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REACTION OF THE SOLVATED ELECTRON AND MONOMERIC METAL SPECIES WITH TOLUENE AND BENZENE IN HEXAMETAPOL. HYDROGEN ATOM MOBILITY.

Jacques-Emile Dubois and Guy Dodin
(Laboratoire de Chimie Organique Physique de la Faculté des Sciences de Paris,
Associé au C.N.R.S., 1, rue Guy de la Brosse, Paris 5° - France).

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Benzene has been variously reported to behave in alkali metal-hexametapol (HMPA) solutions, either a) reacting with the solvated electrons (1) generated by the electrolysis of alkali metal salts or b) stabilizing the metallic species (2) obtained by direct metal addition to HMPA.

Absorption and e.p.r. spectroscopy shows that the metal solutions are strictly similar (at least for dilute solutions) whether prepared by electrolysis or metal dissolution. Moreover, under the electrolysis conditions no electrochemical reduction of benzene occurs. Thus, the equivocal behaviour of benzene must be related to the difference in the metal concentrations involved in these studies.

We now wish to report the results of a study of the reaction of benzene and toluene with metal (lithium or sodium)/HMPA solutions at two very different metal concentrations (10^{-5} and 0.2 M).

Weak solutions were prepared by electrolysis of a 0.2 M solution of lithium or sodium perchlorate at a platinum electrode, in the presence of water (0.1 M) which serves as a proton-donor : at this concentration no reaction between water and the solvated electron is observed, but at a higher one (0.5 M) reduction to hydrogen occurs. Benzene and toluene (0.5 to 1.0 M) are reduced to 1,3-cyclohexadiene and 1-methyl-1,4-cyclohexadiene respectively. Further reductions to cyclohexene and isomeric methylcyclohexenes follow (3).

However, in concentrated metal solutions (0.2 M) obtained by direct dissolution of the metal in HMPA, the radical anions of naphthalene and biphenyl are formed from benzene (2.0 M), as shown by e.p.r. spectroscopy (Figure 1). The components of the composite spectrum were readily separated ; the computed spectrum was similar to that observed. At lower benzene concentration (1.0 M), a five-band spectrum (intensities : 1 4 6 4 1 ; coupling constant : 2.6 G) corresponding to that reported (4) for the biphenylene radical anion, was initially observed.

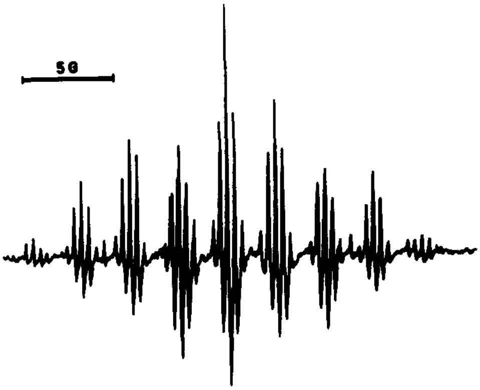


Figure 1. - Composite e.p.r. spectrum of biphenyl and naphthalene radical anions.

Reaction with toluene (2.0 M) leads to a more complex spectrum (the central line corresponds to the signal of the solvated electron) (Figure 2). The spectrum was assigned to a mixture of dimethylbiphenyl radical anions (5), but only the 4,4'-derivative could be positively identified ($a^{CH_3} = 5.6$ G, $a_2^H = 2.72$ G, $a_3^H = 0.5$ G). No products resulting from metallation of the methyl group were detected (6).

Extension of current theories regarding the structure of metal-ammonia solutions (7) to HMPA provides an interpretation of these results. At low concentrations, the solvated electron would be the predominant species and lead to Birch reduction of the benzene ring ; the formation of the conjugated diene, in the case of benzene,is attributable to the low proton-donor concentration (8). At higher concentrations, the metal monomer becomes an important constituent of the medium and leads to a metallation reaction (2) with the substitution of labile hydrogen atoms, the ring hydrogen atoms being apparently the more labile under these conditions.

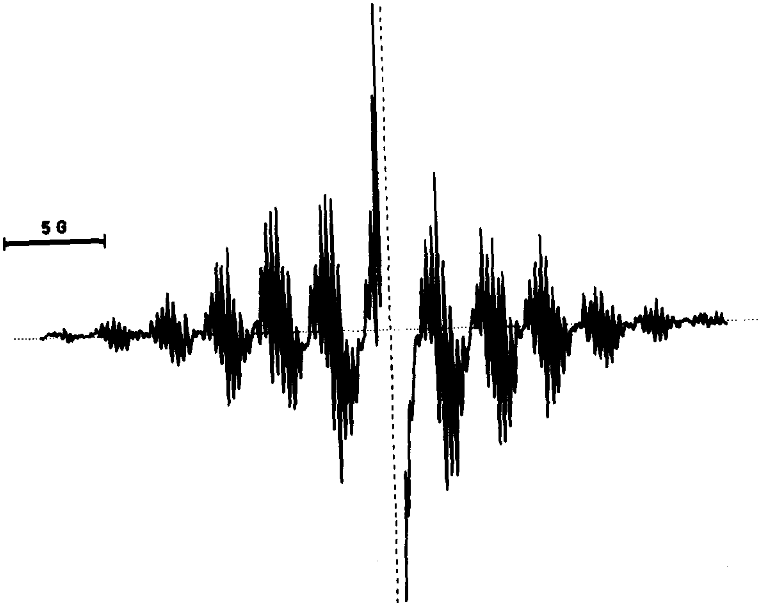
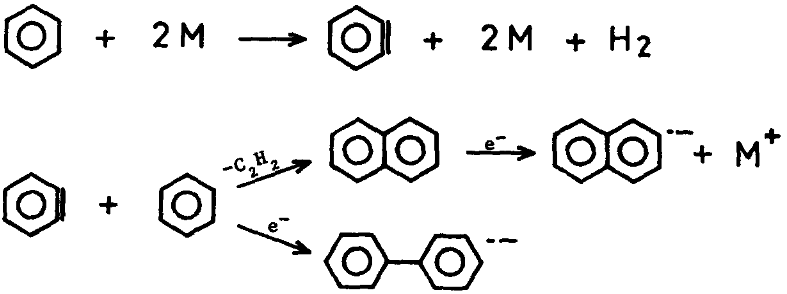
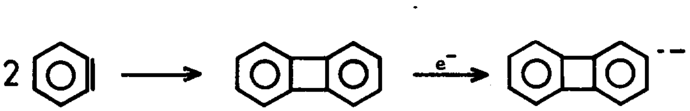


Figure 2.- Composite e.p.r. spectrum of a mixture of dimethyl biphenyl radical ions.

These various results support a mechanism similar to that of electron impact decomposition or pyrolysis of benzene (9), involving the initial formation of benzyne.



The formation of the biphenylene radical anion can be reasonably attributed to the dimerization of benzyne (10).



The high lability of the ring hydrogen atoms has already been mentioned in metallation of toluene in octane (11) and in the mono- and dimetallation of benzene in benzene by aliphatic alkali derivatives (12). Moreover, our observations are consistent with the reported condensation of anisol to biphenyl by means of Na/K alloy in THF/DME mixtures (6b).

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