VOLUME 70, NUMBER 7 JOC Perspective APRIL 1, 2005

Crossing Conventional Boundaries in Half a Century of Research[†]

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Received November 22, 2004

An overview of the research of the Olah group over five decades—ranging from synthetic reagents and methods to mechanistic—structural studies to new hydrocarbon chemistry and the development of methanol based fuels and hydrocarbon synthesis—is presented.

I was born, educated, and started my career in Hungary. Having been forced to leave my native country after the failure of the 1956 revolution, I joined 200 000 refugees who were seeking freedom and a better life in the West. While growing up in my school years I never thought about becoming a scientist, not the least a chemist. I attended for eight years a very strict “gimnázium” (combined junior high and high school) of a Roman Catholic teaching order where I received a very good general education. The emphasis was on the humanities, history (even philosophy), languages, etc., with less emphasis on the natural sciences, although I had an inspiring physics teacher who later became a nationally recognized pioneer of science education. My memories of my chemistry classes are much more vague and left not much of an impression on me. In any case, my interest, until I entered the university at the end of World War II in the fall of 1945, was very much in the humanities. It was the realization that I needed to choose a profession which also would allow me to make a living in a war-devastated small country which opened my mind to other fields. After I took an initial chemistry course I fell in love with it and still feel the same way today. A few years ago I wrote my autobiographical reflections (*A Life of Magic Chemistry*).[1a] If anybody is interested in more personal aspects of my life, these are discussed there.

After completing my studies at the Technical University of Budapest I became an Assistant Professor in the Institute of Professor Geza Zemplen, a renowned natural product and carbohydrate chemist of his time and a former student of Emil Fischer. Thus, in a way I am a scientific grandson of Fischer and was listed as such in the tabulation of his school commemorating the centennial of his Nobel Prize of 1902.

Early Carbohydrate and Natural Product Studies

I started my research with Zemplen in the area of glycosides, particularly of digitalis heart glycosides found in the colorful foxglove plants, which grew extensively in some areas around Lake Balaton. Their chemistry was pioneered by another Fischer student, Arthur Stoll, and the Swiss pharmaceutical company Sandoz for many years used the Hungarian natural source as the basis of their production. My research resulted in significantly improved processes for both lanataglucoside and derived digitoxin, which the Hungarian pharmaceutical company Richter successfully commercialized.

Around 1950, I came across a paper by the German carbohydrate chemist Micheel who succeeded in preparing pentaacetylglucosyl fluoride and found that it could be deacetylated to the relatively stable free fluorohydrin. This gave me the idea that the selective synthesis of α- or β-glycosides could be achieved by treating either acetofluoroglucose (or other fluorinated carbohydrates) or, if they're relatively stable, deacetylated free fluorohydrins with the appropriate aglucons (assuming Walden inversion in both cases). Zemplen's reaction to my idea was, not unexpectedly, negative.

Early Organofluorine Chemistry[2–6]

To try to pursue organofluorine chemistry in post-war Hungary was indeed far fetched. Zemplen thought that the study of fluorine compounds, which necessitated “outrageous” reagents such as hydrogen fluoride, was

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[†] It was my usual practice during my career that, whenever I felt that I had substantially achieved my goals and fulfilled my interest in a specific field of research, I wrote (or edited) a book or comprehensive to review of it. The interested reader may want to consult these for details. They also contain extensive references to my 1300 research papers, reviews, and book chapters. I am most grateful for the contribution of all my former students and associates which made our joint work possible and whose names can be found in the references. Portions of the text and graphics have been reprinted with permission from ref 1. Copyright 1995 and 2001 John Wiley & Sons, Inc.

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Published on Web 03/24/2005

foolish. It became increasingly clear that my ideas and interests were not matching his. Eventually, however, I prevailed and with some of my early dedicated associates (including Attila Pavlath and Steven Kuhn) we started to study organic fluorides. Laboratory space and particularly fume hoods were scarce in the Zemplen institute. I was not welcome to "pollute" space intended for "real chemistry". However, at the top floor of the chemistry building overlooking the Danube and badly damaged during the war was an open balcony used to store chemicals. In an unexpected gesture Zemplen allowed me the use of this balcony. With some effort we enclosed it, installed two old fume hoods, and we were soon ready for research in what was referred to as the "balcony laboratory".

Carrying out fluorine research in post-war Hungary was not easy. There was no access to such basic chemicals as anhydrous HF, FSO_3H, or BF_3, and we had to prepare them ourselves. HF was prepared from fluorspar (CaF_2) and sulfuric acid, and its reaction with SO_3 (generated from oleum) gave FSO_3H. By treating boric acid with fluorosulfuric acid we made BF_3. Handling these chemicals and their use in a laboratory equipped with the barest of necessities was indeed a challenge. It was in the early 1950s that an unexpected present came from Hans Meerwein, who somehow read our early publications and started correspondence with a young unknown Hungarian chemist. He subsequently arranged a gift of a cylinder of boron trifluoride and sent it to us. What a wonderful gesture and help it was! Through my initial research work involving reactions of fluorinated carbohydrates, I became interested in Friedel−Crafts acylation and subsequently alkylation reactions with acyl and alkyl fluorides with boron trifluoride. This also was the beginning of my long-standing interest in electrophilic aromatic and later aliphatic substitution reactions.[2,3]

$$\mathrm{ArH + RCOF \xrightarrow{BF_3} ArCOR + HF}$$

$$\mathrm{ArH + RF \xrightarrow{BF_3} ArR + HF}$$

These studies at the same time aroused my interest in the mechanistic aspects of the reactions, including the complexes of RCOF and RF with BF_3 (and eventually with other Lewis acids) as well as the complexes they formed with aromatics. I isolated for the first time at low temperatures arenium tetrafluoroborates (the elusive σ-complexes of electrophilic aromatic substitutions), although I had no means at the time to pursue their structural study. Thus, my long fascination with the chemistry of carbocationic complexes began.

$$\mathrm{ArH + HF + BF_3 \rightleftharpoons ArH_2^+\ BF_4^-}$$

$$\mathrm{ArH + RF + BF_3 \rightleftharpoons ArHR^+\ BF_4^-}$$

Another aspect of my early research in Budapest, which was carried out at the Chemical Research Institute of the Academy of Sciences from 1954 to 1956, was in nitration chemistry, specifically in the preparation of nitronium tetrafluoroborate, a stable nitronium salt. I was able to prepare it in a simple and efficient way from nitric acid, hydrogen fluoride, and boron trifluoride.

$$\mathrm{HNO_3 + HF + 2BF_3 \rightarrow NO_2^+BF_4^- + BF_3{\cdot}H_2O}$$

This salt turned out to be remarkably stable and a powerful, convenient nitrating agent for a wide variety of aromatics (and, later, also aliphatics). Over the years, this chemistry was further developed, and nitronium tetrafluoroborate is still widely used as a commercially available nitrating agent.

$$\mathrm{ArH + NO_2^+BF_4^- \rightarrow ArNO_2 + HF + BF_3}$$

$$\mathrm{RNH_2 + NO_2^+BF_4^- \rightarrow RNHNO_2}$$

$$\mathrm{ROH + NO_2^+BF_4^- \rightarrow RONO_2}$$

In the course of my studies I also introduced silver tetrafluoroborate, $AgBF_4$, as a metathetic cation forming agent suitable to form varied ionic (electrophilic) reagents.

$$\mathrm{RCl + AgBF_4 \rightarrow R^+BF_4^- + AgCl}$$

Meerwein himself subsequently used this reagent extensively.

My early research on organofluorine compounds that I started in 1950 centered on new methods of their preparation and use in varied reactions. At the time, I also started cooperative research with the Medical University of Budapest on the study of their pharmacological effect and particularly on their use in cancer research. Our joint publications from 1952 to 1953 must be among the earlier ones in this intriguing field. The pursuit of the biological activity of fluorinated organic compounds clearly was a worthwhile early effort as progress in this still rapidly expanding field was remarkable.

In October 1956, Hungary revolted against the Soviet rule, but the uprising was soon put down by drastic measures following intense fighting with overwhelming Soviet forces and much loss of life. Budapest was again devastated, and the future looked bleak. Our research laboratories were themselves not damaged during the fighting, but our spirit was broken. During the short-lived days of freedom a small revolutionary committee was formed in our Institute to which I was elected. There was a nearly unanimous support for the spontaneous uprising of 1956 in Budapest, but it could not on its own prevent the oppression and terror which returned with the Soviet forces. Consequently, in November and early December of 1956 some 200 000 Hungarians, mostly of the younger generation, fled their homeland. With my family (my older son was born in 1954) and most of my small research group, who also decided that this was the only path to follow, we joined the torrent of refugees seeking a new life in the West.

After fleeing Hungary, we eventually got to London in early December where an aunt of my wife lived. We were warmly welcomed. During our stay in London for the first time I was able to meet some of the chemists whose work I knew from the literature and admired. I found them most gracious and helpful. In particular, Christopher Ingold and Alexander Todd extended efforts on behalf of a young, little known Hungarian refugee chemist in a way that I will never forget and for which I will always be grateful.

We did not intend to settle in England and moved in the spring of 1957 to Canada, where my mother-in-law lived in Montreal, having remarried there after the war. While initially I was looking for an academic position, none came along, but a few industrial research possibilities opened up. Of these I chose that of the Dow Chemical Company.

In the 1950s it was a general trend for major American chemical companies to establish European research laboratories. Some examples of such laboratories were Cyanamid in Geneva, Union Carbide in Brussels, and Monsanto in Zurich. Dow, instead of Europe, established in Canada an Exploratory Research Laboratory in 1955. This small laboratory (with a staff of perhaps 15−20) had a significant degree of freedom and close contact with Dow research in Midland, MI, just a 2 h drive across the border from our location in Sarnia, Ontario just north of Detroit.

As a chemist it was easy for me to fit into the new environment. Science is international and even has its own language sometimes called scientific English, i.e., English with a foreign accent. The initial language difficulty many immigrants face is thus much easier to overcome in the technical-scientific field. Dow also hired two of my former Hungarian co-workers. It was thus possible to restart active research soon after our arrival at Dow. I am very grateful for the opportunity and support given to me. I should also mention that in an industrial laboratory, located within a chemical plant complex, nobody thought of working extra long hours, weekends, etc., except for some “strange” scientists. What I did “after hours” was conceded to be research in which I could pursue my own interests.

My years at Dow (I eventually transferred to Dow’s Eastern Research Laboratory in the Boston area) were productive and rewarding. It was during this period in the late 1950s that my breakthrough work on long-lived stable carbocations, which in a way already started back in Hungary, was carried out. Dow was and is a major user of Friedel−Crafts-type chemistry, including the manufacture of ethylbenzene for styrene production by the reaction of benzene with ethylene. This was long assumed to involve cationic intermediates (i.e., carbocations) which were, however, never directly observed or studied. My work thus also had practical significance for Dow and, in a modest way, helped to improve the large-scale industrial process.

Positive carbon ions (carbocations as I named them later) were first suggested by Meerwein as reaction intermediates in the acid-catalyzed rearrangement of camphene hydrochloride to isobornyl chloride. It was Ingold, Hughes, and their collaborators starting in the late 1920s who carried out detailed kinetic and stereochemical investigations on what became known as nucleophilic substitution at saturated carbon and polar elimination reactions. Their work relating to unimolecular nucleophilic substitution and elimination, called S_N1 and E1 reactions, where formation of carbocations is the slow rate-determining step, laid the foundation for the role of electron-deficient carbocationic intermediates in organic reactions.[7]

In the 1930s, Frank Whitmore generalized these concepts in a series of papers to include many other organic reactions. Carbocations, however, were generally considered to be unstable and transient (short-lived), as they could not be directly observed. Leading investigators such as P. D. Bartlett, C. D. Nenitzescu, S. Winstein, D. J. Cram, M. J. S. Dewar, J. D. Roberts, P. v. R. Schleyer, and others have contributed fundamentally to the development of modern carbocation chemistry. The chemistry of carbocations, as probably the most important organic reaction intermediate, is well reviewed, and I do not need to repeat it here. Direct observation and study of stable, long-lived carbocations, such as of alkyl cations in the condensed state, remained, however, for a long time an elusive goal.

My work on long-lived carbocations dates back to the late 1950s at Dow and resulted in the first direct observation of alkyl cations using antimony pentafluoride as an extremely strong Lewis acid and later using other highly acidic (superacidic) systems (such as $HF-SbF_5$, FSO_3H-SbF_5, etc.).

The chemistry of stable, long-lived (or persistent) carbocations, as they became known, thus began, and its progress was fast and widespread. From an industrial laboratory, publication of research is not always easy. I would therefore like to thank again the Dow Chemical Company for allowing me not only to carry out the initial work, but also to publish the results.

During my years with Dow I also did much other research studying varied reactions and their mechanistic aspects, developing new reagents, and starting to explore superacid chemistry.[5]

Superacids as defined by R. J. Gillespie, a pioneer of their study, are acids stronger than 100% sulfuric acid or, in case of Lewis acids (as we suggested), than aluminum trichloride. The name incidentally was given by J. B. Conant of Harvard for unusually strong acids, such as perchloric acid, which he found capable of protonating weak bases such as carbonyl compounds.

In the summer of 1965, I moved back to academia in Cleveland and I took on my duties as professor and chairman of the Chemistry Department of Western Reserve University.

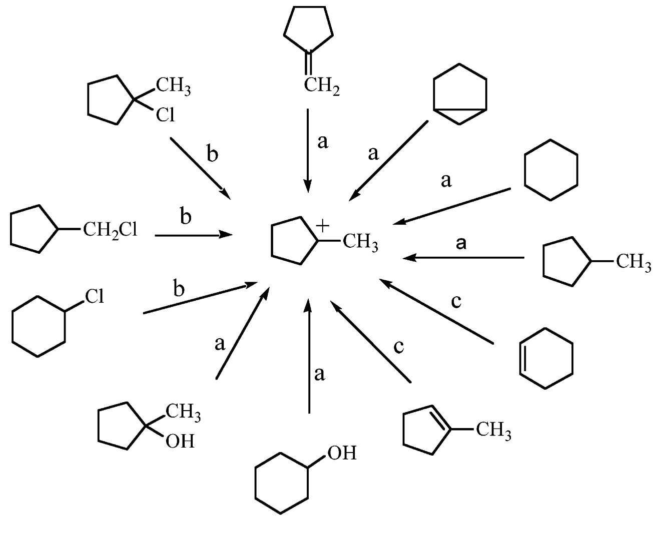
The transition back to academic life was surprisingly easy for me. My group grew and reached 15−20, about equally divided between graduate students and postdoctorals, the optimal size of group for me. I always felt that in order to be an effective research advisor and mentor I must have close and regular personal contact with all of my young associates, which is not always possible in large groups.

One achievement of my Cleveland years I am proud of was to have succeeded in combining the chemistry departments of Western Reserve University and neighboring Case Institute of Technology. The two departments occupied practically adjacent buildings, and it became obvious in the year following my arrival that it would make sense to join the two into a single, stronger department. We achieved this by 1967 with surprisingly little friction, and I was asked to stay on for a while as the Chair of the joint department. I never had administrative ambitions and was anxious to get out of such, which I did in 1969. The merging of the two chemistry departments was so successful that it prompted the complete combining of Western Reserve University with Case Institute of Technology by 1970 into Case Western Reserve University, which continues as a very successful university.

During my Cleveland years I also initiated an active seminar program with the participation of many leading chemists who came to visit us. This allowed the creation of a lively and stimulating atmosphere in the department benefiting students and faculty alike. I organized in 1969 the first of many subsequent international research symposia. This symposium on carbocation chemistry was attended by many of the major investigators in the field (Nenitzescu, Brown, Winstein, Dewar, Schleyer, Gillespie, Saunders, and others). When I moved to Los Angeles, these symposia became regular annual events. My own group held regular weekly meetings and research seminars, which remained a permanent feature over the years. On the basis of our mutual interest, Ned Arnett and John Pople with their research groups from Pittsburgh joined us at regular intervals and we had joint monthly meetings alternating between Cleveland and Pittsburgh.

My research during the Cleveland and subsequent years centered on continued and extended study of carbocations in varied superacidic systems as well as exploring the broader of superacid chemistry, including varied ionic systems and reagents. I should mention again that it was Ron Gillespie who pioneered much of the inorganic chemistry of superacids. His contribution and our interaction was of great value to the development of the field.

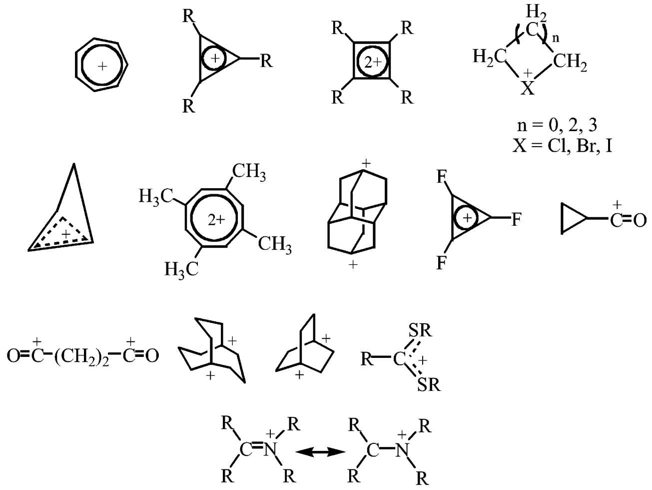
The study of persistent carbocations using superacidic media also necessitated low nucleophilicity solvents such as SO_2, SO_2ClF, SO_2F_2, etc. Varied precursors could be used under appropriate conditions, as shown for example in the case of the preparation of the methylcyclopentyl cation.



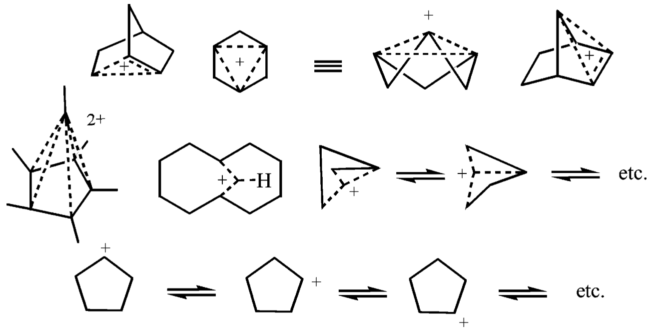
[a]FSO_3H-SbF_5 [b]SbF_5/SO_2 [c]$HF/SbF_5/SO_2$

During our prolonged research we were able to show that practically all conceivable carbocations could be prepared and studied under what became known as "stable ion conditions" in superacidic media. We also succeeded in preparing various carbodications and studied their structure.[5,6,8]

We reported over the years on a wide variety of carbocations and carbodications in over 300 publications including those of aromatically stabilized nature, as well as those stabilized by heteroatoms. Some illustrative ions are shown.



Besides static carbocations much interest centered on and effort was put into studying the question of whether certain carbocations represent rapidly equilibrating or static (bridged), delocalized systems.



This question was of particular significance in the so-called norbornyl or nonclassical ion controversy (*vide infra*).

Superacid Chemistry and Catalysis[5]

In 1927, Conant observed that weak organic bases such as carbonyl compounds (ketones and aldehydes) are capable of forming salts with perchloric acid in nonaqueous solvents. Because of the ability of perchloric acid to protonate such weak bases, he called this acid system a superacid. According to Gillespie, who did much of the fundamental work on the inorganic aspects of acid systems, all protic acids stronger than 100% sulfuric acid are considered as superacids. Thus, perchloric acid ($HClO_4$), fluorosulfuric acid (HSO_3F), hydrofluoric acid (HF), and trifluoromethanesulfonic acid (CF_3SO_3H) are superacids. The H_0 (Hammett) acidity function of $HClO_4$ is -13; of CF_3SO_3H, -14.1; of HF, -15.0 (if entirely dry); and of FSO_3H, -15.1. Conjugate Bronsted−Lewis superacids are much stronger. The acidity of HSO_3F increases from H_0 −15.1 to −21.0 on addition of 25 mol % of SbF_5. HSO_3F-SbF_5 (Magic acid) of 1:1 molar composition, which I used extensively in my study of carbocations and other systems, has an H_0 value of about −23.

Fluoroantimonic acid is an even stronger acid. The acidity of 1:1 $HF-SbF_5$ can reach H_0 −28. Thus, these superacidic systems can be 10^{16} times stronger than 100% sulfuric acid! The large complex fluoroanions facilitate dispersion of the negative charge and thus contribute to increased acidity of the solvated proton ($H_2SO_3F^+$, H_2F^+). The name Magic Acid was coined in my laboratory, after a Christmas party in the 1960s, by one of my postdoctorals (J. Lukas). A candle (of paraffin wax) left from a cake was dissolved in the acid system and the solution showed an excellent NMR spectrum of the *tert*-butyl cation, inspiring the name for “magic properties”. The name for the acid eventually found its way into the literature and is now a registered trademark.

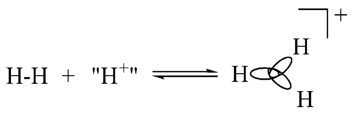
Related superacid systems in which SbF_5 is replaced by other Lewis acids such as AsF_5, TaF_5, NbF_5, or BF_3 are of lower acidity than Magic Acid or fluoroantimonic acid. However, $HF-TaF_5$, $HF-NbF_5$, and $HF-BF_3$ are very useful superacids as they will not cause oxidative side reactions.

Superacids are also very effective catalysts for a variety of electrophilic transformations of saturated and aromatic hydrocarbons. Superacids such as CF_3SO_3H and FSO_3H catalyze isomerization and alkylation reactions of hydrocarbons (frequently in conjunction with some HF). Such reactions are of substantial practical interest as they decrease the environmental and safety hazards associated with using highly volatile HF itself. Conjugate superacids, due to their very high acidity, affect acid-catalyzed reactions effectively at relatively low temperatures, offering additional advantages.

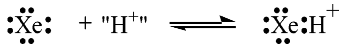
The conjugate superacids of triflic acid (and related perfluoroalkanesulfonic acids) with Lewis acid halides such as SbF_5 also show greatly increased acidity. With boron trifluoride triflatoboric acid, $CF_3SO_3H_2^+$ $B(O_3SCF_3)_4^-$, is formed, i.e., the conjugate superacid of triflic acid and boron tris(triflate).

Superacids protonate a variety of very weak bases including methane and other saturated hydrocarbons. Facile proton−deuterium exchange, cracking, and cleavage reactions of alkanes take place readily. Even molecular hydrogen undergoes proton−deuterium exchange in superacid media. Evidence for the protonation of halogens, carbon dioxide, and even xenon was also obtained.

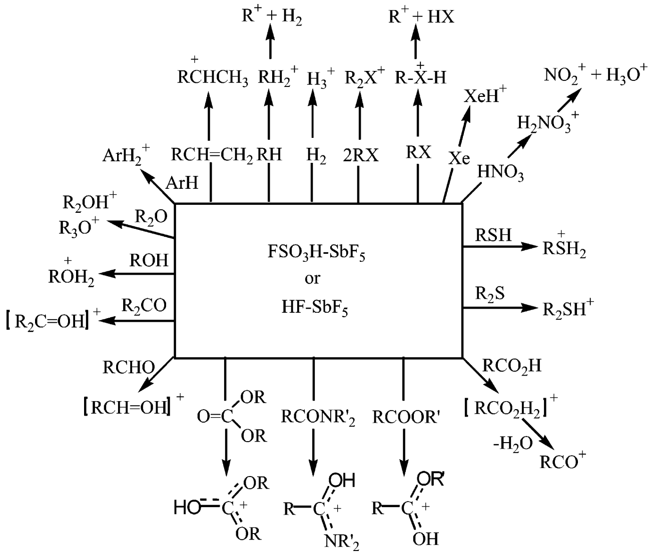
Dihydrogen (H_2), a σ donor base, is similarly protonated to H_3^+ by superacids as was shown by studies using isotopic labeling. The structure of H_3^+ involves two electron-three center (2e-3c) bonding.



Nonbonded electron pair donors (*n-donors*) are also readily protonated (or coordinated) with superacids. Remarkably, this includes even the long-considered “inert” gas xenon.



The protonation of some π-, σ-, and *n*-bases and their subsequent ionization to carbocations or onium ions are depicted as follows.



Besides liquid superacidic systems, I also studied solid superacids as catalyst systems. My work involved *inter alia* the use of antimony pentafluoride complexed to fluorographite, the use of longer chain perfluoroalkanesulfonic acids, as well as of perfluorinated resinsulfonic acid (such as Nafion-H), and some acidic Zeolites complexed with Lewis acids. Most of my research centered on the use of Nafion-H as a highly efficient catalyst for hydrocarbon conversion reactions. Alkylation reactions became particularly useful including those using solid equivalents of HF, such as polyvinylpyridium polyhydrogen fluorides, which was used in a modification of the Alkad process.

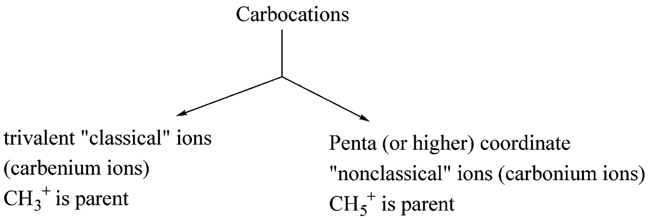
General Concept of Carbocations[5−11]

After the direct observation of stable, long-lived carbocations in highly acidic (superacid) systems became widely used, it led me to the recognition that a more general concept of carbocations exists. In addition to trivalent ions, five-coordinate (and higher) carbocations exist, and they are the key to electrophilic reactions at single bonds in saturated hydrocarbons (alkanes, cycloalkanes).

In 1972, I offered a general definition of carbocations based on the realization that two distinct classes of carbocations exist (carbocation seemed to be the logical name for all cations of carbon compounds, as the negative ions are called carbanions).[6,11]

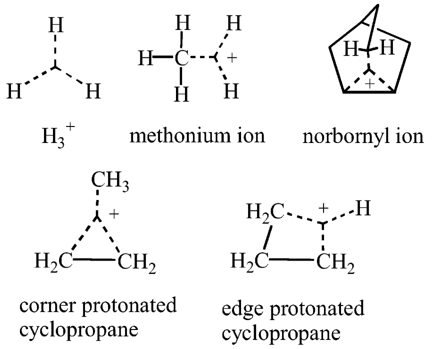
(a) Trivalent {“classical”} carbenium ions contain an sp^2-hybridized electron-deficient carbon atom, which tends to be planar in the absence of constraining skeletal rigidity or steric interference. The carbenium carbon contains six valence electrons and thus is highly electron deficient. The structure of trivalent carbocations can always be adequately described by using only two-electron, two-center bonds (Lewis valence bond structures). CH_3^+ is the parent for trivalent ions.

(b) Penta-coordinate (or higher) {"nonclassical"} carbonium ions, which contain five-coordinate (or higher) carbon atoms. They cannot be described by two-electron, two-center single bonds alone but also necessitate the use of two electron, three (or multi) center bonding. The "carbonium" ions are electron deficient due to sharing of two electrons between three (or more) atoms. CH_5^+ can be considered the parent for carbonium ions.

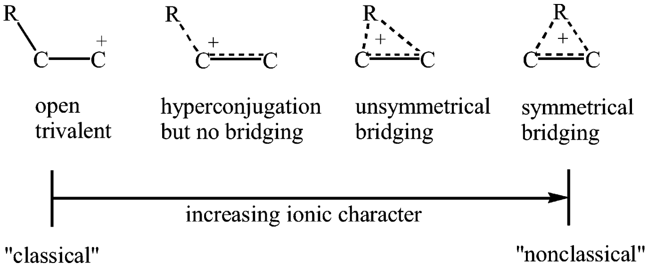


There are the limiting cases, but it should be clear that in carbocationic systems there always exist varying degrees of delocalization. This can involve participation by neighboring n-donor atoms, π-donor groups, or σ-donor C−H or C−C bonds.

Trivalent carbenium ions are the key intermediates in electrophilic reactions of π-donor unsaturated hydrocarbons. At the same time, pentacoordinated carbonium ions are the key to electrophilic reactions of σ-donor saturated hydrocarbons through the ability of C−H or C−C single bonds to participate in carbonium ion formation. Some typical nonclassical ions are as follows.



Whereas the differentiation of limiting trivalent (classical) and *penta* or higher *coordinate* (nonclassical) ions serves a useful purpose of establishing the significant differences between these ions, it must be again emphasized that these represent only the extremes of a continuum and there exists a continuum of charge delocalization comprising both intra- and intermolecular interactions.



"Every Scientist Needs Good Enemies": The Nonclassical Ion Controversy and Its Significance"

One of the major contemporary chemical controversies in which I was inadvertently involved developed in the 1950s and centered around the structure of the seven-carbon-containing bicyclic carbocation, the 2-norbornyl (bicyclo[2.2.1]heptyl) cation.

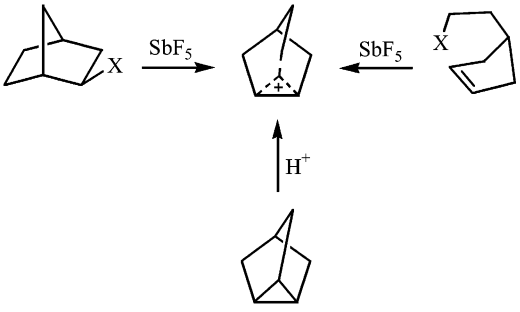
Meerwein, while studying the mechanism of the Wagner rearrangement, based on his studies of the rate-accelerating effect of some Lewis acids, made the far-sighted suggestion that the reaction proceeds through an ionic intermediate, i.e., the norbornyl cation. Hence, this type of transformation is now known as the Wagner−Meerwein rearrangement.

The structure of the norbornyl cation became controversial (the "nonclassical ion" controversy) following Wilson's original suggestion in 1939 of a mesomeric, σ-delocalized, carbocationic intermediate in the camphene hydrochloride−isobornyl chloride rearrangement. In 1949−1952, Winstein and Trifan reported on solvolytic studies of *exo*- and *endo*-2-norbornyl brosylates (p-bromobenzenesulfonates) and postulated the intermediacy of a σ-delocalized, symmetrically bridged norbornyl ion intermediate. The *endo*-reactant was found to solvolyze in acetic acid (aqueous acetone and aqueous dioxane) to give substitution products of exclusively *exo* configuration while the *exo*-brosylate gave exclusively *exo*-product and was markedly more reactive in acetolysis than the *endo*, by a factor of 350.

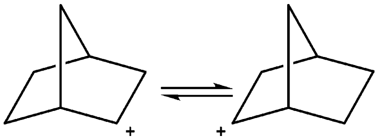
Winstein, one of the most brilliant chemists of his time, concluded that "it is attractive to account for these results by way of the bridged (nonclassical) formulation for the *norbornyl cation involving accelerated rate of formation from the exo precursor (by anchimeric assistance)*". His formulation of the norbornyl cation as a σ-bridged species stimulated other workers in the solvolysis field to interpret results in a variety of systems in similar terms of σ-delocalized, bridged carbonium ions.

H. C. Brown (the pioneer of hydroboration chemistry) in contrast concluded that in solvolysis both 2-*exo* and 2-*endo* norbornyl esters (brosylates, etc.) undergo reaction by anchimerically unassisted ionization and that the singular rate and product characteristics of the system are attributable to steric effects, particularly hindrance to ionization of the *endo* isomers. Explaining results of his extensive solvolytic studies, he suggested that high *exo*/*endo* rate and product ratios *do not necessitate* σ-participation as an explanation. In other words *exo* is not fast, but *endo* is slow. His suggestion for the structure of the norbornyl cation was that of a rapidly equilibrating pair of regular trivalent ions (classical ions).

My own involvement with the norbornyl ion controversy goes back to 1960−1962 when I succeeded in developing a general method for preparing and studying persistent (long-lived) alkyl cations. Whereas previous investigators, by necessity, were able to study the norbornyl and related ions only indirectly (by kinetic and stereochemical studies), my newly discovered methods allowed their preparation and study as persistent (long-lived) species. Without repeating here the now well-known history of the direct study of the structure of the norbornyl cation, it turned out to be the σ-delocalized "nonclassical" ion (using J. D. Robert's terminology) bringing the long-standing controversy to a conclusion.



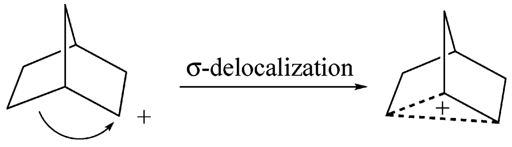
Besides experimental structural studies (NMR, IR, Raman, and ESCA, etc.), extensive quantum mechanical studies were also carried out at ever-increasing levels and showed that the equilibrating so-called classical ion is not even an energy minimum.



This is the way that the so-called nonclassical ion controversy ended. The related experimental facts, restudied many times, were never in question, only their interpretation. Intensive, critical studies of a controversial topic of course help to eliminate the possibility of any errors. One of my favorite quotations is that by George von Bekesy, a fellow Hungarian-born physicist who studied fundamental questions of the inner ear and hearing (Nobel Prize in Medicine, 1961). *"[One] way of dealing with errors is to have friends who are willing to spend the time necessary to carry out a critical examination of the experimental design beforehand and the results after the experiments have been completed. An even better way is to have an enemy. An enemy is willing to devote a vast moment of time and brain power to ferreting out errors both large and small, and this without any compensation. The trouble is that really capable enemies are scarce; most of them are only ordinary. Another trouble with enemies is that they sometimes develop into friends and lose a good deal of their zeal. This way the writer lost his three best enemies. Everyone, not just scientists, needs a few good enemies!"*

The intramolecular σ-delocalization in the norbornyl ion system aroused my interest in studying whether similar electrophilic interactions and reactions of C−H or C−C bonds are possible in intermolecular systems. This led to my subsequent discovery of related intermolecular interactions and of the general electrophilic reactivity of single bonds.

I realized that the formation of the σ-delocalized 2-norbornyl cation from 2-norbornyl precursors represented the equivalent of an intramolecular σ-alkylation where a covalent C_1-C_6 bond provided the electrons for the 2e-3c-bonded bridged ion (by σ-participation).



Although many believe that too much effort was expanded on the "futile" norbornyl ion controversy, I feel that in a broader sense it eventually resulted in significant insights and consequences to chemistry. What started out as a structural problem of a relatively simple carbocation affected, in a fundamental way, our understanding of the chemical bonding in electron-deficient carbon compounds. This extended Kekule's concept of the limiting ability of carbon to bond simultaneously to no more than four other atoms or groups, to the realization of five, six, or even seven coordination in certain electron-deficient carbon systems (what I call hypercarbon system). An equally significant consequence of the norbornyl cation studies was the realization of the ability of saturated C−H and C−C single bonds to act as two-electron σ-donors toward strong electrophiles, such as carbocations or other highly reactive reagents in superacidic systems. These transformations of C−H and C−C bonds are not only intramolecular but have also been found subsequently in intermolecular transformations and electrophilic reactions. The key for this reactivity lies in the ability to form two-electron, three-center (2e-3c) bonds (familiar in boron and organometallic chemistry). The electrophilic chemistry of saturated hydrocarbons (including that of the parent methane) rapidly evolved based on the recognition of the concept and significance of hypercoordinated carbon, in short hypercarbon chemistry (*vide infra*). The long drawn out nonclassical norbornyl ion controversy thus led to an unexpected significant new chapter of chemistry. As it frequently happens in science, the drive for understanding (for whatever reason) of at the time rather isolated, and even relatively unimportant, problems can eventually lead to significant new concepts, new chemistry, and even practical applications. It justifies the need for exploration and study in the context of fundamental (basic) research even if initially no practical reasons or uses are indicated. The beauty of science lies in finding the unexpected, and as Niel Bohr was quoted to have said "you must be prepared for a surprise", but at the same time you must also understand what your findings mean and what they can be used for. To me this is the lesson of the norbornyl ion controversy. I strongly believe it was not a waste of effort pursuing it, and eventually it helped to advance chemistry to new areas of significance, which still continue to emerge.

From Kekulé's Four-Valent Carbon to Higher Coordinate Hypercarbon Chemistry[11]

One of the cornerstones of the chemistry of carbon compounds (organic chemistry) is Kekule's concept proposed in 1858 of the tetravalency of carbon. It was independently also proposed by Couper who, however, got little recognition. Kekulé realized that carbon can bind at the same time to not more than four other atoms or groups. It can, however, at the same time use one or more of its valences to form bonds to another carbon atom. In this way, carbon can form chains or rings, as well as multiple bonded compounds.

Kekulé's four-valent carbon was explained later based on the atomic concept including the "rule of eight" valence electrons of the electron pair concept and that of covalent shared electron pair bonding (2e-2c Lewis-bond), which Langmuir further developed. It was Lipscomb who in the 1950s introduced the two-electron, three center (2e-3c) bonding concept into boron chemistry, explaining also the bridged structure of diborane.

It is remarkable that chemists for so long resisted making the connection from boron to electron-deficient carbon, which, after all, are analogues. It was my good fortune to be able to generalize the concept of five and higher coordinate carbon and to develop a field that I suggested to be called hypercarbon chemistry.

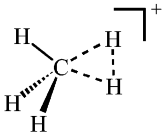
Organic chemists who deal with carbon compounds (or perhaps more correctly with hydrocarbons and their derivatives) considered for a long time that 2e-3c bonding was limited to some "inorganic" or at best "organometallic" systems, and they have seen no relevance to their field. The discussed long drawn out and sometimes highly personal nonclassical ion controversy was accordingly limited to the structural aspects of some carbocations of little interest of the general chemical community.

The close relationship of electron-deficient carbocations with their neutral boron analogues was pointed out in our 1971 paper with DeMember and Commeyras, discussing *inter alia* the close spectral (IR and Raman) similarities between isoelectronic $^{+}C(CH_3)_3$ and $B(CH_3)_3$. My colleagues Bob Williams, Surya Prakash, and Leslie Field did a fine job of carrying the carbocation:borane and polyborane analogy much further and also reviewed the topic in depth in our book, *Hypercarbon Chemistry*.[11,12]

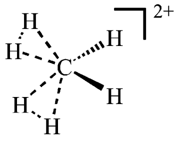
It was based on my extensive study of stable, persistent carbocations, reported in some 300 publications, that I was able to develop the general concept of carbocations referred to previously. Accordingly, in higher coordinate (hypercoordinate) carbonium ions of which protonated methane CH_5^+ is the parent, besides two-electron, two-center Lewis bonding, two-electron, three-center bonding is involved.

Extensive ab initio calculations, including ever improved high-level studies, reconfirmed the preferred C_s symmetrical structure for the CH_5^+ cation which we originally suggested with Klopman in 1969. The structure can be viewed as a proton inserted into one of the σ C−H bonds of methane to form a 2e-3c bond between carbon and two hydrogen atoms (or CH_3^+ binding H_2 through a long, weaker bonding interaction). At the same time, we pointed out that facile bond to bond (isotopal) proton migration can take place through low barriers to identical or other possible structures, which are energetically only slightly less favorable. This led later to Schleyer's suggestion of a fluxional, delocalized structure.

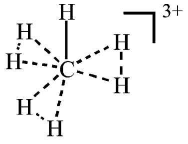
With Lammertsma and Simonetta in 1982 we studied the parent six-coordinate diprotonated methane (CH_6^{2+}), which has two 2e-3c bonding interactions in its minimum-energy structure (C_{2v}). On the basis of ab initio calculations carried out with Rasul, we have more recently found that the seven-coordinate triprotonated methane (CH_7^{3+}) is also an energy minimum and has three 2e-3c bonding interactions in its minimum energy structure (C_{2v}). These results indicate the general importance of 2e-3c bonding in protonated alkanes.



CH_5^+ C_s



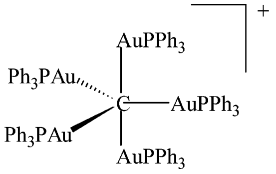
CH_6^{2+} C_{2v}

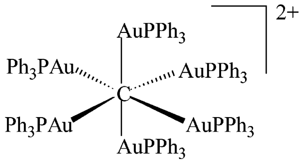


CH_7^{2+} C_{3v}

We also searched for a minimum-energy structure of tetraprotonated methane, CH_8^{4+}. However, CH_8^{4+}, remains even computationally elusive, as charge−charge repulsion appears to have reached its prohibitive limit. The isoelectronic triply charged boron analogue BH_7^{3+}, however, was found calculationally to be an energy minimum.

Protonated methanes, their homologues , and derivatives are experimentally indicated in superacid chemistry by hydrogen−deuterium exchange experiments, as well as by core electron (ESCA) spectroscopy of their frozen matrixes. Some of their derivatives could even be isolated as crystalline compounds. Schmidbaur in recent years has prepared gold complex analogues of CH_5^+ and CH_6^{2+} and determined their X-ray structures. The monopositively charged trigonal bipyramidal $\{[(C_6H_5)_3PAu]_5C\}^+$ and the dipositively charged octahedral gold complex $\{[(C_6H_5)_3PAu]_6C\}^{2+}$ contain five- and six-coordinate carbon, respectively. Considering the isolobal relationship (i.e., similarity in bonding) between LAu^+ and H^+, the gold complexes represent the isolobal analogues of CH_5^+ and CH_6^{2+}.

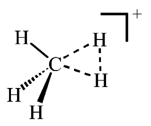




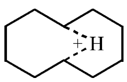
The remarkable stability of the gold complexes is due to significant metal−metal bonding. However, their isolation and structural study is remarkable and greatly contributed to our knowledge of higher coordinate carbocations.

As carbon is a first-row element unable to extend its valence shell, *hypervalency* cannot exist in carbon compounds, only hypercoordination. Hypercarbon compounds contain one or more hypercoordinated carbon atoms bound not only by 2e-2c but also 2e-3c (or >3c) bonds.

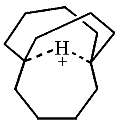
The discovery of a significant number of hypercoordinate carbocations ("nonclassical" ions) initially based on solvolytic studies and subsequently as observable, stable ions in superacidic media shows that carbon hypercoordination is a general phenomenon in electron-deficient hydrocarbon systems. Some characteristic nonclassical carbocations are as follows.



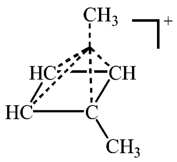
Olah
Hogeveen



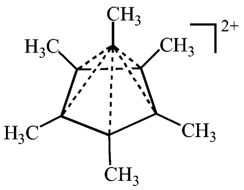
Sorensen



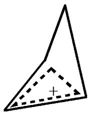
McMurry



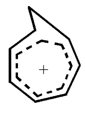
Musamune



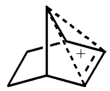
Hogeveen



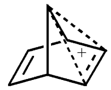
Olah



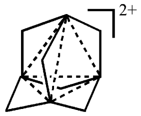
Pettit
Winstein



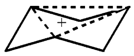
Gassman
Winstein
Olah



Winstein
Olah

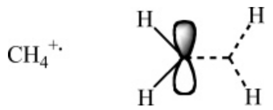


Schleyer



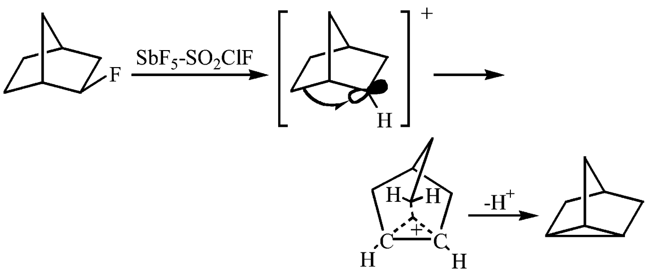
Musamune
Olah

The parent molecular ions of alkanes such as CH_4^+ (observed in mass spectrometry), according to our early theoretical calculations with Klopman of 1971, also prefer a planar hypercarbon structure.



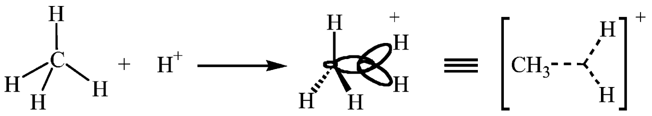
The CH_4^{2+} ion, as calculated more recently by Radom, has a similar planar C_{2v} structure.

The formation of the discussed σ-delocalized norbornyl cation via ionization of 2-norbornyl precursors in low nucleophilicity, superacidic media can be considered, as mentioned, as an analogue of an intramolecular Friedel–Crafts alkylation in a saturated system. Indeed deprotonation gives nortricyclane.

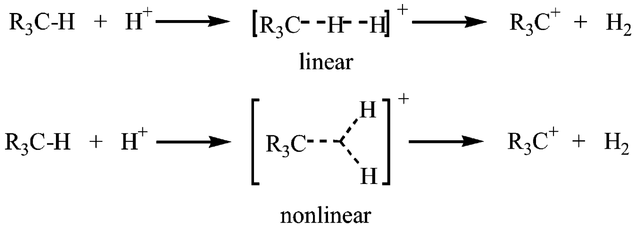


This realization led me to study related possible intermolecular electrophilic reactions of saturated hydrocarbons. Not only protolytic reactions, but a broad scope of reactions with varied electrophiles (alkylation, formylation, nitration, halogenation, oxygenation, etc.) were found to be feasible when using superacidic, low nucleophilicity reaction conditions.

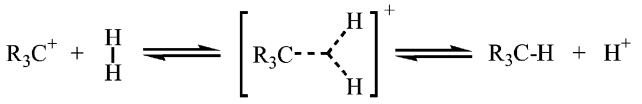
Protonation (and protolysis) of alkanes is readily achieved with superacids. The protonation of methane to CH_5^+ takes place through proton insertion into the C–H bonds.



Acid-catalyzed isomerization reactions of alkanes, as well as alkylation and condensation reactions, are initiated by protolytic ionization. Available evidence indicates off-linear but not necessarily triangular transition states.

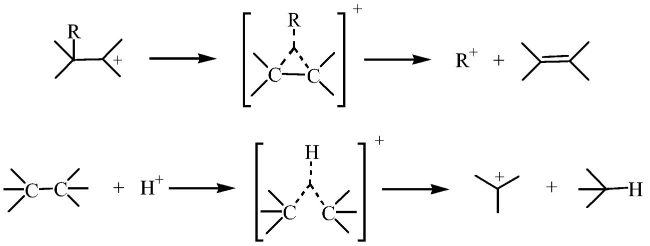


The reverse reaction of the protolytic ionization of hydrocarbons to carbocations, i.e., the reaction of trivalent carbocations with molecular hydrogen giving their parent hydrocarbons, involves the same five-coordinate carbonium ions.



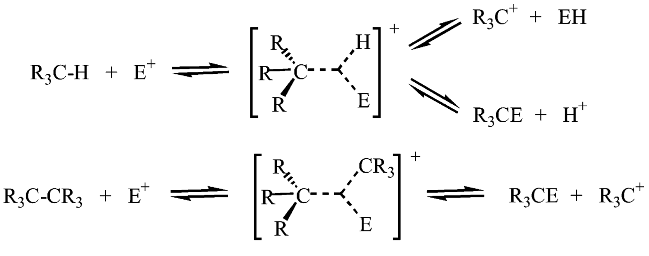
The isomerization of butane to isobutane in superacids is illustrative of a protolytic isomerization, where no intermediate olefins can be present in equilibria with carbocations.

The superacid catalyzed cracking of hydrocarbons (a significant practical application) involves not only eventual formation of trivalent carbocationic sites leading to subsequent β-cleavage but also direct C–C bond protolysis.[13]



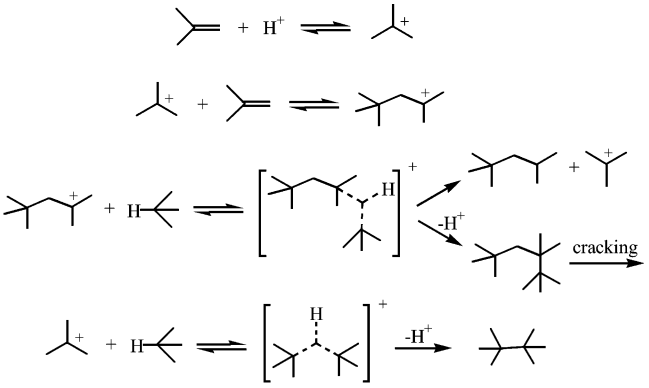
Whereas superacid ($HF–BF_3$, $HF–SbF_5$, $HF–TaF_5$, $FSO_3H–SbF_5$, etc.) catalyzed hydrocarbon transformations were first explored in the liquid phase, subsequently solid acid catalyst systems, such as those based on Nafion-H, longer chain perfluorinated alkanesulfonic acids, fluorinated graphite intercalates, etc., were also developed and utilized for heterogeneous reactions. The strongly acidic nature of some zeolite catalysts was also successfully explored in cases such as H-ZSM-5 at higher temperatures.

Not only protolytic hydrocarbon reactions but a whole range of varied electrophilic reactions can be carried out on alkanes under superacidic conditions.[13]



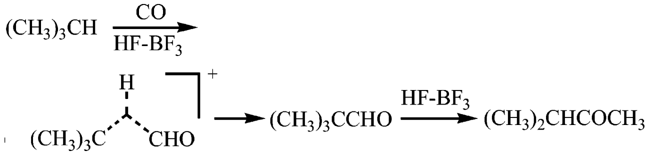
E = D^+, H^+, R^+, NO_2^+. Cl^+, Br^+, I^+, HCO^+, etc.

Alkylation of isoalkanes with alkenes is of particular significance. The industrially used alkylation of isobutane with isobutylene to isooctane is, however, de facto alkylation of the reactive isobutylene and not of the saturated hydrocarbon. Isobutane only acts as a hydride transfer agent and a source of the *tert*-butyl cation, formed via intermolecular hydride transfer. In contrast, when the *tert*-butyl cation is reacted with isobutane under superacidic conditions in the absence of isobutylene, the major fast reaction is still hydride transfer, but a detectable amount of 2,2,3,3-tetramethylbutane, the σ-alkylation product is also obtained. With sterically less crowded systems σ-alkylation is becoming more predominant.

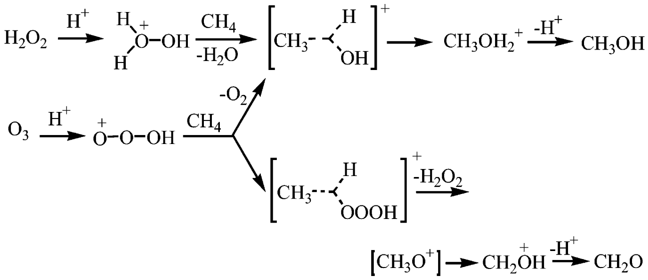


A fundamental difference exists between conventional acid-catalyzed and superacidic hydrocarbon chemistry. In the former, trivalent carbenium ions are always in equilibrium with the parent olefins which play the key role, whereas in the latter, hydrocarbon transformations take place without the involvement of olefins through the intermediacy of five-coordinate carbocations.

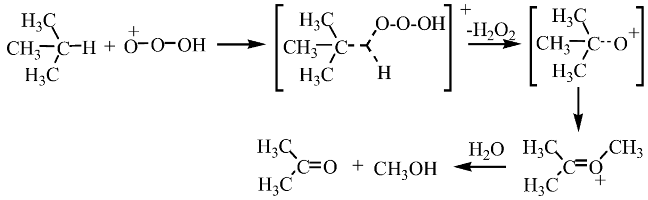
The reaction of trivalent carbocations with carbon monoxide giving acyl cations is the key step in the well-known and industrially used Koch−Haaf reaction for preparing branched carboxylic acids from alkenes or alcohols. For example, in this way isobutylene or *tert*-butyl alcohol are converted into pivalic acid. In contrast, based on the superacidic activation of carbon monoxide (*vide infra*) we found it possible to formylate isoalkanes to aldehydes, which subsequently rearrange to the corresponding branched ketones. These are effective high-octane gasoline additive oxygenates. Illustrative is the conversion of isobutane into isopropyl methyl ketone, or isopentane into isobutyl methyl ketone. In this reaction no branched carboxylic acids (Koch−Haaf products) are formed.



The superacid-catalyzed electrophilic oxygenation of saturated hydrocarbons, including methane with hydrogen peroxide (via $H_3O_2^+$) or ozone (via HO_3^+), allowed the efficient preparation of oxygenated derivatives.



As the protonation of ozone removes its dipolar nature, the electrophilic chemistry of HO_3^+, a very efficient oxygenating electrophile, has no relevance to conventional ozone chemistry. Illustrative is the superacid-catalyzed reaction of isobutane with ozone giving acetone and methyl alcohol, the aliphatic equivalent of the industrially significant Hock reaction of cumene.



I wrote in the conclusion of my 1972 paper on the general concept of carbocations “The realization of the electron donor ability of shared (bonding) electron pairs, including those of single bonds, should rank one day equal in importance with that of unshared (nonbonding) electron pairs recognized by Lewis. Now we can not only explain the reactivity of saturated hydrocarbons and in general of single bonds in electrophilic reactions, but indeed use this understanding to explore new areas of carbocation chemistry.”

This was one of the few times that I ever made a prediction of the possible future significance of my chemistry. More than a quarter of century later I take some satisfaction that I was correct and indeed hypercarbon chemistry has taken a significant place on the wide palette of chemistry.

Onium Ion Chemistry[14]

In my research on superacidic chemistry, besides the study of reactions of hydrocarbons and their carbocationic intermediates, I also pursued over the years with much interest various onium cations and dications as well as derived synthetic reagents.

Onium ions are the positively charged higher valency (higher-coordination) ions of nonmetallic elements. They can be obtained by protonation (alkylation, etc.) of their lower valency parents or by ionization of appropriate precursors. Many onium ions are isolable as stable salts and are also recognized as electrophilic reaction intermediates. Onium ions which I studied in superacidic media or as isolated salts included alkyl oxonium ions, acyl cations, carboxonium, carbosulfonium, carbazonium ions, as well as various oxonium, sulfonium, selenonium, telluronium, phosphonium, halonium, siliconium, and boronium ions. I have reviewed these fields with Laali, Wang, and Prakash. My studies are also reviewed in some detail in my monographs entitled *Onium Ions*[14] and *Halonium Ions*.[15]

It was Meerwein who pioneered the chemistry of organic oxonium ions. He introduced trialkyloxonium ions in the form of their tetrafluoroborate or hexachloroantimonate salts as efficient alkylating agents. They became widely used reagents known as Meerwein salts. In my research we have found the related hexafluorophosphate salts to be superior, not only because of their enhanced stability but also due to their excellent solubility in relatively low nucleophilicity solvents such as methylene chloride. I also studied various new tertiary oxonium ions, including cyclic systems. Proto and alkyl peroxonium ions were also studied. Whereas tertiary alkyloxonium ions were well recognized and widely used prior to my studies, with my superacid chemistry I was able to prepare a wide variety of acidic secondary and even primary oxonium ions. We studied not only structural and mechanistic aspects of these ions but also their utility in synthetic chemistry.

With Sommer and Namanworth in the 1960s we first showed that primary and secondary alcohols are protonated in FSO_3H-SbF_5 (SO_2, SO_2ClF) solution at −60 °C. We were able to observe well-resolved NMR spectra of the static protonated species. At more elevated temperatures they cleave to carbonium ions. The kinetics of these cleavage reactions could be followed by NMR spectroscopy. Studies were subsequently extended to protonated ethers and various other oxonium ion systems. Our investigations on oxonium ions were extended to related sulfonium, selenonium and telluronium ions. Using NMR spectroscopy the relative stability of these onium ions could be compared with those of oxonium ions.

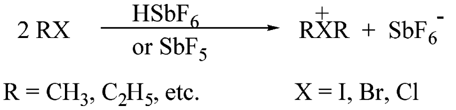
Halonium Ions[15]

Organic halonium ions of acyclic or cyclic nature have been studied both as reaction intermediates and preparative reagents. Hartman and Meyer prepared the first diphenyliodonium salt in 1894. Open-chain (acyclic) halonium ions, R_2X^+ (X = Cl, Br, I) were, however, unknown until our studies. In 1937, Roberts and Kimball, in a daring mechanistic proposal of the time, suggested that the addition of bromine to olefins involves a stereospecific trans-addition through cyclic three-membered ring bromonium ion intermediates. Preparation and direct study of these cyclic halonium ions, however, were achieved only through our investigations. We have studied not only three- membered ring halonium ions but also 4-, 5-, and 6-membered cyclic halonium ions and even bicyclic systems under long-lived stable ion conditions.

Of particular interest to me were our successful studies where we obtained for the first time stable dialkylhalonium ions, which could be isolated as stable salts and used as selective alkylating agents.

Although Meerwein's trialkyloxonium and dialkoxycarbenium salts are widely used as transfer alkylating agents, they lack selectivity and generally are incapable of C-alkylation.

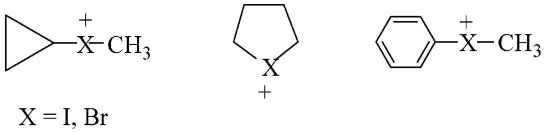
In contrast, dialkylhalonium salts such as dimethylbromonium and dimethyliodonium fluoroantimonates, which we prepared from excess alkyl halides with antimony pentafluoride or fluoroantimonic acid and isolated as stable salts (the less stable chloronium salts were obtained only in solution), are very effective alkylating agents for heteroatom compounds (Nu = R_2O, R_2S, R_3N, R_3P, etc.) and for C-alkylation of arenes and alkenes.



$$2\,RX \xrightarrow[\text{or } SbF_5]{HSbF_6} R\overset{+}{X}R + SbF_6^-$$

R = CH_3, C_2H_5, etc. X = I, Br, Cl

As the nature of the halogen atom can be varied, these salts show useful selectivity in their alkylation reactions. We also prepared various other halonium ions and studied their alkylating ability.



Later, mixed alkyl aryl, cyclopropyl, vinyl, and even cubyl halonium ion systems were obtained and investigated. The interesting 7-bromoniumbicyclo[2.2.1]heptane was obtained by the ionization of *trans*-1,4-dibromocyclohexane. This demonstrated the first 1,4-transannular participation in a six membered ring involving bromine atom. Acidic hydrido and dihydridohalonium ions were also studied through superacidic halogen protonation. Divalent, disubstituted fluoronium ions, however, still remain unknown in the condensed phase, although stabilization of carbenium ions by adjacent halogens including fluorine is well established.

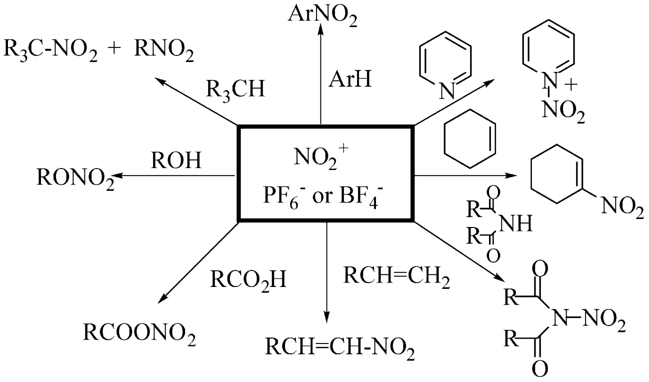
Azonium Ions and Nitration Chemistry[14,16]

Another topic of particular interest in my research was the continuation of my early work started in Hungary on the preparation and use of nitronium salts in nitration reactions.

Conventional nitration of aromatic compounds uses mixed acid (mixture of nitric acid and sulfuric acid). The water formed in the reaction dilutes the acid and spent acid disposal is becoming a serious environmental problem in industrial applications.

Further, due to its strong oxidizing ability, mixed acid is ill suited to nitrate many sensitive compounds. I have developed a series of efficient new nitrating agents and methods to overcome these difficulties. The use of readily prepared and isolated stable nitronium salts, such as $NO_2^+BF_4^-$, was extended and they became commercially available. They nitrate aromatics in organic solvents generally in close-to-quantitative yields, as well as a great variety of other organic compounds.

Some of the nitration reactions we studied with NO_2^+ salts were the following:



I have also found that *N*-nitropyridinium salts such as $C_5H_5N^+NO_2BF_4^-$ are convenient transfer nitrating reagents in selective, clean reactions. Transfer nitrations are equally applicable to C- as well as to O-nitrations allowing, for example, safe, acid-free preparation of alkyl nitrates and polynitrates from alcohols (including that of nitroglycerine).[17]

To solve some of the environmental problems of mixed acid nitration it was also possible to replace sulfuric acid with solid superacid catalysts. This allowed developing a novel, clean, azeotropic nitration of aromatics with nitric acid over solid perfluorinated sulfonic acid catalysts (Nafion-H). Water formed is continuously azeotroped off by an excess of aromatics, thus preventing dilution of acid. As disposal of spent acids in solution nitration represents a serious environmental problem, the use of solid acid catalysts represents a substantial improvement.

In the course of our studies we also continued structural studies on nitronium ions including ^{15}N and ^{17}O NMR investigations in acidic media to prove their activation mechanism. I also studied a wide scope of nitration and nitrosation chemistry with nitronium and nitrosonium salts over the years.

My extensive studies on nitration chemistry were reviewed in our monograph *Nitration* (written with Malhotra and Narang).[16] It is my colleague Surya Prakash who continues in the Loker Institute his independent extensive research on nitration and high energy nitrogen compounds in which I play only a very modest role.

Besides nitronium and related ions I also carried out research on various other azonium ions.

My studies of azonium ions included the preparation of various classes of these ions in superacids as well as their methylated (alkylated) analogues. *Inter alia N*-alkylnitrilium ions (originally prepared by Meerwein), protonated nitriles, protonated and alkylated imines (carbazonium ions), new diazonium ions, etc. were studied. Of particular interest was the investgation of unusual new diazonium ions.

We prepared amino-, hydroxy-, and methoxydiazonium ions and studied them by ^{15}N NMR spectroscopy and theory. Chemical reactivity of the aminodiazonium ion as an electrophilic aminating agent for aromatics was explored. The intermediacy of the parent diazonium ion (HN_2^+), i.e., protonated dinitrogen was also demonstrated.

In the study of the reaction of isotopically labeled ammonium and tetrafluoroammonium ions with LiH(D) and HF_2^- attempts were made to search for five coordinate neutral NH_5 and NF_5 systems. Results on the parent ammonium system, however, remained inconclusive, as no free H^- (only LiH) was involved in the reactions. In the reactions of NF_4^+ salts with $H^{18}F_2^-$, as studied with Christe and Schrobilgen, only $^{18}F^{19}F$ was formed indicating no exchange involving the intermediacy of NF_5. It was considered that, even with fluorine substituents, NF_5 is sterically too congested. At the same time, NH_5 may have transitory existence.

Studies of Miscellaneous Onium Ions[14]

My studies on organic carbonium ions including alkonium and the parent methonium ion (CH_5^+) discussed previously represent studies of the onium ions of carbon. Carbonium ions are the onium ions of carbon obtained by protonation and related electrophilic coordination of alkanes. Evidence for related boronium and alonium ions was obtained by the protonation of boranes and alanes, respectively, together with hydrogen−deuterium exchange studies. Further protonation of BH_5, obtained by protonation of borohydride (BH_4^-), indicated the formation of BH_6^+. Evidence of siliconium ions was obtained by the reaction of trialkylsilanes with HI/DI/AlI$_3$ which resulted in hydrogen−deuterium exchange. We also obtained evidence for H_3^+, the hydrogenonium ion, in superacidic solutions. H_2, HD, and D_2 show hydrogen−deuterium exchange in superacids even at room temperature.

Studies in Organometallic Chemistry[4,13]

My research on occasion involved organometallic systems, particularly in connection with elemento-organic carbocationic systems and their chemistry. I studied a series of stable mercurinium ions, including alkenemercurinium ions in mercuration studies of olefins, as well as aromatic mercuration. I also studied various organometallic stabilized carbocations such as bis(cyclopentadienyl)iron (ferrocenyl) cations and iron tricarbonyl substituted cations.

I followed up my early work on the preparation of various organophosphorus and arsenic compounds with later studies involving their superacidic and Friedel−Crafts-type preparation, including a novel preparation of triphenylphosphine.

With Prakash and Liang we carried out ^{13}C NMR studies of the trialkyl-, tricyclopropyl-, and triarylaluminum dimers and probed the nature of the bridging five coordinate carbons. Our cooperation with Lester Andrews led to studies of the elusive aluminum dichloride. Its intriguing chemistry resulted in the preparation of various organoaluminum compounds from hydrocarbons. With Prakash, we also restudied the intriguing Max Fischer polymerization of ethylene with $AlCl_3/Al/TiCl_4$, a forerunner of the Ziegler polymerization.

From 1969 onward, we attempted to study persistent trivalent alkylsilicenium ions, the silicon analogues of trivalent carbocations. We found, however, that due to the high affinity of silicon for fluorine, oxygen, etc., present in many superacidic systems, generally no persistent silicenium ions could be observed. It was only by using highly crowded systems, that it became possible to obtain stable silicenium ions (Reed).

Polymer Chemistry[13]

During my career I occasionally studied some new aspects of ionic and coordination polymerization, related to my interest in Friedel−Crafts and organometallic chemistry. I also used stable carbocationic and other ionic initiator complexes. In this regard I studied the polymerization of α-olefins mediated by stable carbocationic salts and related mechanistic aspects of cationic polymerization (polycondensation) of π, σ, and n-donor monomers. Studies were also directed at cationic ring-opening polymerization with new Lewis acids and cationic complexes.

As mentioned, we restudied with Prakash in the 1980s the low-pressure polymerization of ethylene with Al, $AlCl_3$, and $TiCl_4$ following Max Fischer's work of the early 1940s (Fischer, M. DBP 874,215, 1943, applied for in 1943). Although Fischer used $AlCl_3$, his polymerization was found to be not of cationic, Friedel−Crafts' nature, but a forerunner to Ziegler's coordinative polymerization. A mixture of $AlCl_3$ and Al is known to react with ethylene to give ethylaluminum sesquichloride (Nash and Hall). We showed with L. Andrews that the system can also produce in situ $(AlCl_2)_2$ that can add to ethylene to give organoalanes. Added $TiCl_4$ in both cases forms active Ziegler catalysts.

My polymer studies in the late 1980s also resulted in the discovery of Friedel−Crafts type novel dehydrohalogenative polymerization of acetyl chloride via in situ formed ketene to polyketene, which contains 70% of the enol form, i.e., poly(hydroxy acetylene). Polyketene formation is a general reaction for all substituted acetyl halides.

New Synthetic Reagents and Reactions

Organic synthesis is most frequently considered to involve the synthesis of target molecules, usually of natural or biological origin and significance. Synthesis of complex target molecules involves multistep reaction sequences. Increasingly, multicomponent reactions in a combinatorial approach are also used to prepare large libraries of compounds. After identification of individual active compounds, they must be synthesized by more conventional means. Development of new reagents and reactions are, however, also important for a synthetic chemist. Over the years, my interests centered on these latter aspects, i.e., the development of new and improved methods, reagents, and reactions. As I mentioned, my early scientific career began with an interest in organofluorine chemistry and reagents.

During my whole career I continued my early fascination with organofluorine compounds and fluorine chemistry. This primary synthetic work was reviewed (more recently with Chambers and Prakash in our monograph *Synthetic Fluorine Chemistry* in 1992).[4] I will therefore only mention one aspect. Fluorination of organic compounds frequently requires special techniques not usually available in the average laboratory. Reactions with the most generally used and inexpensive fluorinating agent, anhydrous hydrogen fluoride, must be carried out under pressure in special equipment due to its relatively low boiling point (20 °C) and corrosive nature. It is also an extremely toxic and dangerous material to work with. "Taming" of anhydrous hydrogen fluoride was thus a challenge.

I have found a simple way for carrying out anhydrous hydrogen fluoride reactions at atmospheric pressure in the usual laboratory equipment by using the remarkably stable complex formed between pyridine and excess hydrogen fluoride. HF (70%) and pyridine (30%) form a liquid complex, $C_5H_5NH^+(HF)_xF^-$, showing low vapor pressure at temperatures up to 60 °C. The reagent (pyridinium polyhydrogen fluoride, sometimes called Olah's reagent) enables one to carry out a wide variety of synthetically very useful fluorination reactions safely and under very simple experimental conditions.[4,14]

The other area of synthetic research I pursued during my whole career involved Friedel−Crafts and related reactions. I developed many new synthetic methods and reactions over the years in this wide and diverse field. Again, these were well reviewed, including in my book and reviews on Friedel−Crafts Chemistry, and no further repetition is given here.

Many other new synthetic reagents and methods evolved in our research over the years. Following unsuccessful efforts to prepare long-lived trivalent alkylsilicenium ions from silyl iodides with Tse-Lok Ho, we found that trimethylsilyl iodide (TMSI), with strong hard−soft character of the Si−I bond, is capable of bringing about varied synthetic transformations including cleavage of esters, ethers, etc. under mild conditions. TMSI developed into a most useful and widely used reagent.

In later work, primarily through the efforts of my colleague Surya Prakash, TMS-CF_3 was explored as a trifluoromethylalkylating agent.

As already mentioned, I explored many synthetic applications of superacidic systems, particularly those of trifluoromethanesulfonic acid (triflic acid). One interesting application was the finding that sodium borohydride in triflic acid medium was a powerful reducing agent capable of the reductive isomerization of polycyclic hydrocarbons, $C_{4n+6}H_{4n+12}$ to their respective diamondoid hydrocarbons, adamantane, diamantane and triamantane. The efficacy of this ionic hydrogenation system was also demonstrated by the reduction of CO_2 and CO.

Comprehensive reviews on my synthetic efforts have been published and will thus not be repeated here. The widely used Fieser and Fieser series (now continued by T. L. Ho) and other review sources also contain good documentation of my newly developed synthetic reagents and reactions.

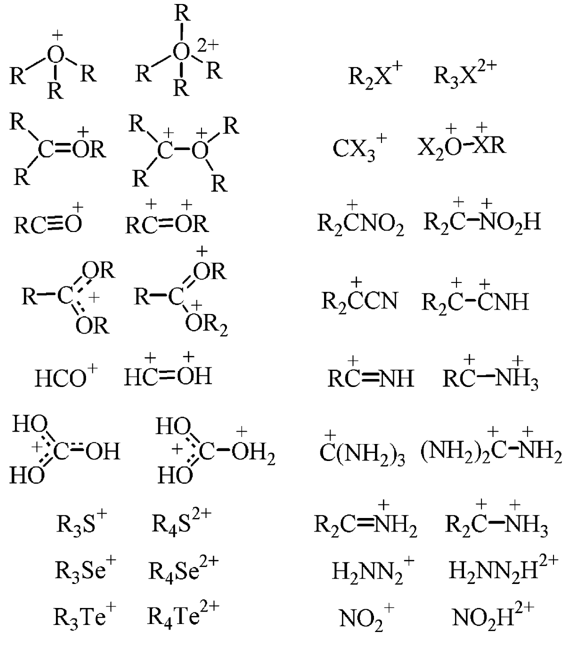
From Superacids to Superelectrophiles and Superelectrophilic Activation[18]

In 1994 I was awarded the Nobel Prize in chemistry. I have described in my autobiographical book the wonderful events connected with the festivities in Stockholm. I only want to emphasize that the Prize was really the recognition of the joint efforts of so many of my colleagues and students in the Olah group over the years. I was fortunate to represent them.

The Nobel Prize frequently puts so many new responsibilities and preoccupations on the shoulders of the winners, that it drastically changes their lives and affects their ability (or desire) to continue active research. I was blessed not to be affected by this and feel that my research of the past decade following the Prize was (and still continues to be) perhaps the most interesting and may be the most important of all my work.

As discussed, a significant part of my previous research was based on the study of superacid systems and their chemistry. The acids used turned out to be many billions or even trillions of times stronger than previously recognized strong acids such as concentrated sulfuric acid.

My work on carbocations and acidic onium ions under superacidic long-lived stable ion conditions led to new reactions and the characterization of many of the intermediates involved in these reactions. I increasingly realized in recent years that electrophiles that are capable of further interaction (coordination) with strong Bronsted or Lewis acids can be activated to *superelectrophiles* with greatly enhanced reactivity. The resulting enhancement of reactivity is substantial compared to that of the parent electrophiles under conventional conditions. Superelectrophiles are, thus, electrophiles with doubly electrodeficient (dipositive) nature whose reactivity substantially exceeds that of their parent electrophiles. We studied *inter alia* the protolytic or electrophilic activation of acyl cations: protonated CO, CO_2, COS, carbonic and thiocarbonic acids, heteroatom-substituted carbocations (and some of their boron analogues), halonium ions, azonium ions (including nitronium ion), and carbazonium ions in superacidic and related strongly electrophilic media. Both experimental chemical studies and theoretical calculations of the involved systems were carried out. As prototypes for protolytically activated onium ions, the protohydronium dication H_4O^{2+} (diprotonated water) and its sulfur analogue, the protosulfonium dication (H_4S^{2+}), were found to be of particular significance. The protoacetyl and protoformyl dication (diprotonated carbon monoxide), diprotonated carbonic acid and carbon dioxide, diprotonated hydrogen cyanide and nitriles, as well as the protonitronium dication, among others, were studied which laid the foundation for the emerging chemistry of superelectrophiles. The protonitronium dication was subsequently directly detected by H. Schwarz in electron-impact mass spectra, whereas we obtained ^{17}O NMR evidence for its formation.



Polyprotonated carbonic acid, esters, and diazonium ions were also investigated by theoretical calculations and experiments. The gitonic (proximal) vs distonic (distant) nature of onium dications was defined and discussed. In highly acidic media even alkyl cations are further protonated. The structure of the protio-*tert*-butyl dication was established by hydrogen/deuterium exchange studies and theoretical calculations.

Superelectrophiles are highly reactive species. They are the *de facto reactive intermediates* in many electrophilic reactions in superacidic systems (including those involving solid superacids) and should be differentiated from energetically lower-lying, *stable intermediates*, which can be observed and even isolated. However, these lower energy intermediates may not be sufficiently reactive without further activation.

It is recognized that many of the observed superelectrophilic reactions proceed when assisted by only electrophilic solvation by the superacids without the intervention of distinct dipositive intermediates. This is certainly the case in reactions with suitable nucleophiles, such as π-donor arenes and olefins or substrates containing n-donor heteroatoms, but not necessarily with weak σ-donor alkanes or highly deactivated π systems. Protosolvolytic (electrophilic) activation always should be considered in this context.

Application of the concept of superelectrophilic activation to organic syntheses led to a series of synthetically useful reactions. Several superelectrophilic nitration methodologies were developed. Benzaldehyde has been activated in superacids leading to the efficient preparation of triarylmethanes via condensation with aromatics. Isatin has been reacted with a number of aromatic compounds using superacidic activation to give 3,3-diaryloxindoles, in a combinatorial approach. Such oxindoles have applications in the pharmaceutical field. The field continues to rapidly develop further.

Hydrocarbon Research in the Loker Institute

Hydrocarbons from natural fossil fuels (oil, gas, coals) were formed over the eons. They are, however, nonrenewable resources on our human time scale. Upon combustion their carbon content forms carbon dioxide and hydrogen is converted into water. The industrial revolution that began just over two centuries ago was fueled by coal. In the second part of the 19th century mankind began to use oil and natural gas, which in the 20th century became a most significant part of our energy sources and raw materials for the chemical and petrochemical industries. Our hydrocarbon resources are, however, finite. With the greatly increased population of the earth (6 billion at present and, in all probability, it will reach 9−10 billion by the middle of the 21st century) and with vast demands for energy and materials, we must find new, efficient, and environmentally friendly ways to produce hydrocarbons by synthesis from renewable or recyclable sources.

My research in recent years in the context of the Loker Hydrocarbon Research Institute at the University of Southern California centered on developing new chemistry and methods directed toward these goals.

Some of our work involved development of more efficient and environmentally friendly methods to utilize presently existing petroleum resources. The isomerization of straight- chain alkanes into branched ones of much higher octane numbers is of substantial interest in producing high-octane gasoline without toxic additives. Isomerization with superacidic system at lower temperatures was studied, where equilibrium composition favors branched isomers. Our work included the highly efficient FSO_3H-HF system.

Acid-catalyzed alkylation of alkenes with isoalkenes also produces high octane branched alkylates. Anhydrous HF is a widely used acid catalyst in industry for the alkylation process. However, HF is highly volatile and toxic. In case of accidental release into the atmosphere it forms a toxic aerosol cloud that can harm or kill people in populated areas. I have discovered an efficient and safe way to minimize the safety and environmental hazard of HF alkylation by complexing excess HF with a suitable base such as a pyridine in ratios of 9:1 to 20:1 to form liquid onium polyhydrogen fluorides, which are ionic liquids of decreased volatility.[11] In these ionic liquids there is an equilibrium with some free HF, which promotes the alkylation process. The bulk of HF, however, is present in its complexed form. In case of an accidental release, the liquid complex can be easily washed down with water and neutralized. The process was commercialized by UOP-Texaco under the name ALKAD.

Superacidic systems were also found in our work to be efficient for upgrading heavy oils, and even for coal liquefaction. We studied, for example with Otto Strausz of Edmonton, the ability of superacids in upgrading Alberta heavy oils obtained from tar sand. Similarly, superacidic $HF-BF_3$-catalyzed depolymerization coupled with ionic hydroliquefaction of coals was found in our work to be an efficient new way of coal liquefaction necessitating only moderate temperatures and pressures.

We have also developed efficient superacidic methods to directly upgrade natural gas liquids to commercially useful high-octane gasoline.

The Methanol Economy[19]

The major direction of my ongoing research is to develop a new approach to hydrocarbons independent of Fischer−Tropsch chemistry. It centers on the use of methyl alcohol as the source for ethylene and propylene, and subsequently for all of the various hydrocarbons and products presently produced from oil or natural gas. My friend and colleague Professor Surya Prakash, besides carrying out his own independent significant research, is playing an increasingly major role in our ongoing cooperative effort. We have discovered bifunctional acid−base catalysis, such as by WO_3 on Al_2O_3, for the efficient conversion of methyl alcohol or dimethyl ether, as well as other substituted methanes (methyl halides, methyl mercaptans, etc.) to ethylene, propylene, and their derived hydrocarbons. Our work with these catalysts was independent of the industrially developed zeolite-based processes (Mobile, Union Carbide, UOP) for converting methyl alcohol into olefins (ethylene, propylene) and hydrocarbons. More importantly, our approach is based on new ways for obtaining the needed methanol (or dimethyl ether) either by direct selective oxidative conversion of still available natural gas (methane) without going through syn-gas based Fischer−Tropsch chemistry or by catalytic (as well as electrochemical) hydrogenation of atmospheric carbon dioxide.

As mentioned, all hydrocarbons, upon their combustion, produce carbon dioxide and water. As carbon dioxide is an efficient a greenhouse gas, excessive burning of fossil fuels contributes to global warming. We are involved in intensive research on the chemical recycling of carbon dioxide to methyl alcohol and its derivatives as useful fuels and raw materials for production of hydrocarbons. At the same time, removal of excess CO_2 from our atmosphere should mitigate global warming. We have discovered new ways of reductive recycling of atmospheric carbon dioxide to methanol involving either catalytic hydrogenation or the reverse use of our methanol fuel cell, wherein carbon dioxide in water is electrocatalytically reduced to methanol.

The hydrogenative production of methanol from carbon dioxide necessitates the use of much energy (which eventually can be provided by safe atomic energy or alternative energy sources). This can also be considered as an effective and safe way for energy storage. In contrast, the much discussed “hydrogen economy” is based on the use of highly volatile hydrogen, which must be handled under high pressure and using special materials and conditions (in order to minimize explosion hazards). No infrastructure exists for this, whereas liquid methanol can be easily stored and transported.

Methanol in its own right is an excellent fuel which can be blended with gasoline. It also has the potential when made by recycling of carbon dioxide for making mankind independent of our diminishing fossil fuel sources. What I call the “methanol economy” is an approach using methanol, based on direct conversion of methane or eventually recycling of atmospheric carbon dioxide with hydrogen generated from water, as a fuel as well as raw material for synthetic hydrocarbons. As part of our research on the use of methanol, with my colleague Surya Prakash and cooperation with colleagues from Caltech-JPL (Jet Propulsion Laboratory), we also developed a new type of direct methanol oxidation fuel cell that does not use prior reforming to produce hydrogen (through syn-gas and its separation). This new fuel cell promises many useful applications and, after nearly a decade of effort, now generates much interest for industrial commercialization.

In summary, I believe that methanol will increasingly become a key fuel, as well as a raw material for production of hydrocarbons. Its production from atmospheric carbon dioxide and water would represent an inexhaustible source for hydrocarbons, independent of fossil fuels and also a way to mitigate global warming caused by the greenhouse effect of carbon dioxide.

Concluding Remarks

In my years of research, which always gave me much pleasure, it was the German chemist Hans Meerwein who was my role model. Meerwein, whose fundamental studies touched various subjects, never wanted his work to be placed into any specific subsection of chemistry. He considered himself a Chemist (I am using the capital C deliberately) not to be narrowed into any specialty. His fundamental study of 1922, where he first observed rate acceleration in the acid-catalyzed hydrolysis of 2-norbornyl esters, and his suggestion that the related norbornyl carbocation is involved in the reaction, started what was to become physical organic chemistry. Meerwein himself, however, did not remain in this field. He was hurt by the very negative response of many of his colleagues to his work and by the rejection by the leading journals of the time of his subsequent follow-up papers. He decided not to pursue his studies in the field and to prove himself-by carrying out other, synthetically oriented research (Meerwein−Pondorf reduction, Meerwein oxonium salts, etc.). He was interested in developing new reagents and reactions, but not in the synthesis of complex target molecules. He also did some pioneering work in polymer chemistry. The ring-opening polymerization of THF was the result of Meerwein's ideas pursued in cooperation with industry. He also was the first to produce linear polyethylene (ahead of Ziegler and Natta) by BF_3-catalyzed dediazotization of diazomethane. He called his product polymethylene, which perhaps explains why it did not become widely recognized. Although Meerwein's name is regretfully not on the list of chemistry Nobel Prize winners, in my view he was a true giant of our profession who always strongly believed in the universality of chemistry. I hope that his shining example will be followed by future generations.

Meerwein is of course not the only example of leading chemist's broad interest and contributions to chemistry without narrow dividing lines. Emil Fischer, the leading organic chemist of his time, also made many fundamental contributions to carbohydrates, glycosides, peptides, early enzyme chemistry (lock and key concept), etc., and thus should be credited with having started the field of biochemistry.

R. B. Woodward, besides his classical studies on the total synthesis of complex molecules of generally significant biological activity, also was interested in structural-mechanistic problems. The Woodward−Hoffmann orbital symmetry rules probably would have brought him a second Nobel Prize if not for his untimely death. He also made major contributions to other areas, such as to the suggestion of the structure of ferrocene, a keystone of organometallic chemistry.

Our Priestly Medalist of last year, E. J. Corey, besides his fundamental contributions to organic synthesis and the development of the principle of retrosynthesis, also enjoyed exploring the computational methodology of synthesis. He even was once involved in studying the structural problem of the norbornyl cation.

I mention these examples to emphasize that I am proud and unapologetic for being a Chemist, with no hyphenation and subcategories. I also believe that chemistry continues to be the central science bridging, in a way others, such as physics and biology.

I always easily crossed the conventional boundaries of chemistry (organic, inorganic, physical, etc.) and always enjoyed the wide scope and opportunities which it offers. My own research over more than half a century covered many diverse fields. Although I am considered an organic chemist, much of my most interesting chemistry evolved from the use of new inorganic systems and reagents, including superacids and ionic compounds. I always used, to my best ability, new physical and spectroscopic methods. I am sure Meerwein would be satisfied knowing that I also always tried to be just a Chemist.

We recently published with my friend and colleague, Professor Surya Prakash, a collection of my selected chemical research papers, together with commentaries under the title *Research Across Conventional Lines*.[18] For those interested, it contains considerable details of my research of 50 years and a complete bibliography of my publications and patents.

On a personal note I concluded my autobiographical book with the following:

"My long journey, which started in my native Budapest on the banks of the river Danube and took me to the shores of the Pacific Ocean, was not always an easy one. Human nature, however, helps to block out memories of hardship and difficulties. They fade away and you look back remembering mostly the positive aspects of your life. I followed my own principles and went my own way. It helped that I inherited a strong, perhaps on occasion stubborn nature with a determination to follow the pathway to my goals and that I worked hard to achieve them. It was and still is a rewarding life experience, which I shared with my wife Judy, including our common profession. Her love, understanding for my many shortcomings and obsession with my work, her strength to keep the Olah family on course can not be thanked in simple words, I am glad that our sons have not followed us into the area of science. George an MBA is the CFO of a financial company in Los Angeles and Ron, a physician, is practicing internal medicine in close-by Pasadena. With our daughters in law, Sally and Cindy and our three adorable grandchildren, Peter, Kaitlyn, and Justin, we are blessed with a wonderful family. What else could I ever have asked for?" I could not conclude my Essay any better.

Acknowledgment. I am grateful to Mrs. Katherine Loker and her late husband Donald for their generous support of my work in the Loker Institute of USC in Los Angeles. Various government agencies and private foundations supported over the years different aspects of my research. Dr. Thomas Mathew and Ms. Jessie J. May are thanked for their help in preparing the manuscript and the figures (schemes).

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JO040285O