ROLE OF THE AROMATIC OXIDATIVE COUPLING REACTION IN FUEL CHEMISTRY

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In the temperature range of 300° to 500°C bituminous coals pass through one or more plastic stages, but after each occurrence continued heating causes solidification (1). In the direct liquefaction of coals or processing of coal-derived liquids at pyrolytic temperatures catalytic surfaces become fouled with carbonaceous deposits (2,3,4). In jet fuels the presence of heterocyclic aromatic compounds containing nitrogen in the rings causes sludge to form (5). Carbazoles and related compounds tend to form carbonaceous electrode deposits at anodes in electrochemical cells.

Each of these effects is caused by an increase in molecular weight which might arise from a number of different chemical reactions. However, in these specific oxidation-reduction reactions a favored oxidation half reaction is the oxidative coupling of aromatic ring structures. The first clue to the operation of aromatic oxidative coupling as a route to products of higher molecular weight and lower solubility resulted from the observation of electrode film formation on anodes when coal-derived liquids were being examined electrochemically (6).

EXPERIMENTAL

The electrode films formed by anthracene oil and SRC-II type product oils derived from Blacksville No. 9 coal were studied by means of cyclic voltammetry and double potential step chronoamperometry. A Princeton Applied Research Model 170 Electrochemistry System was employed. The electrolyte was tetrabutyl ammonium fluoroborate, and solvents were acetonitrile for the anthracene oil and tetrahydrofuran for SRC-II type product oils.

DISCUSSION

Anthracene oil and many samples of SRC-II type product oil from the 1000 pound per day pilot plant at Pittsburgh Energy Technology Center (PETC) were examined electrochemically and found to form electrode deposits under oxidizing conditions. Successive voltammetric traces show the insulating effect of the film deposited by anthracene oil (Figure 1a). Progressive changing of the switching potential toward more cathodic potentials shows a decrease (Figure 1b) and elimination (Figure 1c) of the film-forming tendency.

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In a different experiment the initial potential of an SRC-II type solute was held at +1.000 volt for different lengths of time, and the resulting films were reduced in the voltammetric scan toward more cathodic potentials. The peak heights reflect the currents used to reduce the films formed by oxidation at +1.000 volt. A linear variation in peak height with time is shown (Figure 2). In these samples the films are much more reactive than those formed from anthracene oil.

The films formed on anodes proves the reaction to be an oxidation. The formation of electrode films, which, depending on conditions, varied from soft, brown, and soluble to hard, glossy, black, and insoluble in pyridine, proves an increase in molecular weight. The presence of reactive aromatic structures in coals and coal-derived liquids (7) suggests the operation of the aromatic oxidative coupling reaction. Table I comprises a list of selected compounds that undergo oxidative coupling.

As reported by Dworkin and others(8) and illustrated with anthracene, $C_{14}H_{10}$, aromatic oxidative coupling proceeds by way of a radical cation intermediate.

Oxidations:

$$C_{14}H_{10} \longrightarrow C_{14}H_{10} + e^-$$

$$C_{14}H_{10} + C_{14}H_{10} \longrightarrow C_{28}H_{10} + 2H^+ + 2e^-$$

Reduction:

$$C_{14}H_{10} + 2H^+ + 2e^- \longrightarrow C_{14}H_{12}$$

Net Reaction:

$$3C_{14}H_{10} \longrightarrow C_{28}H_{18} + C_{14}H_{12}$$

Many common reagents and catalysts cause radical cation formation which initiate aromatic oxidative coupling. These include H_2SO_4 (9,10),oxidizing agents in acidic media (9,11,12,13), Lewis acids (14-26), halogens (27), $Ag(ClO_4)$ and iodine (28,29), and metal salts (30,31). Free radical cations are also formed by such solid catalytic surfaces as gamma-alumina (32), silica alumina (33), and zeolites (34). They may also be generated by photoionization (35,36,37) and electrochemical oxidation(38). Both radical cations and radical anions were generated at PETC by electrolysis of SRC-II type solutes in an ESR cavity (39).

In support of this information Ross and Blessing report, "In the absence of an H-donor, then, oxidative crosslinking takes place within the coal upon heating, yielding a product even less soluble in solvents such as pyridine than was the starting coal" (40). Others have reported the same behavior (41,42). Thus, one may conclude that Lewis acids cause oxidative hydrogen transfer from hydrogen donors or oxidative polymerization through a sequence of coupling reactions. Other radical cation forming catalysts and reagents may be expected to behave similarly.

CONCLUSIONS

Aromatic structures may polymerize by a stepwise, oxidative coupling reaction, initiated by formation of radical cations. Common reagents and catalysts cause radical cations to form.

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Table I

Compounds Susceptible to Oxidative Coupling

Compounds	References	Compounds	
Benzene	43	Triphenylamines	49,50,51
p-Xylene	44	Anilines	52
Mesitylene	44	Carbazoles	53,54
Durene	44	Iminobibenzyls	55
Phenolic Tetrahydro-isoquinolines	45,46,47	o-Phenylenedianine	56
Catechol Ethers	48	Dibenzothiophene	57

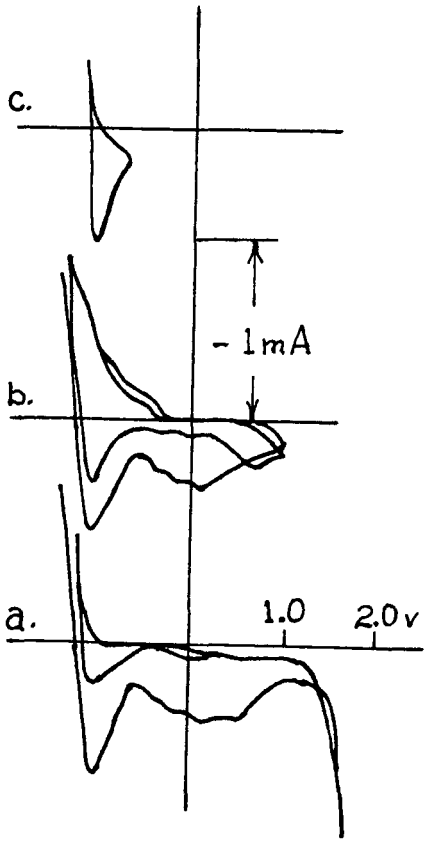

Figure 1. Effect of Film Formation on Voltammograms of Anthracene Oil.

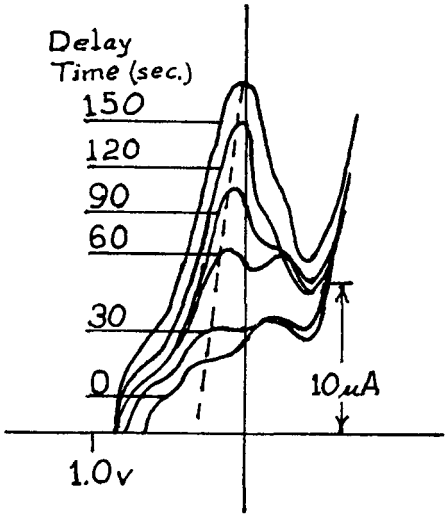

Figure 2. Effect of Film Formation on Voltammogram of SRC-II Type Liquids.