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ALKALINE HYDROLYSIS OF ACTIVATED AROMATIC SUBSTRATES IN AQUEOUS DMSO

K. Bowden* and R.S. Cook

Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex

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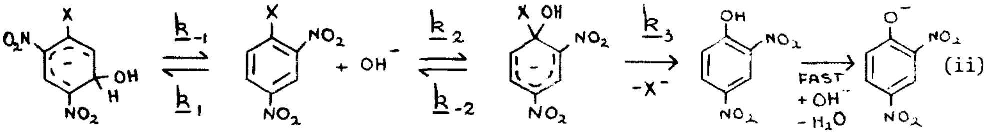
Recent studies have investigated the incidence and structure of Meisenheimer complexes(1), and have demonstrated addition at both the 1- and 3- positions(2). The present study reveals evidence for the presence of both addition complexes as intermediates in nucleophilic aromatic substitutions in aqueous dimethyl sulphoxide (DMSO).

Rates of hydrolysis for several activated aromatic substrates have been measured in aqueous DMSO containing tetramethylammonium hydroxide at 30.0°. 1-Substituted-2-nitrobenzenes and 1-substituted-4-nitrobenzenes show a linear correlation between log k and the acidity function J-, where J- is given(3) by expression (i). H- is the known acidity function for the system, and a_w is the activity of water. The correlations have slopes from 0.64 to 1.0, which

$$J_- = H_- + \log a_w \qquad \text{(i)}$$

appear to reflect the extent of covalent-bond formation in the transition state.

Analogous correlations for the hydrolysis of 1-substituted-2,4-dinitrobenzenes are also linear with slopes from 0.48 to 0.88. However, these pass through a rate maximum in the region 55-70 mole percent DMSO, the rate then falling with increasing DMSO concentration. The deviations from linearity coincide with the first appearance of a transient reaction intermediate (λ_{max} = 515 mμ) in the solutions on initial mixing. The latter absorption is consistent with the intermediates being of Meisenheimer (cyclohexadienide) structure(2). The intermediates become increasingly stabilised as the DMSO concentration is raised, and their rates of decomposition are asymptotic to the overall reaction rate at high basicities. The deviations from linearity observed in the correlations are therefore attributed to an increasing contribution to the overall reaction rate from the rate of decomposition of the intermediate(4). The leaving-group order of the halogens remains Cl>Br>I throughout the region where the rate of decomposition of the intermediate becomes important. This indicates that the step which becomes kinetically important at high DMSO concentrations is not the intermediate-decomposition step of the Bunnett mechanism(5). If this step was kinetically important, the leaving-group order I>Br>Cl would be expected. Furthermore, the ρ value for the hydrolysis of 2,4-dinitrophenyl 3'-substituted phenyl ethers has been found to be + 0.75 (correlation coefficient, 0.995) in 27 mole percent DMSO, and -0.86 (correlation coefficient, 0.990) in 83 mole percent DMSO. The small, negative ρ value in solutions rich in DMSO confirms that the latter step cannot yet have become kinetically important or ρ would expect to be large and positive. At very high DMSO concentrations, the rates normally begin to increase again with increasing DMSO content and this is followed by reversals of leaving group order. The above results lead to the following suggested reaction scheme (equation (ii)) for nucleophilic substitutions of 1-substituted-2,4-dinitrobenzenes in aqueous DMSO.



(ii)

At low DMSO concentrations, k_2 is rate determining. The contribution to the overall reaction rate from k_{-1} increases as the DMSO concentration is raised, and k_{-1} approaches becoming rate determining. At very high DMSO concentrations, k_3 will become rate determining.

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