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The Reaction of Aryl Radicals with Metallic Electrodes

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Attempts were made to study the homogeneous chemical reactions of α-naphthyl radicals by cathodic generation from the corresponding diazonium salt. Voltammetric measurements at platinum, gold and mercury electrodes showed in every case that very little current was passed before the electrode became completely deactivated by reaction of the radicals with the metallic surfaces. Under similar conditions, the diazonium salts are cleanly reduced to the radicals by homogeneous reductants. That it is the radicals rather than the salts which cause the deactivation of the electrodes was clearly demonstrated by carrying out voltammetric oxidations in the presence of the salt and showing that deactivation does not occur until reduction of the diazonium ions is attempted. The reduction potential of the α-naphthyl radical was estimated to be less than −1.6 V *vs.* the Ag^+/Ag electrode in acetonitrile by chronoamperometric experiments.

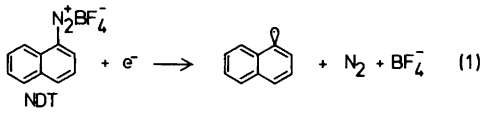
The polarographic reduction of a number of arenediazonium ions has been studied by Elofson and coworkers.[1-6] Product studies have implicated the corresponding radicals as intermediates. The isomer distribution of phenylated pyridines obtained from the electrolytic reduction was almost identical to that found for the decomposition of benzoyl peroxide when both reactions were conducted in pyridine.[4] The diazonium ions are reduced at potentials close to 0 V *vs.* the SCE, a potential where few organic compounds are electroactive. Thus, the reduction of diazonium ions appeared to be an ideal means to study the reactions of aryl radicals by voltammetric techniques.

Aryl radicals have been recently postulated as intermediates in several reduction processes. Hawley and coworkers[7] observed reductive cleavage of halogen from *p*-halonitrobenzenes and proposed a mechanism involving loss of halide ion from the anion radical to produce the neutral aryl radical. The same mechanism was later proposed by Saveant and coworkers[8-10] to account for the cathodic cleavage of halogen from substituted benzophenones. More recently, Pinson and Saveant[11,12] have observed nucleophilic substitution of halide ion during reduction of haloaromatics and have proposed the aryl radicals as intermediates in these reactions in analogy to the homogeneous reactions studied by Bunnett and co-workers.[13]

This study was initiated in order to determine the nature of the reactions of aryl radicals in electrochemical systems produced by reduction of the diazonium ions. It was hoped that the product distributions obtained and the kinetics of the reactions could be used to evaluate the mechanisms previously proposed for the other systems.

RESULTS

Preliminary experiments revealed that the peak current during linear sweep voltammetry for the reduction of 1-naphthalene diazonium tetrafluoroborate (NDT) at stationary platinum, gold or mercury electrodes was far less than that expected for a one electron process as in eqn. (1). This can readily be seen by a comparison of cyclic voltammograms for the reduction of tetracyanoethylene (TCNE), which gives a stable anion radical, shown in



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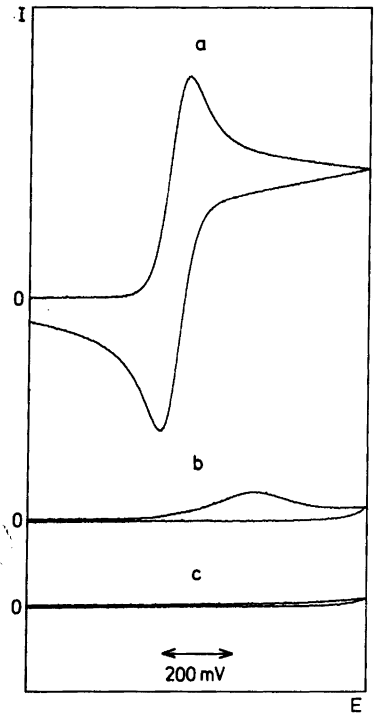


Fig. 1. Cyclic voltammograms for the reduction (a) tetracyanoethylene (3 mM) and (b) NDT (3 mM) in acetonitrile containing Bu_4NBF_4 (0.1 M). (c) Same as (b), second cycle. Voltage sweep rate = 100 mV s^{-1}. Start potential +0.3 V, switching potential −0.7 V.

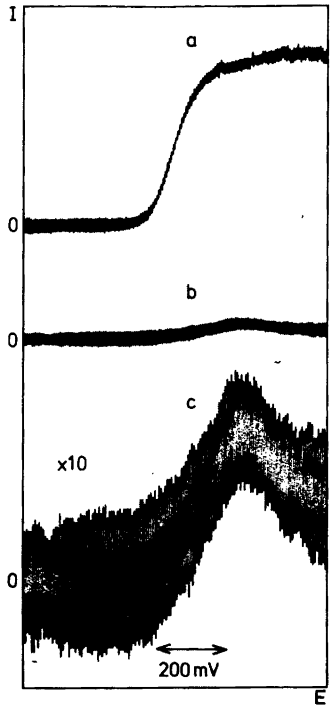


Fig. 2. Rotating disk electrode voltammograms for the reduction of (a) TCNE and (b) NDT in acetonitrile containing Bu_4NBF_4 (0.1 M). (c) Same as (b) with the current × 10. Voltage sweep rate = 100 mV s^{-1}. Start potential 0 V, end potential −2.0 V.

Fig. 1a, and that for the reduction of NDT (Fig. 1b). Since the concentrations of TCNE and NDT in acetonitrile were the same (3.0 mM) and the diffusion coefficients would not be expected to differ greatly, the peak currents were expected to be nearly the same. The peak current observed during the reduction of NDT is obviously much too low to correspond to the transfer of one electron per equivalent of substrate. A further noteworthy feature of the NDT voltammogram is the unusual shape with the current approaching zero after the peak and the complete disappearance of the peak on the second cycle (Fig. 1c). Such behaviour is only consistent with the deactivation of the electrode by a product of the electrode reaction.

One possibility for the deactivation mechanism is that the nitrogen generated in (1) is trapped at the electrode accompanied by the formation of an insulating film of gas. While this was not thought to be very likely, it could not be excluded from the stationary electrode studies. Therefore, the reduction was carried out at a platinum rotating disc electrode (RDE). Under these conditions any gas trapped on the electrode would be carried away by the solution which is rapidly passing over the electrode surface. The response of NDT is once again compared to that for TCNE in Fig. 2. The RDE voltammogram for the reduction of TCNE (Fig. 2a) shows the characteristic rapid rise in current as the potential passes $E_{rev} + 120$ mV and then settles to a constant plateau at potentials more negative than $E_{rev} - 120$ mV where charge transfer is controlled by the transport of substrate to the electrode surface. The response of NDT at the RDE is quite different. Instead of a constant current plateau, a peak is observed in the current-voltage curve after which the current rapidly diminishes (Fig. 2b). Once again the maximum current, *i.e.*

that at the peak, is much lower than that observed at the plateau for the reversible one electron reduction of TCNE. Thus, we conclude that the deactivation of the electrode during reduction of NDT is not due to a film of nitrogen gas.

The results described thus far do not convincingly eliminate adsorption of the substrate NDT on the electrode as the deactivating mechanism. In order to investigate this possibility, the cyclic voltammogram for the oxidation of 4-bromo-*N*,*N*-dimethylaniline (BNMA) in acetonitrile was recorded. The cyclic voltammogram recorded after the addition of an equivalent amount of NDT to the solution was unchanged and is shown in Fig. 3a. The reason for selecting this process is that the oxidation takes place at a convenient positive potential for the comparison and we have recently studied the reaction in detail.[14] The feature of greatest interest in these experiments is that when the potential was only scanned in the positive direction where NDT is not electroactive, its presence did not influence the voltammetric response for BDMA while scanning first to negative potentials where NDT is reduced (Fig. 3b) resulted in a positive shift of about 300 mV in the oxidation peak and the current was significantly diminished. This indicates that the insulating layer formed on the electrode during NDT reduction remains at positive potentials to cause the oxidation of BDMA to take place at an apparently higher potential. The insulating layer on the electrode was readily removed by rinsing with acetone or rubbing on tissue. Such treatment restored the voltammogram for the oxidation of BDMA to that shown in Fig. 3a.

At potentials more negative than −0.2 V where the NDT reduction peak appears, electrode deactivation is even more severe. This is illustrated by the voltammetry for the reversible reduction of nitrobenzene in acetonitrile (Fig. 4a) and that measured in the same solution after adding NDT (Fig. 4b). In the absence of complications the reversible one electron reduction gave the expected response (Fig. 4a). After adding NDT the electrode

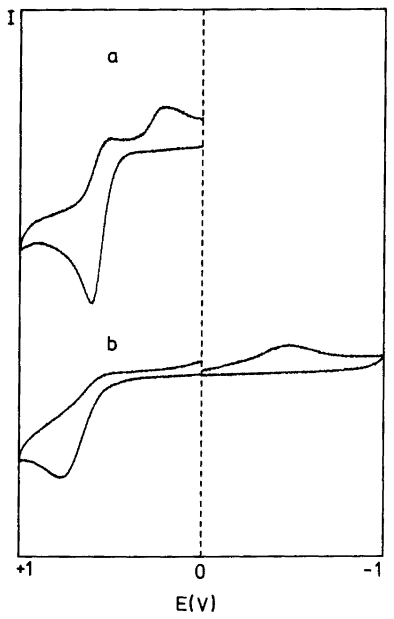


Fig. 3. Cyclic voltammograms (a) for the oxidation of 4-bromo-*N*,*N*-dimethylaniline and (b) for the reduction of NDT followed by oxidation of 4-bromo-*N*,*N*-dimethylaniline in acetonitrile containing Bu_4NBF_4 (0.1 M). Voltage sweep rate = 100 mV s^{-1}.

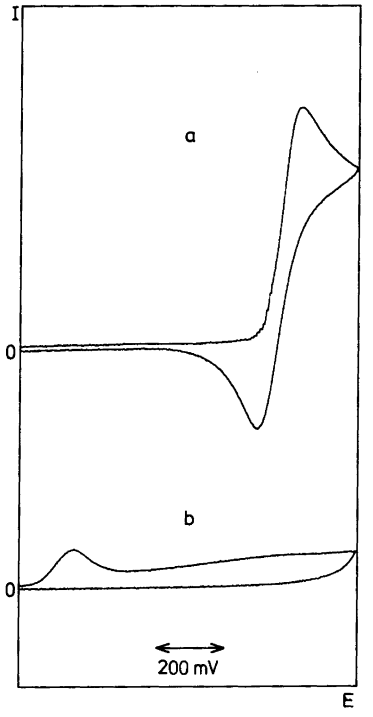


Fig. 4. Cyclic voltammograms for the reduction of (a) nitrobenzene and (b) NDT in the presence of nitrobenzene in acetonitrile containing Bu_4NBF_4 (0.1 M). Voltage sweep rate = 100 mV s^{-1}. Start potential 0 V, switching potential −2 V.

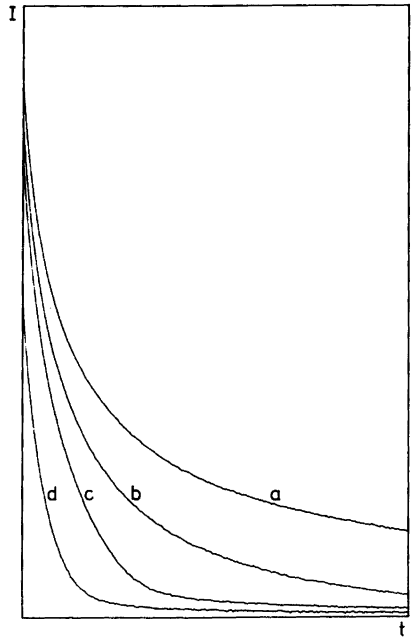


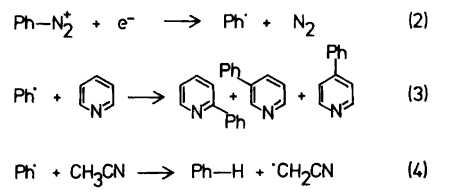
Fig. 5. Current-time curves for the potential step reduction of NDT in acetonitrile. Step potential *vs.* Ag^+/Ag equal to −1.6 V (a), −1.5 V (b), −1.3 V (c) and −1.0 V (d). Bu_4NBF_4 (0.1 M) was the supporting electrolyte. The time difference between the left and right hand margins is 1 ms.

became completely deactivated (Fig. 4b) and the reduction of nitrobenzene was not observed at all.

The results of a series of potential step experiments are illustrated in Fig. 5 which shows current-time curves recorded after stepping to increasingly negative potentials. Curve (d) shows that very little current is passed before the electrode is deactivated when the potential was stepped to −1.0 V *vs.* Ag^+/Ag. Deactivation still occurred but somewhat more slowly when the potential was stepped to −1.3 V. Considerably more current was observed at −1.5 V and when the potential was stepped to −1.6 V the current decay was very nearly described by the theoretical relationship, $It^{\frac{1}{2}} = \text{constant}$. These measurements indicate that the reduction potential of the α-naphthyl radical is somewhat less than −1.6 V *vs.* Ag^+/Ag in acetonitrile.

DISCUSSION

At first glance, the results presented here appear to be inconsistent with the reports on the electrolytic reduction of aryldiazonium salts by Elofson.[4] The reduction of benzene diazonium tetrafluoroborate in the presence of pyridine in acetonitrile resulted in the formation of an isomeric mixture of phenylpyridines along with benzene, believed to arise from the following reactions.[4] However, it is not clear that the reactions are necessarily cathodic reactions. The same product mixture was obtained simply by allowing the reactants to stand over mercury.[4] We also find that preparative scale reductions of arene diazonium salts can be carried out at mercury cathodes under constant current conditions which force the reaction to take place in spite of electrode filming. It is known that pyridine forms adducts with diazonium ions[15] and the homolysis of the adducts has been reported as a convenient source of aryl radicals.[16] Isomer ratios have been reported for the attack of aryl radicals generated in this manner on pyridine and various other aromatic compounds.[16] Similarly, diazonium ions are known to



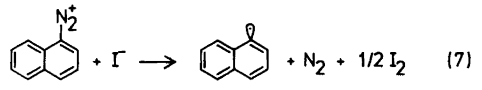
decompose homolytically in dimethyl sulfoxide, presumably by the mechanism outlined below.[17]

$$Ar-N_2^+ + O=S(Me)_2 \rightarrow Ar-N=N^{\cdot +}\cdots O=S(Me)_2 \quad (5)$$

$$Ar-N=N^{\cdot +}\cdots O=S(Me)_2 \rightarrow Ar^{\cdot} + N_2 + (O=S(Me)_2)^{\cdot +} \quad (6)$$

A similar mechanism could be written to account for the pyridine promoted decomposition.

The α-naphthyl radical can be efficiently generated by homogeneous electron transfer between iodide ion and NDT.[16] When reaction (7) is carried out in acetonitrile containing carbon tetrachloride, products arising from the α-naphthyl radical (including naphthalene, 1-chloronaphthalene and 1-iodonaphthalene) account for the NDT consumed. Thus, favorable reaction pathways exist for the radical in acetonitrile leading to identifiable products.



The discussion above strongly suggests that the deactivation of electrodes during the reduction of NDT in acetonitrile is not due to a polymeric film from homogeneous reactions of the α-naphthyl radical. Since the radical rapidly reacts with acetonitrile to give naphthalene, this would be expected to be a preferred reaction pathway which would preclude the formation of polymers. It is our conclusion that the radicals react with the metallic electrodes thereby blocking the surface to further electrode reactions. While the detailed nature of surface blockage is of considerable interest, it is beyond the scope of this paper.

The deactivation of electrodes during oxidation or reduction of organic compounds is not an unusual observation and the fact that the phenomenon occurs during reduction of NDT is not of special interest in itself. The significance in this case is that the α-naphthyl radical is implicated as the reactive intermediate arising from the reduction and has been postulated as an intermediate during the cathodic reduction of 1-bromonaphthalene.[12] When the latter reaction is conducted in acetonitrile, naphthalene is a major product. The question is then, is it reasonable that α-naphthyl radical generated by cathodic cleavage of 1-bromonaphthalene reacts with a hydrogen atom donor in the solvent-electrolyte system while the same radical generated from the diazonium salt does not escape from the electrode? An affirmative answer can be given to this question on the basis of two facts; (a) our results indicate that the radical is reduced at somewhat lower potentials than −1.6 V, well below the reduction potential of 1-bromonaphthalene which precludes the reaction of the radical with the electrode and (b) the relative rates of cleavage of the 1-bromonaphthalene anion radical and reaction of the radical with hydrogen atom donors[12] is such that the radical thus generated does not reach the electrode.

An obvious consequence of the results presented here is that the reduction potential of NDT measured at metallic electrodes has no thermodynamic significance and cannot be used in the correlation of other properties of the ions. Even if the reaction of the radical with the electrode did not take place, the fact that the loss of nitrogen from the intermediate radical is apparently very rapid requires that the potentials measured must reflect this kinetic step. Therefore, the correlations discussed by Elofson[5] must be considered with some reservation.

EXPERIMENTAL

The instrumentation, cells, electrodes, reference electrodes and solvent purification procedures were the same as previously reported.[17] NTD was prepared according to a well-known procedure[18] and purification was accomplished by repeatedly dissolving the salt in acetonitrile and precipitation with ether. Decomposition temp. 104 – 105 °C (lit.[19] 105 – 106 °C).

Reduction of naphthalenediazonium tetrafluoroborate by iodide ion in acetonitrile/carbon tetrachloride (6/1). A solution of NDT (0.5 mmol) was added at room temperature to a solution of Bu_4NI (1.0 mmol). After a few minutes, durene (0.522 mmol) was added as a GLC standard, followed by an aqueous ether work-up procedure. Analysis showed the product mixture to consist of naphthalene (0.0327 mmol), 1-chloronaphthalene (0.0486 mmol) and 1-iodonaphthalene (0.390 mmol) accounting for 94 % of the NDT consumed.

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