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NUCLEOPHILICITY AND BASICITY IN ANODE PROCESSES. II.
THE ECEC$_{N(B)}$ MECHANISM.

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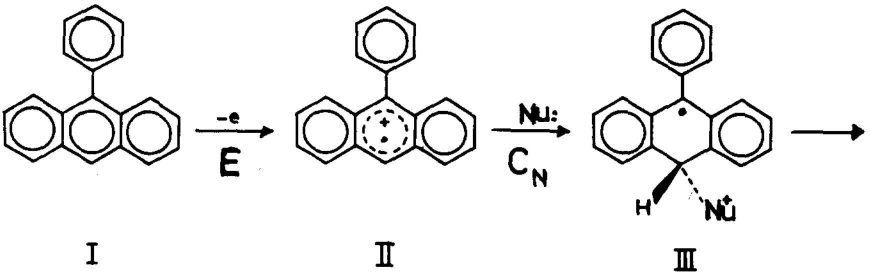
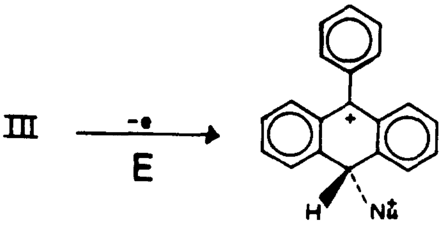
In the preceding paper a method was developed for distinguishing between nucleophilic behavior toward positive carbon centers and protons during the reaction of nucleophiles with cation-radicals generated at the anode (1). The two mechanisms may be described as EC$_N$E (when the homogeneous chemical reaction between the two electron transfer steps involves the interaction of a nucleophile with the positive carbon center) or EC$_B$E (when proton abstraction by the nucleophile is the homogeneous step). Anodic substitution reactions had previously been shown to involve the ECE mechanism (2).

We now report duality in mechanisms of reaction of a nucleophile with the intermediate formed by the EC$_N$E mechanism. The EC$_N$E mechanism for the reaction of 9-phenylanthracene with a nucleophile is illustrated in equation 1. Examination of the structure of the intermediate after the EC$_N$E process, IV, reveals that there are now two possible sites for reaction with the nucleophile, the positive carbon center at the 9-position or the proton at the 10-position.

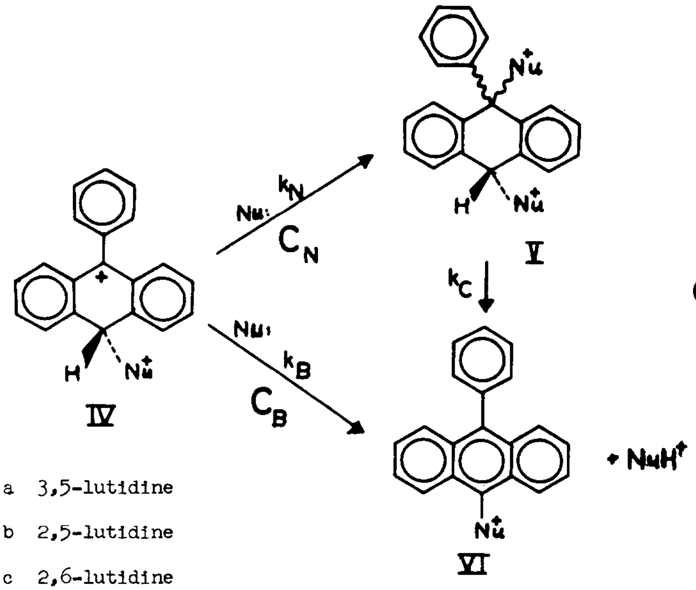




IV

(eqn.1)

The voltammogram of 9-phenylanthracene in acetonitrile in the presence of the unhindered nucleophile, 3,5-lutidine shows a 2e oxidation peak (EC_NE) at +1.0 v (all potentials refer to the saturated calomel electrode, SCE, and the supporting electrolyte was lithium perchlorate in all cases) and a smaller peak at +1.4 v. The voltammograms in the presence of the more hindered bases 2,5-lutidine and 2,6-lutidine (1) show 2e oxidation peaks at +1.0 v and second 2e peaks at +1.4 v. Controlled potential coulometry of 9-phenylanthracene in the presence of any of the three nucleophiles (at +1.1 v) results in the passage of 2.0 Faradays per mole of substrate. The voltammograms of the three solutions all show an oxidation peak at +1.4 v. The height of the oxidation peak for the solutions containing the hindered nucleophiles was precisely the same as the original oxidation peak at +1.0 v of the solutions before coulometry. However, the solution obtained from controlled potential coulometry of 9-phenylanthracene in the presence of 3,5-lutidine exhibited a voltammetric oxidation peak at +1.4 v 0.38 times as great as that of the original solution at +1.0 v. After heating to the boiling point of the solvent for one hour and allowing the solution to cool, voltammetric analysis showed the oxidation peak at +1.4 v to be as large as that of the other two solutions indicating that a chemical reaction was occuring to produce the oxidizable intermediate. The product of this reaction was isolated and the structure shown to be VIa (on the basis of elemental analysis and the nmr spectrum). Thus, the chemical reaction occuring after electrolysis is the conversion of Va to VIa (eqn. 2). The rate of this reaction was found to be much too low to account for the production of VI during the time-scale of cyclic voltammetry (the half-life of Va in the electrolysis medium was found to be $\gtrapprox$ 6 hours at 27°C). The conversion of the 9,10-dipyridinium salt from anthracene to the 9-pyridylanthracene salt by the action of warm base has been reported (3).



(eqn.2)

a 3,5-lutidine

b 2,5-lutidine

c 2,6-lutidine

We can conclude from our data that $k_B >> k_N$ when the nucleophile is 2,5-lutidine or 2,6-lutidine. When the nucleophile is 3,5-lutidine $k_B = 0.6\ k_N$ (determined by measurement of the peak heights for the oxidation at +1.0 v and +1.4 v of the solution of 9-phenylanthracene and 3,5-lutidine or measurement of the peak height at +1.0 v before coulometry as compared to that at +1.4 v after coulometry, both methods giving the same value). Thus, nucleophilic attack at the positive carbon center at the 9-position is inhibited when the nucleophile is hindered.

The voltammograms of 9-phenylanthracene in the presence of 3,5-lutidine and 2,5-lutidine are illustrated in figures 1-A and 1-B respectively.

References

1. V. D. Parker and L. Eberson, See preceding paper.
2. V.D. Parker, G. Manning, and R. N. Adams, J. Electroanal. Chem. In press.
3. H. Lund, Acta Chem. Scand., 11, 1323 (1957).

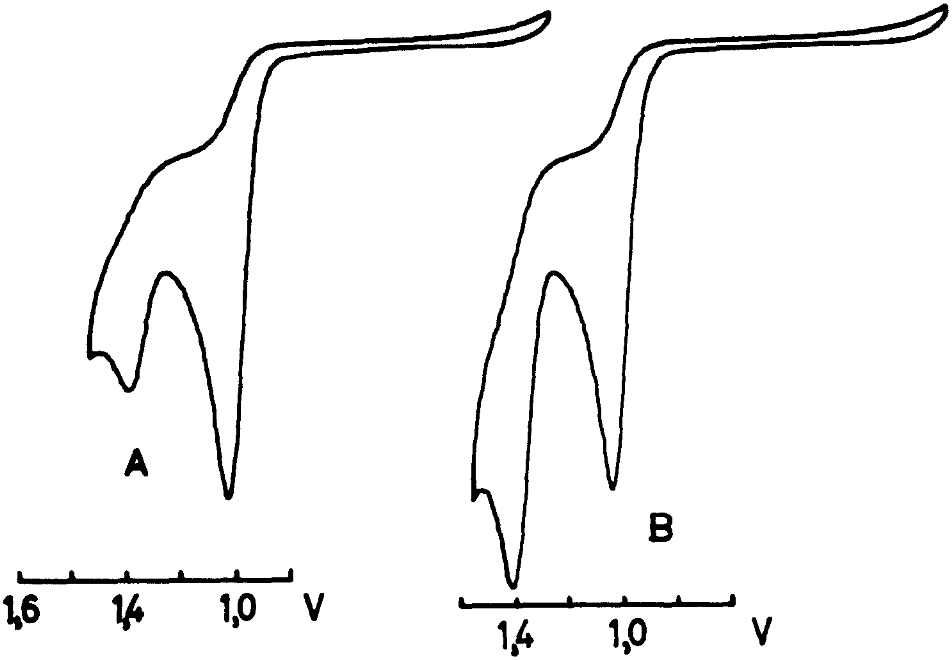


Figure 1. Voltammograms of 9-phenylanthracene in the presence of 3,5-lutidine (A) and 2,5-lutidine (B).