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Review Summary

The inductive effect – the present position

In the following we summarize the main conclusions from the preceding three articles with the intention of pointing out the essential facts and the most important points at issue.

There is a universal electrical effect observable in all systems XGY, where X, G and Y are substituent, skeletal group and reactive functional group, respectively. The effect may be observed by varying the substituent and measuring some quantity localized on Y or alternatively the energy of the whole molecule or ion. In the latter case, the effect can be defined in exact thermodynamic terms as the reaction enthalpy of an isodesmic reaction [Eqn. (1), p. 266]. This effect was first called an inductive effect, but later many authors referred to it as a field effect. Inherent in these names are concepts of the nature of the transmission of the universal effect. One of us called it the localized electrical effect, but this term has not been generally accepted. At present we have no simple term which would denote only the universal effect and nothing else. Such a term is sorely needed.

In molecules with a skeletal group Z such that conjugation between X and Z is excluded and the distance between them is great enough to exclude any short-range interaction, the universal effect is the only electrical effect that is observed. This is expressible by a substituent constant [Eqn. (5), p. 266]; such constants include σ_I, σ_F and σ_1, all of which are equivalent. Quantitative predictions can be made when the reaction constant and substituent constants are known. With less accuracy, predictions can be made for substituents for which the parameters are unknown [Eqn. (1), p. 286]. When the structure of G does not satisfy the above requirement, an additional electrical effect is assumed to occur. This additional effect can be evaluated by substracting from the total electrical effect the calculated value of the universal effect.

The long-standing dispute about the nature of the transmission of the universal effect, through space (field effect, *F* effect) or through bonds (inductive effect, sigma-inductive effect, *I* effect) in no way affects the use of substituent constants in modelling the universal effect. The problem cannot be approached through quantum chemical calculations as these can provide energies of particular molecules or charges on atoms but do not provide evidence on the mode of transmission. The two models originally proposed, the classical (Kirkwood–Westheimer) field effect [Eqns 6 and 7, p. 267] and the classical inductive effect of Derick, Lewis, Branch and Calvin [Eqn. (8), p. 268] are not well defined and are not in good agreement with experiment. The two new models, the modified field effect [Charton, Eqn. (10), p. 277] and, to a lesser extent, the modified inductive effect [Exner and Fiedler, Eqn. (9), p. 268] provide better models. The tests described in our papers are not entirely unambiguous. All of the models are approximate to a greater or lesser degree. The mode of transmission problem cannot be solved completely by recourse to sophisticated model compounds of unusual structure.

Whatever the name may be, the universal electrical effect is a general phenomenon observed throughout quantitative chemistry, organic, inorganic and polymer chemistry, biochemistry and physical properties. It deserves a more important place in textbooks than it ordinarily has, as it is far more than a means for explaining the acidity of chloroacetic acids.

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