

Superacid Chemistry

Second Edition

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SECOND EDITION

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SUPERACID CHEMISTRY



In memory of Katherine Bogdanovich Loker, Benefactor and Friend

PREFACE TO THE SECOND EXTENDED AND UPDATED EDITION

More than 20 years passed since the publication of our book on Superacids. The book became out of print and much progress since was made in the field, which is gaining increasing interest and significance. Hence, it seems warranted to provide the interested reader with a comprehensively updated review and discussion of the field with literature coverage until early 2008. The title has been changed to “Superacid Chemistry” to reflect enormous progress in the field. Some aspects of superelectrophilic activation are also discussed (for more elaborate coverage, readers are referred to G. A. Olah and D. A. Klump, “Superelectrophiles and Their Chemistry” Wiley-Interscience, 2008). Our friend and colleague, Árpád Molnár joined us as a coauthor and made an outstanding contribution to the revised new edition of our book, which we hope will be of interest and use to the chemical community. Our publisher is thanked for arranging the new revised edition.

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October 2008

PREFACE TO THE FIRST EDITION

The chemistry of superacids, that is, of acid systems stronger than conventional strong mineral Brønsted acids such as sulfuric acid or Lewis acids like aluminum trichloride, has developed in the last two decades into a field of growing interest and importance. It was J. B. Conant who in 1927 gave the name “superacids” to acids that were capable of protonating certain weak bases such as carbonyl compounds and called attention to acid systems stronger than conventional mineral acids. The realization that Friedel–Crafts reactions are, in general, acid catalyzed with conjugate Lewis–Brønsted acid systems frequently acting as the de facto catalysts extended the scope of acid catalyzed reactions. Friedel–Crafts acid systems, however, are usually only 10^3 to 10^6 times stronger than 100% sulfuric acid. The development in the early 1960s of Magic Acid, fluoroantimonic acid, and related conjugate superacids, 10^7 to 10^{10} times stronger than sulfuric acid, added a new dimension to and revival of interest in superacids and their chemistry. The initial impetus was given by the discovery that stable, long-lived, electron-deficient cations, such as carbocations, acidic oxonium ions, halonium ions, and halogen cations, can be obtained in these highly acidic systems. Subsequent work opened up new vistas of chemistry and a fascinating, broad field of chemistry is developing at superacidities. Because acidity is a term related to a reference base, superacidity allows extension of acid-catalyzed reactions to very weak bases and thus extends, for example, hydrocarbon chemistry to saturated systems including methane.

Some years ago in two review articles (*Science* 206, 13, 1979; *La Recherche* 10, 624, 1979), we briefly reviewed some of the emerging novel aspects of superacids. However, we soon realized that the field was growing so fast that to be able to provide a more detailed survey for the interested chemist a more comprehensive review was required. Hence, we welcomed the suggestion of our publisher and Dr. Theodore P. Hoffman, chemistry editor of Wiley-Interscience, that we write a monograph on superacids.

We are unable to thank all of our friends and colleagues who directly or indirectly contributed to the development of the chemistry of superacids. The main credit goes to all researchers in the field whose work created and continues to enrich this fascinating area of chemistry. Professor R. J. Gillespie’s pioneering work on the inorganic chemistry of superacids was of immense value and inspiration to the development of the whole field. Our specific thanks are due to Drs. David Meidar and Khosrow Laali, who helped with the review of solid superacid systems and their reactions. Professor E. M. Arnett is thanked for reading part of our manuscript and for his thoughtful comments.

Finally we would like to thank Mrs. R. Choy, who tirelessly and always cheerfully typed the manuscript.

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CONTENTS

Preface to the Second Edition	xvii
Preface to the First Edition	xix
1. General Aspects	1
1.1. Defining Acidity	1
1.1.1. Acids and Bases	1
1.1.2. The pH Scale	3
1.1.3. Acidity Functions	4
1.2. Definition of Superacids	6
1.2.1. Range of Acidities	7
1.3. Types of Superacids	9
1.3.1. Primary Superacids	10
1.3.2. Binary Superacids	10
1.3.3. Ternary Superacids	10
1.3.4. Solid Superacids	10
1.4. Experimental Techniques for Acidity Measurements (Protic Acids)	11
1.4.1. Spectrophotometric Method	11
1.4.2. Nuclear Magnetic Resonance Methods	13
1.4.2.1. <i>Chemical Shift Measurements</i>	15
1.4.2.2. <i>Exchange Rate Measurements Based on Line-Shape Analysis (DNMR: Dynamic Nuclear Magnetic Resonance)</i>	18
1.4.3. Electrochemical Methods	20
1.4.4. Chemical Kinetics	20
1.4.5. Heats of Protonation of Weak Bases	22
1.4.6. Theoretical Calculations and Superacidity in the Gas Phase	22
1.4.7. Estimating the Strength of Lewis Acids	23
1.4.8. Experimental Techniques Applied to Solid Acids	27
References	29
	vii

2. Superacid Systems	35
2.1. Primary Superacids	35
2.1.1. Brønsted Superacids	35
2.1.1.1. <i>Perchloric Acid</i>	35
2.1.1.2. <i>Chlorosulfuric Acid</i>	36
2.1.1.3. <i>Fluorosulfuric Acid</i>	37
2.1.1.4. <i>Perfluoroalkanesulfonic Acids</i>	38
2.1.1.5. <i>Hydrogen Fluoride</i>	40
2.1.1.6. <i>Carborane Superacids $H(CB_{11}HR_5X_6)$</i>	41
2.1.2. Lewis Superacids	42
2.1.2.1. <i>Antimony Pentafluoride</i>	42
2.1.2.2. <i>Arsenic Pentafluoride</i>	44
2.1.2.3. <i>Phosphorus Pentafluoride</i>	44
2.1.2.4. <i>Tantalum and Niobium Pentafluoride</i>	44
2.1.2.5. <i>Boron Trifluoride</i>	44
2.1.2.6. <i>Tris(pentafluorophenyl) Borane</i>	45
2.1.2.7. <i>Boron Tris(trifluoromethanesulfonate)</i>	46
2.1.2.8. <i>Aprotic Organic Superacids (Vol'pin's Systems)</i>	46
2.2. Binary Superacids	47
2.2.1. Binary Brønsted Superacids	47
2.2.1.1. <i>Hydrogen Fluoride–Fluorosulfuric Acid</i>	47
2.2.1.2. <i>Hydrogen Fluoride–Trifluoromethanesulfonic Acid</i>	47
2.2.1.3. <i>Tetra(Hydrogen Sulfato)Boric Acid–Sulfuric Acid</i>	47
2.2.2. Conjugate Brønsted–Lewis Superacids	47
2.2.2.1. <i>Oleums–Polysulfuric Acids</i>	47
2.2.2.2. <i>Fluorosulfuric Acid–Antimony Pentafluoride ("Magic Acid")</i>	49
2.2.2.3. <i>Fluorosulfuric Acid–Sulfur Trioxide</i>	53
2.2.2.4. <i>$HSO_3F-MF_n(SO_3F)_{5-n}$; $n = 3, 4$, $M = Nb, Ta$</i>	53
2.2.2.5. <i>Fluorosulfuric Acid–Arsenic Pentafluoride</i>	54
2.2.2.6. <i>Perfluoroalkanesulfonic Acid–Based Systems</i>	54
2.2.2.7. <i>Hydrogen Fluoride–Antimony Pentafluoride (Fluoroantimonic Acid)</i>	56
2.2.2.8. <i>Hydrogen Fluoride–Phosphorus Pentafluoride</i>	59
2.2.2.9. <i>Hydrogen Fluoride–Tantalum Pentafluoride</i>	60

2.2.2.10. Hydrogen Fluoride–Boron Trifluoride (Tetrafluoroboric Acid)	60
2.2.2.11. Conjugate Friedel–Crafts Acids ($HX-AlX_3$, etc.)	61
2.3. Ternary Superacids	62
2.3.1. $HSO_3F-HF-SbF_5$	62
2.3.2. $HSO_3F-HF-CF_3SO_3H$	63
2.3.3. CF_3SO_3H-HF –Lewis Acid	63
2.3.4. $HSO_3F-SbF_5-SO_3$	63
2.4. Solid Superacids	63
2.4.1. Zeolitic Acids	64
2.4.2. Polymeric Resin Sulfonic Acids	65
2.4.2.1. Lewis Acid-Complexed Sulfonic Acid Resins	65
2.4.2.2. Perfluorinated Polymer Resin Acids	66
2.4.3. Enhanced Acidity Solids	68
2.4.3.1. Brønsted Acid-Modified Metal Oxides: $TiO_2-H_2SO_4$; $ZrO_2-H_2SO_4$	68
2.4.3.2. Lewis Acid-Modified Metal Oxides and Mixed Oxides	69
2.4.3.3. Lewis Acid-Complexed Metal Salts	70
2.4.4. Immobilized Superacids (Bound to Inert Supports)	71
2.4.4.1. Superacids Immobilized on Solid Supports	71
2.4.4.2. Graphite-Intercalated Superacids	72
2.4.4.3. SbF_5 -Fluorinated Graphite, SbF_5 -Fluorinated Al_2O_3	74
References	75
3. Carbocations in Superacid Systems	83
3.1. Introduction	83
3.1.1. Development of the Carbocation Concept: Early Kinetic and Stereochemical Studies	83
3.1.2. Observation of Stable, Long-Lived Carbocations	84
3.1.3. General Concept of Carbocations	85
3.2. Methods of Generating Carbocations in Superacids Systems	87
3.3. Methods and Techniques in the Study of Carbocations	88
3.3.1. Nuclear Magnetic Resonance Spectra in Solution	88
3.3.2. ^{13}C NMR Chemical Shift Additivity	89
3.3.3. Isotopic Perturbation Technique	90
3.3.4. Solid-State ^{13}C NMR	90
3.3.5. X-ray Diffraction	91

3.3.6.	Tool of Increasing Electron Demand	91
3.3.7.	Core Electron Spectroscopy	91
3.3.8.	Infrared and Raman Spectroscopy	92
3.3.9.	Electronic Spectroscopy	92
3.3.10.	Low-Temperature Solution Calorimetric Studies	92
3.3.11.	Quantum Mechanical Calculations	93
3.4.	Trivalent Carbocations	93
3.4.1.	Alkyl Cations	93
3.4.1.1.	<i>Early Unsuccessful Attempts</i>	93
3.4.1.2.	<i>Preparation from Alkyl Fluorides in Antimony Pentafluoride Solution and Spectroscopic Studies</i>	94
3.4.1.3.	<i>Preparation from Other Precursors</i>	108
3.4.1.4.	<i>Observation in Different Superacids</i>	112
3.4.2.	Cycloalkyl Cations	112
3.4.3.	Bridgehead Cations	116
3.4.4.	Cyclopropylmethyl Cations	120
3.4.5.	Alkenyl Cations	123
3.4.6.	Alkadienyl and Polyenylic Cations	125
3.4.7.	Arenium Ions	126
3.4.8.	Ethylenearenium Ions	132
3.4.9.	Propargyl and Allenylmethyl Cations (Mesomeric Vinyl Cations)	134
3.4.10.	The Phenyl Cation	139
3.4.11.	Arylmethyl and Alkylarylmethyl Cations	140
3.4.12.	Carbocations and Polycations	147
3.4.13.	Aromatic Stabilized Cations and Dications	157
3.4.14.	Polycyclic Arene Dications	162
3.4.15.	Fullerene Cations	164
3.4.16.	Heteroatom-Stabilized Cations	167
3.4.16.1.	<i>Halogen as Heteroatom</i>	167
3.4.16.2.	<i>Oxygen as Heteroatom</i>	172
3.4.16.3.	<i>Sulfur as Heteroatom</i>	192
3.4.16.4.	<i>Nitrogen as Heteroatom</i>	195
3.4.17.	Carbocations Complexed to Metal Atoms	204
3.5.	Equilibrating (Degenerate) and Higher (Five or Six) Coordinate (Nonclassical) Carbocations	206
3.5.1.	Alkonium Ions (Protonated Alkanes $C_nH_{2n+3}^+$)	206
3.5.1.1.	<i>The Methonium Ion (CH_5^+)</i>	207

3.5.1.2.	<i>Multiply Protonated Methane Ions and Their Analogs</i>	212
3.5.1.3.	<i>Varied Methane Cations</i>	214
3.5.1.4.	<i>Ethonium Ion ($C_2H_7^+$) and Analogs</i>	216
3.5.1.5.	<i>Proponium Ions and Analogs</i>	218
3.5.1.6.	<i>Higher Alkonium Ions</i>	219
3.5.1.7.	<i>Adamantonium Ions</i>	224
3.5.2.	<i>Equilibrating and Bridged Carbocations</i>	225
3.5.2.1.	<i>Degenerate 1,2-Shifts in Carbocations</i>	225
3.5.2.2.	<i>The 2-Norbornyl Cation</i>	229
3.5.2.3.	<i>The 7-Norbornyl Cation</i>	239
3.5.2.4.	<i>The 2-Bicyclo[2.1.1]hexyl Cation</i>	240
3.5.2.5.	<i>Degenerate Cyclopropylmethyl and Cyclobutyl Cations</i>	241
3.5.2.6.	<i>Shifts to Distant Carbons</i>	246
3.5.2.7.	<i>9-Barbaralyl (Tricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-yl) Cations and Bicyclo[3.2.2]nona-3,6,8-trien-2-yl Cations</i>	253
3.5.2.8.	<i>The 1,3,5,7-Tetramethyl- and 1,2,3,5,7-Pentamethyl-2-adamantyl Cations</i>	257
3.5.3.	<i>Homoaromatic Cations</i>	258
3.5.3.1.	<i>Monohomoaromatic Cations</i>	259
3.5.3.2.	<i>Bishomoaromatic Cations</i>	260
3.5.3.3.	<i>Trishomoaromatic Cations</i>	265
3.5.3.4.	<i>Three-Dimensional Homoaromaticity</i>	266
3.5.4.	<i>Pyramidal Cations</i>	267
3.5.4.1.	<i>(CH)₅⁺-Type Cations</i>	267
3.5.4.2.	<i>(CH)₆²⁺-Type Dications</i>	270
References		273

4. Heterocations in Superacid Systems 311

4.1.	<i>Introduction</i>	311
4.2.	<i>Onium Ions</i>	311
4.2.1.	<i>Oxonium Ions</i>	311
4.2.1.1.	<i>Hydronium Ion (H_3O^+)</i>	311
4.2.1.2.	<i>Primary Oxonium Ions [ROH_2^+]</i>	313
4.2.1.3.	<i>Secondary Oxonium Ions [$RR'OH^+$]</i>	319
4.2.1.4.	<i>Tertiary Oxonium Ions</i>	322
4.2.1.5.	<i>Aurated Oxonium Ions</i>	328

4.2.1.6.	<i>Hydrogen Peroxonium Ion ($H_3O_2^+$) and Derivatives</i>	329
4.2.1.7.	<i>Ozonium Ion (HO_3^+)</i>	330
4.2.2.	Sulfonium Ions	331
4.2.2.1.	<i>Hydrosulfonium Ion (H_3S^+)</i>	331
4.2.2.2.	<i>Primary Sulfonium Ions</i>	332
4.2.2.3.	<i>Secondary Sulfonium Ions</i>	334
4.2.2.4.	<i>Tertiary Alkyl(Aryl)Sulfonium Ions</i>	335
4.2.2.5.	<i>Halosulfonium Ions</i>	340
4.2.2.6.	<i>Sulfonium Ions with Other Heteroligands</i>	342
4.2.3.	Selenonium and Telluronium Ions	350
4.2.3.1.	<i>Hydridoselenonium and Hydridotelluronium Ions</i>	350
4.2.3.2.	<i>Acidic Selenonium and Telluronium Ions</i>	351
4.2.3.3.	<i>Tertiary Selenonium and Telluronium Ions</i>	352
4.2.3.4.	<i>Haloselenonium and Halotelluronium Ions</i>	356
4.2.3.5.	<i>Aurated Selenonium and Telluronium Ions</i>	357
4.2.3.6.	<i>Polychalcogen Dications</i>	358
4.2.4.	Halonium Ions	360
4.2.4.1.	<i>Acyclic (Open-Chain) Halonium Ions</i>	362
4.2.4.2.	<i>Cyclic Halonium Ions</i>	372
4.2.5.	Onium Ions of Group 15 Elements	381
4.2.5.1.	<i>2-Azoniallene and Derived Cations</i>	381
4.2.5.2.	<i>Diazonium Ions</i>	383
4.2.5.3.	<i>Nitronium Ion (NO_2^+)</i>	390
4.2.5.4.	<i>Nitrosonium Ion (NO^+)</i>	392
4.2.5.5.	<i>Ammonium, Phosphonium, Arsonium, and Stibonium Ions</i>	394
4.3.	Enium Ions	397
4.3.1.	Enium Ions of Group 13 Elements	397
4.3.1.1.	<i>Borenium Ions</i>	397
4.3.1.2.	<i>Alumenium Ions</i>	400
4.3.2.	Enium Ions of Group 14 Elements	401
4.3.2.1.	<i>Silicenium Ions</i>	401
4.3.2.2.	<i>Germanium Ions</i>	411
4.3.2.3.	<i>Enium Ions of Other Group 14 Elements</i>	413
4.3.3.	Enium Ions of Group 15 Elements	415
4.3.3.1.	<i>Nitrenium Ions</i>	415
4.3.3.2.	<i>Phosphenium Ions</i>	417
4.3.3.3.	<i>Enium Ions of Other Group 15 Elements</i>	423

4.3.4.	Enium Ions of Group 16 Elements	424
4.3.4.1.	<i>Oxenium Ions</i>	424
4.3.4.2.	<i>Enium Ions of Other Group 16 Elements</i>	425
4.4.	Homo- and Heteropolyatomic Cations	426
4.4.1.	Halogen Cations	427
4.4.1.1.	<i>Iodine Cations</i>	427
4.4.1.2.	<i>Bromine Cations</i>	430
4.4.1.3.	<i>Chlorine Cations</i>	432
4.4.2.	Interhalogen Cations	433
4.4.2.1.	<i>Triatomic Interhalogen Cations</i>	433
4.4.2.2.	<i>Pentaatomic Interhalogen Cations</i>	436
4.4.2.3.	<i>Heptaatomic Interhalogen Cations</i>	437
4.4.3.	Polyatomic Cations of Group 16 Elements	438
4.4.3.1.	<i>The O_2^+ Cation</i>	438
4.4.3.2.	<i>Polysulfur Cations</i>	439
4.4.3.3.	<i>Polyselenium Cations</i>	441
4.4.3.4.	<i>Polytellurium Cations</i>	444
4.4.3.5.	<i>Polyheteroatom Cations</i>	445
4.4.4.	Mixed Polyheteroatom Cations of Group 15, 16, and 17 Elements	447
4.4.4.1.	<i>Polyheteroatom Cations of Nitrogen and Sulfur</i>	447
4.4.4.2.	<i>Polyheteroatom Cations of Halogens with Oxygen or Nitrogen</i>	448
4.4.4.3.	<i>Polyheteroatom Cations of Chalcogens with Halogens</i>	450
4.5.	Cations of Group 6–12 Elements	453
4.5.1.	Homoleptic Metal Carbonyl Cations	453
4.5.2.	Other Cations of Group 6–12 Elements	456
4.6.	Miscellaneous Cations	460
4.6.1.	Hydrogen Cations	460
4.6.1.1.	<i>H^+ Ion</i>	460
4.6.1.2.	<i>H_3^+ Ion</i>	460
4.6.2.	Cations of Noble Gases	460
	References	465
5.	Superacid-Catalyzed Reactions	501
5.1.	Conversion of Saturated Hydrocarbons	501
5.1.1.	Sigma-Basicity: Reversible Protonation or Protolysis of C–H and C–C Bond	503

5.1.1.1. Deuterium–Hydrogen Exchange Studies	505
5.1.2. Electrochemical Oxidation in Strong Acids	520
5.1.3. Isomerization of Alkanes	524
5.1.4. Cleavage Reactions (β -Cleavage versus C–C Bond Protolysis)	539
5.1.5. Alkylation of Alkanes and Oligocondensation of Lower Alkanes	543
5.2. Alkylation of Aromatic Hydrocarbons	554
5.2.1. Alkylation with Alkenes	554
5.2.2. Alkylation with Alcohols and Cyclic Ethers	560
5.2.3. Alkylation with Alkyl Halides	566
5.2.4. Alkylation with Carbonyl Compounds and Derivatives	577
5.2.5. Alkylation with Acid Derivatives	585
5.2.6. Isomerization and Transalkylation of Alkylbenzenes	586
5.2.7. Alkylation with Miscellaneous Reagents	589
5.2.8. Cyclialkylation	595
5.3. Acylation of Aromatics	608
5.4. Carboxylation	618
5.5. Formylation	627
5.6. Thio- and Dithiocarboxylation	632
5.7. Sulfonation and Sulfonylation	633
5.8. Nitration	636
5.9. Nitrosonium Ion (NO^+)-Induced Reactions	643
5.10. Halogenation	647
5.10.1. Halogenation of Nonaromatic Compounds	647
5.10.2. Halogenation of Aromatic Compounds	655
5.11. Amination	659
5.12. Oxyfunctionalization	660
5.12.1. Oxygenation with Hydrogen Peroxide	661
5.12.1.1. Oxygenation of Alkanes	661
5.12.1.2. Oxygenation of Aromatics	663
5.12.1.3. Oxygenation of Natural Products	666
5.12.2. Oxygenation with Ozone	667
5.12.3. Oxygenation Induced by Nafion Resins	672
5.12.4. Oxygenation by Other Methods	674
5.13. Superacids in Protection Group Chemistry	676
5.14. Superacids in Heterocyclic Chemistry	680
5.14.1. Synthesis of Heterocycles	680
5.14.1.1. Preparation of Oxacycloalkanes	680

5.14.1.2. <i>Synthesis of Nitrogen Heterocycles</i>	685
5.14.1.3. <i>Heterocycles with Two or Three Heteroatoms</i>	689
5.14.2. Ring-Opening of Oxygen Heterocycles	696
5.15. Dehydration	698
5.16. Superacids in Carbohydrate Chemistry	700
5.17. Rearrangements and Cyclizations	706
5.17.1. Rearrangements and Cyclizations of Natural Products	706
5.17.2. Phenol–Dienone Rearrangements	722
5.17.3. Other Rearrangements and Cyclizations	724
5.18. Ionic Hydrogenation	727
5.19. Esterification and Ester Cleavage	734
5.20. Additions	735
5.20.1. Cycloadditions	735
5.20.2. Other Additions	738
5.21. Ritter Reactions	742
5.22. Polymerization	744
5.23. Miscellaneous Reactions	750
References	756
Outlook	789
Index	791