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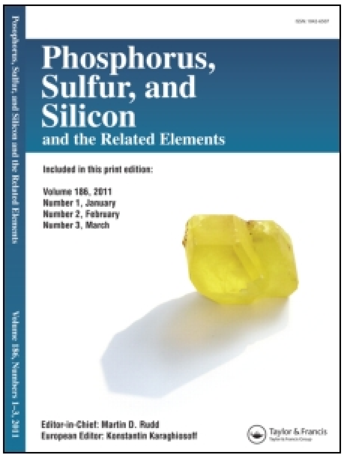

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The Separation of Steric and Electronic Effects in the Reaction of Benzenesulphonyl Chloride with Carboxylate Ions in Aqueous Solution

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Keywords: sulphonyl chlorides; aliphatic acids; linear free energy relationships

The kinetics of the reaction of benzenesulphonyl chloride with twentyfive carboxylate ions, R.COO $^-$, in 2% dioxan are reported. Eight compounds are accommodated in either a Bronsted-type or a σ^I plot. Pivalate and formate ions require a linear combination with Taft's steric factor, E_s. Although E_s has been shown [1] to be related to r, where r is the radius of a symmetrical group, R_3C, E_s correlates just as well with r^{-1}, as predicted by the Born equation for steric inhibition by solvent exclusion. Steric effects are shown using the methods previously applied to *a priori* calculations of electrostriction [2], to be due to steric exclusion of solvent from the vicinity of carboxy-group. Anions having adjacent groups either carrying a charge or capable of hydrogen bonding deviated in the same manner as the corresponding pK_a values, thus all hydrogen malonates are less reactive than σ^I

would predict and in particular for the hydrogen 2,2-diethylmalonate, known to form a strong intramolecular hydrogen-bond [3], no reactivity could be detected. Acetate ions, mono- or di-substituted by a polar group, showed small deviations due to different through space interactions of the differing conformers of the acid in the pK_a values and the transition state in the formation of a mixed anhydride. In conclusion although the Taft σ^* values do carry a small steric factor due to imbalance of solvent interactions between the defining transition states, E_s values seem as good as any other parameter, provided the limitations Taft recognised are considered.

A provisional ρ value for the reaction of arenesulphonyl chlorides with acetate ion is given and the transition state charge distribution for all reactions of sulphonyl chlorides in water discussed briefly. In particular the linear relationship [2] between the partial charges on sulphur and chlorine in the transition states and the *a priori* calculations of Hammett ρ values are briefly considered.

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