \times 10^{-11}$	1.8
	$\text{NaClO}_4$	1625	2230	605	$2.5 \times 10^{-11}$	1.3
AN	$\text{Me}_4\text{NI}$	1920	2650	730	$1.5 \times 10^{-13}$	2.1
	$\text{Et}_4\text{NI}$	1915	2585	680 <sup>c</sup>	$1.0 \times 10^{-12c}$	14
	$n\text{-Pr}_4\text{NI}$	1910	2650	740	$1.0 \times 10^{-13}$	1.4
	$n\text{-Bu}_4\text{NI}$	1905	2655	750	$7.0 \times 10^{-14}$	1.0
	$\text{NaClO}_4$	1900	2560	660 <sup>d</sup>		

<sup>a</sup> Potential in mV vs. SCE. <sup>b</sup>  $\Delta E^\circ = E_2^\circ - E_1^\circ$  in mV. <sup>c</sup> At -35°, extrapolated to 11°, all other measurements at +11°. <sup>d</sup> No oxidation current for the dianion.

by a graphical procedure corrected the potentials. When the peak potentials were plotted as functions of the peak current, points for the second charge transfer fell on a straight line with slope identical with that for the first charge transfer. The potential difference between the two lines is equal to  $\Delta E^\circ$  for the two charge transfers, and the intercept of the extrapolated lines at zero current is equal to the corrected peak potential. The procedure is illustrated by Figure 5 for the reduction of perylene (PE) in THF containing  $n\text{-Bu}_4\text{NBF}_4$  (0.18 M) in the presence of suspended alumina using two electrodes differing greatly in surface area. The advantage of using electrodes with very small area in order



**Figure 5.** Peak potentials plotted vs. peak currents for the reduction of PE in THF at a large ( $\sim 20 \text{ mm}^2$ , solid circles) and a small ( $\sim 2 \text{ mm}^2$ , open circles) platinum electrode at +10.6°. Data obtained by varying voltage sweep rate from 32 to 600 mV/sec.  $n\text{-Bu}_4\text{NBF}_4$ , 0.18 M.

to minimize the effect of ohmic drop during voltammetric measurements is evident from the figure. In spite of the fact that the applied potential sweep is nonlinear in the highly resistant THF solutions, the peak potentials are shifted linearly with the ohmic drop, and no nonlinear second order effects were observed.

**The Effect of the Nature of the Supporting Electrolyte on the Voltammetry of Perylene and Anthracene.** The effects of the counterions on the differences in the potentials of the first and second charge transfers for PE and AN in DMF are summarized in Table IV. A uniform decrease in  $\Delta E^\circ$  was observed with decreasing cation size in going from  $n\text{-Bu}_4\text{N}^+$  to  $n\text{-Pr}_4\text{N}^+$  to  $\text{Et}_4\text{N}^+$  ions, while a substantial increase was observed in going from  $\text{Et}_4\text{N}^+$  to  $\text{Me}_4\text{N}^+$  as the counterion. Furthermore, additional experiments in which  $\text{Et}_4\text{N}^+$  ions were added to solutions containing either  $\text{Me}_4\text{N}^+$  or  $n\text{-Bu}_4\text{N}^+$  ions resulted in values of  $\Delta E^\circ$  approaching that when only  $\text{Et}_4\text{N}^+$  was present.  $\Delta E^\circ$  for PE in the presence of sodium ion was intermediate between that observed in the presence of  $\text{Me}_4\text{N}^+$  and  $n\text{-Bu}_4\text{N}^+$  ions.

Special care must be taken to obtain reduction potential data in the presence of sodium ions. The electrode very easily becomes deactivated either when there is oxygen present in the solution or when sodium is reduced on the electrode.

**The Effect of the Supporting Electrolyte Concentration on  $\Delta E^\circ$ .** The data in Table IV were found to be very nearly independent of the concentration of the supporting electrolyte in DMF. On the other hand, in THF, the value of  $\Delta E^\circ$  for both PE and AN was found to be profoundly affected by the salt concentration. Data obtained during voltammetric measurements on solutions of widely varying salt concentration are summarized in Table V. For both PE and AN, plots of  $\Delta E^\circ$  vs.  $\log (n\text{-Bu}_4\text{NBF}_4)$  were linear (Figure 6).

Table V. The Effect of Supporting Electrolyte Concentration on  $\Delta E^\circ$  in THF<sup>a</sup>

$(n\text{-Bu}_4\text{NBF}_4)$ , $M$	$\Delta E^\circ_{\text{PE}}$ , mV	$(K_{\text{disp}})_{\text{PE}}$	$\Delta E^\circ_{\text{AN}}$ , mV	$(K_{\text{disp}})_{\text{AN}}$
0.01	450	$1.5 \times 10^{-8}$		
0.02	470	$5.5 \times 10^{-9}$	605	$2.5 \times 10^{-11}$
0.04	490	$2.5 \times 10^{-9}$	630	$8.5 \times 10^{-12}$
0.06			640	$6.0 \times 10^{-12}$
0.10	520	$7.5 \times 10^{-10}$	650	$4.0 \times 10^{-12}$
0.20	545	$3.0 \times 10^{-10}$	685	$9.5 \times 10^{-13}$
0.42	565	$1.0 \times 10^{-10}$		
0.50			720	$2.5 \times 10^{-13}$
0.62	580	$6.5 \times 10^{-11}$		
1.00	590	$4.5 \times 10^{-11}$	735	$1.5 \times 10^{-13}$

<sup>a</sup> Temperature 10°.

Difficulties were encountered when attempts were made to make similar series of measurements in the presence of sodium ions. For PE, it was possible to measure reversible potentials for both charge transfers at very low concentrations of NaBPh<sub>4</sub>, and the values of  $\Delta E^\circ$  were comparable to those listed in Table V. However, the amount of salt could not be increased significantly without encountering serious problems with deactivation of the electrode which resulted in very irreversible voltammograms for the second charge transfer, rendering the measurements meaningless. Another problem which appeared to be greater with NaBPh<sub>4</sub> than with *n*-Bu<sub>4</sub>NBF<sub>4</sub> is that the former salt appears to adsorb on alumina making the exact concentration uncertain.

**The Effect of Temperature on  $\Delta E^\circ$ .** The values of  $\Delta E^\circ$  were not greatly affected by the temperature. The maximum temperature effect observed was of the order of 50-mV lowering of  $\Delta E^\circ$  for a 100° temperature decrease. In THF,  $\Delta E^\circ$  for PE decreased only 11 mV for a 40° lowering of the temperature.

## Discussion

The difference in experimental conditions used in this study as compared with previous studies of the voltammetric reduction of aromatic hydrocarbons which has allowed us to observe reversible anion radical-dianion redox couples is that our measurements are made in the presence of suspended alumina. This technique was developed in connection with the study of cation radical-dication equilibria, in which case the function of the suspended alumina was that of a very effective nucleophile scavenger.<sup>16</sup> This work has shown that suspended alumina is just as effective as an electrophile scavenger, particularly proton donors, and even very reactive dianions such as that from anthracene can be observed using slow sweep cyclic voltammetry carried out in the presence of alumina. It should be emphasized that all the lengthy and tedious purification procedures on solvents used in previous studies failed to allow for the observation of reversible reduction of the anion radicals studied here. In this study, we were able to directly use reagent grade solvents without any pretreatment and achieve the desired results. This is not to say that solvent purification should be abandoned for voltammetric studies<sup>20</sup> since impurities could have effects other than bringing about irreversible redox couples.

The effect of conducting voltammetric measurements in the presence of alumina is dramatically brought out by the voltammograms illustrated in Figures 1 and 3. Chrysene is very difficult to reduce, the peak potential for the first charge transfer being -2.25 V in DMF. In the absence of alumina, the voltammogram consists of a single reversible one-electron redox couple; the second charge transfer is obscured by the background current. However, when neutral alumina is suspended in the solution, the background cur-

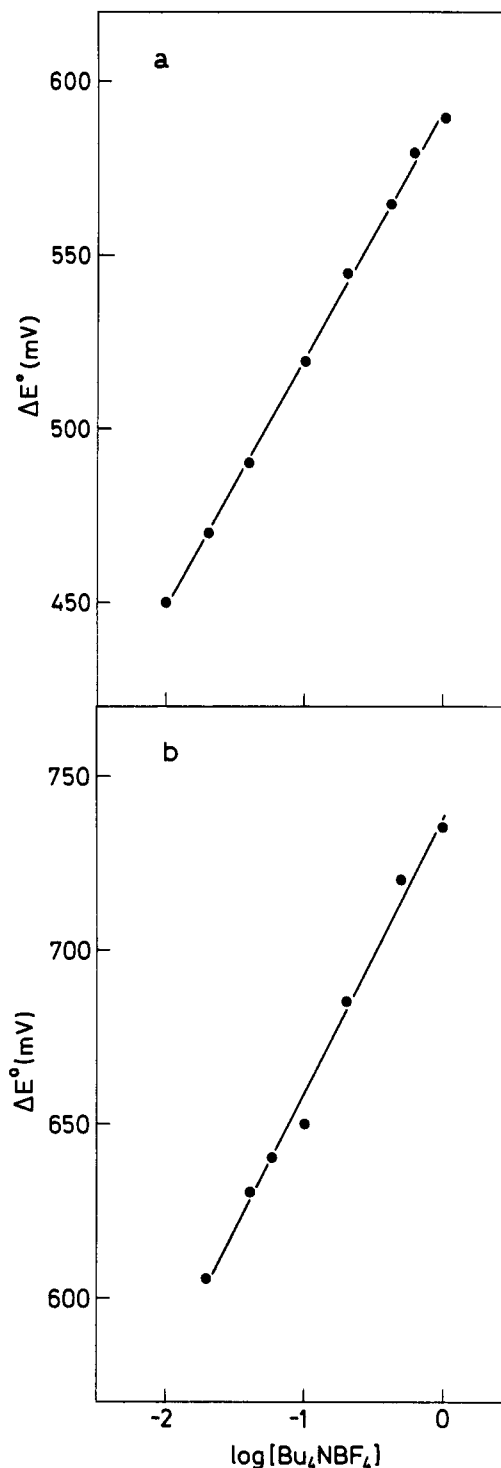
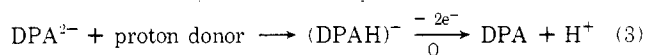
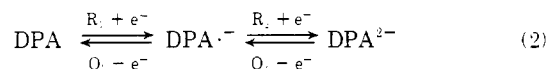


Figure 6. Difference in potentials for the first and second charge transfers ( $\Delta E^\circ$ ) for the reductions of (a) PE and (b) AN in THF plotted as functions of supporting electrolyte concentration.

rent is shifted out beyond -3.0 V, and the reduction peak for the second reversible charge transfer was observed at -2.75 V (Figure 1). The corresponding redox couples for DPA are observed at less negative potentials and, at -30°, the first couple is reversible and the second irreversible in the presence of some but not sufficient amounts of alumina (Figure 3a,b). When the cathodic sweep is continued into the background current region and held for 15 sec, the return sweep revealed oxidation current for the dianion (Figure 3c).<sup>21</sup> This experiment identifies the species reacting with the dianion as being a solvent impurity, which is destroyed by the background current, rather than either the

solvent or the electrolyte. The reactions are summarized below.



The effect of the size of the tetraalkylammonium ion of the supporting electrolyte on the reduction of PE and AN is illustrated by the data in Table IV.<sup>22</sup> The potential of the first reduction step for PE in DMF is more or less independent of the supporting electrolyte cation when the latter is  $\text{Me}_4\text{N}^+$ ,  $\text{Et}_4\text{N}^+$ , or  $n\text{-Pr}_4\text{N}^+$  and is equal to about  $-1.62$  V. On the other hand,  $\Delta E^\circ$  is equal to  $595$  mV in the presence of the largest ion and only  $545$  mV in  $\text{Et}_4\text{N}^+$  containing solutions. Upon going to  $\text{Me}_4\text{N}^+$ , a maximum value of  $\Delta E^\circ$  ( $610$  mV) was observed. Sodium ion had very nearly the same effect upon the potentials as  $\text{Me}_4\text{N}^+$  ion. For anthracene, the first charge transfer is nearly independent of the supporting electrolyte, and  $\Delta E^\circ$  is nearly the same for all the electrolytes ( $740$  mV) with the exception of  $\text{Et}_4\text{N}^+$  in which case a significantly lower value ( $670$  mV) was observed. We rationalize the cation effect in the following manner. Both  $n\text{-Pr}_4\text{N}^+$  and  $n\text{-Bu}_4\text{N}^+$  have long enough saturated carbon chains so that the ion pairs formed between the dianions and these two counterions are weaker than that for the smaller  $\text{Et}_4\text{N}^+$  ion which forms contact ion pairs with the dianions.<sup>23</sup> The even smaller ion ( $\text{Me}_4\text{N}^+$ ) can interact more strongly with the solvent and thus form solvent-separated ion pairs. It has been demonstrated that  $\text{Bu}(\text{isoamyl})_3\text{N}^+$  ions are not coordinated with either THF or dimethoxyethane, the Stokes radii being identical ( $4.2$  Å) in both solvents.<sup>25</sup> The latter supports the contention that  $n\text{-Bu}_4\text{N}^+$ ,  $n\text{-Pr}_4\text{N}^+$ , and  $\text{Et}_4\text{N}^+$  form contact ion pairs rather than solvent-separated ion pairs with the dianions with  $\text{Et}_4\text{N}^+$  forming the strongest pairs because of its smaller size. A test of the above hypothesis is as follows. Of the four cations,  $\text{Et}_4\text{N}^+$  is proposed to form the strongest ion pairs. Thus, if small amounts of  $\text{Et}_4\text{N}^+$  are added to solutions containing excess of the other three ions, the voltammetry should be very similar to that when  $\text{Et}_4\text{N}^+$  is the cation of the supporting electrolyte. The latter was in fact observed during voltammetric measurements in DMF. That results obtained in the presence of sodium ion are similar to those obtained when  $\text{Me}_4\text{NI}$  was the supporting electrolyte is consistent with the fact that  $\text{Na}^+$  is known to form solvent-separated ion pairs.

A number of electrochemical investigations have dealt with ion-pairing effects.<sup>6a,26,27</sup> The effect of tetraalkylammonium ions on the reversibility of alkali metal ion reduction has been discussed<sup>26</sup> in terms of the size of the ions. Reductions were found to be irreversible in the presence of  $\text{Me}_4\text{N}^+$  and  $\text{Et}_4\text{N}^+$  ions and reversible in the presence of the larger ions. The latter was attributed to preferential adsorption of the smaller ions on the electrode surface. Cyclic voltammetry of anthracene in HMPT in the presence of  $\text{Li}^+$ ,  $\text{Bu}_4\text{N}^+$ , and  $\text{Et}_4\text{N}^+$  showed that the potential of the first charge transfer for the reduction was independent of the cation but that the potential difference between first and second charge transfers became increasingly less in going from  $\text{Li}^+$  to  $\text{Bu}_4\text{N}^+$  to  $\text{Et}_4\text{N}^+$ .<sup>27</sup> The latter was interpreted in terms of increasing strength of ion pairs. It should be pointed out that the anion radical-dianion couple was irreversible under the conditions of the latter study.<sup>27a</sup> Peover<sup>27b</sup> makes the following statement: "In these solvents (those of low dielectric constant) solvation of the tetraalkylammonium ions is apparently so weak that they are smaller and therefore interact more strongly with large diffuse anions than do alkali metal cations".

The ability of  $\text{Et}_4\text{N}^+$  to form a contact ion pair with the dianion of DPA is brought out dramatically by the voltammograms in Figure 2. At  $-36^\circ$ , the second charge transfer to DPA is decidedly irreversible in DMF containing  $n\text{-Bu}_4\text{N}^+$  ( $0.2$  M) with the peak separation for the anodic and cathodic segments being of the order of  $200$  mV (Figure 2a). Adding a smaller amount of  $\text{Et}_4\text{N}^+$  ( $0.02$  M) resulted in the observation of a reversible charge transfer (Figure 2b). The latter behavior was not observed with either PE or AN. We attribute the irreversibility in the presence of only  $n\text{-Bu}_4\text{N}^+$  ions to the fact that the 9,10-positions of DPA, where MO calculations indicate the charges would be concentrated,<sup>28</sup> are sterically inaccessible to two of the large cations approaching from the same side. Neither PE or AN, both planar molecules without interfering substituents, have stringent steric requirements for solvation of the respective ions.

As stated in the introduction, one of the primary objectives of this work was to evaluate disproportionation equilibrium constants from reversible redox potentials. This objective has been achieved. From the data in Table I, we can see that the disproportionation constants for all the hydrocarbon ions are exceedingly small in DMF. Perhaps more surprising is the fact that  $K_{\text{disp}}$  for  $\text{PE}^{\cdot-}$  varied only by a factor of 35 over the entire range of solvents investigated (Table III) at a constant supporting electrolyte concentration. Although small differences in  $K_{\text{disp}}$  were observed, the magnitude of the effect is almost negligible. The variations in  $K_{\text{disp}}$  that do occur appear to be unrelated to the dielectric constant of the solvent. By far the most significant finding is the very great dependence of  $K_{\text{disp}}$  for both  $\text{PE}^{\cdot-}$  and  $\text{AN}^{\cdot-}$  in THF (Table V and Figure 6) upon the salt concentrations.<sup>29</sup> In fact,  $\Delta E^\circ$  for both systems was found to vary linearly with the logarithm of the salt concentration. A 100-fold increase in salt concentration brought about a 300- and 600-fold decrease in  $K_{\text{disp}}$  for  $\text{PE}^{\cdot-}$  and  $\text{AN}^{\cdot-}$ , respectively (Figure 6). The latter observation provides an obvious means of evaluating possible disproportionation mechanisms. If a disproportionation equilibrium is involved either during or before the rate-determining step of a reaction of an anion radical, the overall rate of the reaction should increase proportionately to the increase in  $K_{\text{disp}}$  as the salt concentration is varied.

In conclusion, we emphasize once again that the measurements reported in this paper were on solutions containing tetraalkylammonium ions and that the disproportionation equilibrium constants obtained differ substantially from values measured on alkali metal ion containing solutions.<sup>10</sup> Work is now in progress to determine if there are any real discrepancies between the two sets of data.

## Experimental Section

The procedure for carrying out voltammetric measurements in the presence of suspended neutral alumina has been described in detail.<sup>16</sup> The apparatus used for voltammetric measurements has been described.<sup>31</sup> The electrodes used for the measurements were either commercial platinum inlay (Beckmann Pt Button) or much smaller electrodes designed by Moe.<sup>32</sup> The small electrodes were constructed from a 0.6-mm platinum wire sealed in soft glass and polished on a surface of ground glass. Reference electrodes were either commercial saturated aqueous calomel electrodes or, in cases when only potential differences were measured, silver wires. A coiled platinum wire served as the counter electrode. An undivided cell cooled with either tap water or a cryostat was used. From 10 to 30 g of Woelm W 200 neutral alumina grade super I (stored under argon) was added to 50.0 ml of solution, on which measurements were to be made, and the mixture was stirred during a few minutes, while the oxygen was blown out of the solution with argon.

Solvents were purified by standard procedures before use.<sup>19</sup> Reagent grade hydrocarbons were recrystallized before use.

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- (22) It should be emphasized that, although tetraalkylammonium ions are capable of acting as proton donors, no reactions were observed between the anion radicals or dianions with the electrolytes on the time scale of the measurements. The latter is evident from the voltammograms in Figures 1, 2, and 4 and the voltammetric data.
- (23) The Stokes radii for the tetraalkylammonium ions have been calculated to be equal to: 4.71 ( $n\text{-Bu}_4\text{N}^+$ ), 3.92 ( $n\text{-Pr}_4\text{N}^+$ ), 2.81 ( $\text{Et}_4\text{N}^+$ ), and 2.04 Å ( $\text{Me}_4\text{N}^+$ ).<sup>24</sup> The Stokes radius of  $\text{Na}^+$  in THF has been determined to be of the order of 4.0 Å.<sup>25</sup>
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## Stereochemistry of Carbene Rearrangements. Correlation of ab Initio Molecular Orbitals as an Aid to the Investigation of the Electron Redistribution Mechanism

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**Abstract:** Nonempirical LCAO-MO-SCF calculations employing a double  $\zeta$  basis set have been carried out to examine the reaction profile of the rearrangement of methylcarbene to ethylene. The investigation also involved a charge distribution analysis on the basis of which a mechanism for the electron redistribution process has been proposed. This mechanism has been further supported by a detailed study of the change in molecular orbital density contours along the reaction coordinate. An energy level correlation diagram for the singlet carbene to ethylene process, based on the calculated MO distribution pattern, shows no correlations between bonding levels in the reactant and antibonding levels in the product. Thus the reaction is predicted to be thermally allowed in the Woodward-Hoffmann sense.

The thermal rearrangement of carbenes to olefins is well known<sup>1</sup> to organic chemists. Since carbenes could conceivably exist as singlets or triplets, this reaction could, in principle, involve either the conversion of a singlet carbene to an olefin in its ground state, or the conversion of a triplet carbene initially to an excited triplet olefin which rapidly decays to its ground state. Orbital symmetry considerations<sup>2</sup> to predict which of the above conversions should be favored cannot be utilized because of the lack of a common symmetry element in reactant and product. An alternative qualita-

tive quantum mechanical approach, which is based on the correlation of nodal characteristics of the molecular orbitals involved in a reaction and does not require any symmetry considerations, is the so called "MO Following technique".<sup>3</sup> It was reported<sup>3</sup> that application of this technique to the carbene rearrangement predicts the ground state process to be "allowed" and thus preferred. However, this approach is truly applicable only to molecules whose electronic ground state is unquestionably singlet. It is clear that, in the present case, the choice of the favored conversion depends entirely