A Study of Substituent Effect on the Oxidative Strengths of *N*-Chloroarenesulphonamides: Kinetics of Oxidation of Leucine and Isoleucine in Aqueous Acid Medium

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To study the variation of oxidative strengths of *N*-chloro-arenesulphonamides with substitution in the benzene ring, six mono- and five di-substituted *N*-chloro-arenesulphonamides are employed as oxidants for studying the kinetics of oxidation of two neutral amino acids, L-leucine and L-isoleucine in aqueous acid medium. The *N*-chloro-arenesulphonamides studied are of the constitution: $ArSO_2NaNCl{\cdot}H_2O$ (where Ar = C_6H_5, 4-$CH_3C_6H_4$, 4-$C_2H_5C_6H_4$, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 2,3-$(CH_3)_2C_6H_3$, 2,4-$(CH_3)_2C_6H_3$, 2-CH_3-4-ClC_6H_3, 2,4-$Cl_2C_6H_3$, and 3,4-$Cl_2C_6H_3$). The reactions show second order kinetics in [oxidant], fractional order in [amino acid] and inverse dependence on $[H^+]$. Addition of the reduced product of the oxidants or variation in ionic strength of the medium has no significant effect on the rates of oxidations. A two-pathway mechanism is considered to explain the experimental results. Effective oxidizing species of the oxidants is Cl^+ in different forms. Therefore the oxidising strengths of *N*-chloro-arenesulphonamides depend on the ease with which Cl^+ is released from them. The study reveals that the introduction of substituent in the benzene ring of the oxidant affects both the kinetic and thermodynamic data for the oxidations The electron releasing groups such as CH_3 generally inhibit the rates, while electron-withdrawing groups such as Cl enhance this ability, as the electron withdrawing groups ease the release of Cl^+ from the reagents and hence increase the oxidising strengths. The on E_a and log$A$ and validity of the Hammett and isokinetic relationships for the oxidations are also analysed.

Key words: Kinetics, Oxidation, Leucine, Isoleucine, *N*-Chloroarenesulphonamides