

Contents

| | |
|---|----------|
| Preface | page vii |
| 1 The Hammett $\sigma\rho$ relationship | 1 |
| 1.1. <i>Introduction</i> | 1 |
| 1.2. <i>The Hammett equation</i> | 1 |
| 1.3. <i>The reaction constant ρ</i> | 7 |
| 1.4. <i>The substituent constant σ</i> | 11 |
| 1.5. <i>The σ^0 scale</i> | 17 |
| 1.6. <i>The effect of solvent on σ values</i> | 20 |
| 1.7. <i>Problems</i> | 24 |
| 2 Elucidation of reaction mechanisms | 27 |
| 2.1. <i>Introduction</i> | 27 |
| 2.2. <i>Modified substituent constants</i> | 27 |
| 2.3. <i>The σ^- substituent constant</i> | 28 |
| 2.4. <i>The σ^+ substituent constant</i> | 31 |
| 2.5. <i>Diagnosis of reaction mechanisms</i> | 33 |
| 2.6. <i>Aromatic nucleophilic substitution</i> | 38 |
| 2.7. <i>Aromatic electrophilic substitution</i> | 40 |
| 2.8. <i>Nucleophilic aliphatic substitution</i> | 49 |
| 2.9. <i>Condensations of carbonyl compounds with amine derivatives</i> | 57 |
| 2.10. <i>Free radical and multicentre reactions</i> | 63 |
| 2.11. <i>Conclusion</i> | 66 |
| 2.12. <i>Problems</i> | 67 |
| 3 The separation of inductive, resonance and steric effects; application of the Hammett equation to aliphatic systems | 69 |
| 3.1. <i>Introduction</i> | 69 |
| 3.2. <i>The evaluation of inductive effects</i> | 70 |
| 3.3. <i>Esterification and ester hydrolysis: the Taft equation</i> | 75 |
| 3.4. <i>The evaluation of resonance effects</i> | 83 |

| | | |
|-------|--|-----|
| 3.5. | <i>The Yukawa–Tsuno equation</i> | 86 |
| 3.6. | <i>Some attempts to evaluate <i>o</i>-substituent constants</i> | 92 |
| 3.7. | <i>Problems</i> | 94 |
| 4 | Application of the Hammett equation to data other than side chain reactivities of substituted benzenes | 96 |
| 4.1. | <i>Heteroaromatic systems</i> | 96 |
| 4.2. | <i>The heteroatom as reaction site</i> | 96 |
| 4.3. | <i>The heteroatom as substituent</i> | 99 |
| 4.4. | <i>The heteroatom as part of the communicating system between reaction site and substituent</i> | 103 |
| 4.5. | <i>Five-membered ring heteroaromatic compounds; the extended selectivity treatment</i> | 104 |
| 4.6. | <i>Polycyclic systems: biphenyl</i> | 108 |
| 4.7. | <i>Polycyclic systems: naphthalene</i> | 111 |
| 4.8. | <i>Non-bonding molecular orbital theory</i> | 111 |
| 4.9. | <i>Application of the Hammett equation to spectral measurements</i> | 126 |
| 4.10. | <i>Problems</i> | 130 |
| 5 | Thermodynamic aspects of the Hammett equation | 133 |
| 5.1. | <i>Introduction</i> | 133 |
| 5.2. | <i>Basic thermodynamic formulae</i> | 138 |
| 5.3. | <i>The Hammett equation: a linear free energy relationship</i> | 142 |
| 5.4. | <i>The isokinetic relationship</i> | 144 |
| 5.5. | <i>Internal and external contributions to ΔH and ΔS</i> | 150 |
| 5.6. | <i>The Hammond postulate</i> | 152 |
| 5.7. | <i>Problems</i> | 159 |
| | Problem discussion | 161 |
| | References | 188 |
| | Index | 193 |