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ON THE MECHANISM OF THE ELECTROCHEMICAL AROMATIC SUBSTITUTION BY CYANIDE ION

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Recently Tsutsumi and co-workers reported on the direct introduction of cyano groups into aromatic compounds by the electrolytic oxidation of inorganic cyanide in the presence of the aromatic compound (1). These workers found that when a solution of sodium cyanide and anisole was electrolyzed a mixture of o-cyanoanisole (38%) and p-cyanoanisole (62%) was obtained. They concluded that electrochemically generated cyano radical attacks aromatic compounds at points of high electron density to form aromatic nitriles.

Experiments had previously been conducted in our laboratory in which solutions of sodium cyanide and aromatic compounds in methanol were electrolyzed to form aromatic nitriles. We interpret our results to indicate that the aromatic compound is oxidized in a two electron oxidation to an electrophilic intermediate which reacts with cyanide ion to form the aromatic nitrile. The removal of the electrons at the anode surface may be assisted by the approach of cyanide ion as suggested by Eberson and Nyberg for the acetoxylation of naphthalene (2). It has been shown by Leung, Herz, and Salzberg that the anodic acetoxylation of naphthalene occurs at anode potentials below which acetate ion is oxidized to the radical (3). Therefore the mechanism, at least in the case of acetoxylation, for this type of aromatic substitution is anodic oxidation of the aromatic substrate followed or assisted by reaction with the ionic species.

In the case of cyanide ion and anisole the ease of oxidation is reversed [+0.96 v. for cyanide (4) in aqueous solution and +1.67 v. for anisole (2) in acetic acid, both values are versus the standard calomel electrode], that is, cyanide oxidizes more readily than anisole. In order to distinguish between the two mechanisms, the oxidation of cyanide ion in the presence of anisole in methanol was conducted at an anode potential of +1.2 v.. At this potential only cyanide ion was oxidized. Gas chromatographic analysis failed to show the presence of cyanoanisoles. When electrolysis of an identical solution was carried out at an anode potential of +2.0 v. gas chromatographic analysis showed the presence of cyanoanisoles, which were identified by IR and mass spectroscopy. These results are best interpreted to indicate that although cyanide ion is anodically oxidized to the radical it does not react with the aromatic hydrocarbon. The formation of aromatic nitriles at higher anode potentials indicates that oxidation of the aromatic species produces an electrophilic intermediate which reacts with cyanide ion to form aromatic nitrile.

Schmidt and Meinert had previously failed to trap the cyano radical with easily substituted organic compounds such as N,N-dimethylaniline and 1,3-cyclohexadiene (5). They were able to obtain solutions of oxamidines when the oxidation of cyanide ion was conducted in the presence of o-cresol or aniline in pyridine. Formation of the oxamidines is attributed to reaction of the phenol or amine with electrochemically generated cyanogen.

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