Reactions of Aromatic Anion Radicals and Dianions. IX.*

The Preparation of Stable Anion Radical Solutions Containing

Tetra-alkylammonium Ions

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A technique was developed for the electrochemical synthesis of aromatic anion radicals in solvents containing tetraalkylammonium ions. The technique consists of cycling the substrate-solvent-electrolyte system under vacuum through a column of active alumina until all interfering impurities are removed. Under these conditions, it was found that the perylene and anthracene anion radicals could be formed by electrolysis of the parent compounds in N,N-dimethylformamide containing tetrabutylammonium fluoroborate. The resulting solutions were found to be stable for several weeks.

An important aspect of radical ion chemistry is the relative reactivities of the mono- and dicharged ions of aromatic hydrocarbons and related compounds. A number of kinetic studies have been carried out on reactions of both cation and anion radicals. A significant number of these reactions have been observed to follow rate laws second order in the ion radical and are often inhibited by the presence of the parent aromatic compound.[2] Recent studies have shown that the observation of second order in radical ion kinetics is insufficient evidence for the disproportionation mechanism.[3] Thus, there is a need for direct measurements on the rates of reactions of the doubly charged intermediates to verify the

occurrence of the disproportionation mechanism. One such verification has been reported for the cyclization of the tetraphenylethylene cation radical and dication to yield the phenanthrene.[4]

In this paper we report an approach to the study of the reactions of aromatic dianions *via* solutions of pure anion radicals produced by electrolysis. The reason that it is necessary to have solutions of anion radicals free from the parent compound in order to study the dianion reactions is as follows. When a dianion is generated at an electrode surface from a solution of the parent compound it is very short-lived because upon diffusing from the electrode surface it encounters the parent compound diffusing toward the electrode and the resulting comproportionation reaction produces the anion radical. Such reactions are usually highly exothermic and occur at diffusion controlled rates thus making the study of other slower reactions difficult or even impossible. This problem can be overcome if it is possible to prepare stable solutions of the radical ions.

Contrary to the common belief that aromatic anion radicals are sufficiently basic to react with tetraalkylammonium ions, we find that the ion radicals of perylene (PE), anthracene (AN) and naphthalene (NA) are stable in DMF containing tetrabutylammonium fluoroborate (TBAF). The key feature of this technique, described in detail below, is based upon earlier work [5] involving contacting electrolytic solu-

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* Parts I—VIII, see Ref. 1.

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tions with active alumina with the new feature of carrying out the entire preparation under vacuum.

EXPERIMENTAL

Cell description. The apparatus, shown in Fig. 1, was constructed from standard glassware (Quickfit) and PTFE stopcocks. The cell consisted of three removable sections (1 to 3, Fig. 1). A Teflon tube was used to connect the column containing alumina to the reservoir 3. Parts 1 and 2 constituted the electrochemical cell proper while section 3 was used for the initial rinsing and filling operations. The apparatus was connected to a standard vacuum line such that each section could be independently evacuated or filled with dry nitrogen. The working compartment of the cell (1) was equipped with three electrodes held in position with an aged rubber stopper. Electrode *a* was a Pt-spiral which served as the working electrode for preparative experiments and as the counter electrode when voltammetric measurements were made. Experience has shown that the surface condition of the Pt electrode has a marked influence on the maximum at-

tainable concentration of anion radical and often an Hg pool was used as cathode in order to achieve the desired conversions. In these cases, the Pt wire was used as an electrical contact. The remaining two electrodes consisted of an Ag wire *b* as a reference and a Pt wire *c* (1 mm diameter) sealed into soft glass as the working electrode for voltammetric measurements. A second Pt spiral sealed into section 2 of the apparatus served as the secondary electrode during the electrolyses.

Experimental procedure. A suitable volume (up to 500 ml) of electrolyte solution was prepared containing the substrate (*ca.* 1 mM; the exact concentration was determined by voltammetry) and supporting electrolyte (up to 0.5 M). The stopper holding the electrodes was removed and the solution introduced through a column of neutral alumina. The electrodes were replaced and section 1 was evacuated (to *ca.* 0.1 mmHg) together with section 3. Dry nitrogen was then admitted to section 1, stopcock B was opened and the solvent transferred to the reservoir 3. Section 1 and the column containing active alumina were then evacuated and solvent introduced into the column *via* tap D. When the column was filled, tap A was partially opened and a slow stream of solvent was admitted to the cell. Adjustment of stopcocks A and D ensured that the column remained filled with solvent. When all of the solvent had been introduced, tap A was closed and the cell evacuated once again. The solution was then vigorously stirred to ensure thorough washing of the electrodes and cell walls. The solution was then returned to the reservoir 3 by application of vacuum to 3 and nitrogen to 1. The alumina treatment and rinsing operations could be applied indefinitely but usually two rinses were sufficient to produce a solvent/cell system which contained very low quantities of reactive impurities such as oxygen or water. The effectiveness of the procedure was easily checked at each stage by cyclic voltammetry, noting the character of the solvent cut-off and the voltammetric behaviour of the substrate in comparison with results obtained under known inert conditions, *i.e.* in the presence of neutral alumina. When satisfactory voltammetric results were observed, section 3 and the alumina column were removed. The cell was filled with dry nitrogen and section 2 of the apparatus was evacuated. Tap F was then closed and tap E opened slowly so that the secondary electrode compartment was completely filled with solution. The cell was then evacuated to the vapor pressure of the solution. Electrolysis was then accomplished by connecting a constant current power supply to the Pt electrode *a* in the cell and to the secondary electrode in section 2. At the start of the electrolysis tap F was opened so that there was a slight flow of solution into the reservoir. At the same time, tap E was adjusted to have the minimum opening with-
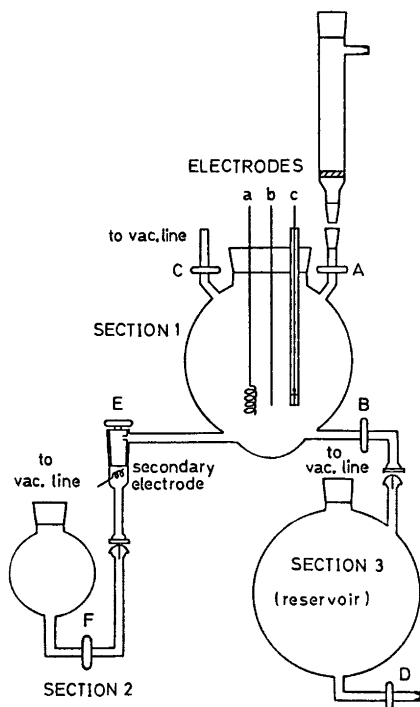

ELECTRODES
a b c

to vac. line
C   A

SECTION 1

E   B

to vac. line   secondary   to vac. line
                    electrode

SECTION 3
(reservoir)

F   D

SECTION 2

Fig. 1. Apparatus for the purification of solvent-electrolyte systems and the electrochemical preparation of solutions of reactive intermediates.

out interferring with the electrolysis current. The restriction caused by tap E increase the flow velocity into the secondary compartment and thus prevents products generated at the secondary electrode from diffusing into cell 1. This method of separating the anode and cathode compartments was found to be superior for minimizing contamination of the working electrode solution than the more usual methods employing glass frits. The progress of the electrolysis as well as the concentration of the electrogenerated species could be followed by slow sweep voltammetry (about 20 mV s^{-1}) while the solution was stirred. The resulting current-potential curve is similar to that obtained at a rotating electrode and measurement of the plateau currents gave the concentration ratio of the parent and generated species.

Materials. The success of this technique for preparing solutions of reactive intermediates relies upon the purity of the solvent and supporting electrolyte. It has been found that due to the effectiveness of the alumina treatment together with the recycling of the electrolyte solutions through the cell in a closed system, standard purification procedures yield an acceptable grade of solvent and special handling and purification techniques are not necessary.

For this study, DMF (Kebo) was passed through a column of active neutral alumina (ICN; W200 neutral, super grade 1) and then fractionally distilled under reduced pressure. The product was stored over anhydrous CuSO$_4$.[6] Storage over this material appears to preserve the quality of DMF for several weeks. The solvent gradually assumes a deep green color presumably due to the dissolution of copper amine complexes accompanying the slow decomposition of DMF. The copper-containing compounds are easily removed by percolation of the solvent through a column of neutral alumina.

Tetrabutylammonium fluoroborate (TBAF) was prepared from the hydrogen sulfate and aqueous fluoroboric acid.

Reagent grade tetramethylammonium iodide was recrystallised from water and dried under reduced pressure before use.

Nitrogen was purified by passing through a solution of the triphenylmethanide ion[7] in pyridine, then through concentrated sulfuric acid and finally through a column of active neutral alumina.

RESULTS AND DISCUSSION

The effectiveness of the system was evaluated by recording the voltammograms for the reduction of compounds which are known to give reactive anions. Fig. 2 shows the cyclic voltammograms in DMF for the reduction of
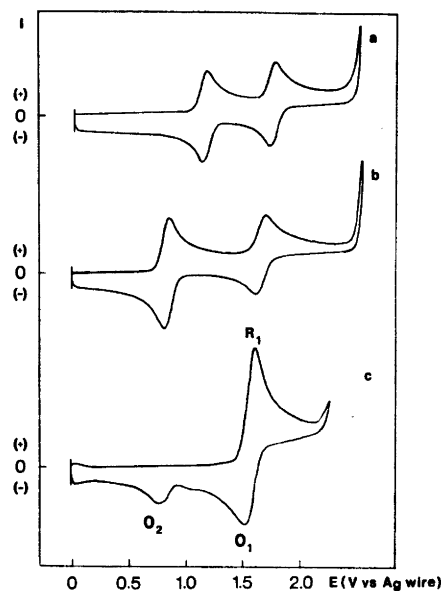

Fig. 2. Cyclic voltammograms for the reduction of perylene (a) and azobenzene (b) in DMF/TBAF at platinum and 3,8-dimethyl-2-methoxyazocine (c) in DMF/TMAI at mercury. Voltage sweep rate equal to 100 mV s^{-1}.

perylene, azobenzene, and 3,8-dimethyl-2-methoxyazocine (DMMA).

Cyclic voltammetric measurements for the reduction of aromatic hydrocarbons and related compounds in aprotic solvents such as DMF or acetonitrile usually result in the observation of a reversible couple for the first electron transfer and an irreversible peak for the reduction of the anion radical to the dianion. The reason for this behaviour is that the highly basic dianions undergo rapid, irreversible protonation reactions even in carefully purified solvents and thus no oxidation current for the dianions is observed. The nature of the protonating species has recently been conclusively shown to be neither solvent nor electrolytic.[1]

Recently,[1] it has been found that it is possible to detect the reversible reduction of anion radicals to reactive dianions by carrying out voltammetric measurements with neutral alumina suspended in the solvent electrolyte system. A careful comparison of the results obtained for the reduction of aromatic hydro-

carbons, for example perylene (Fig. 2, Curve a), using the vacuum-alumina purification system with those from voltammetry carried out in the presence of alumina confirms that the present technique is very effective in removing reactive impurities from the solvent, electrolyte and cell. Of interest is the character of the solvent cut-off. Both for this technique and the suspended alumina method the solvent cut-off is very sharp and at a high cathodic potential (about -2.95 V $vs.$ SCE). The latter value is close to the published potential for the reduction of DMF.[8] Systems that contain small amounts of reducible impurities such as water generally do not give rise to distinct voltammetric peaks but exhibit rather broad background currents with much less well-defined cut-off potentials. It must be stated that although reactive intermediates can be generated in the presence of alumina under voltammetric conditions, $i.e.$ in the immediate vicinity of the electrode, such solutions are unsuitable for the preparative scale generation of these intermediates.

The electrochemical reduction of a number of aromatic azo compounds in DMF has been reported by Sadler and Bard[9] using a cell connected to a high vacuum line. Solvent was distilled under vacuum into the cell which contained substrate and supporting electrolyte. The cell was then brought up to atmospheric pressure by admitting pure helium. Voltammetry of azobenzene at both Hg and Pt electrodes showed reversible formation of the anion radical but irreversible further reduction to the dianion which was thought to be due to rapid protonation of the dianion by unspecified proton donors in the solvent-electrolyte system. The authors[9] pointed out that the EC behaviour of the second electron transfer was consistent with the a.c. polarographic results of Aylward $et\ al.$.[10] reported for the reduction of azobenzene in DMF. In the present investigation, as illustrated by the voltammogram for azobenzene in DMF (Fig. 2, Curve b), the reduction in fact involves two consecutive reversible electron transfers when the impurities of the solvent-electrolyte system are reduced to a very low level. This result emphasizes that not only must the solvent be carefully purified in a closed atmosphere as in the work of Sadler and Bard[9] but that the electrolyte

and the electrode-cell assembly must also be freed from impurities.

The voltammogram for the reduction of DMMA in DMF (Fig. 2, Curve c) affords confirmation of the low level of impurities achieved by the vacuum-alumina technique. Anderson and co-workers[11] in describing a vacuum cell suitable for the voltammetry of compounds giving very reactive intermediates used the reduction of DMMA in DMF as a test of the effectiveness of their system. DMMA is reduced in a single two-electron step to the dianion and their results were interpreted as a very slow electron transfer for the formation of the dianion with a peak potential separation of $ca.$ 0.9 V (cyclic voltammetry theory predicts a peak separation of 28 mV at 25 °C for a fast electron transfer). As the figure shows, when DMMA was reduced in DMF in the presence of Me_4NI as supporting electrolyte using the vacuum-alumina technique, a voltammogram was obtained showing quasi-reversible electron transfer ($R_1 - O_1$ about 90 mV) in agreement with other recent published work on this compound.[1] The peak separation $O_2 - R_1$ corresponds closely with that reported by Anderson[11] which suggests that under their conditions the dianion was completely protonated during the time scale of the electrochemical measurement. The presence of O_2 on our voltammogram shows that our systems is not quite as effective as having active alumina present in the cell.[1] The reduction of DMMA thus represents a very useful test of the impurity level in an electrochemical system. As shown in Fig. 2, Curve a, the dianion of perylene is insufficiently reactive on the voltammetric time scale to reveal these extremely low impurity levels.

The ability to obtain electrochemical solvents of very high purity has enabled us to prepare, by electrolysis, stable solutions of aromatic hydrocarbon anion radicals in the presence of various tetraalkylammonium counter ions. Thus, reduction of perylene in DMF containing tetrabutylammonium fluoroborate yielded a stable solution (little change in anion radical concentration after 4 weeks). As we have already noted, these results are interesting in view of the general acceptance that such anions would be rapidly protonated by the tetraalkylammonium ions. The fact that the radical ion solutions slowly decay suggests reaction via

the dianions and work is in progress to determine the exact nature of the decomposition.

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