

Cambridge University Press

978-0-521-29014-2 - Electrophilic Halogenation: Reaction Pathways Involving Attack by Electrophilic Halogens on Unsaturated Compounds

Peter B. D. de la Mare

Index

[More information](#)

## Index

---

- aceneaphthylene, chlorination of, 76, 80, 102–4, 105
- acetaldehyde, 188–90, 193
- acetals, 190
- acetamidonaphthalenes, fluorination of, 59–60
- acetamido substituent, 67–8, 71
- acetanilide, and derivatives, 37, 67–8, 118
- acetic acid, as solvent, 30, 35, 37, 56, 65ff, 88–90, 91, 102, 103, 105, 119, 127–8, 131ff, 142, 148, 150, 155, 161, 162, 167, 175, 178, 187, 191, 201–2, 207
- acetic anhydride, 191–2  
as solvent, 51
- acetone, 179–80, 183–4
- acetonitrile, as solvent, 169
- acetophenones, substituted, 185
- 3-acetoxycholesta-3,5-diene, 152
- acetoxyl, as substituent, 40
- acetoxylation, by addition–elimination, 51
- N*-acetyl carbazole, 201–2
- N*-acetyl-2,3-dimethylindole, 200
- acetylenic compounds, 92–3, 114–15, 116, 133, 169–71
- acetyl hypochlorite, *see* chlorine acetate
- acidity functions, 10, 107, 125, 181
- acids  
as catalysts, 9, 31, 66, 107–10, 134, 136–7, 179ff, 206ff  
general, *see* general acids  
Lewis, *see* Lewis acids
- acrylic acid, and derivatives, 67, 172
- acrylonitrile, 120
- activated processes, 3
- activation, free-energy of, 14–15  
*see also* energy of activation
- active hydrogen, 177ff
- addition, definition of, 17
- addition–elimination pathways, 51–2, 54, 91–2, 155–8, 209–12
- aldehydes, halogenation of, 188–90
- aldoses, oxidation of, 189
- alkyl and aryl migrations, 50–1, 86–7, 122, 148–9, 156–8, 163–4, 174
- alkyl aryl sulphenate esters, 178
- alkyl aryl sulphides, 157, 178
- allene and methyl-substituted derivatives, 43, 93–4, 114–15
- allenic cations, 149, 162
- allyl bromide, and derivatives, 51, 144–5, 147, 163
- allyl chloride, and derivatives, 81, 111–13, 144–5, 147, 163
- allyl derivatives, halogenation of, 125, 144–5, 147, 163
- allylic rearrangement, 73, 156–7
- allyl trimethylammonium perchlorate, 125
- aluminium chloride, 208  
as catalyst for additions, 114–15  
*see also* Lewis acids
- amines, aromatic, *see* aniline
- aminopyridines, 212
- anchimeric effect, 40  
*see also* neighbouring-group interaction
- aniline, and derivatives, 5ff, 118–19, 153, 156–8, 164–5, 169  
*see also* acetanilide; dimethylaniline

- anisole  
 bromination of, 150, 183, 198  
 charge-transfer complexes of, 25  
 chlorination of, 100  
 iodination of, 165
- antimony pentachloride, 120, 122
- antimony pentafluoride, 41
- aromatic aldehydes, oxidation of, 190
- aromatic hydrocarbons, polycyclic, 67, 126–7
- aromatic side-chain–nucleus rearrangement, 46, 119, 176
- Arrhenius parameters, *see* energy of activation; entropy of activation
- arylethylenes, *see* ethylenes, aryl-substituted; styrene; styrenes, substituted
- arylpropenes, *see* styrenes, substituted
- astatine, 20, 23, 34
- auric chloride, chlorination by, 123
- axial–equatorial rearrangement, 157
- azidocarbon disulphide, 41
- azulenes, iodination of, 165
- bases, as catalysts, 9, 178, 192  
*see also* nucleophiles
- benzamido-substituent, as neighbouring group, 147–8
- benzene, and derivatives  
 bromination of, 1  
 chlorination of, 64  
 iodination of, 166  
 nitration of, 42  
 solvent, 142, 173  
 substitution in, 67; *see also* partial rate factors
- benzene iododichloride, 34–5, 96, 97
- benzocyclobutene, 149
- benzofuran, 59, 199–201
- benzothiophene, 199–201
- benzoyloxy-substituent, 167
- benzyl phenyl ketones, 185
- biphenyl, and derivatives, 60, 67, 87–8
- Bredt's rule, 186
- bromide ions  
 participation of, in halogenations, 132ff  
 rearrangements, catalysts for, 137  
*see also* nucleophiles
- brominations, *see* bromine  
 of kinetic order greater than one, 131ff, 158
- bromine, molecular, as brominating agent, 126ff, 154, 180ff, 197–8, 199, 201, 202, 207–12
- bromine acetate, 150, 166
- bromine azide, 152–3
- bromine cations, 125–6, 206–8  
*see also* halogen cations
- bromine chloride, 9, 23, 145, 149–50, 153
- bromine diquinoline perchlorate, 205, 208
- bromine fluoride, 23, 149–50, 173
- bromine trifluoride, 23
- N*-bromoacetamide, protonated, 9
- bromoacetone, 185
- N*-bromoanilides, 150
- N*-bromo-*t*-butylamine, 152
- bromodeboronation, 126
- bromodecarboxylation, 128
- bromodechromiation, 177–8
- bromodesilylation, 126
- bromodesulphonation, 128, 136
- bromonium cations, 112, 129, 145–6
- bromophenols, isomerisation of, 136
- 3-bromopropene, *see* allyl bromide
- bromosteroids, rearrangement of, 137
- bromo-substituent, 40, 127
- N*-bromosuccinimide, 151, 152
- bromoxyleneols, isomerisation of, 136
- butadiene, and derivatives, 49, 69, 82–3, 104, 149, 156–8, 163–4, 168
- butan-2-one, 185–6, 193
- butenes, *see* ethylenes, alkyl-substituted
- t*-butylbenzene, 72, 108, 125
- t*-butylcyclohexanone, 183–4
- t*-butylcyclohexene, 151
- t*-butylethylene, 145
- t*-butylhemimellitene, 135
- t*-butyl hypobromite, 151, 178
- t*-butyl hypochlorite, 35, 36, 96, 104–6, 107, 116
- 1-*t*-butyl-2-phenylethylenes, 78
- t*-butyl substituent, 71, 127  
 displacement of, 72
- camphorquinone, 186
- carbazole, 201–2
- carbenes, 42, 43–4
- carbomethoxy-substituent, 136
- carbon tetrachloride, as solvent, 98, 99, 100, 142, 150, 154, 161, 183–4, 185, 207, 209
- carbonyl compounds,  $\alpha\beta$ -unsaturated, 66, 77–8, 134, 194

- carboxylic acids, and esters, 190–2
- carboxy-substituent, displacement of, 72
- catalysts
- acid, 9, 31, 66, 107–10, 134, 136–7, 179ff, 206ff
  - base, 9, 178, 192; *see also* nucleophiles
- chain (radical) reactions, *see* homolytic reactions
- charge-transfer complexes, 24–5, 32
- chloride ions, participation, in halogenations, 66, 74–6, 82ff, 122
- N*-chlorination, 37
- chlorine, molecular, as chlorinating agent, 64ff, 138, 180ff, 197–8, 201–2
- chlorine acetate, 35, 96, 101–4, 107, 115–16, 166
- chlorine azide, 96, 120
- chlorine cations, 101, 107–10, 116–17
- see also* halogen cations
- chlorine fluoride, 23, 96, 97
- chlorine monoxide, 35, 96, 100–1
- N*-chloroacetamide, 35, 96
- N*-chloroacetanilide, 35, 96, 117
- chlorobenzene, as solvent, 106
- N*-chlorobenzene sulphonamide, 35, 96, 117
- chlorodecarboxylation, 72
- N*-chlorodimethylamine, 117–18
- chloroethylene, 81
- chloroform, as solvent, 59, 76, 137, 143, 164, 168, 172, 210
- chlorolactonisation, 79–80
- N*-chloro-*N*-methylaniline, 118–19
- N*-chloromorpholinium cation, 119
- chloronium cations, 69–70, 75, 94, 112, 114–15, 163
- 3-chloropropene, *see* allyl chloride
- chloro-substituent, 11, 40
- N*-chlorosuccinimide, 118
- cholestan-3-one, 187–8
- cholest-2-ene, 75
- cholest-5-en-3-one, bromination of, 155–8
- cholesterol, and derivatives, 145–6, 156–8, 173
- chromium, displacement of substituted, 177–8
- cinnamaldehyde, 66
- cinnamate ion, 72
- cinnamic acid, and derivatives, 67, 77, 99, 102–4, 172
- colligation, definition of, 2
- complexes
- charge-transfer, 24–5, 32
  - molecular, 53–4, 126, 138ff, 160, 162, 169, 204
  - $\sigma$ , 53–4, 139–40, 161, 169, 204
- concerted (synchronous) processes, 3, 15, 17, 43–7, 54, 103–4, 132–3, 135–6, 169–71
- conjugated carbonyl compounds, *see* carbonyl compounds
- conjugated dienes, 69
- see also* butadiene; isoprene
- conjugative effect, 11, 38ff
- co-ordination, definition of, 2
- co-ordination numbers, of halogen compounds, 21
- copper(II) bromide, 180
- copper(II) chloride, 121–2, 180, 186
- covalent halides, 30
- as sources of electrophilic halogen, 34ff
- cyanogen, 41
- N*-cyanoquinolinium ion, 211
- cyclic transition states, 37, 46, 57, 83, 98, 104, 122, 148, 151, 167, 171–2, 191
- cycloalkenes, 75, 98, 122, 143, 151
- cyclohexane
- derivatives of, 148
  - as solvent, 160
- cyclohexenes
- bromination of, 143, 151
  - chlorination of, 122
- cyclohexyl methyl ketone, 185
- cyclopentadiene, 149, 178
- cyclopropanes, bromination of, 177
- deboronation, bromo-, 126
- decarboxylation
- bromo-, 128
  - chloro-, 72
  - iodo-, 175
- deiodination
- iodo-, 169–71
  - proto-, 166
- demercuration, 46
- iodo-, 161
- demetallations, halogeno-, 177–8
- desilylation, 50, 72
- bromo-, 126
  - iodo-, 161
  - nitro-, 47
- destannylation, iodo-, 161
- desulphonation, 72
- bromo-, 128, 136

Cambridge University Press

978-0-521-29014-2 - Electrophilic Halogenation: Reaction Pathways Involving Attack by Electrophilic Halogens on Unsaturated Compounds

Peter B. D. de la Mare

Index

[More information](#)

226

Index

- deuterium isotope effects, *see* isotope effects
- p*-diacetamidobenzene, 67–8
- di-*t*-butylethylene, 75
- 2,6-di-*t*-butylphenol, and derivatives, 127–8
- 1,2-dichloro-1,2-dihydronaphthalene, 77
- 2,4-dichloro-1-naphthol, 74
- 2,3-dichloroprop-1-ene, 114
- Diels–Alder reaction, 43
- dienes, conjugated, 69  
*see also* butadiene; isoprene
- dienones, rearrangement to phenols and naphthols, 36, 73–4, 88, 127–9, 136–7, 141–4, 153, 156–7, 160–1
- diethylchloroamine, 119
- diethyl ether, as solvent, 162, 196
- diethyl malonate, 9, 190–2, 194
- diffusion control, of reaction rates, 182–3, 191
- 9,10-dihydro-9,10-etheno-anthracene, 163–4
- dimedone enol methyl ether, 183
- dimethoxymethane, 190
- dimethoxystilbene, 164
- 2,6-dimethylacetanilide, 67–8
- 1,1-dimethylallyl alcohol, 147
- N,N*-dimethylaniline, 135, 160, 198, 212
- 2,3-dimethylbenzothioephene, 201
- dimethylformamide, as solvent, 143, 161, 178, 186
- 1,5-dimethylnaphthalene, 135
- 3,4-dimethylphenol, and derivatives, 89–91
- dimethyl sulphoxide, as solvent, 143, 152
- 2,4-dinitrobenzenesulphenyl chloride, 47
- 2,4-dinitrotoluene, 58
- dioxan, as solvent, 63, 110, 111, 143, 154
- dioxan dibromide, 143
- 1,1-diphenylethylene, and derivatives, 55, 61–2
- displacements, terminology, 18
- disproportionation, of *p*-bromophenol, 137
- double-bond rearrangement, 17, 49, 59, 69, 82–5, 87–91, 104–5, 149, 152, 156–8, 160–1, 168, 200
- electrophiles (electrophilic reagents)  
classification of, 42–3  
definition of, 2  
electrophilicity, relative, 36ff
- elimination  
homolytic, 155–8  
of iodine, 169–71  
enamines, 184, 206
- energy diagrams, 2–5, 84, 85
- energy of activation, 3, 14, 138
- enol esters, 59, 152
- enol ethers, 183
- enols, and enolisation, 180, 182, 186, 187, 191, 192
- enthalpy of activation, *see* energy of activation
- entropy of activation, 14, 138
- environmental effects, 8ff, 30  
*see also* solvent effects
- epoxidation, 44
- ethyl acetoacetate, 194
- ethylene  
bromination of, 129–30  
chlorination of, 1, 80, 121  
*see also* ethylenes, alkyl- and aryl-substituted
- ethylene dichloride, as solvent, 32
- ethylenes, alkyl-substituted, 70, 74, 93, 99, 129–31, 133, 144–5  
*see also* isobutene; propene
- ethylenes, aryl-substituted, 139, 144  
*see also* 1,1-diphenylethylene; 1- and 2-phenylprop-1-ene; styrene; styrenes, substituted
- ethylene sulphonate ion, 125
- ferric chloride, 154
- fluorine, molecular, reactions of, 55ff
- fluorobenzene, 60, 63
- fluorochloromethanes, as solvent, 55, 56, 59
- fluoro-substituent, 40
- fluorosulphuric acid, as solvent, 31, 33
- formate ion, oxidation of, 189
- free-energy  
of activation, 14–15; *see also* energy of activation  
linear relationships, 12; *see also* reaction constants, Hammett; substituent constants, Hammett
- free-radical reactions, *see* homolytic reactions
- fumaric acid, and derivatives, 78
- furan, and derivatives, 196–9
- general acids, 9, 31, 181
- D-glucal, 97, 195

- D-glucal triacetate, 77, 168, 173
- halide ions, 28ff, 66, 74–6, 82ff, 122, 132ff, 137, 166ff, 170ff
- halogenation, definition of, 18
- halogen cations, 20–1, 31ff, 101, 107–10, 116–17, 125–6, 165–6, 206–9
- halogen migrations, 50–1, 110–15, 137
- N*-halogeno-compounds, 35, 178, 180  
*see also under N*-bromo-, *N*-chloro-, *N*-iodo-
- halogenocyclohexa - 2,5 - dienones, *see* dienones
- halogenodemetalations, 177–8
- halogens, physical properties of, 19ff
- Hammett acidity function, *see* acidity functions
- Hammett equation, 12  
*see also* reaction constants, Hammett; substituent constants, Hammett
- Hell-Volhard-Zelinskii halogenation, 191
- heterocyclic compounds, 195ff
- heterolysis, definition of, 2
- hexamethylbenzene, 73
- 'hexamethyl-Dewar-benzene', 123
- hex-1-ene, 168
- homolysis, definition of, 2
- homolytic reactions, 9, 43, 55, 64, 142, 159, 177
- hydrocarbons, aromatic polycyclic, 67, 126–7
- hydrogen chloride, addition of, to propene, 42  
*see also* hydrogen halides
- hydrogen fluoride, as solvent, 173
- hydrogen halides  
as catalysts: for halogenation, 60; for isomerisations, 136–7, 181–2  
properties of, 30
- hydroxybenzoic acids, 128
- hydroxyl, as substituent, 11, 40, 171
- hydroxylation, 167–8
- hydroxypyridines, 212
- hyperconjugation, 12, 197  
*see also* no-bond resonance
- hypobromites, organic, 151, 178
- hypobromous acid; and cations and anions derived from, 125–6, 145, 147, 154, 162–3, 178, 194, 208–9
- hypochlorites, organic, 35, 36, 38, 96, 104–6, 107, 116
- hypochlorous acid; and cations and anions derived from, 35, 37, 100, 107–10, 111–15, 145, 162–3, 178, 194
- hypofluorites, organic, 58–60
- hypohalites, organic, 35, 36, 96, 104–6, 107, 116, 151, 178, 192
- hypoiodous acid; and cations and anions derived from, 32, 162–3, 189–90
- imidazole, 202–3
- indene, 63
- indole, 199–201
- inductive effect, 11, 38ff
- interhalogen compounds, 180  
*see also under individual compounds*
- intermediates, 4ff
- intermolecular reactions, 17
- intramolecular reactions, 17, 50, 119, 182  
*see also under* rearrangement
- iodide ions, participation of in iodinations, 166ff, 170ff
- iodine, molecular, as iodinating agent, 159ff, 174, 180ff, 196–7, 199, 202–3
- iodine acetate, 166–8
- iodine azide, 172–4
- iodine bromide, 132
- iodine carboxylates, 166ff
- iodine cations, 159, 160, 165–6, 174  
*see also* halogen cations
- iodine chloride, 23–4, 161ff
- iodine dipyridine cation, 168, 205
- iodine diquinoline perchlorate, 32
- iodine fluoride, 172–4
- iodine isocyanate, 168
- iodine nitrate, 168–9
- iodine trichloride, 96, 99
- N*-iodoanilides, 166
- iododecarboxylation, 175
- iododemercuration, 161
- iododesilylation, 161
- iododestannylation, 161
- iodolactonisation, 171–2
- iodonium cations, 112, 160, 163
- iodo-substituent, 40
- N*-iodosuccinimide, 173
- iodotrifluoromethane, 36
- ion-pairs, 30, 53–4, 138, 140–4, 204
- ipso-position, attack at, 46, 47, 49, 50, 72, 126, 127, 128, 136, 161, 166, 169–71, 175, 177–8
- isobutene, 50, 70, 73, 113–14  
*see also* ethylenes, alkyl-substituted
- iso-oxazole, 203
- isoprene, 83, 105
- isoquinoline, 210

Cambridge University Press

978-0-521-29014-2 - Electrophilic Halogenation: Reaction Pathways Involving Attack by Electrophilic Halogens on Unsaturated Compounds

Peter B. D. de la Mare

Index

[More information](#)

228

Index

- isotope effects, 10, 46, 47–8, 65, 125, 128, 135–6, 165–6, 175, 181, 188, 189, 193, 203
- ketones, 180ff
- kinetic control, of product-proportions, 16, 48, 82–4, 186
- kinetic isotope effects, *see* isotope effects
- kinetic methods, 7ff
- kinetic order, 17  
high, in bromine, 131, 139, 158; in iodine, 161ff  
zeroth, in halogen, 180ff
- lactonisation  
chloro-, 79–80  
iodo-, 171–2
- lead tetrafluoride, 62
- Lewis acids, 9, 30–1, 41, 96, 120–1, 137  
*see also* aluminium chloride, *etc.*
- linear free-energy relationships, 12  
*see also* reaction constants, Hammett; substituent constants, Hammett
- localisation energies, 110, 127
- maleic acid, and derivatives, 78
- mandelic acid, and derivatives, 192
- Markownikoff orientation, 80ff, 111–14, 162, 168, 174
- mechanisms, classification of, 16ff
- mercuric acetate, 35, 166
- mercury, displacement of, *see* demercuration
- mesitylene, 108, 110
- 1-mesityl-1-methylethylene, 142–3
- mesityl oxide, 134
- metal halides, *see* Lewis acids
- metallation, 120
- methanol, as solvent, 56, 57, 130, 145, 185
- methoxybenzene, *see* anisole
- methoxy substituent, 40
- 2-methoxynaphthalene, 106
- p*-methoxystyrene, 47
- p*-methylacetanilide, 67
- methyl cinnamate, 70
- methylene chloride, as solvent, 93, 143, 153, 173
- methylethylenes, *see* ethylenes, alkyl-substituted
- methyl hypochlorite, 96
- 1-methylnaphthalene, 88–9
- 2-methyl-5-nitroisocarbostyryl, 211
- methyl substituent, 40, 67, 127, 129–30
- methyl vinyl sulphone, 134
- mixed halogens, *see* interhalogen compounds
- molecular bromine, *see* bromine
- molecular chlorine, *see* chlorine
- molecular complexes, *see* complexes, molecular
- molecular fluorine, 55ff
- molecular iodine, *see* iodine
- molecularity, of reactions, definition of, 16, 17  
*see also* kinetic order
- molybdenum chloride, 122
- naphthalene, 52, 58, 84–5, 87, 106, 108, 110  
derivatives of, 74, 106, 135
- naphthols, rearrangement to dienones, 160–1
- naphtholsulphonic acids, and ions, 128, 136, 160–1
- neighbouring-group interaction (participation), 40, 48–9, 69, 73ff, 111–15, 129, 163–4, 171–2  
*see also under* rearrangement
- neopentane, 22, 64
- neopentyl ethylene, 51
- nitration, 50, 51, 52
- nitrenium cations, 119
- nitric acid, 175
- nitrobenzene, 58, 60, 125
- nitro-compounds, aliphatic, 192
- nitrodesilylation, 47
- nitroethane, 194
- nitromethane, as solvent, 117–18, 143, 154
- nitrosamine rearrangement, 46
- $\beta$ -nitrostyrene, 82
- nitro-substituent, 40
- p*-nitrotoluene, 117
- no-bond resonance, 32  
*see also* hyperconjugation
- norbornene, 86
- 19-norcholestanones, 188
- nuclear quadrupole resonance and bonding, in trihalide ions, 26–7
- nucleophiles  
capture of, by carbocations, 98, 158, 162  
definition of, 2  
*see also* bases, as catalysts; solvents, nucleophilic

- one-stage (synchronous) processes, *see* concerted (synchronous) processes
- orbital hybridisation, d-, and bonding in trihalide ions, 27–8
- orientation
- of addition, 48–9, 56–7, 60, 80–2, 93, 110–15, 145–6, 162, 173–4
  - of substitution, 66ff, 71, 108–10, 126–7, 136, 153–4, 184–6, 195ff
- Saytzeff, 113
- see also ortho: para* ratios; Markownikoff orientation; partial rate factors
- ortho: para* ratios, 71, 175–6
- see also* orientation of substitution; partial rate factors
- oxazole, 203
- oxidation, of aldehydes by halogens, 189–90
- 2-oxobicyclo[2,2,2]octane-1-carboxylic acid, and esters, 182
- ozone, as electrophile, 42, 52
- [2,2]-paracyclophanes, 136
- partial rate factors, 66–7, 71, 108, 154, 198, 202
- see also* orientation
- 1,3-pentadiene, 69
- penta-iodide ion, 28
- pentamethylbenzene, 166
- pentamethylbenzoic acid, 175
- n-pentane, as solvent, 142, 143
- pent-4-enoic acid, 171–2
- pentenols, 171
- peracetic acid, 162, 166
- perchloryl fluoride, 63, 180
- periodic acid, 175
- peroxides, organic, 9
- phenanthrene, 55, 56, 76–7, 91–2, 102–4, 105, 108, 110
- phenanthridinium cation, 207
- phenol, and derivatives, 63, 88–91, 119, 127–8, 152, 156–8, 166, 176, 183
- isomerisation of, 136
- phenols and naphthols, rearrangement to dienones, 36, 73–4, 88, 127–9, 136–7, 141–4, 153, 156–7, 160–1
- phenol sulphonic acids, 128
- phenyl acetate, 88
- phenylacetic acid, and substituted derivatives, 191–2
- phenylacetylene, 92–3, 116, 133, 194
- 1-phenylbutadiene, 83
- 1-phenylcyclopropane, 177
- phenyldichloroamine, 35, 96
- phenylethylene, *see* styrene
- phenyl hypo-iodite, 176
- 1-phenylprop-1-ene, 56–8, 77
- 2-phenylprop-1-ene, 70–1
- phenylpropenes, substituted, 146–7
- phenylpropionic acid, and anion, 170–1
- phenyl substituent, 67–8, 71
- phosphorus tribromide, 191
- piperylene, 69
- polycyclic aromatic hydrocarbons, 67, 126–7
- polyhalide ions, 25ff
- 'positive bromine', *see* bromine cations
- 'positive chlorine', *see* chlorine cations
- 'positive iodine', *see* iodine cations
- product-proportions
- kinetic control, of, 16, 48, 82–4, 186
  - thermodynamic control of, 16, 82–4, 163–4, 186
- see also* partial rate factors; *ortho: para* ratios
- propene, 42, 70, 82, 100, 111, 162
- derivatives of, 111, 148; *see also* methylethylenes; allyl derivatives
- propionic acid, and anion, 170–1
- propylene, *see* propene
- prototropic rearrangement, 177ff, 203, 212
- pseudo-halogens, 41
- pyrazole, 202–3
- pyridine, and derivatives, 204–12
- catalyst for halogenation, 120, 153
  - hydrotribromide, 143
  - solvent, 63, 162, 168–9
- pyridine N-oxide, 206–8, 210–11
- pyrone, 211–12
- pyrrole, 196–9
- pyrrolidone hydrotribromide, 194
- quinoline, 204–12
- quinoline N-oxide, 210–11
- quinones, 134
- radical-cations, 33, 60–1
- radical (chain) reactions, *see* homolytic reactions
- rate-limiting step, 4
- reaction constants, Hammett, 66–7, 71, 106, 125, 129, 130, 131, 133, 143, 151, 165, 175, 185, 190, 192, 198–9
- reaction co-ordinate, 3ff, 15

Cambridge University Press

978-0-521-29014-2 - Electrophilic Halogenation: Reaction Pathways Involving Attack by Electrophilic Halogens on Unsaturated Compounds

Peter B. D. de la Mare

Index

[More information](#)

230

Index

- reagents, electrophilic, classification of, 42–3
- rearrangement, 54
- alkyl and aryl migration, 50–1, 86–7, 122, 148–9, 156–8, 163–4, 174
  - allylic, 73, 156–7
  - aromatic side-chain–nucleus, 46, 119, 176
  - axial–equatorial, 157
  - dienones to phenols and naphthols, 36, 73–4, 88, 127–9, 136–7, 141–4, 153, 156–7, 160–1
  - double-bond, 17, 49, 59, 69, 82–5, 87–91, 104–5, 149, 152, 156–8, 160–1, 168, 200
  - halogen migration, 50–1, 110–15, 137
  - nitrosamine, 46
  - prototropic, 177ff, 203, 212
  - ring–chain tautomeric, 148, 177
- regiospecificity, *see* orientation
- replacement, with rearrangement, *see under* rearrangement
- replacements, terminology, 18
- reversibility
- of bromination, 136–7
  - of iodination, 159ff
- ring–chain rearrangement, 148, 177
- Saytzeff orientation, 113
- Schiff bases, 204
- selenocyanogen, 41
- selenophen, 198
- silver acetate, 167
- silver benzoate, 167
- silver halides, 33, 108–10, 173
- silver sulphate, as catalyst for halogenations, 116–17, 174, 207–8
- sodium phenylpropiolate, 170–1
- solvent effects, 8ff, 20, 29, 30, 65, 106, 127, 140–4, 163
- solvents
- nucleophilic, capture of, 47, 49–50, 54, 78–80, 105, 111–13, 143, 147, 162
  - pre-equilibria with, 65–6
- solvolysis, of aryl dimethyl carbinyl halides, 12, 13, 40
- stannic chloride, 122
- stereochemical effects, *see* stereochemistry
- stereochemistry
- of additions, electrophilic: bromine, 139–41, 146–8; chlorine, 74ff, 101–4, 122; fluorine, 56–7; iodine, 160–3, 166–8, 170–4
  - of some halogen compounds, 21ff
  - symbolism, 18
  - steric effects, 13ff, 38, 71, 127
  - secondary, 68–9, 130–1, 175–6
  - steroidal olefins, 59–60, 75, 145–6, 155–8, 173
  - steroids, 187–8 (*see also* steroidal olefins)
  - structural effects, 11, 12, 38ff, 133
  - see also* partial rate factors; *ortho*:*para* ratios; substituent constants
  - styrene, 80–1, 105, 120, 174
  - styrenes, substituted, 68–9, 70–1, 98, 129–31, 143, 146–7, 151
- substituent
- acetamido, 67–8, 71
  - acetoxyl, 40
  - benzamido, 147–8
  - benzoyloxy, 167
  - bromo, 40
  - t-butyl, 71, 127
  - carbomethoxy, 136
  - carboxy, 72
  - chloro, 11, 40
  - fluoro, 40
  - hydroxyl, 11, 40, 171
  - iodo, 40
  - methoxyl, 40
  - methyl, 40, 67, 127, 129–30
  - nitro, 40
  - phenyl, 67–8, 71
  - sulphonic acid, 72, 128, 136
  - trimethylsilyl, 47, 50, 72, 126, 161
- substituent constants, Hammett, 12, 13, 39, 40, 44, 66, 125, 133, 151
- substituent effects, 164
- see also* partial rate factors; substituent constants
- substitution
- with rearrangement, *see under* rearrangement
  - terminology, 18
- substrates, classification, 42
- sulphones, 179
- sulphonic acid substituent, 72, 128, 136
- sulphoxides, 178
- sulphur dioxide, as solvent, 41, 177, 190
- sulphuric acid, as solvent, 116, 174, 206–7
- sulphuryl chloride, 35, 96, 106, 180, 186, 196, 199



Cambridge University Press

978-0-521-29014-2 - Electrophilic Halogenation: Reaction Pathways Involving Attack by Electrophilic Halogens on Unsaturated Compounds

Peter B. D. de la Mare

Index

[More information](#)*Index*

231

- synchronous processes, *see* concerted (synchronous) processes
- temperature effects, 14, 138
- termolecular additions, 44–5, 66, 132–3, 169–71, 173, 174
- tetrahydrofuran, 173
- tetrakis(*p*-methoxyphenyl)ethylene, 139
- tetramethylbenzenes, and derivatives, 73, 98
- thallium salts, 153–4, 162, 172
- thermodynamic control of product-proportions, 16, 82–4, 163–4, 186
- thermodynamic factors, 15–16
- thiane, 32
- thiazole, 202–3
- thiocyanogen, 41
- thionyl chloride, as solvent, 209
- thiophene, and derivatives, 63, 196–9
- toluene, 49, 52, 58, 67, 105, 108, 121
- transition-metal fluorides, 62–3
- transition states, 3ff, 37
  - cyclic, *see* cyclic transition states
- tribromide ions, 26ff, 132–4
- tribromobenzene, 178
- trichloride ions, 26ff
- trifluoroacetic acid, 61, 98
- trifluoromethanol, as solvent, 60
- trihalide
  - anions, 13, 26, 132–4
  - cations, 31, 175
- tri-iodide
  - anion, 26ff
  - cation, 175
- trimethylbenzoic acid, 175
- trimethylsilylbenzene, 72
- trimethylsilyl substituent, displacement of, 47, 50, 72, 126, 161
- triphenylene, 108, 110
- 1,3,5-tris (*N,N*-dialkylamino) benzenes, 144
- vinylacetylene, 149
- vinyl azides, 174
- vinyl bromide, 134
- vinyl cations, 92–3, 115
- water, as solvent, 37, 100, 107ff, 111, 125ff, 145, 160, 165, 170, 171, 172, 178, 180ff, 188ff, 192ff, 196–7, 208, 211, 212
- Wijs' solution, 24
- xenon difluoride, 60–2
- xenon tetrafluoride, 62
- xylenes, 51, 108, 110, 129
  - solvent, 176
- zeroth order kinetics, 180ff
- zinc chloride, as catalyst
  - for bromination, 132
  - for iodination, 162