

INDEX

- ab initio* calculations
estimated activation energies, for
 superelectrophilic
 electrocyclizations 47–48
of superelectrophiles
energies of LUMOs, 49
estimation of electronic chemical
 potential, 49–50
estimation of electrophilicity indexes,
 49–50
estimation of chemical hardness,
 49–50
estimation of NBO charges, 49
estimation of NMR chemical shifts,
 50–52
superelectrophilic isodesmic reactions,
 48–49
- Acenaphthenequinone
condensation with deactivated arenes,
 141–142
diprotonated in superacid, 141–142
superelectrophilic, in polymer synthesis,
 142
- Acenaphthenequinone
condensation with benzene, 141
diprotonated in superacid, 141
- Acetic acid
diprotonated, calculated NMR chemical
 shifts, 51–52
diprotonated, calculated structure and
 stability, 212
- Acetoacetamide
condensation with benzene, 199
diprotonation, 199–200
- Acetoacetic acid, diprotonation and NMR
 study, 199–200
- Acetone, diprotonated, 86–88, 157, *see*
 also carboxonium ions
- N*-Acetylpyridinium salts
condensation with benzene, 205
protonation in CF₃SO₃H, 205
- Acetyl cation
electrophilic solvation, 154
superelectrophilic
 from AlCl₃, 154
 reactions with arenes, 155

- Acetylene dication (CHCH^{2+}), structure and stability, 132
- N*-Acetyl-4-piperidone, diprotonation, 258
- Acyl cations
- long-lived, 5
 - monocationic, 269
 - superelectrophilic, 153–155
 - acetyl cation, 153–155
 - from AlCl_3 , 90
 - from HF-BF_3 , 86
 - studied by theoretical methods, 58
 - pivaloyl cation, from AlCl_3 , 154
 - propenoyl cation, 219
 - propionyl cation, 249
- N*-Acyliminium salts, superelectrophilic
- calculated structures, stabilities, and reactions, 207–208
 - evidence for, 207–208
 - in AlCl_3 , 205–206
 - in $\text{CF}_3\text{SO}_3\text{H}$, 207–208
 - reactions with weak nucleophiles, 205–208
- Acyl-transfer, from amides, 267
- Adamanta-1,3-diyl dication
- attempted preparation, 188
 - calculated structure and relative stability, 189
- 2,6-Adamantanedione, diprotonation, 257
- 2,6-Adamantanediyl dication
- attempted preparation, 236
 - calculated structure and relative stability, 189
- Adipic acid, 259
- Adrenaline, formation of dication, 224–225
- Aliphatic 1,3-carbocation, deprotonation, 13
- Aliphatic diesters, diprotonated
- calorimetric studies, 260
 - NMR studies, 260
- Aliphatic glycols
- diprotonation in superacid, 213
 - superelectrophilic pinacolone rearrangement, 213
- Alkenyl *N*-heterocycles, diprotonated, 250–251
- Alkoxy alcohols
- diprotonated, 214
 - superelectrophilic pinacolone rearrangement, 214
- Alkylthioalkylation reaction, with deactivated arenes, 19–20
- Aminoacetals
- forming ammonium-carbenium dications, 204, 225–226
 - forming 1,3-carboxonium-ammonium dications, 204
 - reactions with benzene, 204
- α -Aminoacids
- diprotonation in superacid, 204
 - triprotonation in superacid, 204
- Aminoalcohols
- formation of dications in superacid, 37, 224
 - observation of dications in $\text{FSO}_3\text{H-SbF}_5$, 37, 224–225
 - reactions with arenes in $\text{CF}_3\text{SO}_3\text{H}$, 37, 224
- Aminobutyric acids, diprotonation
- cleavage to acyl-ammonium dications, 262–263
 - NMR studies, 262–263
- 5-Amino-1-naphthol, diprotonation, calculated structures, stabilities, and properties, 266
- NMR studies, 266
 - reactions with weak nucleophiles, 266
- Ammoniaborene dication ($\text{NH}_3\text{BH}^{2+}$)
- structure and stability, 129
 - generation using charge stripping mass spectroscopy, 128–129
- Ammonium group
- activation of adjacent carboxonium ions, 262–268
 - activation of adjacent carbocations, 224
- Ammonium-carbenium dications
- from aminoacetals, 225
 - from aminoalcohols, 224
 - from heterocycles, 225
- Aniline *N*-oxides, formation of geminal dications, 111–113
- reactions in superacid, 111–113

- p*-Anisaldehyde diprotonation
decreased neighboring group
participation, 268–269
NMR studies, 268–269
- Aprotic superacids, 90–91
- Aromatic dications, 12
- Aromatic diesters, diprotonation, 260
- Arsonium dications, 272
- Aryldiazonium dications, 173
- 3-Arylindenones, diprotonated, in triflic acid, 85
- Aspartic acid, triprotonated, 204
- Atomic charge (q_i), 266
- Aza-polycyclic aromatic compounds, 255
- Azonium ions, long-lived, 5
- Benzaldehyde, diprotonated
calculated structures and stabilities, 160
reactions in superacid, 127–128, 158–160
- Benzene elimination, 255
- Benzophenone cyanohydrin, 226
- Benzopinacol, reaction in superacid, 134–135
- Benzoquinone monooxime, 268
- Benzoyl cation, superelectrophilic,
reactions with arenes, 155
- Bicyclic hydrazinium ions
methods of preparation, 169–170
structures, 169
- 1,4-Bicyclo[2.2.2]octadiyl dication, 235–236
- Bi-dentate interaction
with hydrogen bonding catalysts, 93–94
with solid acids, 93
- 1,1'-Binaphthalene-2,2'-diyl dications, 241
- Biological systems, 93–94, 148–150
- 1,1'-Biphenyl-2,2'-diyl dications, 241
- 1,8-Bis(diarylmethyl)naphthalene dications
effects of charge-charge separation, 239–240
preparation and study, 239–240
- Bis(1,3-dioxolanium) dications
calculated structures and stabilities, 261
NMR studies, 260–261
- Bis(fluorenyl) dication, 12–13
- Bis-acyl dications
observation by NMR, 269–270
reactions with arenes, 269–270
- 1,1'-Bisadamanta-3,3'-diyl dication, 237
- Bis-carboxonium ions, diprotonated
1,2,3-indanetrione, 199
1,3-indanedione, 199
2,4-pentanedione, 198–199
- Bis-sulfonium dications, 271
- Boron and aluminum-centered systems, 128–131
- Boron-based ions, superelectrophilic,
studied by theoretical methods, 71
- p*-Bromoanisole, dialkylated, 276
- 2,3-Butanedione
condensation with benzene, 140–141
diprotonation in $\text{CF}_3\text{SO}_3\text{H}$, 140–141
monooxime, diprotonation in $\text{CF}_3\text{SO}_3\text{H}$, 143
- Calorimetric studies
bis-acyl dications, 270
protonation of diesters, 260
protonation of diketones, 257
- Camphor, 245
- β -Carbenium-acyl dications
calculated structures and stabilities, 219
generation in superacid, 218
- 1,3-Carbenium-carbonium dications, 192
- Carbenium ions, superelectrophilic,
studied by theoretical methods, 64–66
- Carbenium-nitrilium dications, 226
- 1,3-Carbenium-oxonium dications, 213–215
- Carbocations
crystalline, 7–8
historical background, 1
long-lived, 5
- Carbon dioxide
protosolvated, 163
superelectrophilic, from Al/AlCl_3 , 91

- Carbonic acid, diprotonated, 163
- Carbonium ions, superelectrophilic, studied by theoretical methods, 60–64
- Carbonyl group
 electrophilic and protosolvation, 5
 electrophilic strength, 4–5
 LUMO, 5
 protonation, 4
 inductive effects of trifluoro and trichloromethyl groups, 22
see also carboxonium ions
- α -Carbonyl nitromethanes, superelectrophilic reactions with benzene, 223–224
- Carbonylation, of dimethyl ether, 116
- Carborane anions, 7–8
- Carboxonium ions
 activating adjacent electrophilic sites, 247
 long-lived, 5
 silylated, 8
 superelectrophiles, 156–164
 superelectrophilic
 diprotonated acetaldehyde, 157
 diprotonated acetone, 157
 from $\text{FSO}_3\text{H}\cdot\text{SbF}_5$, 86–87
 from $\text{HF}\cdot\text{BF}_3$, 86–88
 generated in triflic acid, 82–83
 hydride abstraction, 157
 observation of by NMR, 37–38
 piperidones, 205, 262
 pivaldehyde, 8, 214–215
 promoting rearrangements, 160–163
 studied by theoretical methods, 53–58
- Carboxonium-carbenium 1,3-dications, 194–198
- Carboxonium-vinyl dication, 197–198
- Carboxylation
 of alkyl groups, 243–244
 superelectrophilic with CO_2 , from AlCl_3 , 91
- Carboxylic acids, diprotonated, 88–89, 211–212
- CCl_2^{2+}
 reaction with Cl_2 , 45
 structure and stability, 109
- CF_2^{2+}
 gas phase reactions, 45, 109
 structure and stability, 109
- CF_3^{2+} ion, gas phase formation and reactions, 167–168
- C-H σ -bond protonation, from $\text{HF}\cdot\text{SbF}_5$, 89
- $\text{CH}_2\text{XH}^{2+}$ (X = F, Cl, Br, I) dications, 167
- Chalcone, diprotonation in superacid, 195
- Charge-charge separation
 effect on amino acid ionization, 204
 effecting heats of protonation, 257
 effecting pK_{R^+} values, 238–239
 effecting relative stabilities, 251–253
 in 1,8-Bis(diarylmethyl)naphthalene dications, 238–239
 in charge migration reactions
 aza-polycyclic aromatic compounds, 254–255
 butorphanol, 254
 structural effects, 254–255
 in the Nazarov reaction transition state, 106
 in oxyfunctionalizations, 245–246
 in remote functionalization, 244
 in retopinacol rearrangements, 161
 isomerization of 1,4-dialkyl-1,4-cyclohexyl dications, 234
 isomerization of 1,5-manxyl dication, 234–235
- Chiral dications
 1,1'-Binaphthalene-2,2'-diyl dications, 241
 from 2-oxazolines, 224
 from aminoalcohols, 224
 redox behavior, 241
- N*-Chlorosuccinimide, diprotonated, from $\text{H}_2\text{O}\cdot\text{BF}_3$, 91–92
- Cinnamic acids,
 diprotonation, observation by NMR, 196
 reactions in superacid, 195–196
- Cobalt-stabilized propargyl cations, electrophilicities, 2
- Coulombic explosion, 43
- Coulombic repulsive effects
 alkylation of bromoanisole, 276

- alkylation of dihaloalkanes and dihaloarenes, 275
- ionization of dicarboxylic acid fluorides, 270
- protonation of *o*-methoxybenzene-diazonium ion, 274
- tris(1,3-dioxolanium) trication, 262
- Cryoscopic experiments, 222, 258
- Cyclizations, superelectrophilic
- aza-polycyclic aromatic compounds, 255
 - cyclodehydration, 25–26, 157–158
 - 1,2-ethylenedications
 - ab initio* calculations, cyclization energetics, 137
 - cyclization kinetics and thermodynamics, 136
 - cyclizations to fluorene products, 134–139
 - cyclizations to phenanthrene products, 134–139
 - Grewe cyclization, 249–259
 - Houben-Hoesch reaction, 26–27, 82–83, 146
 - indanones, 195–196
 - Nazarov reaction, 25, 48, 106, 157–158
 - Pictet-Spengler reaction, 28–29, 82–83, 147
 - tetralones, 246–248
- Cyclodehydration of
- 1,3-diphenyl-1-propanone
 - kinetic studies, 25–26
 - pK_{BH^+} , 26
 - activation parameters, 158
 - evidence for superelectrophiles, 157–158
 - use of CF_3SO_3H , 25–26
 - 1,4-Cyclohexanedione, diprotonation, 257
- Cyclohexenone
- diprotonated in $HF-SbF_5$, 194
 - isomerization in superacid, 194
- Cyclopropyl-stabilized 1,3-carbocation
- calculated and experimental NMR data, 189–190
 - method of preparation, 189
- 1,3-Dehydro-5,7-adamantane dication, 12–13
- Diacetylbenzenes, diprotonation, 257
- Diadamanta-4,9-diyl dication, 237
- Dialkylhalonium ions
- formation of geminal superelectrophiles, 119–121
 - superelectrophilic
 - evidence for, 120
 - in the alkylation of arenes, 119
 - structures and stabilities, 120
- 2,2-Diaryl-1,3-indanediones, superelectrophilic rearrangement, 162–163
- Diazenes, dialkylation, 170
- Diazenium dications, methods of preparation, 171
- Diazoles, dialkylation, 170
- Diazomethane
- diprotonation, 172
 - formation of methyldiazonium dication, 172
- Diazonium dications
- calculated structures and stabilities, 171–172
 - diprotonated diazomethane, 172
 - diprotonated dinitrogen ($N_2H_2^{2+}$), 172
- Dibromonium dications, 275
- 1,2-Dicarbonyl compounds, formation of superelectrophiles, 140–143
- Dicarboxylic acid fluorides, reactions to bis-acyl dications, 269–270
- Dicarboxylic acids, diprotonation
- cleavage to acyl cations, 258–259
 - cryoscopic studies, 258
 - NMR studies, 258–259
- Dicationic carbon dioxide (CO_2^{2+})
- formed in the gas phase, 163
 - reactions with H_2 , 164
- 2,4-Dichloro-2,4-dimethylpentane, ionization in superacid, 188
- 1,4-Dihalocubanes, formation of dihalonium ions, 276
- Dihalogen dications ($HXXH^{2+}$, X = Cl, Br), 178
- Dihydro[5]helicene dication, 242
- Diiodonium dications, 275
- Diketones, diprotonation, 140–143, 257
- Dimethyl oxonium ion
- carbonylation, 116
 - superelectrophilic, 115–116

- Dimethylbromonium ion, protosolvation, structures and stabilities, 121, 167
- Dimethylperoxide
alkylation, 175–176
formation of a vicinal dication, calculated structure and stability, 176
- Dimethylsulfoxide
NMR studies from superacid, 177–178
protonation and diprotonation
calculated structures and stabilities, 177–178
GIAO-MP2 NMR data, 177–178
- Diols, diprotonated, 272–273
- 1,3-Dioxane, superacidic ring opening, 213
- Diprotonated
acetaldehyde, 157
acetone, 157
ammonia (NH_5^{2+})
analogous gold complex, 111
calculated structure and stability, 110–111
from gas phase reaction, 110–111
butane ($\text{C}_4\text{H}_{12}^{2+}$), calculated structures and stabilities, 242–243
formaldehyde ($\text{CH}_2\text{OH}_2^{2+}$)
calculated structure and stability, 157
observation in gas phase, 157
reaction with isoalkanes, 157
hydrogen sulfide (H_4S^{2+})
analogous gold complex, 118
calculated structure and stability, 117
evidence for its formation, 117
imines
evidence for, 147
superelectrophilic cyclizations, 147–148
methane (CH_6^{2+})
analogous gold complex, 108
calculated structure and stability, 108
methyl halides, calculated structures and stabilities, 121
nitriles, 145
propane ($\text{C}_3\text{H}_{10}^{2+}$), calculated structures and stabilities, 192–193
 α,β -unsaturated ketones, 194–195
water (H_4O^{2+})
analogous gold complex, 114–115
calculated NBO charges, 105–106
calculated NMR chemical shifts, 51–52
evidence for its formation, 113–114
calculated structure and stability, 114
- Distonic superelectrophiles
1,4-carbocations, 233–234
acyl-carbenium dications, 248–249
acyl-carbonium dications, 248–249
ammonium-carboxonium dications, 262–268
aryl-stabilized carbocations, 237–238
bis-carbonium dications, 242–243
bis-carboxonium dications, 257–262
bis-oxonium dications, 272–274
carbenium-carbonium dications, 243
carbo-ammonium dications, 249–256
carbocationic systems, 232–243
carbo-halonium dications, 256
carbo-phosphonium dications, 256
carboxonium-carbenium dications, 244, 246–247
carboxonium-carbonium dications, 244
cyclopropyl-stabilized, 233–234
dihalonium dications, 274–276
structural requirements, 231–232
sulfur-based dications, 270–271
- Disulfonium dications
methods of preparation, 176–177
reactions, 176–177
- Dithiocarbenium ions, electrophilicities, 2
- Electrocyclization
 α -(methoxycarbonyl)diarylmethanol
NMR observation of
superelectrophiles, 40–41
kinetic studies, 136–137
effects of acidity, 30–31
- Electron transfer, involving HCX^{2+} ions ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$), 109
- Electrophile, strength, 2–5
- Electrophiles, historical background, 1
- Electrophilic activation involving phosphonium, 208
- Electrophilic solvation, 11, 283
- Electrophilicity, 2–3
- Enones
Superelectrophilic

- 3-arylindenones, diprotonated, in triflic acid, 85, 194
- chalcone, 195
- cyclohexenone, 194
- from AlCl_3 , 91
- from HUSY zeolite, 92
- mestyl oxide, 194
- Ester cleavage
 - $\text{A}_{\text{ac}}1$, 209
 - superelectrophilic
 - evidence for superelectrophiles, 209–210
 - need for low temperatures, 99
 - NMR studies, 209–210
- Esters, diprotonated
 - calculated structures and stabilities, 210
 - reactions with arenes, 211
- Ethane dication ($\text{CH}_3\text{CH}_3^{2+}$), structure and stability, 132
- Ethylacetoacetate, diprotonation and NMR study, 199–200
- Ethylene dication ($\text{CH}_2\text{CH}_2^{2+}$)
 - formation in gas phase, 131–132
 - halogenated derivatives, 132
 - hyperconjugation, 126
 - calculated structure and stability, 131–132
- 1,2-Ethylenedications
 - ab initio* calculations, cyclization energetics, 137
 - cyclization kinetics and thermodynamics, 136
 - cyclizations to fluorene products, 135–139
 - cyclizations to phenanthrene products, 135–139
 - evidence for, in fluorene cyclization, 139
 - observation by NMR, 136
- Ethylene glycol, diprotonated, 214
- Ethyleniminium, protonated, calculated structures and stabilities, 146–147
- Ethynyl pyridines, diprotonated, 250–251
- Fluorooxonium dications (FOH_3^{2+} and $\text{F}_2\text{OH}_2^{2+}$), 114
- Fluorosulfonic acid (FSO_3H), use in forming superelectrophiles, 85
- Formic acid, diprotonated, calculated structure and stability, 212
- Formyl cation
 - Gatterman-Koch formylation, 151
 - superelectrophilic
 - calculated structures and stabilities, 153
 - evidence for, 151–153
 - from $\text{HF}\cdot\text{BF}_3$, 88
 - from $\text{CF}_3\text{SO}_3\text{H}$, 84
 - reaction with adamantane, 23
 - reactions with isoalkanes, 22, 151
- Freidel-Crafts acylation
 - reactions of deactivated arenes, 21
 - superelectrophilic acetyl and benzoyl ions, 33
 - involvement of diprotonated esters, 211
 - use of amide derivatives, 267
- Gatterman reaction
 - evidence for superelectrophiles, 145
 - $\text{p}K_{\text{BH}^+}$ of hydrogen cyanide, 32
 - use of $\text{CF}_3\text{SO}_3\text{H}\cdot\text{SbF}_5$, 82–83
 - use of superacids, 32
- Gitionic superelectrophiles
 - 1,3-carbocations, 187–193
 - carbon-carbon vicinal systems, 131–144
 - carbon-halogen vicinal systems, 164–168
 - carbon-nitrogen vicinal systems, 145–151
 - carbon-oxygen vicinal systems, 151–164
 - carboxonium-centered 1,3-dications, 193–212
 - geminal
 - azocations, 110–113
 - carbocations, 108–110
 - delocalization of charge, 105–106
 - halocations, 119–121
 - oxo and sulfocations, 113–119
 - structural considerations, 105–107
 - halogen-centered vicinal-dications, 178–179
 - nitrogen-centered vicinal systems, 168–175
 - noble gas-centered vicinal systems, 179–180

- Gitionic superelectrophiles (*contd.*)
 oxygen and sulfur-centered vicinal
 dications, 175–178
 vicinal, structural considerations,
 125–128
 Glutamic acid, triprotonated, 204
 Glutaric acid, 259
 Grewe cyclization, 249–250
 Guanidinium ion, protonated dication,
 148

 H₂O-BF₃, use in forming
 superelectrophiles, 91–92
 H₄Se²⁺ dication, analogous gold complex,
 118
 H₄Te²⁺ dication, 118
 H₅S³⁺
 calculated
 NBO charges, 106
 structure and stability, 119
 analogous gold complexes, 119
 Halocarbonyl cations, superelectrophilic,
 155–156
 Halogenation, superelectrophilic
 N-halosuccinimides, 201
 Halonium ions, superelectrophilic
 (H₃X²⁺), calculated structures and
 stabilities, 120–121
 Halonium ions
 long-lived, 5
 superelectrophilic, studied by theoretical
 methods, 72–74
N-Halosuccinimides
 superelectrophilic
 calculated structures, stabilities, and
 reactions, 201–203
 reactions with deactivated arenes,
 201–203
 Hammett acidity scale, 6
 Hammett equation, 2
 HCX²⁺ ions (X = F, Cl, Br, I)
 gas phase reactions, 108–109
 calculated structures and stabilities,
 108–109
 Heliomethonium dication (CH₄He²⁺), 180
 Helium dimer dication, He₂²⁺, 12
N-Heteroaromatic compounds,
 diprotonation, 205–206
 2,5-Hexanedione, diprotonation, 257

 HF-BF₃, use in forming
 superelectrophiles, 86–88
 HF-SbF₅, use in forming
 superelectrophiles, 88–89
 Houben-Hoesch reaction
 involving diprotonated nitriles, 146
 superelectrophilic
 kinetic studies, 26–27
 use of CF₃SO₃H-SbF₅, 82–83
 HUSY zeolite, use in forming
 superelectrophiles, 92–93
 Hydrazinium dications
 methods of generation, 168–170
 inductive effects, 126–127
 Hydrazoic acid, diprotonated (H₂N₃H²⁺),
 172
 Hydride transfer, from alkanes or
 cycloalkanes
 to diprotonated naphthols, 91–92
 to superelectrophilic
 acetyl ion, 8–9
 carboxonium ions, 86–87, 157
 trihalomethyl cations, 164–166
 Hydrogen peroxide, studies of protonated
 products, 175
 Hydroxyalkylation
 2,2,2-trifluoroacetophenone, 5
 acetophenone, 5
 superelectrophilic
 N-acetylpyridinium salts, 205
 N-acetyl-4-piperidone, 258
 2,3-butanedione, 31
 carboxonium ions, 38
 diprotonated acetoacetamide, 199
 isatin, 20
 parabanic acid, 20, 203
 4-piperidones, 205, 262
 phosphonium-substituted ketones, 208
 reactions involving deactivated
 arenes, 20–21
 use of low temperature, 98
 with chloral, 21–22
 Hydroxyanilines
 formation of geminal dications,
 111–112
 reactions in superacid, 111–112
 Hydroxycarboxylic acids, diprotonation,
 268
 Hydroxyethers, diprotonation, 273–274

- Hydroxyquinolines
diprotonation
 calculated structures, stabilities, and properties, 264–266
 ionic hydrogenation, 264–265
 LUMO energies, 264–265
 reactions with arenes, 264–265
 superelectrophiles from AlCl₃, 264
- Hyperconjugation, ethylene dication, 126
- Hypercoordinate ions, superelectrophilic, studied by theoretical methods, 63
- Imines, diprotonated
 from CF₃SO₃H, 82–83
 reactions of, 28–29
- Iminium ions, electrophilicities, 2
- Indenones, diprotonated, 85, 194–195
- Inductive effects, fluorine-substitution, 5
- Infrared and Ramen spectroscopy, use in the study of superelectrophiles, 41–42
- Iodination, of alkanes and cycloalkanes, at low temperature, 96–97
- Ionic hydrogenation
 hydroxyquinolines, 38–39, 264–265
 1-naphthol, 248
 5-Amino-1-naphthol, 266
 carbonic acid, 163
 methanol, 116
- Isatin, superelectrophilic
 condensation with arenes, 142–143
 polymer formation, 142–143
- Isoformyl cation, 151
- Isopentenoyl cation, protonation, calculated structures and properties, 219
- Isopropyliminium, protonated, calculated structures and stabilities, 147
- Isoxazolidines, formation of dications, 216
- Ketoacids
 diprotonation
 cleavage to acyl-carboxonium dications, 257–258
 NMR studies, 257–258
 α -ketoacids
 condensation with benzene, 140–141
 diprotonated, 140
 α -Ketoesters, diprotonated, 140
- Kinetic studies
 estimating nucleophilicities and electrophilicities, 2–3
 use of NMR, 40
 cyclodehydration, 157–158
 Nazarov reaction, 157–158
 Houben-Hoesch reactions, 146
 Pictet-Spengler reaction, 27–28, 147
 stereomutation, role of superelectrophile, 27
- Koch-Haaf carbonylation, superelectrophilic, effect of temperature, 97–98
- Lactic acid
 diprotonation, 213
 formation of lactide in superacid, 213
- β -Lactone, ring opening via superelectrophile, 210
- Lewis acids, electrophilic solvation, 90
- Linear free-energy relationships, 2–3
- Lysine, triprotonated, 204
- Magic acid (FSO₃H-SbF₅)
 use in stable ion conditions for NMR, 86
 acidity range, 6
- Malonic acid, diprotonation and NMR study, 201
- Malonyl fluoride
 preparation of the diacyl dication, 217
 reaction with SbF₅, 217
- Mass-spectroscopy
 charge stripping, 42
 electron ionization, 42
 electrospray ionization, 43
 photoionization, 42
 observation of protoacetyl dication, 44, 155
 observation of protoformyl dication, 153
 observation of protonitronium dication, 43–44
- Mesityl oxide
 diprotonated
 observation by NMR, 194
 reaction with cyclohexane, 194

- Mesityl oxide (*contd.*)
 superelectrophile, AlCl₃ electrophilic solvation, 194
- Metal-free dehydrogenase enzyme, 93–94
 model studies related to, 148–150
- Metallocene catalysts, 7
- Methane
 dicationic ions from mass spectrometry, 108
 diprotonation, 108
 triprotonation, 108
- Methanol
 reactions in superacid, 115–116
 self-condensation, 116–117
- Methionine, triprotonated, 204
- Methyl acetate
 protonation and reaction in superacid, 209–210
 synthesis from dimethyl ether, 118
- 9-Methyl-9-fluorenyl cation, protonation, 191
- Methyl halides, diprotonation
 calculated structures and stabilities, 121, 167
 NBO charges, 167
- Methyl oxonium ion (CH₃OH₂²⁺),
 formation of geminal superelectrophile, 115
 superelectrophilic
 alkylation of arenes, 115
 reaction with hydrogen, 115
- Methyleniminium ion, protonated
 calculated structures and stabilities, 146
 observation in gas phase, 146
- Multi-dentate interaction
 with hydrogen bonding catalysts, 93–94
 with solid acids, 93
- Multiply-charged ions, fragmentation and rearrangements, 12–13
- Nafion-H, use in forming
 superelectrophiles, 92
- Naphthols
 diprotonated
 from AlCl₃, 91–92
 from HF-SbF₅, 89
 reactions with weak nucleophiles, 248
- 2-Naphthol
 protonation and electrophilic solvation, 195
 superelectrophilic ionic hydrogenation, 195
- Naphthyl ethers, diprotonation, 195
- Nazarov reaction
 in superacid, 157–158
 superelectrophilic
 ab initio calculations, 48
 delocalization of charge, 106
 kinetic studies, 25, 157–158
 use of low temperature, 98
 use of CF₃SO₃H, 25
- Neighboring group participation,
 decreasing
 in superelectrophilic activation, 4, 10, 283
 in enzymatic activation, 24
 shown by NMR, 238
 influencing rotational barriers, 268
- NH₃²⁺ dication, structure and stability, 111
- Ninhydrin
 condensation with arenes, 162–163
 superelectrophilic rearrangement, 162–163
- Nitration
 reactivities with deactivated arenes, 18–19, 173–174
 superelectrophilic reactions, 173–174
 superelectrophilic, use of low temperature, 98
- Nitriles, diprotonated, 26–27
- Nitrilium ions, protonation to form
 superelectrophiles, 145
- Nitroethylene
 diprotonated
 evidence for, 220
 reaction with benzene, 220
 reaction in CF₃SO₃H, 35
- Nitrogen-based ions, superelectrophilic,
 studied by theoretical methods, 66–69
- Nitronic acids
 diprotonation, 223
 reactions with arenes, 223
- Nitronium ion
 protosolvation, 174

- reactivities with deactivated arenes, 18–19, 173–174
- superelectrophilic
¹⁷O NMR study, 175
calculated structures and stability, 175
electrophilic solvation with AlCl₃, 173–174
formation in superacids, 173–174
from fluorosulfonic acid, 85
from triflatoboric acid, 84
from CF₃SO₃H, 82–83
study by infrared and Ramen spectroscopy, 41
with AlCl₃, 90
long-lived, 5
reactions with alkanes, 9
- 2-Nitropropene, diprotonated, reaction with benzene, 220
- Nitrosobenzene, formation of geminal dication, 113
- β*-Nitrostyrene, reaction in CF₃SO₃H, 35–36
- Nitro-substituted benzenes, diprotonation
NMR studies, 222–223
reactions with benzene, 222–223
- Nitro-substituted naphthalenes
diprotonation in superacid, NMR studies, 35–36
reaction in CF₃SO₃H, 35–36
- Nitro-substituted olefins
diprotonation in superacid, NMR studies, 35–36, 222
reactions with benzene, 220–222
superelectrophiles from CF₃SO₃H, 82–83
- NMR
necessity of low temperature for studies of superelectrophiles, 99–101
use in the study of superelectrophiles, 34–40
- Noble gas clusters, 44, 179
- Nucleophiles
historical background, 1
strength, 2–5
- Nucleophilicity, 2–3
- Olefinic amines
diprotonated, 250
reactions with arenes, 250
- Oleum (H₂SO₄-SO₃), use in forming superelectrophiles, 82
- Organosulfurane (IV) dications, 118
- Oxalic acid, diprotonated, 140
- Oxalyl chloride
attempted preparation of the oxalyl dication, 216–217
reaction with SbF₅, 216–217
- Oxalyl dication (+OCCO+), calculated structure and stability, 216–217
- Oxamide dication, 142
- Oxazolines
diprotonation, 215
reaction with arenes, 215
ring opening to distonic superelectrophiles, 215
- Oxonium ions
long-lived, 5
superelectrophilic
from FSO₃H-SbF₅, 86–87
from HF-BF₃, 88
from HF-SbF₅, 88–89
from triflatoboric acid, 84–85
studied by theoretical methods, 58–59
see also diprotonated water
trialkylloxonium salts (Meerwein salts, R₃O⁺X⁻)
formation of geminal superelectrophiles, 115
superelectrophilic alkylation of arenes, 115
- Oxyfunctionalization, 245–246
- Ozone, reactions in superacid, 176, 246
- Pagodane dication, 12–13
- Parabanic acid, superacid promoted reactions with arenes, 203
- Phenalenone, 190
- Phenylenediyl dications, pK_{R+} values, 239
- 2,2'-*p*-Phenylene-di-2-propanol, ionization to superelectrophile, 238
- 3-Phenylpropynoic acid, diprotonation, 197–198
- Phosphonium dications, 272

- Phosphonium ions, superelectrophilic, studied by theoretical methods, 69
- Phosphonium-carboxonium dications, 208
- Phthalic acid, 259
- Pictet-Spengler reaction, kinetic study and role of superelectrophiles, 27
- Pimelic acid, 259
- Pinacolone rearrangement, 213
- Piperidones
condensation with benzene, 205
diprotonated, 205
4-piperidone, 262
- Pivaldehyde
diprotonated, 88
superelectrophilic rearrangement
calculated structures and stabilities, 214–215
conditions, 214–215
- Pivaloyl cation, superelectrophilic, from AlCl_3 , 154
- pK_{R^+} value, definition, 3
- p*-Methoxybenzene-diazonium ion, protonation, 274
- Pnictogenocarbenium ions ($\text{CH}_2\text{XH}^{2+}$, X = P, As, Sb)
calculated isodesmic reactions of superelectrophiles, 151
protonation, 150–151
- Polycyclic aromatic hydrocarbons, superelectrophilic gas phase route, 45–46
- Polymer, catalysts, 7–8
- Polymer, polycarbonate and bisphenols, 4
- Polymer synthesis, 285
- 1,3-Propanediol
diprotonation, NMR studies, 272–273
diprotonation, rearrangement to propanal, 272–273
- Propenoyl cation, protonation, calculated structures and properties, 219
- Propionyl cation
evidence for acyl-carbonium dication, 249
protosolvated, calculated structures and stabilities, 249
- Protio-adamantyl dications ($\text{C}_{10}\text{H}_{16}^{2+}$), calculated structures and stabilities, 189
- Proto-*tert*-butyl cation
evidence for, 144
NBO charges, 125–126
- Protoacetyl dication ($\text{CH}_3\text{COH}^{2+}$)
calculated NMR chemical shifts, 51–52
from $\text{HF}\cdot\text{BF}_3$, 153–154
gas phase observation, 44, 155
generation in the gas phase, 155
isodesmic reaction, 48–49
reaction isobutane, 153–154
- Protoformyl dication (HCOH^{2+}), generation in the gas phase, 153
- Protonated iminium dications, 146–147
- Protonitronium dication (HONO^{2+})
calculated NMR chemical shifts, 51–52
calculated structure and stability, 175
gas phase observation, 43–44
generation in the gas phase, 175
- Protosolvated
alkylcarbenium ions, 143–144
alkylcarbenium ions, leading to 1,3-carbocations, 191–192
tert-butyl cation, 144
2-propyl cation, 144
- Protosolvation
acetyl cation, 8–10, 153–154
activated complex, 128
nitronium salts, 9–10
- Pyruvic acid
cleavage to acetyl cation in superacid, 218
diprotonated, 218
- Quantum mechanical Coulombic repulsion energy, 106
- 2-Quinolinol, superelectrophilic ionic hydrogenation, 197
- Rare gas clusters, 43–44
- Retropinacol rearrangement
calculated energetics, 161
promoted by superacids, 160–161
reactions in $\text{CF}_3\text{SO}_3\text{H}$, 29–30
superelectrophilic, 29–30
- Selectfluor[®], 271–272
- Silicenium ions, 8
- Solid acids, use in forming superelectrophiles, 92–93

- Stannyl cation, 7–8
- Stereomutation, kinetic study and role of
 superelectrophile, 27
- Steroid chemistry, 245
- Succinic acid, 259
- Succinic anhydride, diprotonation
 equilibrium with acyl-carboxonium
 dication, 201
 NMR study, 201
- Sulfonium ions, long-lived, 5
- Sulfonium ions
 superelectrophilic
 from $\text{FSO}_3\text{H}\cdot\text{SbF}_5$, 86–87
 studied by theoretical methods,
 69–71
- Sulfuric acid, use in forming
 superelectrophiles, 82
- Superacidic media, 5–6, 283
- Superacids
 Brønsted, definition, 6
 $\text{CF}_3\text{SO}_3\text{H}\cdot\text{SbF}_5$, acidity range, 6
 $\text{FSO}_3\text{H}\cdot\text{SbF}_5$, acidity range, 6
 $\text{HF}\cdot\text{BF}_3$, acidity range, 6
 $\text{HF}\cdot\text{SbF}_5$, acidity range, 6
 $\text{H}_2\text{SO}_4\cdot\text{SO}_3$, acidity range, 6
 nucleophilicity of, 5–6
 properties, 5–6
- Superelectrophilic activation
 effect on LUMO, 93
 historical background, 8
 in acyl-transfer, 267
- Superelectrophiles
 calculational methods and studies,
 46–74
 chemical hardness, 49–50
 classes and categories, 10–11
 effecting equilibria, 128
 electronic chemical potential, 49–50
 electrophilicity index, 49–50
 enzyme system, 23–24, 148–150
 experiments requiring of low
 temperatures, 95–100
 from reactions with Lewis acids, 90–92
 gas-phase studies, 42–46
 in situ generation, 81
 kinetic studies, 24–33
 necessity for elevated temperatures,
 95–96
 partial protonation, 107
 reactions in the gas phase, 44–46
 reactivities
 with alkanes or alkyl groups, 22–23
 with deactivated arenes, 18–19
 with hydrogen, 23–24
 profiles, 18–24
 spectroscopic studies, 33–42
 Wheland intermediates, 190
- Terephthaloyl fluorides, reactions to
 bis-acyl dications, 270
- Terpene chemistry, 244–245
- tert*-Butyl cation, protosolvation, from
 $\text{HF}\cdot\text{SbF}_5$, 89
- Tetraaryl-1,2-ethylene dications
 charge delocalization, 125–126
 chiral derivatives, 132–134
 NMR study, 34
 X-ray crystallography, 34
- Tetrahydropyridines
 diprotonation, 225
 reactions with arenes, 225, 250
- Tetrakis(dimethylamino)ethylene dication
 methods of preparation, 143
 structure, 143
- Tetrakis-(*p*-dimethylaminophenyl)-
 ethylenedication
 methods of preparation, 134
 structure, 134
- Tetralones, 246–248
- Tetramethylammonium ion
 calculated structures and stabilities of
 protonated dications, 168
 protosolvation in superacid, 168
- Tetramethylhexathiaadamantane, 235
- Tetramethylhydrazine, formation of the
 hydrazinium dication, 169
- 2,3,3,4-Tetramethyl-2,4-pentanediol,
 ionization in superacid, 188
- Tetranisylethylene dication
 chemistry of, 133
 methods of preparation, 132–133
 ^{13}C NMR, 134
- Tetraphenylethylene dication
 cyclization, 134–135
 methods of generation, 134–135
 reaction in superacid, 134–135
- Theoretical calculations, kinetic stability
 of superelectrophiles, 11

- Thioalkylcarbenium ion
 superelectrophilic reactions, 19–20
 superelectrophilic, from AlCl_3 , 91
- Thiourea, diprotonated, study by infrared and Ramen spectroscopy, 42
- Tri(*p*-nitrophenylmethyl)cation, pK_{R^+} value, 3
- Trialkyloxonium salts (Meerwein salts, $\text{R}_3\text{O}^+\text{X}^-$)
 formation of geminal superelectrophiles, 115
 superelectrophilic alkylation of arenes, 115
- Trialkylselenonium salts ($\text{R}_3\text{Se}^+\text{X}^-$)
 alkylation of arenes, 118
 formation of geminal superelectrophiles, 118
- Trialkylsulfonium salts ($\text{R}_3\text{S}^+\text{X}^-$)
 alkylation of arenes, 118
 formation of geminal superelectrophiles, 118
- Trialkyltelluronium salts ($\text{R}_3\text{Te}^+\text{X}^-$)
 alkylation of arenes, 118
 formation of geminal superelectrophiles, 118
- Trications, one-carbon, 110
- Triflatoboric acid ($2\text{CF}_3\text{SO}_3\text{H}-\text{B}(\text{O}_3\text{SCF}_3)_3$), use in forming superelectrophiles, 84–85, 115
- Triflic acid ($\text{CF}_3\text{SO}_3\text{H}$)
 use in forming superelectrophiles, 82–83
 with $\text{CF}_3\text{CO}_2\text{H}$, use in kinetic studies, 85
 with SbF_5 , use in forming superelectrophiles, 82–84
- Triflic anhydride, use with triflic acid, 82
- Trifluoroacetic acid
 protosolvated, 211
 diprotonated
 calculated structure and stability, 211–212
 cleavage reactions, 211–212
- Trihalomethyl cations
 protosolvation, from $\text{HF}-\text{SbF}_5$, 89
 superelectrophilic
 calculated structures and stabilities, 165–167
 effect of temperature, 96–97
 evidence for, 164–166
 from AlCl_3 and AlBr_3 , 91
 isodesmic reactions, 166
 reactions with alkanes and alkyl groups, 164–166
- Trihydrobromonium ion (H_3Br^{2+}), formation in superacid, 121
- Trimethylene methane dication, 190
- Triphenylmethyl cation
 historical background, 1
 pK_{R^+} value, 3
 reaction with superelectrophilic nitronium ion, 19
- Triprotonated hydrogen sulfide (H_5S^{3+})
 analogous gold complex, 119
 structure and stability, 119
- Triprotonated methane (CH_7^{3+}), calculated structure and stability, 108
- Triprotonated water (H_5O^{3+}), 119
- Tris(1,3-dioxolanium) trication, 261–262
- Trivalent dicationic nitrogen species (R_3N^{2+}), in superacid reactions, 111–113
- Tscherniac amidomethylation, superelectrophilic, 207
- Two-electron three center bonding, 108
- Unsaturated amides
 diprotonated
 from HUSY zeolite, 92
 from Nafion-H, 92
 reactions with arenes, 197
 superelectrophilic, from AlCl_3 , 91
- Unsaturated carboxylic acids
 diprotonation, 246–247
 reactions with arenes, 246–247
see also cinnamic acid
- Unstable 1,3-carbocations, 188
- UV-visible spectroscopy, use in the study of superelectrophiles, 40–41
- Varying degree of protonation, of superelectrophiles, 27, 127
- Vicinal superelectrophiles, *see* superelectrophiles
- Vinyl dications, 250–251

- Wallach rearrangement, involvement of
aryldiazonium dications, 172–173
- Weakly coordinating anions, 7–8
- Xenon difluoride, 179
- X-ray crystal structure
tetraarylethylene dications, 34
1,8-Bis(diarylmethyl)naphthalene
dications, 238–239
- tetrakis(dimethylamino)ethylene
dication, 143
- Zeolites, electrostatic fields, 284
- Zucker-Hammett Hypothesis, applied to
the study of superelectrophiles,
25

