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Voltammetry in Benzene and Chlorobenzene. The Behaviour of Ions of Aromatic Compounds in Nonpolar Media

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By employing minute working electrodes, it was found possible to measure well defined redox potentials of aromatic hydrocarbons in the nonpolar solvents, benzene and chlorobenzene. Both solvents were found to have large accessible anodic and cathodic potential ranges. Anions appear to be exceptionally stable in benzene, the reversible formation of a trianion-radical being observed. Both the anion radical and dianion of perylene were formed reversibly under cyclic voltammetric conditions in benzene while the cation radical was found to adsorb strongly to the electrode. The latter behaviour was rationalized in terms of stronger ion-pairing between the anions and supporting electrolyte cations taking place stabilizing the anions while similar strong interactions involving the cation radicals are absent. Due to the inertness of chlorobenzene, its wide voltammetric potential range, and the ready solubility of tetrabutylammonium salts in the solvent, chlorobenzene was suggested to be an excellent solvent for the study of reversible oxidation and reduction of aromatic compounds.

Voltammetric studies are generally confined to solvents of relatively high dielectric constants. Exceptions to this rule can be found, for example ethers such as tetrahydrofuran and 1,2-dimethoxyethane have found limited use. The latter are exceptional in that the ethereal oxygens provide sites for coordination of cations and thus they are good solvents for many salts which can be used as supporting electrolytes. Studies in the ethereal solvents have revealed much information regarding the ion-pairing properties of anions derived from aromatic compounds.[1]

The present investigation was initiated in order to determine the behaviour of organic ions generated at electrodes in nonpolar solvents which have no special solvating features for either anions or cations. The ultimate goal would be to be able to do electrochemistry in a saturated hydrocarbon solvent such as hexane. However, a stringent requirement for a voltammetric solvent is that it is capable of dissolving supporting electrolyte salts, a property not shown by hexane. Thus, it was necessary to choose benzene, a somewhat more polar and less inert hydrocarbon, as the least polar solvent likely to have the necessary features for voltammetric studies. Here, we report results of voltammetric studies on redox reactions of aromatic hydrocarbons in benzene and chlorobenzene.

RESULTS AND DISCUSSION

Voltammetry in benzene. Tetrahexylammonium perchlorate was found to be sufficiently soluble in benzene for voltammetric studies. Attempts to measure voltammograms for the reduction of perylene (PE) in benzene containing Hex_4NClO_4 (up to 0.5 M) at a commercial platinum disk electrode (area ≈ 25 mm^2) failed; no current which could be ascribed to the reduction of PE was observed. However, measurements made using electrodes fabricated by polishing the cross section of fine platinum wire embedded in soft glass (see experimental section) resulted in well defined voltammetric peaks for the two consecutive one electron reductions of PE.

The dependence of the voltammetric characteristics for the reduction of PE in benzene

Table 1. Reduction of perylene in benzene/hex$_4$NClO$_4$ or DMF/Bu$_4$NBF$_4$ at a micro mercury electrode.

[Hex$_4$NClO$_4$]/M	ν/mVs^{-1} [a]	ΔE_p^1/mV [b]	ΔE_p^2/mV [b]	$\Delta E°_{1,2}$/mV
0.1	61.8	*ca.* 350	*ca.* 320	695
	156	370	320	695
	309	390	315	685
	618	415	310	690
0.15	61.8	180	200	590
	156	200	200	595
	309	205	195	610
	618	215	200	620
0.2	61.8	*ca.* 150	160	580
	156	140	160	590
	309	135	155	600
	618	135	160	605
0.25	61.8	140	*ca.* 150	580
	156	120	130	600
	309	110	130	605
	618	100	125	605
0.3	61.8	120	*ca.* 150	595
	156	95	120	600
	309	90	115	605
	618	85	115	600
0.2 [c]	61.8	100	110	570
	156	90	100	570
	309	85	90	570
	618	70	75	570

[a] Voltage sweep rate. [b] Difference in potential of oxidation and reduction peaks on cyclic voltammograms. [c] DMF/Bu$_4$NBF$_4$.

upon supporting electrolyte concentration and voltage sweep rate is shown in Table 1. The symbols, ΔE_p^1 and ΔE_p^2, refer to the potential differences between the oxidation and reduction peaks measured from cyclic voltammograms for the first and second charge transfers to PE, respectively. The differences in $\Delta E°$ for the two charge transfers, referred to as $\Delta E°_{1,2}$ in Table 1 were estimated from the differences in peak potentials for the consecutive reductions. The electrode used was constructed from a 0.03 mm diameter platinum wire and the exposed surface was covered with Hg just prior to making the measurements. Voltammetric data for the reduction of PE in dimethylformamide (DMF) containing Bu$_4$NBF$_4$ (0.2 M), a well defined system,[2] at the same micro electrode is included for comparison at the end of Table 1. At an electrolyte concentration of 0.1 M, the peak separations for both charge transfers are very large (>300 mV) indicating a major contribution of uncompensated resistance. The same effect, although to a lesser degree, was observed when the salt concentration was 0.15 M with the peak separation increasing with increasing voltage sweep rate in the expected manner. Curiously, the effect of increasing the voltage sweep rate reversed upon increasing the electrolyte concentration to 0.2 M; *i.e.* increasing the sweep rate resulted in decreasing the peak separation for the first charge transfer. The same trend continued with further electrolyte concentration increases, with the effect of uncompensated resistance becoming relatively unimportant.

Cyclic voltammetry theory requires that ΔE_p for a reversible one electron transfer at a planar electrode be equal to 58 mV at 25 °C.[3]

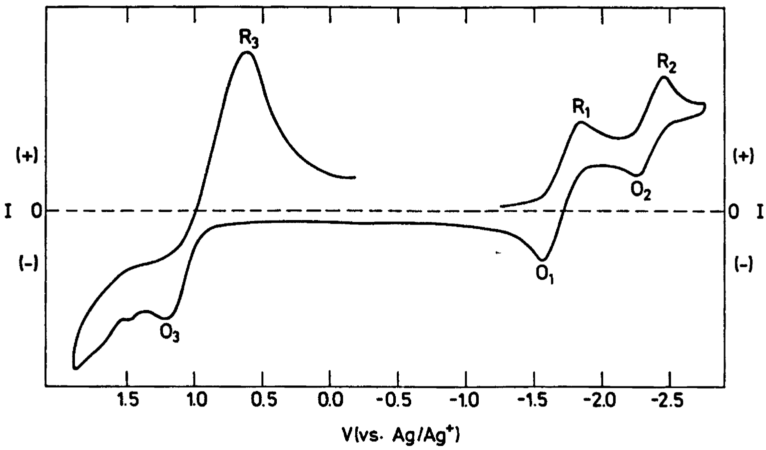


Fig. 1. Cyclic voltammograms showing consecutive reductions (R_1 and R_2) and the oxidation (O_3) of perylene in benzene containing tetrahexylammonium perchlorate (0.2 M) at a micro platinum electrode (diameter = 0.03 mm). Voltage sweep rate: 156 mV/s.

The theoretical relationships are followed for the reduction of PE in DMF at planar electrodes.[2] The voltammetric behaviour of the PE in DMF system using the micro electrode of this study is informative. Firstly, the peak separations (as high as 110 mV) are much greater than the theoretical values and secondly, the ΔE_p values which should be independent of sweep rate were found to decrease with increasing sweep rate. The latter forces us to the conclusion that the theoretical relationships for the very small electrodes do not hold since the edge effect becomes very important and modes of mass transport other than planar linear diffusion are operative.

The most frequently desired data from voltammetric studies are potential differences. The data for the reduction of PE in benzene can readily be assessed in the latter respect. It has been found that $\Delta E°$ for PE in DMF ($Bu_4NBF_4 = 0.2$ M) is equal to 565 mV.[2] The same system using the micro electrode gives an acceptable value of 570 mV. Little change in $\Delta E°$ for PE in benzene was observed at electrolyte concentrations greater than 0.15 M and a value of the order of 590 mV, was found very similar to that in DMF in spite of the great difference in the two solvents. We conclude that the potential differences that can be measured in benzene are reliable estimates.

Another aspect of the voltammetric behaviour of PE in benzene is illustrated by the cyclic voltammogram shown in Fig. 1. The reduction is characterized by two reversible redox couples, $R_1 - O_1$ and $R_2 - O_2$, involving the anion radical and the dianion, respectively. On the other hand, the oxidation producing the cation radical is accompanied by severe adsorption (O_3) and a very large reduction peak (R_3), at which the adsorbed cation radical is reduced from the electrode surface, is observed on the reverse sweep. The shape of the voltammogram shows that both the anion radical and the dianion remain in solution upon formation while the cation radical never leaves the electrode surface. Although there are indications that the cation radical is further oxodized on the electrode, no discrete oxidation to the dication can be discerned from the voltammogram. The fact that the anion radical and dianion appear to behave normally even in the nonpolar solvent is indicative that ion-pairing with the Hex_4N^+ ions allows the aromatic anions to go into solution. On the other hand, ion-pairing between the aromatic cations and ClO_4^- ions is probably far less important and thus the cations remain on the electrode.

The unusual stability of aromatic anions in benzene solution is further demonstrated by the voltammetric behaviour of 1,2-bis(9-anthryl)ethane (*1*) shown in Fig. 2. The expected

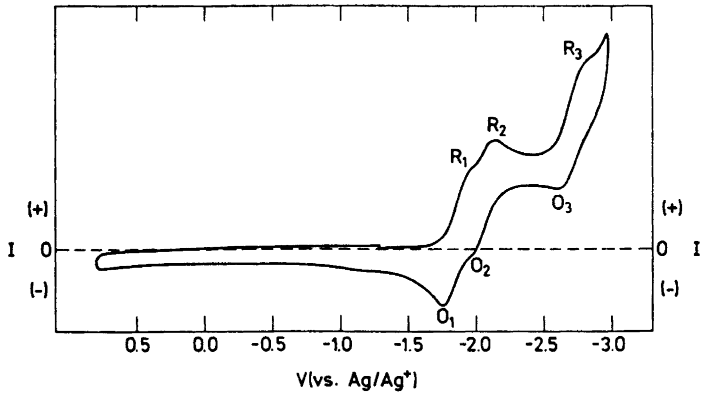
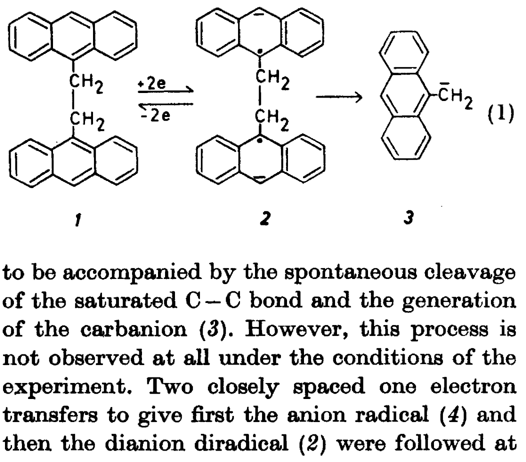
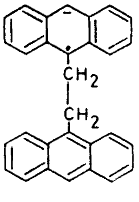


Fig. 2. Cyclic voltammogram showing the consecutive reductions of 1,2-bis(9-anthryl)ethane in benzene containing tetrahexylammonium perchlorate (0.2 M) at a micro platinum electrode (diameter = 0.03 mm). Voltage sweep rate: 156 mV/s.

reaction, which occurs readily in more polar media,[4] is that illustrated by eqn. (1). Formation of the dianion diradical (*2*) was expected



to be accompanied by the spontaneous cleavage of the saturated C – C bond and the generation of the carbanion (*3*). However, this process is not observed at all under the conditions of the experiment. Two closely spaced one electron transfers to give first the anion radical (*4*) and then the dianion diradical (*2*) were followed at more negative potential (~700 mV) by a further reversible one electron transfer to give the trianion radical (*5*).



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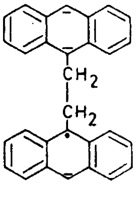

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The saturated C – C bond in the free dianion diradical (*2*) is expected to be severely weakened by the mutual repulsion of the negative charges in the two anthracene moieties. The weakening of the ethane linkage by charge repulsion would in turn be neutralized to a degree by ion-pairing. The fact that the bond remains intact even upon formation of the trianion (*5*) indicates that the extent and strength of ion-pairing in this medium are indeed very great.

The observation of the reversible formation of *5* also points out the very negative cathodic limit of the benzene – Hex_4NClO_4 system. The reduction peak, R_3, which appears at about – 2.8 V. *vs.* SCE is the most negative reversible reduction of an aromatic system that we are aware of. In general the more negative potential necessary to form an anion, the more reactive the intermediate will be.

Voltammetry in chlorobenzene. The more common electrolytic supporting electrolyte, tetrabutylammonium fluoroborate was found to be sufficiently soluble in chlorobenzene for voltammetric studies. The effect of voltage sweep rate and supporting electrolyte concentration for the reduction of PE in chlorobenzene at a micro platinum electrode (diameter = 0.03 mm) is shown in Table 2. In this case the inverse voltage sweep rate relationship, due to the edge effect of the small electrode, was observed at Bu_4NBF_4 greater than 0.1 M. The effect of uncompensated resistance appears

Table 2. Voltammetric reduction of perylene in chlorobenzene at a micro platinum electrode.[a]

Voltage sweep rate/	ΔE_p/mV [b]					
mVs^{-1}/Bu_4NBF_4	0.05 M	0.1 M	0.15 M	0.20 M	0.25 M	0.30 M
618	280	100	85	80	75	80
309	260	110	90	95	80	95
156	250	120	110	100	105	–
61.8	250	150	150	125	120	120

[a] Constructed from a platinum wire, 0.03 mm diameter. [b] Peak potential difference of the reduction and oxidation segments of the first reduction step measured on cyclic voltammograms.

to be important only at very low supporting electrolyte concentration (0.05 M).

The lack of reactivity of chlorobenzene to aromatic hydrocarbon anion and cation radicals as well as the favorable anodic and cathodic potential ranges is illustrated by the cyclic voltammogram for oxidation and reduction of anthracene shown in Fig. 3. Both redox couples are shown to be reversible and the potential range is seen to cover at least 4.0 V. The difference in $E°$ for the oxidation and reduction of anthracene in chlorobenzene under the conditions of this study was found to be equal to 3.32 V as compared to 3.34 V reported recently for the $E°$ difference in acetonitrile.[5]

CONCLUSIONS

When very small electrodes are employed, the nonpolar solvents benzene and chlorobenzene are suitable voltammetric solvents. The theoretical relationships of cyclic voltammetry do not hold for the small electrodes due to diffusion toward and electron transfer at the edges of the electrode which constitute a significant portion of the active area. The potentials measured at the electrodes are, however, significant and it was shown that they compare favourably with those measured at large electrodes in polar solvents.

The use of these new nonpolar solvents should provide valuable information about the effect of ion association on the stability of electrode generated intermediates. That anions undergo strong ion-pairing in benzene was demonstrated by the stability of the trianion radical (*5*) which was observed to be formed reversibly at the very negative potential, −2.8 V.

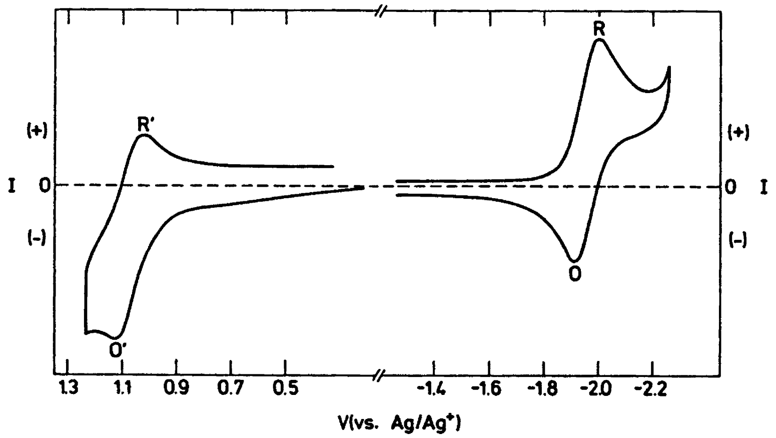

Fig. 3. Cyclic voltammogram for the oxidation and reduction of anthracene in chlorobenzene containing tetrabutylammonium fluoroborate (0.2 M). Voltage sweep rate: 309 mV/s.

EXPERIMENTAL

Tetrahexylammonium perchlorate (Hex_4NClO_4) was prepared by mixing an aqueous solution of Hex_4NBr with an equimolar solution of perchloric acid (70 %). The precipitated salt was dissolved in dichloromethane and washed first with $NaHCO_3$ solution and then with water. After removal of most of the dichloromethane under reduced pressure, the salt was precipitated by the addition of dry ether. The salt was collected and dried over P_2O_5; m.p. 102 – 103 °C. Tetrabutylammonium fluoroborate (Bu_4NBF_4) was prepared in a similar manner from Bu_4NHSO_4 and fluoroboric acid (35 %).

Benzene, BDH Analar, was used as received. Clorobenzene (Kebo) was fractionally distilled before use. Distillation of the solvent did not improve the voltammetric potential range but decreased the residual anodic current.

Micro electrodes were fabricated by sealing fine platinum wire (0.03 mm diameter) into the end of a soft glass tube, then cutting and polishing the end first with emory cloth and finally on a ground glass surface. The polishing procedure was found to be very critical to the performance of the electrodes and repeated treatment was often necessary to obtain the best response. It appears that, owing to the fineness of the wire, minor imperfections in the sealing process markedly affect the performance of the electrodes. Careful polishing removes the portion of the electrode where defects exist. Mercury plating of the polished electrodes was accomplished by electrolytic deposition from an aqueous $Hg(ClO_4)_2$ solution. Examination of these electrodes under a magnifying glass indicated that the mercury coatings were uniform. The effective area of the coated electrodes was estimated by voltammetry to be about twice that of the polished platinum surface.

Voltammetric measurements were conducted in an undivided cell of about 10 ml capacity. The counter electrode was a platinum wire and an $Ag|0.1$ M $AgNO_3|MeCN$ electrode was used as the reference. A Luggin capillary for the reference was found not only to be unnecessary but also to introduce noise into the circuit. The appropriate amount of supporting electrolyte was weighed into the cell together with a small quantity of neutral alumina [2,6] and the solvent was introduced through a short column packed with neutral alumina. The substrate was then added and the solution was deaerated using a stream of dry nitrogen. Due to the small currents associated with the use of the micro electrodes, typically of the order of about 5×10^{-2} μA, electrical screening of the cell was necessary to prevent excessive noise pick up. Once efficient screening had been achieved, noise free voltammograms could be recorded even at the highest sensitivity of the equipment which was 4×10^{-2} μA per cm on the recorder chart. A three electrode voltammetry unit of the type previously described [7] was used along with a Watanabe WX 442 recorder. Our experience indicates that measurements with even smaller electrodes are feasible provided that the constructional difficulties of the micro electrodes can be overcome.

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