Kinetics and Mechanism of Oxidation of Dimethyl Sulphoxide by Mono- and Di-Substituted N,N-Dichlorobenzenesulphonamides in Aqueous Acetic Acid

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In an effort to introduce *N*,*N*-dichloroarylsulphonamides of different oxidising strengths, four mono- and five di-substituted *N*,*N*-dichlorobenzenesulphonamides are prepared, characterised and employed as oxidants for studying the kinetics of oxidation of dimethyl sulphoxide (DMSO) in 50% aqueous acetic acid. The reactions show first order kinetics in [oxidant], fractional to first order in [DMSO] and nearly zero order in [H^+]. Increase in ionic strength of the medium slightly increases the rates, while decrease in dielectric constant of the medium decreases the rates. The results along with those of the oxidation of DMSO by *N*,*N*-dichlorobenzenesulphonamide and *N*,*N*-dichloro-4-methylbenzenesulphonamide have been analysed. Effective oxidising species of the oxidants employed in the present oxidations is Cl^+ in different forms, released from the oxidants. Therefore the introduction of different substituent groups into the benzene ring of the oxidant is expected to affect the ability of the reagent to release Cl^+ and hence its capacity to oxidise the substrate. Significant changes in the kinetic and thermodynamic data are observed in the present investigations with change of substituent in the benzene ring. The electron releasing groups such as CH_3 inhibit the ease with which Cl^+ is released from the oxidant, while electron-withdrawing groups such as Cl enhance this ability. The Hammett equation, $\log k_{obs} = -3.19 + 1.05\,\sigma$, is found to be valid for oxidations by all the *p*-substituted *N*,*N*-dichlorobenzenesulphonamides. The substituent effect on the energy of activation, E_a and log *A* for the oxidations is also analysed. The enthalpies and free energies of activation correlate with an isokinetic temperature of 320 K.

Key words: Kinetics, Oxidation, Dimethyl Sulphoxide, *N*,*N*-Dichloroarylsulphonamides