

## An Electron Spin Resonance Study of the Reduction of Aromatic Compounds by Quaternary Ammonium Amalgams

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OUR colleagues<sup>1</sup> have recently reported the formation of quaternary ammonium amalgams by electrolysis of quaternary ammonium salts at a mercury cathode. These compounds themselves show no e.s.r. signal, but readily transfer electrons to suitable organic substrates forming paramagnetic solutions.

We find that these amalgams produce anion radicals from aromatic hydrocarbons and nitro- or cyano-benzenes, and we have been able to estimate the reduction potentials for the various amalgams in this way.

anions are identical, within experimental error, with those obtained previously by electrolysis<sup>3,4</sup> or alkali-metal reduction<sup>5</sup> (Table). The spectra show no interaction between the anion radicals and the amalgam donors. All the tetra-alkylammonium amalgams, R<sub>4</sub>N/Hg, where R<sub>4</sub> is Me<sub>4</sub>, Et<sub>4</sub>, Pr<sup>n</sup><sub>4</sub>, Bu<sup>n</sup><sub>4</sub> or dodecyl trimethyl were found to reduce biphenyl and therefore have a reduction potential in excess of -2.7 v (against S.C.E.). This observation has since been confirmed<sup>6</sup> by direct measurement of the potentials of the amalgams. Sodium amalgam (-2.1 v against S.C.E.) does not

TABLE

### Observed coupling constants (gauss)

Anion radical	Coupling constants	Reduction potentials <sup>7</sup> (against S.C.E.)
Naphthalene	$A_1 = A_4 = A_5 = A_8 = 4.88$ $A_2 = A_3 = A_6 = A_7 = 1.83$	-1.50
Anthracene	$A_1 = A_4 = A_5 = A_8 = 2.65$ $A_2 = A_3 = A_6 = A_7 = 1.49$ $A_9 = A_{10} = 5.36$	-1.94
Biphenyl	$A_2 = 2.63$ $A_3 = 0.40$ $A_4 = 5.27$	-2.70
Terephthalonitrile	$A_H = 1.69$ $A_N = 1.94$	—
Nitrobenzene	$A_N = 10.00$ $A_3 = A_5 = 1.00$ $A_2 = A_6 = 3.36$ , $A_4 = 3.78$	-0.62
m-Dinitrobenzene	$A_N = 3.93$ $A_2 = 2.80$ $A_5 = 1.08$ $A_4 = A_6 = 4.44$	-0.39

Well-resolved e.s.r. spectra of the anion radicals are obtained when a dilute (*ca.* 10<sup>-3</sup>M) solution of the hydrocarbon or the nitro- or cyano-substituted aromatic compound in dry *NN*-dimethylformamide is shaken *in vacuo* with the tetra-alkyl ammonium amalgam. The technique is basically the one normally employed for alkali-metal reductions,<sup>2</sup> except that the quaternary ammonium amalgam is now used as the reducing agent.

In all cases the coupling constants for the radical

reduce biphenyl. Attempts to reduce benzene or benzene derivatives containing electron-donating groups, such as methyl, have so far failed, presumably because their reduction potentials are much more negative.

Similar studies on the corresponding phosphonium, sulphonium, and oxonium compounds will be reported in detail subsequently.

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