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A KINETIC ISOTOPE EFFECT IN THE TRICYANOVINYLATION OF DIMETHYLANILINE

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In a recent paper Rappoport (1) reported an investigation of the mechanism of the reaction between dimethylaniline and tetracyanoethylene in which the formation of both a charge-transfer complex (2) and a σ-complex were observed, the latter complex being a stable Wheland-type intermediate (3). The abstraction of a proton from the σ-complex has been suggested as the rate-determining step in the formation of the final product.

We have observed a kinetic isotope effect in the rate of formation of the final product of the reaction between tetracyanoethylene and dimethylaniline and its deutero-derivatives, this result being consistent with the proposed mechanism (1). For the reaction between tetracyanoethylene and 4-deuterodimethylaniline, and between tetracyanoethylene and 2,4,6-trideuterodimethylaniline, $k_H/k_D = 3.6 \pm 0.1$ at 22°, both reactions being carried out in chloroform solution containing 1% by weight of ethanol. This value may be compared with the isotope effects found in other electrophilic substitution reactions involving aromatic amines, in which a zwitterionicintermediate may be formed without loss of a proton (4).

The formation of charge-transfer complexes in electrophilic aromatic substitution reactions may be concurrent with, or may precede the formation of a Wheland-type intermediate, the degree to which this intermediate is formed in the transition state being greater, the more reactive the aromatic compound (5). Alternatively, charge-transfer complex formation may lead to complete electron transfer from the donor to the acceptor molecule (6). Our investigations of the mechanism of reactions between dialkylanilines and tetracyanoethylene (7) show that the formation of a charge-transfer complex between the free base and tetracyanoethylene is not essential to the formation of the σ-complex, but that in organic solvents some charge-transfer complex formation is always observed. The rate of the reaction charge-transfer complex ⟶ σ-complex increases with the electron releasing power of the substituents on the nitrogen atom of the dialkylaniline, but the rate of the reaction σ-complex ⟶ final product shows no such relationship.

The electron donating ability of the dialkylanilines, as measured by the wavelength of maximum absorption of the dialkylaniline-tetracyanoethylene charge-transfer complex, shows a large increase from dimethylaniline (λ_{max} 675 mμ, ϵ 3200) to diethylaniline (λ_{max} 835 mμ, ϵ 3000), with smaller increases to di-n-butylaniline (λ_{max} 845 mμ, ϵ ca. 2800), all values referring to chloroform solutions. The visible absorption spectrum, together with e.s.r. measurements indicates that complete electron transfer occurs in diethylaniline-tetracyanoethylene solutions in solvents of moderate polarity (e.g. chloroform, ethyl acetate). The absorption maxima assigned to the anion occur at ca. 400 mμ, 416 mμ, these values corresponding with the absorption maxima for the 1,1,2,3,3-pentacyanopropenide anion (8). The rapid disappearance of the absorption band due to the charge-transfer complex, and the lack of any significant amount of 4-tricyanovinyl N,N-diethylaniline in the reaction mixture are in agreement with this assignment. Similar results are obtained for the higher dialkylanilines, and also for N,N-diethyl p-toluidine-tetracyanoethylene solutions in which no 4-tricyanovinylation can occur.

This ability of diethylaniline to form highly stable reaction intermediates with electron acceptors was also observed in the bromination of aromatic amines (9).

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