

Index

- accuracy of Hammett correlation, 7, 100
 acetaldehyde hydrate, acid catalysed
 dehydration, 82
 acetophenone, resonance effects in, 13
 acid dissociations, 6
 acetic acids, 76, 77, 82
 alcohols, 82
 amidonium ions, 172
 anilinium ions, 8, 28–9
 arenium ions, 123, 125
 benzoic acids, 1–2, 4, 7, 8, 18, 23, 25,
 26, 135, 142–4, 164
 bicyclo[2.2.2]octane carboxylic acids,
 71–3, 74
 bicyclo[2.2.1]heptane carboxylic acids,
 73
 biphenyl 4-carboxylic acids, 131, 180
 cinnamic acids, 8
 ethano-bridged dihydroanthracene
 carboxylic acids, 74
 formic acids, 134–6
 1-hydroxypyridinium ions, 104–5
 malonic acid, 73
 naphthoic acids, 118–19, 132, 180
 phenols, 8, 29–31, 67, 104, 166
 phenylacetic acids, 8, 19
 phenylphosphonic acids, 3, 4, 8
 phenylpropionic acids, 8, 19
 protonated benzaldehydes, 172
 pyridine acetic acids, 101
 pyridine carboxylic acids, 99–101,
 103–4
 pyridinium ions, 96–9
 pyrrole 2-carboxylic acids, 107
 quinoline 2-carboxylic acids, 132,
 182–3
 succinic acids, 73
 activated complex, *see* transition state
 acylium ions, 169, 171, 187
 additions to double bonds
 bromine, 83
 chlorine, 83
 additions to double bonds—*cont.*
 dichlorocarbene, 83
 2,4-dinitrosulphenyl chloride, 83, 95,
 176
 2-nitrobenzenesulphenyl chlorides,
 94–5, 176
 additivity of substitution effects, 26, 67,
 103, 107, 164–6
 alkylbenzenes, α hydrogen abstraction
 by radicals, 63–4
 alternant hydrocarbons, 112–26
 anchimeric assistance, 51
 1-anilino-2-naphthol, *see* 1-bromo-2-
 naphthol
 Arrhenius activation energy, 141, 159,
 183
 2-arylethyl *p*-toluene sulphonates, solvo-
 lysis, 51–3, 124–6
 azobenzenes, basicity, 89
 azulene, 113
 Beckmann rearrangement, 89
 Bell–Evans–Polanyi principle, *see* Ham-
 mond postulate
 bell-shaped rate–acidity profiles, 59
 benzamides, basic hydrolysis, 24–5,
 161–2
 benzenesulphonyl chlorides, hydrolysis
 catalysed by pyridines, 136–8
 benzylation of amines, 8, 11
 benzhydryl chlorides, methanolysis, 89
 benzyl, NBMO coefficients, 114–15
 benzyl *p*-toluene sulphonates, hydro-
 lysis, 49–51
 benzylamines, as nucleophiles, 40
 biphenyl, electrophilic substitution, 43,
 45, 108–11
 Boltzmann's constant, 140
 1-bromo-2-naphthol, substitution of
 bromo group with anilines, 53–5
 Brønsted equation, 27, 156
 butadiene, 113

- carbonium ions, 31, 49–53, 55–7, 114, 124–5, 172, 186–7
- carbanions, 114, 115
- chlorobenzene, substitution of chloro group by methoxide ions, 159, 185–6
- N-p*-chlorobenzylidene aniline, from *p*-chlorobenzaldehyde and aniline, 58
- 1-chloro-2,4-dinitrobenzene
 substitution of chloro group by benzylamines, 40
 substitution of chloro group by phenoxide ions, 154–5
- 1-chloro-2- and 4-nitrobenzene
 substitution of chloro group by methoxide ions, 159, 185–6
 substitution of chloro group by piperidine, 39
- compensation law, *see* isokinetic relationship
- conformational free energies of mono-substituted cyclohexanes, 78
- cyclobutanes, from tetracyanoethylenes and substituted styrenes, 66
- cyclohexenes, addition of 2,4-dinitrobenzenesulphenyl chloride, 94–5, 176–7
- diazine esters, basic hydrolysis, 102–3
- diazoacetophenones, decomposition in acetic acid, 89, 90–1
- 1,4-dichloro-2-nitrobenzene, substitution of chloro group by phenoxide ions, 154–5
- dielectric constant, 74
- diffusion controlled reactions, 157
 nitration, 43
- dimethyl sulphoxide, 75, 176
- diphenyldiazomethanes, decomposition in benzoic acid, 89
- 2,6-dimethylbenzoyl chlorides, hydrolysis, 67, 169
- dipole moments, 127
- electronic effects of substituents
 acetyl, 13, 14
 acetylamino, 25, 162
 alkyl, *see individual names*
 amino, 15, 16, 18, 23, 90
 ammonium, 23
 aza, 99–103
 azonium, 99–103
 benzoyl, 87–8
 bromo, 15, 73
 electronic effects of substituents—*cont.*
t-butyl, 16, 73, 128
 carbomethoxy (ethoxy), 14, 73, 97–8
 carboxylate, 132, 180
 chloro, 15, 73
 cyano, 14, 73, 97–8
 cyclopropyl, 25, 162
 ethyl, 16, 73, 128
 fluoro, 15
 formyl, 14
 hydroxy, 162
 iodo, 15, 25, 163–4
 isobutyryl, 15
 isopropyl, 16, 73, 128
 methoxy, 15, 16, 18, 73, 116
 methyl, 2, 16, 73, 128
 methylsulphonyl, 25, 163
 methylsulphoxy, 25, 163
 nitro, 2, 14, 73, 97–8, 117
 β -nitrovinyl, 25, 162
 phenyl, 25, 108–11, 162
 phenylazo, 87–8
 picryl, 25, 164
 pivaloyl, 15
 propionyl, 15
 trifluoromethoxy, 25, 163
 trifluoromethyl, 25, 162
 trimethylammonium, 12, 17, 73, 128
- electrophilic aromatic substitution (S_EAr), 40–9, 55–7, 91–2, 104–6, 118–23
 acetylation, 43–5, 106, 109
 benzoylation, 160, 186–187
 benzylation, 159, 186–187
 bromination, 43–5, 89, 106, 109, 125
 bromodeboronation, 89
 chlorination, 43–5, 106, 109, 125
 deuterodeprotonation, 125
 ethylation, 43–5, 109
 iododeboronation, 106
 mercuration, 154
 mercuridesilylation, 91–2, 109
 nitration, 42–8, 89, 125
 protodegermylation, 109
 protodesilylation, 67, 91, 106, 109, 125, 166–7
 protodestannylation, 91
 protodetrifitation, 106, 109, 118–20, 125
see diffusion controlled reactions,
 furan, pyrrole, thiophene
- eliminations
 E1, 31
 E2, 170

- eliminations—*cont.*
 E1_{cb}, 170
 esters and carbonates, 21–3, 93, 150
 β-arylethyl halides, etc., 68
 encounter pair, 43
 enthalpy changes, 133–59, 183–5
 entropy changes, 133–59, 183–5
 ester hydrolysis, 3–6, 8–10, 19, 68, 75–83, 92–3, 94, 95, 101–3, 118–20, 132, 154–5, 180
 A_{Ac}2, 75, 171–2, 177–8
 A_{Ac}1, 171–2, 177–8
 A_{Al}1, 172, 177–8
 B_{Ac}2, 75
 ethylene oxides, acid catalysed hydrolysis, 82
 extended selectivity treatment, 104–6, 108
 external (environmental) contributions to enthalpy and entropy changes, 150–2

 fluorene
 derivatives, 55–7
 electrophilic substitution, 110
 fluorobenzenes, substitution of fluoro group by methoxide ions, 159, 183–4
 free radical reactions, 63–5
 frequency factor, 141
 fulvene, 113
 furan(s), electrophilic substitution, 104–7

 Gibbs free energy, 1, 133–59, 183–5

 Hammond postulate (*see also* reactivity–selectivity principle), 104, 152–8, 159, 185–7
 Huckel molecular orbital (HMO) theory, 113
 hydrogen bonding, 23, 179
 hyperconjugation, 15–17, 73, 80–1, 162

 inductive effect (*I*), 1, 11–12, 69–86
 transmitted through space (*D*), 12, 130
 transmitted through σ bonds (*I*_σ), 12, 130
 transmitted through π bonds (*I*_π), 12
 infrared (IR) spectra,
 band intensities in monosubstituted benzenes, 127
 carbonyl stretching frequencies, 132, 183
 internal contributions to enthalpy or entropy changes, 122, 150–2

 isoenthalpic series, 144
 isoentropic series, 144
 isokinetic relationship, 144–9
 isotope effects, 40, 68, 154, 170
 isotopic labelling, 53

 kinetic energy, 133

 linear enthalpy–entropy relationship, *see* isokinetic relationship
 linear free energy relationship, 142–4
 Lossen rearrangement of acylhydroxamic acids, 67, 167

 Meisenheimer complex, 38, 175
 mesomerism, *see* resonance
 2-methoxytropone, basic hydrolysis, 132, 181–2
 methyl picrate, reaction with substituted dimethylanilines, 21
 molecular orbital calculations, 27, 111–26, 156
 multicentre reactions, 64–6

 naphthalene, 111, 123
 naphthylmethylene, NBMO coefficients, 115
 nitramide decomposition, 82
 nonalternant hydrocarbons, 113
 non-bonding molecular orbital (NBMO) theory, 111–26
 nuclear magnetic resonance (NMR), 126, 128–31, 156, 179
 Taft's shielding parameters, 128–9
 nucleophilic aliphatic substitution (S_N1, S_N2), 31, 49–57, 96–8, 168, 172
 nucleophilic aromatic substitution (S_NAr), 38–40, 94, 154–5, 159, 173–6, 183–6

 Ogg–Polanyi–Hammond postulate, *see* Hammond postulate
 ortho substituents, 3–5, 92–3

 phenanthrene, 123
 phenylhexachlorobicyclo[2.2.1]heptenes, 129–30
 4-phenyl-4-hydroxy-2-butenes, rearrangement, 89
 2-phenyltriarylcarbinols, cyclodehydration to fluorenes, 55–7
 phenyltrimethylsilanes, 67, 166–7
 p*K*_a's, *see* acid dissociations
 potential energy, 133
 pyridines, quaternisation, 96–8

- pyrolysis of esters and carbonates, 21–3, 93, 150
- pyrrole(s), electrophilic substitution 104–7
- quaternisation
 amines, 8–11, 21
 pyridines, 96–8
- reaction constants, *see* rho values
- reactivity numbers, 121–6
- reactivity–selectivity principle, 153, 159, 186
- resonance effect (*R*), 1, 12–13, 83–6
- rho values (table), 8
 ρ_D, ρ_S, ρ_R , 85–6
- selectivity relationship, 47
- semicarbazone formation, 58–63, 89, 94, 173–4
- sigma values
 σ (table), 3, 101, 117
 σ^0 (table), 18
 σ_o (table), 93
 σ^+ (table), 33, 107, 118
 σ^- (table), 29, 87
 σ^* (table), 80, 82
 σ_I (table), 14, 15, 16, 71, 80, 84, 128
 $\sigma_R, \sigma_R^o, \sigma_R^-, \sigma_R^-$ (table), 14, 15, 16, 84, 127
- solvent effects, 8, 20–4, 74–5, 81–2, 128–9, 152, 154, 176
 on ρ , 8, 152
 on σ , 20–4, 128
- steady state (Bodenstein) approximation, 34
- steric effects, 1, 3–5, 75–83, 92–3
- steric parameter (E_s), 75–83, 92–3
- styrenes, *see* cyclobutanes
- substituent constants, *see* sigma values
- substituents, *see* electronic effects
- symmetrical reactions and equilibria, 142–4
- Taft equation, 75–83, 92–3, 94, 172–3
- tautomerism
 aminobenzoic acids, 23
 3-hydroxypyridine, 131, 179
 isonicotinic acids, 99–101, 132, 180
 quinoline 2-carboxylic acids, 132, 183
 Schiff bases, 130–1, 179
- temperature effects
 on ρ , 147, 152
 on σ , 148–9
- tetracyanoethylene, *see* cyclobutanes
- thermal capacity, 148–9
- thiophene(s), electrophilic substitution, 104–7
- through conjugation, 17–18, 28–9, 31
- trans*-2-(benzoyloxy-)-cyclohexyl *p*-toluene sulphonates, 67, 168–9
- transition state theory, 9, 139–41
- transmission coefficient, 140
- triethylphenoxysilanes, basic hydrolysis, 87–8
- trimethylboron adducts of amines, 150–1
- triphenylcarbinyl chlorides, ethanolsis, 89
- tritionaphthalenes, protodetritiation, 119–21
- ultraviolet (UV) spectra
 benzene, 12
 trimethylanilinium ion, 12
- urethanes, formation from ethyl chloroformate and anilines, 68, 170
- van der Waal's radii, 79
- voltmeter analogy, 11, 156
- Wheland intermediate (σ complex), 40–1, 44, 48, 121
- Woodward–Hoffmann rules, 66
- Yukawa–Tsuno equation, 86–92, 94, 107, 108, 173, 182
- zwitterions
 aminobenzoic acids, 23
 3-hydroxypyridine, 131, 179
 isonicotinic acid, 99
 4-methoxyquinoline 2-carboxylic acid, 183
 reaction of tetracyanoethylene and styrenes, 66