STUDY OF SIGMA INDUCTIVE EFFECTS USING THE PEOE METHOD

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The iterative partial equalisation of orbital electronegativity (PEOE) (1) procedure which could be employed to obtain atomic charges in non conjugated sigma frameworks, is used to study sigma inductive effects. The atomic charges so obtained have been successfully correlated with ESCA core binding energies and acidity constants in non conjugated sigma bonded systems(1). Our calculations of atomic charges on substituted alkanes show that the sigma inductive effect falls off systematically along a saturated framework. The calculated transmission coefficient indicates that this effect is important only over a range of two or three bonds. In a series of halogen substituted acetic acids, it was found that neither the polarily of the O-H bond nor the charge on the acidic hydrogen atom were significantly effected by the substituent, indicating that sigma inductive effects on their acidity are minimal, contrary to popular beliefs. Calculations on the substituted alkanes also confirmed that sigma inductive effects are essentially additive and depends on the number of paths between the substituent and the probe atom. Further, the alkyl substituents were found to have a small, electron withdrawing inductive effect. Our results are in general agreement with findings where alternative methods have been employed(2,3).

References

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