Reaction of the Anthracene Cation Radical with Acetonitrile. A Novel Anodic Acetamidation

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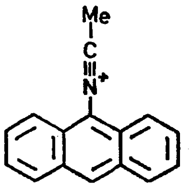
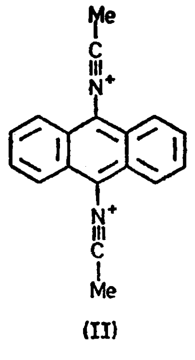
Summary Even in the presence of very small amounts of water hydroxylation is the exclusive reaction of the anthracene cation radical in acetonitrile while in the complete absence of water, high yields of the acetamidation product are obtained.

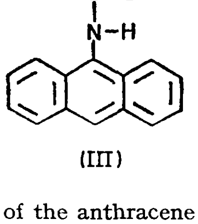
The anodic acetamidation of anthracene has never been observed previously, since the products of oxidation in acetonitrile have always resulted from the reaction of the anthracene cation radical with water.[1] We now report the reaction of the anthracene cation radical with acetonitrile, which takes place when the solvent is made "super-dry" by the water scavenging action of trifluoroacetic acid anhydride (TFAn). Such water-free conditions have recently been used in reversible oxidations of aromatic cation radicals to dications.[2]



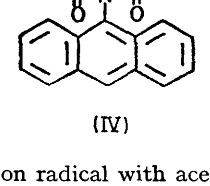
(I)



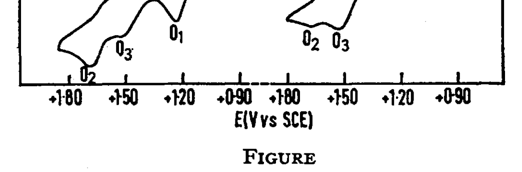
(II)



(III)



(IV)



Figure

The voltammetric behaviour of anthracene (1·0 mm) in water-free acetonitrile is shown in the Figure. Curve (a) shows the cyclic voltammogram which consists of two irreversible 2e oxidation peaks, (O_1) and (O_2) at $+1{\cdot}24$ and $+1{\cdot}69$ V *vs.* the SCE. The first peak (O_1) involves the ece reaction of anthracene to produce the 9-anthranyl nitrilium ion (I) and (O_2) is probably due to the oxidation of (I) to (II). Curves (b), (c), and (d) are the voltammograms taken during constant current coulometry[3] (50 mA) after electrolysis for 2, 4, and 6 minutes, respectively (6·44 minutes required for the 2e oxidation). The experiment showed that 2·0 Faradays per mole were consumed during the oxidation and that (I) is not stable during the coulometric time scale as shown by the appearance of a new oxidation peak (O_3) at

+1·54 V during the electrolysis. The appearance of a reduction peak (R_3) on the cathodic scan along with the magnitude of the current at (O_3) is indicative of a quasi-reversible one electron couple for the new product. The species undergoing oxidation at (O_3) was found to be (IV), which could be prepared in solution by dissolving (III) in acetonitrile containing TFAn.

Preparative scale oxidation of anthracene in acetonitrile-TFAn (25:1) resulted in the formation of (III), isolated yield 82%. The identity of (III) was established from mass and i.r. spectra. The yield of product was very dependent upon the quality of acetonitrile used. Low yields were obtained when reagent grade solvent, passed through neutral alumina immediately before use, was employed. Best results were obtained when carefully distilled acetonitrile was the solvent.[4]

The contrast between results in "super dry" acetonitrile with those in carefully purified solvent using conventional techniques is also illustrated by a comparison of rotating disc (rde) results. Under ordinary conditions the oxidation of anthracene at the rde corresponds to about 4e at low rotation rates with only a small change in n_{app} observed upon increasing ω.[5] In the "super dry" medium we find that at low values of ω the oxidation current corresponds to nearly 2e but that at higher rotation rates the value of the limiting current decreases substantially showing that the reaction between the anthracene cation radical and solvent is slow enough for kinetic measurements to be made.† The pseudo-first-order rate constant, obtained by comparison of limiting current as a function of ω with theoretical working curves, for the reaction between anthracene cation radical and acetonitrile at room temperature was found to be equal to about 125 $\sec^{-1}$.

The effect of TFAn, on the course of the anthracene oxidation in acetonitrile, as a very effective water scavenger is indicated by the fact that voltammetry of anthracene carried out in acetonitrile dried by the action of suspended alumina[2] is nearly identical to that in the Figure. Furthermore, acetamidation is not observed when anthracene is oxidized in acetonitrile containing TFA (5%).

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† In CH_2Cl_2 purified by conventional procedures, the voltammetry of anthracene parallels that in acetonitrile. However, in the presence of TFAn a completely reversible 1e oxidation to the cation radical is observed.

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[2] O. Hammerich and V. D. Parker, *Electrochim. Acta*, 1973, **18**, 537.
[3] V. D. Parker, *Acta Chem. Scand.*, 1970, **24**, 2768.
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