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Preface

Since its conception over thirty years ago, the Hammett equation together with subsequent modifications, all of which owed their motivation to Hammett's original idea, has provided the main basis for quantitative structure reactivity relationships in organic chemistry. The uses of the equation in the great number of research publications employing it can be broadly divided into two categories.

The first is the elucidation of intramolecular interactions of electronic or steric type, typically the manner in which substituents exert their influence on rates of reactions or positions of equilibria.

The second is the investigation of reaction mechanisms, where it is frequently and to best advantage used in conjunction with other physico-chemical techniques, all combining to form a consistent and consequently convincing rationale of the reaction pattern in question.

This book is an attempt to explain these two approaches (and to emphasise the importance of the second) at a level suitable for third year chemistry undergraduates or first year graduate students. Such students, although familar with fundamental qualitative organic chemistry, have often had little or no experience of quantitative assessments of the reactivity of organic molecules. For this reason, exhaustive lists of parameters accompanied by rigorous statistical analysis, possibly of some value to the initiated, but overwhelmingly confusing and indigestible to the beginner, have been avoided. Attention is restricted to detailed consideration of a few familiar reactions and substituents.

However, the simple postulates thus developed can be readily applied to more complicated cases; for this reason, each chapter concludes with a series of problems, taken mostly from recent research papers, and designed to help the student learn to apply the general points included in the text to specific examples of current interest. Perhaps the student will be tempted to try at least some of these for himself. It is impossible to appreciate the concepts of any aspect of physical organic chemistry by lecture attendance and textbook reading alone. Real understanding can only come from supplementation by exercises in which the student calculates and interprets data by himself or possibly in a small discussion group. Through such a process he becomes familiar with the practical meaning to be attached to quantities denoted symbolically in general equations, and thus forms a realistic assessment of the extent of accuracy and degree of validity which he is prepared to accord to such equations.

Consideration of the thermodynamic basis of the equation is delayed until the final chapter. In an elementary treatment, students are prepared to accept the ideas of inductive, resonance, and steric effects without too much questioning. It is only later, when some time has been spent dealing with quantitative approaches such as the Hammett equation or molecular orbital calculations, that they really begin to enquire more critically into the relevance of these concepts, and how and why such theoretical postulates relate to experimentally determined data such as free energy, enthalpy, and entropy changes.

It is impossible in any description of the Hammett equation to avoid controversial material. All aspects are currently under scrutiny; there are many different opinions and conflicting views. In several instances here, points of uncertainty are indicated, but perhaps a degree of simplification is inevitable, for a student must learn what the ideas are before he can effectively appraise them.

Use of the Hammett equation has frequently encountered censure on the grounds that it is empirical, inaccurate, and that the wide diversity of σ value types is confused and ridiculous. There is undoubtedly some truth in this. Certainly one finds quite frequently a measure of significance placed on small order terms which puts credulity under severe strain. However, only the simplest of molecules *in vacuo* can be treated with absolute accuracy; the complete understanding of the complicated systems of organic reactions in solution is a far distant goal, and at the present time theoretical organic chemistry in general is necessarily semi-empirical and approximate. Nevertheless, in terms of the role which it has played in the broad elucidation of electronic effects and reaction mechanisms, the Hammett equation has been of unparalleled utility, to the recognition of which, it is hoped, this volume will in a small measure contribute.

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C.D.J.

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