Electron Transfer as the First Step in Electrophilic Aromatic Substitution

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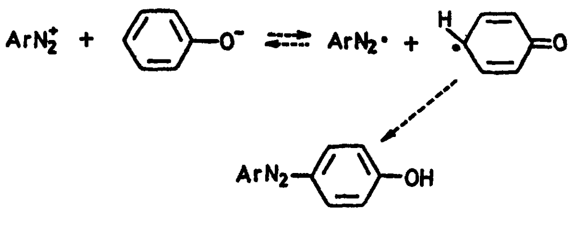
Summary The azo-coupling reaction is shown to proceed *via* radical intermediates.

Electron transfer has been shown to be the first step in S_N1-type nucleophilic substitution.[1,2] Theoretical calculations suggest that electrophilic aromatic substitution proceeds in two steps, the first being electron transfer from substrate to the electrophilic reagent.[3]

Diazonium salts are known to react with substituted *NNN'N'*-*p*-phenylenediamine giving a cation radical of the amine.[4]

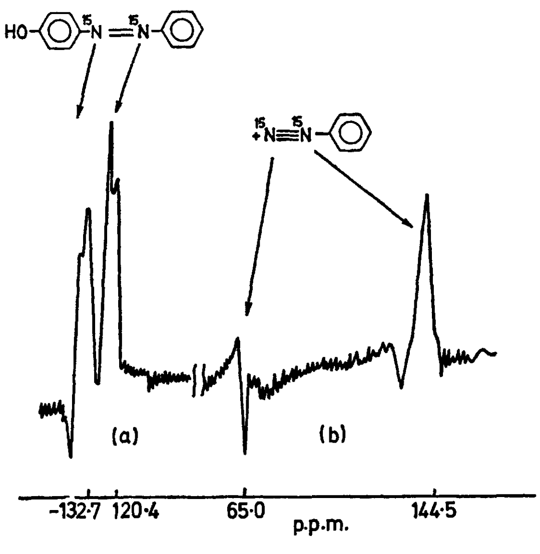


Scheme.

The rates of electron transfer in these reactions were measured by e.s.r. methods in a flow system.[5] The relative rates of electron transfer were found to vary in a similar manner to those of azo-coupling reactions of various *para*-substituted phenyldiazonium salts. This indicates that azo-coupling reactions proceed *via* one electron transfer steps. We report a confirmation of this by CIDNP methods.[6,7]

Reduction of *p*-nitro- or *p*-fluoro-phenyldiazonium tetrafluoroborates by alcoholates of alkali metals in acetone gave strong signals from nitrobenzene and fluorobenzene protons and a negative polarisation of the ^{1}H or ^{19}F n.m.r. spectra. The negative polarisation of the ^{1}H and ^{19}F n.m.r. signals increase with reaction, reach a maximum, become zero, change sign, and then tend to the equilibrium value.

We suggest that the azo-coupling reaction occurs in the two steps shown in the Scheme. The initially formed radical pair which is a result of electron transfer from the phenolate to the diazonium cation recombine to yield the azo-compound. We used diazonium salts containing ^{15}N in both positions. On mixing an acetone solution of phenyldiazonium tetrafluoroborate with methanolic sodium phenolate in the probe of a ^{15}N n.m.r. spectrometer (6 MHz) strongly enhanced signals of the two doublets of the azo-compound were observed (J 15 ± 1 Hz) at 107·3 and 119·6 p.p.m. (reference ${}^{15}NO_2^-$) (Figure a). Strong positive polarisation of the ^{15}N nucleus of the final product was indicated by the fact that after the reaction *i.e.* in the equilibrium state of the nuclear spin system identical signals of very weak intensity could be observed only after a long accumulation period. During the reaction strong polarisation of the diazonium salt was observed at 65·0 p.p.m. and enhanced absorption at 144·5 p.p.m. (reference ${}^{15}NO_3^-$, Figure b). These results indicate that the first step of the reaction, electron transfer, is reversible.



Figure

Thus the azo-coupling reaction must be considered a two step process, the first of which is one electron transfer.

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