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# NUCLEOPHILICITY AND BASICITY IN ANODE PROCESSES. I. METHOD FOR DIFFERENTIATING BETWEEN EFFECTS.

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In general, substances acting as nucleophiles toward carbon centers are also nucleophiles toward protons, i.e. they may act as bases (1). During reactions of intermediates formed at the anode with nucleophiles, the possibility frequently exists that the function of the nucleophile is actually that of a base. For example, anodic substitution on a methyl group of N,N-dimethylaniline has been suggested to involve proton abstraction by a base from the cation-radical of the amine (2). Side-chain anodic oxidation of pentamethylanisole has recently been shown to involve an initial 1e oxidation followed by proton loss, which is made easier by the base, water (3). The purpose of this work was to develop a means of distinguishing between carbon nucleophilic reactions and basic reactions of nucleophiles in anode processes.

The approach used was to study the effect on the reactivity toward cation-radicals, of making the nucleophilic center sterically hindered toward a carbon center without diminishing its basicity toward the proton. The lutidines, I, II, and III provide a series of increasing steric hindrance to nucleophilic reactions of the nitrogen. I, having no methyl groups in the $\alpha$-positions is not hindered, while III, substituted at both $\alpha$-positions is severely hindered.

The stoichiometric interaction of pyridine with cation-radicals has recently been demonstrated (4). Anodic pyridination of anthracene derivatives to stable pyridinium salts was reported several years ago (5).

The substrates chosen were 9,10-diphenylanthracene (DPA, the pyridination of which has been studied (4) ), 9,10-dimethylanthracene (DMA), and 1,4-dimethoxybenzene (DMB). DPA forms a stable cation-radical in acetonitrile (6). DMA (7) and DMB (8) give cation-radicals of limited stability which are, however, stable during the time-scale of cyclic voltammetry. The technique

employed to determine relative reactivities was to determine the dependence of the concentration of the nucleophile on the magnitude of the reduction current for the cation-radical during cyclic voltammetry. Since the concentration of the cation-radical formed at the anode was the same in each case, the relative concentrations of the nucleophiles necessary to eliminate the reduction current is related to the rate constant for the reaction of the nucleophile with the cation-radical. The data are summarized in the Table. Figure 1 demonstrates the cyclic voltammetric technique using the oxidation of DMA in the presence of 2,6-lutidine as an example.

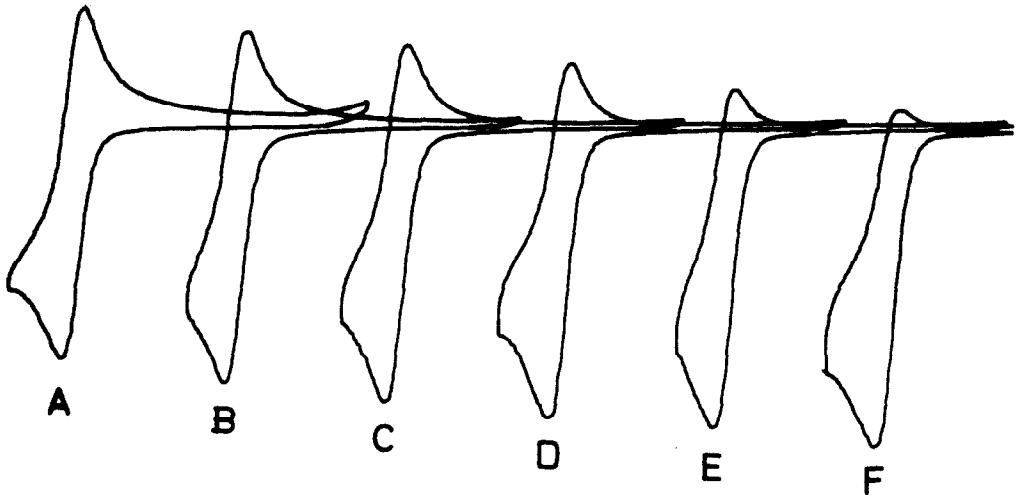



Figure. Oxidation of 9,10-dimethylanthracene (1.0 mM) in the presence of 2,6-lutidine (A, 0 mM; B, 0.25 mM; C, 0.50 mM; D, 0.75 mM; E, 1.0 mM; F, 1.25 mM)

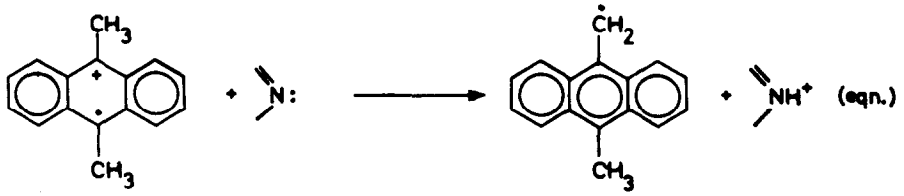
The pyridination of DPA involves attack of the nucleophile on the cation-radical (4). The slightly hindered nucleophile, II is 6.5 times less reactive than unhindered I. I is 37 times as reactive as the hindered nucleophile, III. This system very nicely demonstrates steric inhibition of reactivity toward the positive carbon center. DMB shows the same type of behavior with I being 32 times as reactive as III. However, DPA is about 2 times as reactive toward the unhindered nucleophile, I, as DMB.

Table. Relative reactivities of cation radicals toward 3,5-, 2,5-, and 2,6-lutidine

| Substrate | 3,5-Lutidine, I[a] | 2,5-Lutidine, II[b] | 2,6-Lutidine, III[c] |
|---|---|---|---|
| 9,10-Diphenylanthracene, DPA | 1.0 | 6.5 | 37 |
| 1,4-Dimethoxybenzene, DMB | 2.1 | 35 | 64 |
| 9,10-Dimethylanthracene, DMA | 0.75 | 1.0 | 1.25 |

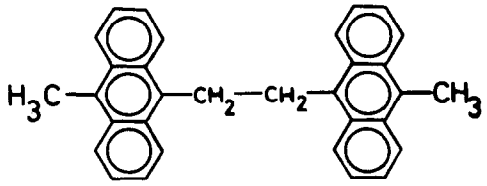
[a] $pK_a$ 6.15 [b] $pK_a$ 6.51 [c] $pK_a$ 6.75

DMA cation-radical shows very little difference in reactivity toward the three nucleophiles, all react in nearly stoichiometric fashion. This is compelling evidence that the site of reaction of DMA cation-radical with the nucleophile is on a methyl proton (eqn).




(eqn.)

This hypothesis is strongly supported by the isolation of the dimer, IV, from the anodic oxidation of DMA in the presence of 2,6-lutidine. A similar dimerization was observed during the cupric chloride oxidation of 9-methoxy-10-methylanthracene (9).




IV

The other two substrates, DMB and DPA, have no available proton sites and can only act as nucleophile acceptors. Both substrates show marked reactivity differences with the degree of steric hindrance of the nucleophile.

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