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Perspective

100 Years of Carbocations and Their Significance in Chemistry[1]

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The centennial of the first report of a stable (persistent) carbocation, the triphenylmethyl cation, serves as the occasion to give a perspective based on recollections of my half century of their search. This included development of general methods to prepare persistent long-lived carbocations in superacidic media, realization of the general concept of carbocations including trivalent and five or higher coordinated ions, as well delineation of their role and significance in chemistry.

1. Early Studies of Triphenylmethyl Cations

Many elements readily form ionic compounds, for example, sodium chloride in which the cationic sodium and anionic chlorine are held together by electrostatic, ionic bonding. Carbon, however, was long considered to lack the ability to form similar ionic compounds, except in very specific, highly stabilized systems, such as triphenylmethyl dyes.

The University of Chicago chemist Stieglitz, while studying salts of imido ethers, raised in 1899 the possibility of ionic hydrocarbon compounds.[2] It was in 1901 that Norris,[3] as well as Kehrman and Wentzel,[4] independently discovered that colorless triphenylmethyl alcohol gave deep yellow solutions in concentrated sulfuric acid. Triphenylmethyl chloride similarly formed orange complexes with aluminum and tin chlorides.

Baeyer should be credited for having recognized in 1902 the saltlike character of the compounds formed.[5] He then suggested a correlation between the appearance of color and salt formation, the so-called "halochromy." Gomberg (who had just shortly before discovered the related stable triphenylmethyl radical), as well as Walden, contributed to the evolving understanding of the structure of related cationic dyes such as malachite green.[6]

Whereas the existence of ionic triarylmethyl and related dyes was thus established around the turn of the twentieth century, the more general significance of carbocations in chemistry long went unrecognized. Triarylmethyl cations were considered an isolated curiosity of chemistry, not unlike Gomberg's triarylmethyl radicals. Not only were simple hydrocarbon cations believed to be unstable, even their fleeting existence was doubted.

2. Kinetic and Stereochemical Studies Indicating Carbocations

One of the most original and significant ideas in organic chemistry was the suggestion by Meerwein that

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[1] Based in part on my Nobel Lecture *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1393, and my autobiographical reflections: A Life of Magic Chemistry; Wiley-Interscience: New York, 2001.

[2] Stieglitz, J. *Am. Chem. J.* **1899**, *21*, 110.

[3] Norris, J. F. *Am. Chem. J.* **1901**, *25*, 117.

[4] Kehrmann, F.; Wentzel, F. *Chem. Ber.* **1901**, *34*, 3815.

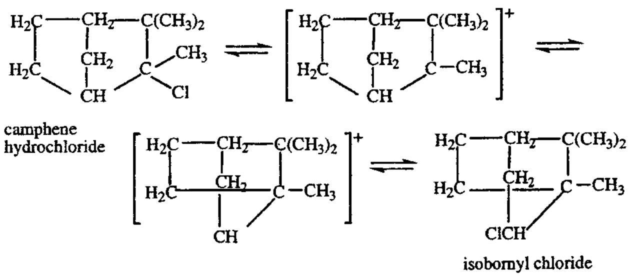
[5] Baeyer, A.; Villiger, V. *Chem. Ber.* **1901**, *35*, 1189; 3013.

[6] (a) Gomberg, M. *Chem. Ber.* **1902**, *35*, 2397. (b) Walden, P. *Chem. Ber.* **1902**, *35*, 2018.

10.1021/jo010438x CCC: $20.00

carbocations (as we now call all the positive ions of carbon compounds) might be intermediates to the course of reactions that start from nonionic reactants and lead to nonionic covalent products.

In 1922, Meerwein, while studying the Wagner rearrangement of camphene hydrochloride to isobornyl chloride with van Emster, found that the rate of the reaction increased with the dielectric constant of the solvent.[7] Furthermore, he found that certain Lewis acid chlorides such as $SbCl_5$, $SnCl_4$, $FeCl_3$, $AlCl_3$, and $SbCl_3$ (but not BCl_3 or $SiCl_4$), as well as dry HCl, which promote the ionization of triphenylmethyl chloride by formation of carbocationic complexes, also considerably accelerated the rearrangement of camphene hydrochloride to isobornyl chloride. Meerwein concluded that the isomerization actually does not proceed by way of migration of the chlorine atom but by a rearrangement of a cationic intermediate. Hence, the modern concept of carbocationic intermediates was born. Meerwein's views were, however, greeted with much skepticism by his peers in Germany, discouraging him from following up on these studies.



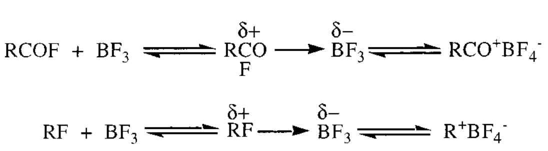
Ingold, Hughes, and their collaborators in England, starting in the late 1920s, carried out detailed kinetic and stereochemical investigations on what became known as nucleophilic substitution at saturated carbon and polar elimination reactions.[8] Their work relating to unimolecular nucleophilic substitution and elimination, called S_N1 and El reactions, in which formation of carbocations is the slow rate-determining step, laid the foundation for the role of electron-deficient carbocationic intermediates in organic reactions.

In the United States in the 1930s, Frank Whitmore in a series of papers generalized these concepts to include many other organic reactions.[9] Carbocations, however, were generally considered to be unstable and transient (short-lived) because they could not be directly observed.

The concept of carbocations slowly grew to maturity through kinetic, stereochemical, and product studies of a wide variety of reactions. 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 contributed fundamentally to the development of modern carbocation chemistry. The role of carbocations as one of the basic concepts of modern chemistry has been well reviewed.[10−12] With the advancement of mass spectrometry, the existence of gaseous carbocations was proven, but this could not give an indication of their structure or allow extrapolation to solution chemistry. Direct observation and study of stable, long-lived carbocations, such as alkyl cations in the condensed state, remained an elusive goal.

3. My Search for Persistent, Long-Lived Alkyl Cations

My search for cationic carbon intermediates started in Hungary while I was studying Friedel−Crafts-type reactions with acyl[13] and subsequently alkyl fluorides catalyzed by boron trifluoride.[14] In the course of these studies, I observed (and, in some cases, isolated) intermediate complexes of either donor−acceptor or ionic nature.

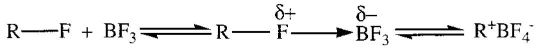


$$RCOF + BF_3 \rightleftharpoons \underset{F}{\overset{\delta+}{RCO}} \longrightarrow \overset{\delta-}{BF_3} \rightleftharpoons RCO^+BF_4^-$$

$$RF + BF_3 \rightleftharpoons \overset{\delta+}{RF} \longrightarrow \overset{\delta-}{BF_3} \rightleftharpoons R^+BF_4^-$$

The idea that ionization of alkyl fluorides to stable alkyl cations could be possible with an excess of strong Lewis acid fluoride that also serves as solvent first came to me in the early 1950s while studying the boron trifluoride-catalyzed alkylation of aromatics with alkyl fluorides. In the course of these studies, I attempted to isolate $RF{:}BF_3$ complexes. Realizing the difficulty of finding suitable solvents that would allow ionization but at the same time would not react with developing, potentially highly reactive alkyl cations, I condensed alkyl fluorides with neat boron trifluoride at low temperatures. I had, however, no access at the time to any modern spectrometers.

All I could do at the time with the $RF{-}BF_3$ complexes was to measure their conductivity. The results showed that methyl fluoride and ethyl fluoride complexes gave low conductivity, whereas the isopropyl fluoride and *tert*-butyl fluoride complexes were highly conducting.[14] The latter systems, however, also showed some polymerization (from deprotonation to the corresponding olefins). The conductivity data thus must have been to some degree affected by acid formation.



$$R{-}F + BF_3 \rightleftharpoons R{-}\overset{\delta+}{F} \longrightarrow \overset{\delta-}{BF_3} \rightleftharpoons R^+BF_4^-$$

My work on long-lived (persistent) carbocations started in the late 1950s while I was working for Dow Chemical in Sarna, Ontario, Canada, and resulted in the first direct observation of alkyl cations.

In Friedel−Crafts chemistry, it was known that when pivaloyl chloride is reacted with aromatics in the presence of aluminum chloride *tert*-butylated products are obtained in addition to the expected ketones. These were assumed to be formed by decarbonylation of the intermediate pivaloyl complex or cation. In the late 1950s, I returned to my earlier investigations of Friedel−Crafts complexes and extended them by using IR and NMR spectroscopy. I studied isolable complexes of acyl fluoride

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(7) Meerwein, H.; van Emster, K. *Chem. Ber.* **1922**, *55*, 2500.

(8) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1953; and references therein; 2nd ed., 1969.

(9) Whitmore, F. C. *J. Am. Chem. Soc.* **1932**, *54*, 3274, 3276; *Ann. Rep. Prog. Chem. (Chem. Soc. London)* **1933**, 177; *Chem. Eng. News* **1948**, 26, 668.

(10) Olah, G. A., Schleyer, P.v. R., Eds. *Carbonium Ions*; Wiley-Interscience: New York, 1968−76; Vols. I−V, and reviews therein.

(11) Bethell, D.; Gold, V. *Carbonium Ions*; Academic Press: London, New York, 1967.

(12) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985.

(13) Olah, G. A.; Kuhn, S. J. *Chem. Ber.* **1956**, *89*, 866.

(14) Olah, G. A.; Kuhn, S. J.; Opal, J. *J. Chem. Soc.* **1957**, 2174.

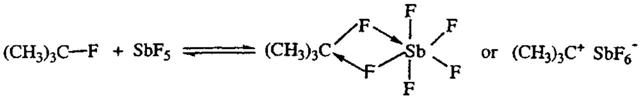
with Lewis acid fluorides, including higher-valence Lewis acid fluorides such as SbF_5, AsF_5, and PF_5.[15-17] In the course of these studies, it was not entirely unexpected that the generated $(CH_3)_3CCOFSbF_5$ complex showed a substantial tendency toward decarbonylation. What was exciting, however, was that it was possible to follow this process by NMR spectroscopy and to observe what turned out to be the first stable, long-lived alkyl cation salt, namely, *tert*-butyl hexafluoroantimonate.

$$(CH_3)_3CCOF + SbF_5 \longrightarrow (CH_3)_3CCO^+SbF_6^- \xrightarrow{-CO} (CH_3)_3C^+SbF_6^-$$

This breakthrough was first reported in 1962 and was followed by further studies that led to methods for preparing various long-lived alkyl cations in solution.

During a prolonged, comprehensive study of attempted ionization of alkyl halides, including fluoride with numerous Lewis acid halides, I finally hit on antimony pentafluoride. It turned out to be an extremely strong Lewis acid and, for the first time, enabled the ionization of alkyl fluorides to stable, long-lived alkyl cations. Neat SbF_5 solutions of alkyl fluorides are viscous, but when diluted with liquid sulfur dioxide the solutions could be cooled and studied at −78 °C. Subsequently, I also introduced even lower-nucleophilicity solvents such as SO_2ClF or SO_2F_2, which allowed studies at even lower temperatures. Following the observation of the decarbonylation of the pivaloyl cation that gave the first spectral evidence for the tertiary butyl cation, *tert*-butyl fluoride was ionized in excess antimony pentafluoride. The solution of the *tert*-butyl cation turned out to be remarkably stable, allowing chemical and spectroscopic studies alike.[16,18]

In the late 1950s, the research director of our laboratory was not yet convinced of the usefulness of NMR spectroscopy. Consequently, we had no such instrumentation of our own. Fortunately, the Dow laboratories in Midland, MI, just 100 miles away, had excellent facilities run by E. B. Baker, a pioneer of NMR spectroscopy, who offered his help. To probe whether our SbF_5 solution of alkyl fluorides indeed contained alkyl cations, we routinely drove in the early morning to Midland with our samples and watched Ned Baker obtain their NMR spectra. *tert*- Butyl fluoride itself showed a characteristic doublet in its ^1H NMR spectrum due to the fluorine−hydrogen coupling ($J_{HF} = 20$ Hz). In SbF_5 solution, the doublet disappeared and the methyl protons became significantly deshielded from $\delta \sim 1.5$ to 4.3. This was very encouraging but not conclusive proof of the presence of the *tert*-butyl cation. If one assumes that, with SbF_5, *tert*-butyl fluoride forms only a polarized donor−acceptor complex, which undergoes fast fluorine exchange (on the NMR time scale), the fluorine−hydrogen coupling would be "washed out," while a significant deshielding of the methyl protons would still be expected. The differentiation of a rapidly exchanging polarized donor−acceptor complex from the long-sought-after ionic $t\text{-}C_4H_9^+$ SbF_6^- thus became a major challenge.



Ned Baker, himself a physicist, showed great interest in our chemical problem. To solve it, he devised a means to obtain the carbon-13 NMR spectra of our dilute solutions, an extremely difficult task at the time before the advent of Fourier transform NMR techniques. Labeling with carbon-13 was possible at the time only to about a 50% level (from $Ba^{13}CO_3$). When we prepared 50% ^{13}C-labeled *tert*-butyl fluoride for ionization in SbF_5, we could, however, obtain at best only a 5% carbocationic solution in SbF_5. Thus, the ^{13}C content in the ionic solution was 10-fold diluted. However, Baker, undaunted, devised what became known as the INDOR (internuclear double resonance) method. Using the high sensitivity of the proton signal, he was able with the double-resonance technique to observe the ^{13}C shifts of our dilute solutions—a remarkable achievement around 1960. The carbon-13 shift of the tertiary carbon atom in $(CH_3)_3CFSbF_5$ of ^{13}C 335.2 turned out to be more than 300 ppm deshielded from that of the covalent starting material. Such very large chemical deshielding (the most deshielded ^{13}C signal at the time) could not be reconciled with a donor−acceptor complex. It indicated rehybridization from sp^3 to sp^2 and at the same time showed the effect of significant positive charge on the carbocationic carbon center.

Besides the *tert*-butyl cation, we also succeeded in preparing and studying the related isopropyl and the *tert*-amyl cations. The isopropyl cation was of particular relevance.

$$(CH_3)_2CHF + SbF_5 \longrightarrow (CH_3)_2CH^+\,SbF_6^-$$

$$(CH_3)_2CFCH_2CH_3 + SbF_5 \longrightarrow (CH_3)_2\overset{+}{C}CH_2CH_3\;SbF_6^-$$

Whereas in the *tert*-butyl cation the methyl protons are attached to carbons that are only adjacent to the carbocationic center, in the isopropyl cation a proton is directly attached to the center. When we obtained the proton NMR spectrum of the $i\text{-}C_3H_7F{-}SbF_5$ system, the CH proton showed up as an extremely deshielded septet at 13.0 ppm, ruling out a polarized donor−acceptor complex and indicating the formation of the $(CH_3)_2CH^+$ ion. The ^{13}C NMR spectrum was also conclusive, showing a very highly deshielded (by $\Delta\delta > 300$) ^+C atom ($\delta^{13}C$ 320.6). The spectrum of the *tert*-amyl cation showed an additional interesting feature due to the strong long-range H−H coupling of the methyl protons adjacent to the carbocationic center with the methylene protons. If only the donor−acceptor complex were involved, such long-range coupling through an sp^3 carbon would be small

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(15) Olah, G. A.; Kuhn, S. J.; Tolgyesi, W. S.; Baker, E. B. *J. Am. Chem. Soc.* **1962**, *84*, 2733.

(16) Olah, G. A. *Rev. Roum. Chim.* (*Buchrest*) **1962**, *7*, 1129 (Nenitzescu issue).

(17) Olah, G. A.; Tolgyesi, W. S.; Kuhn, S. J.; Moffatt, M. E.; Bastien, I. J.; Baker, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 1328.

(18) Preliminary communications and lectures: (a) Olah, G. A. Conference Lecture at 9th Reaction Mechanism Conference, Brookhaven, NY, August 1962. (b) Olah, G. A. Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, NJ, Sep 1962; American Chemical Society: Washington, DC, 1962; p 45. (c) Olah, G. A.; Tolgyesi, W. S.; MacIntyre, J. S.; Bastien, I. J.; Meyer, M. W.; Baker, E. B. Abstracts A, XIX International Congress of Pure and Applied Chemistry, London, June 1963; p 121. (d) Olah, G. A. *Angew. Chem.* **1963**, *75*, 800. (e) Olah, G. A. *American Chemical Society 1964 Petroleum Award Lecture, Reprints*; Division of Petroleum Chemistry; American Chemical Society: Washington, DC, 1964; Vol. 9, No. 7, C31. (f) Olah, G. A. *Intermediate Complexes and Their Role in Electrophilic Aromatic Substitutions*; Conference Lecture at Organic Reaction Mechanism Conference, Cork, Ireland, June 1964; Special Publication No. 19, The Chemical Society, London, 1965. (g) Olah, G. A.; Pittman, C. U., Jr.. In *Advances in Physical Organic Chemistry*; Gold, V., Ed.; Academic Press: London, New York, 1966; Vol. 4, p 305.

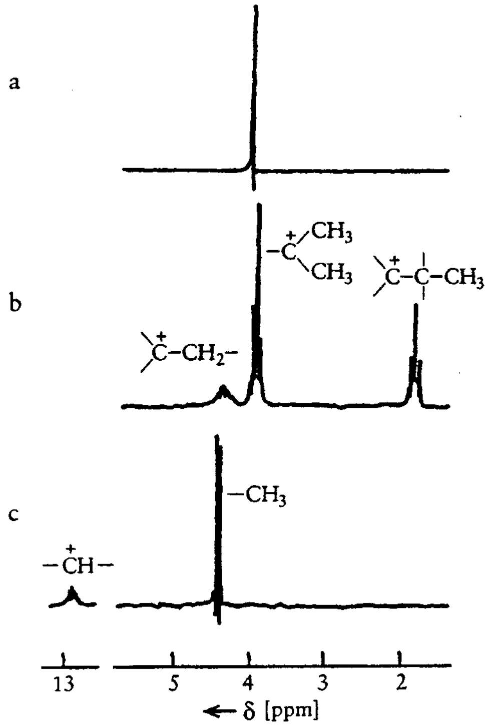
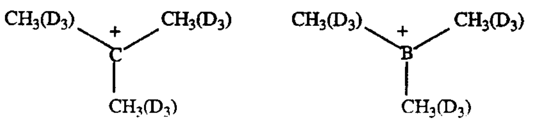


Figure 1. ^{1}H NMR spectra of (a) the *tert*-butyl cation [trimethylcarbenium ion, $(CH_3)_3C^+$]; (b) the *tert*-amyl cation [dimethylethylcarbenium ion, $(CH_3)_3C^+{-}C_2H_5$]; and (c) the isopropyl cation [dimethylcarbenium ion, $(CH_3)_2C^+H$] (60 MHz, in SbF_5/SO_2ClF solution, −60 °C).

(1−2 Hz). Instead, the observed significant coupling (J_{H-H} = 10 Hz) indicated that the species studied indeed had an sp^2 center through which the long-range H−H coupling became effective. Figure 1 reproduces the ^{1}H NMR spectra of the *tert*-butyl, *tert*-amyl, and isopropyl cations. These original spectra are framed and hang in my office as a memento, as are the ESCA spectra of the *tert*-butyl and of the norbornyl cation (vide infra).[19]

IR spectroscopic studies on *tert*-butyl cation was also carried out in neat SbF_5 at room-temperature long before the advent of the Fourier transform methods. Subsequently, in 1968−1970, with DeMember and Commeyras in Cleveland,[20] we were able to carry out more detailed IR and laser Raman spectroscopic studies of alkyl cations. Comparison of the data of unlabeled and deuterated *tert*-butyl cations with those of isoelectronic trimethylboron proved the planar structure of the carbocation.



Our studies also included IR spectroscopic investigation of the observed ions (Figure 2). John Evans, who was at the time a spectroscopist at the Midland Dow laboratories, offered his cooperation and was able to obtain and analyze the vibrational spectra of our alkyl cations. It is rewarding that, some 30 years later, FT-IR spectra obtained by Sunko and his colleagues in Zagreb[21] with low-temperature matrix-deposition techniques and Schleyer's calculations of the spectra showed good agreement with our early work. This was also an early example of the realization that for nearly all carbocations there exists a neutral isoelectronic isostructural boron analogue, which later proved itself so useful in the hands of my colleagues Williams, Prakash, and Field.

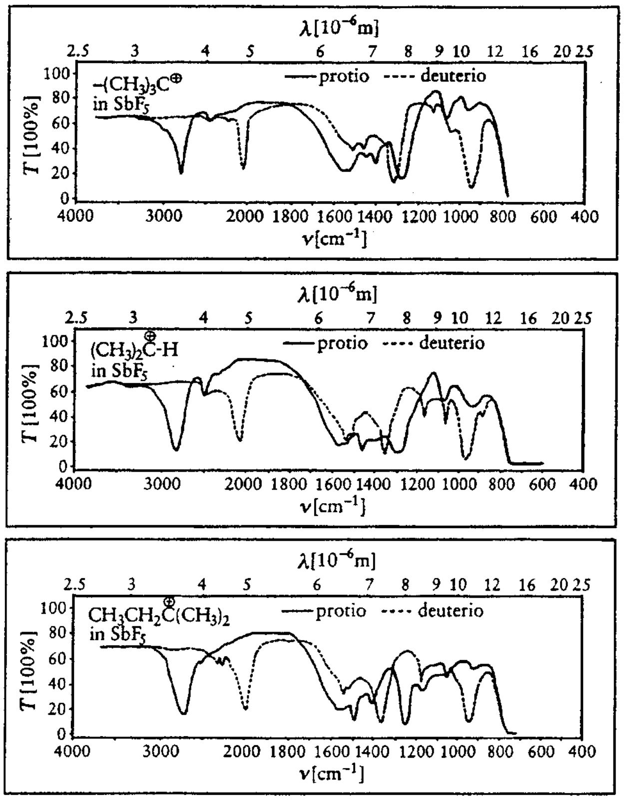


Figure 2. IR spectra of *tert*-butyl (top), isopropyl (center), and *tert*-amyl (bottom) cations. T = transmission.

The chemistry of stable, long-lived (or persistent) carbocations, as they became known, thus began. Many have since contributed to the study of long-lived carbocations. The field rapidly expanded and allowed successful study of practically any carbocationic system. My talented and hard-working former associates and students deserve the lion's share of credit for our work, as do the many researchers around the world who joined in and contributed so much to the development of the field (their work can be found in the references). I would like, however, to mention particularly the pioneering work of Brouwer and Hogeveen,[22] as well as their colleagues at the Shell Laboratories in Amsterdam in the 1960s and 1970s. They contributed fundamentally to the study of long-lived carbocations and related superacidic hydrocarbon chemistry. The first publication from the Shell laboratories on alkyl cations appeared in 1964, following closely my initial reports of 1962−1963.

Subsequent to my study of alkyl cations, a wide spectrum of carbocations as long-lived species was studied using antimony pentafluoride as an extremely strong Lewis acid and later using other highly acidic (superacidic) systems.

Until this time, alkyl cations were considered only transient species. Their existence had been indirectly

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[19] (a) Olah, G. A.; Baker, E. B.; Evans, J. C.; Tolgyesi, W. S.; McIntyre, J. S.; Bastien, I. J. *J. Am. Chem. Soc.* **1964**, *86*, 1360. (b) Olah, G. A. *Chem. Eng. News* **1967**, *45*, 76; *Science* **1970**, *168*, 1798.

[20] Olah, G. A.; DeMember, J. R.; Commeyras, A.; Bribes, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 459 and references therein.

[21] Vancik, H.; Sunko, D. E. *J. Am. Chem. Soc.* **1989**, *111*, 3742.

[22] Brouwer, D. M.; Mackor, E. L. *Proc. Chem. Soc.* **1964**, 147.

inferred from kinetic and stereochemical studies, but no reliable spectroscopic or other physical measurements of simple alkyl cations in solution or in the solid state had been obtained.

4. The Role of Superacids

It was not fully realized until my breakthrough using extremely strong superacids that, to suppress the deprotonation of alkyl cations to olefins and the subsequent formation of complex mixtures by reactions of olefins with alkyl cations, such as alkylation, oligomerization, polymerization, and cyclization, acids much stronger than those known and used in the past were needed.

$$(CH_3)_3C^+ \rightleftharpoons H^+ + (CH_3)_2C{=}CH_2$$

Finding such acids (called "superacids")[23] turned out to be the key to obtaining stable, long-lived alkyl cations and, in general, carbocations. If any deprotonation were still to take place, the formed alkyl cation (a strong Lewis acid) would immediately react with the formed olefin (a good π-base), leading to the mentioned complex reactions.

In the course of my studies, it became increasingly clear that a variety of highly acidic systems besides the originally used antimony pentafluoride systems are capable of generating long-lived, stable carbocations. The work was thus extended to a variety of other superacids. Protic superacids such as FSO_3H (fluorosulfuric acid) and CF_3SO_3H (triflic acid) as well as conjugate acids such as $HF-SbF_5$, FSO_3H-SbF_5 (magic acid), $CF_3SO_3H-SbF_5$, and $CF_3SO_3H-B(O_3SCF_3)_3$ were extensively used. Superacids based on Lewis acid fluorides such as AsF_5, TaF_5, and NbF_5 and other strong Lewis acids such as $B(O_3SCF_3)_3$ were also successfully introduced. The name "magic acid" for the FSO_3H-SbF_5 system was given by Joe Lukas, a German postdoctoral fellow working with me in Cleveland in the 1960s, who after a laboratory Christmas party put remainders of a candle into the acid. The candle dissolved, and the resulting solution gave a clear NMR spectrum of the *tert*-butyl cation. This observation understandably evoked much interest, and the acid used was named "magic." The name stuck in our laboratory. I think it was Ned Arnett who learned about it during one of his visits and subsequently introduced the name into the literature, where it became quite generally used.

I would like to credit especially the fundamental contributions of Ron Gillespie to the inorganic chemistry of strong acids (superacids),[23a,b] which greatly contributed to the development of superacid chemistry. His long-standing interest in fluorosulfuric acid and our studies of SbF_5-containing systems thus found common ground in studies of FSO_3H-SbF_5 (magic acid) systems.[24]

Until the late 1950s, chemists generally considered mineral acids, such as sulfuric, nitric, perchloric, and hydrofluoric acids, to be the strongest acid systems in existence. This has changed considerably as extremely strong acid systems—many billions or even trillions of times stronger than sulfuric acid—have been discovered.

The acidity of aqueous acids is generally expressed by their pH, which is a logarithmic scale of the hydrogen ion concentration (or, more precisely, of the hydrogen ion activity). pH can be measured by the potential of a hydrogen electrode in equilibrium with a dilute acid solution or by a series of colored indicators. In highly concentrated acid solutions or with strong nonaqueous acids, the pH concept is no longer applicable, and acidity, for example, can be related to the degree of transformation of a base to its conjugate acid (keeping in mind that this will depend on the base itself). The widely used so-called Hammett acidity function H_o relates to the half-protonation equilibrium of suitable weak bases. The Hammett acidity function is also a logarithmic scale on which 100% sulfuric acid has a value of H_o -11.9. The acidity of sulfuric acid can be increased by the addition of SO_3 (oleum). The H_o of HF is -11.0 (however, when HF is completely anhydrous, its H_o is $-$ 15, but even a slight amount of water drops the acidity to -11, as shown by Gillespie).

Perchloric acid ($HClO_4$; H_o -13.0), fluorosulfuric acid (FSO_3H; H_o -15.1), and trifluoromethanesulfonic acid (CF_3SO_3H; H_o $-14.$ 1) are considered to be superacids, as is truly anhydrous hydrogen fluoride. Complexing with Lewis acidic metal fluorides of higher valence, such as antimony, tantalum, or niobium pentafluoride, greatly enhances the acidity of all these acids.

In the 1960s, Gillespie suggested calling protic acids stronger than 100% sulfuric acid "superacids." This arbitrary but most useful definition is now generally accepted. It should be mentioned, however, that the name "superacid" goes back to J. B. Conant of Harvard, who used it in 1927 in a paper in the *Journal of the American Chemical Society* to denote acids such as perchloric acid, which he found stronger than conventional mineral acids and capable of protonating such weak bases as carbonyl compounds.[25] My book on superacids, published in 1985 with Surya Prakash and Jean Sommer,[23c] was appropriately dedicated to the memory of Conant. Few of today's chemists are aware of his contributions to this field. Conant subsequently became the president of Harvard University and gave up chemistry, which may explain why he never followed up on his initial work on superacids.

In a generalized sense, acids are electron-pair acceptors. They include both protic (Bronsted) acids and Lewis acids such as $AlC1_3$ and BF_3 that have an electron-deficient central metal atom. In extending the concept of superacidity to Lewis acid halides, those stronger than anhydrous aluminum chloride (the most commonly used Friedel—Crafts acid) are considered super Lewis acids. These superacidic Lewis acids include higher-valence fluorides such as antimony, arsenic, tantalum, niobium, and bismuth pentafluorides. Superacidity encompasses both very strong Bronsted and Lewis acids and their conjugate acid systems.

Friedel—Crafts Lewis acid halides form with proton donors such as H_2O, HCl, and HF conjugate acids such as $H_2O{\cdot}BF_3$, $HCl-AlC1_3$, and $HF-BF_3$, which ionize to $H_3O^+BF_3OH^-$, $H_2Cl^+AlCl_4^-$, and $H_2F^+BF_4^-$, etc. These conjugate Friedel—Crafts acids have H_o values from about -14 to -16. Thus, they are much stronger than

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[23] (a) Gillespie, R. J. *Acc. Chem. Res.* **1968**, *1*, 202. (b) Gillespie, R. J.; Peel, T. E. *Adv. Phys. Org. Chem.* **1972**, *9*, 1; *J. Am. Chem. Soc.* **1973**, *95*, 5173. (c) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985. (d) Gillespie, R. J. *Can. Chem. News* 1991, May, 20.

[24] (a) Bacon, J.; Dean, P. A. W.; Gillespie, R. J. *Can. J. Chem.* **1969**, *47*, 1655. (b) Olah, G. A.; Calin, M. *J. Am. Chem. Soc.* **1968**, *90*, 938.

[25] Hall, N. F.; Conant, J. B. *J. Am. Chem. Soc.* **1927**, *49*, 3047.

the usual mineral acids. Even stronger superacid systems are HSO_3F-SbF_5 (magic acid), $HF-SbF_5$ (fluoroantimonic acid), and $CF_3SO_3H-B(O_3SCF_3)_3$ (triflatoboric acid). The acidity of anhydrous HF, HSO_3F, and CF_3SO_3H increases drastically upon addition of Lewis acid fluorides such as SbF_5, which form large complex fluoroanions facilitating dispersal of the negative charge.

$$2\,HF + 2\,SbF_5 \rightleftharpoons H_2F^+\,Sb_2F_{11}^- \quad \text{fluoroantimonic acid}$$

$$2\,HSO_3F + 2\,SbF_5 \rightleftharpoons H_2SO_3F^+\,Sb_2F_{10}(SO_3F)^- \quad \text{magic acid}$$

$$2\,CF_3SO_3H + B(O_3SCF_3)_3 \rightleftharpoons CF_3SO_3H_2^+\,B(O_3SCF_3)_4^- \quad \text{triflatoboric acid}$$

The acidity function of HSO_3F increases on addition of SbF_5 from −15.1 to −23.0, the acidity of 1:1 FSO_3H-SbF_5 (magic acid). Fluoroantimonic acid is even stronger; with 4 mol % SbF_5, the H_o value for $HF-SbF_5$ is already −21.0, a thousand times stronger than the value for fluorosulfuric acid with the same SbF_5 concentration. The acidity of the 1:1 $HF-SbF_5$ system or those with even higher SbF_5 concentrations reaches H_o −28. Thus, these superacidic systems can be 10^{16} times stronger than 100% sulfuric acid! (A trillion is 10^{12}.)

Related superacid systems in which SbF_5 is replaced by AsF_5, TaF_5, NbF_5, etc. are of somewhat lower acidity but are still extremely strong acids. So is $HF-BF_3$, a very useful superacid that will not cause oxidative side reactions. Ternary superacid systems including, for example, FSO_3H-HF or CF_3SO_3H-HF with Lewis acid fluorides are also known and used.

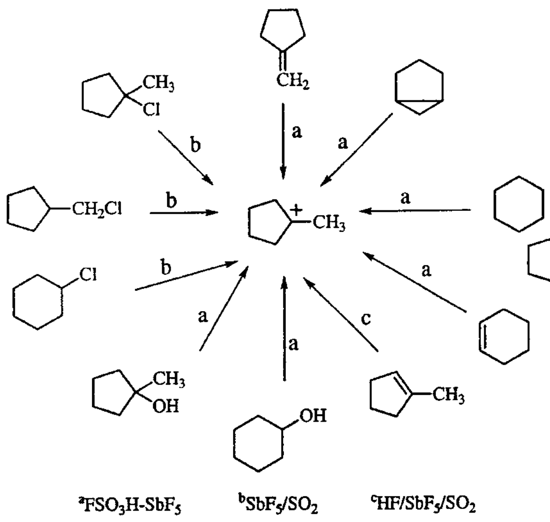
Acids are not limited to liquid (or gaseous) systems. Solid acids also play a significant role. Acidic oxides such as silica, silica−alumina, etc. are used extensively as solid acid catalysts. New solid acid systems that are stronger than those used conventionally are sometimes called solid superacids. However, it must be kept in mind that when carbocations are developing on solid surfaces or zeolitic systems they will coordinate (bind) to nucleophilic sites (oxygen, etc.), and thus only highly stable carbocations will be observable as persistent species on such systems. This of course does not mean that at the involved higher temperatures some equilibrium with carbocationic species could not exist provoking carbocationic reactions.

Solid perfluorinated resin sulfonic acid catalysts, such as those based on the acid form of DuPont's Nafion ionomer membrane resin, and some higher perfluoroalkanesulfonic acids, such as perfluorodecanesulfonic acid, more closely resemble liquid fluorinated superacids.

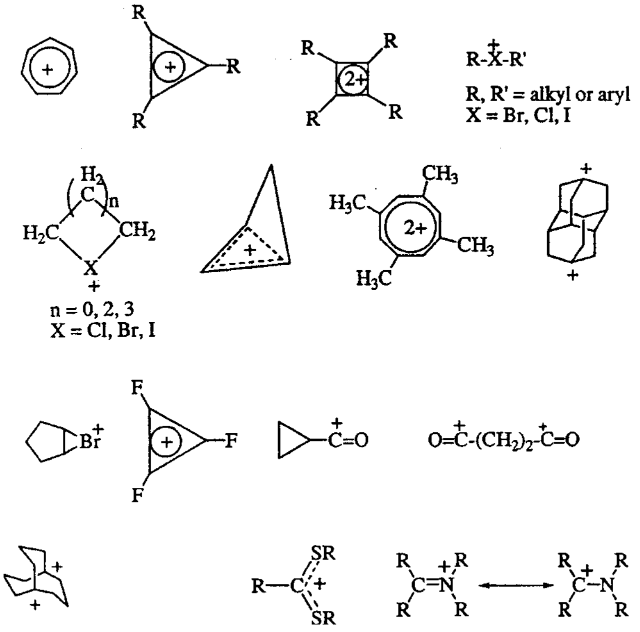
5. Generalization of the Study of Carbocations

After returning to academia in Cleveland in 1965, my research continued and extended the study of carbocations in varied superacidic systems as well as exploration of the broader chemistry of superacids, involving varied ionic systems and reagents. In Cleveland, a main aspect of my research was directed to the exploration of the chemistry of these persistent cations of carbon compounds (carbocations) and the fascinating new area of chemistry opened up by superacids. Particular interest was generated as a great variety of carbocations were found to be readily generated and studied in these enormously strong acid systems.

Over a decade of research, we were able to show that practically all conceivable carbocations could be prepared under what became known as "stable ion conditions" using various very strong acid systems (see discussion of superacids) and low nucleophilicity solvents (SO_2, SO_2ClF, SO_2F_2, etc.).[26] A variety of precursors could be used under appropriate conditions, as shown, for example, in the preparation of the methylcyclopentyl cation.



A wide variety of carbocations and carbodications, including those that are aromatically stabilized as well those as stabilized by heteroatoms, were reported in the nearly 200 publications on the topic during my Cleveland years.



During my Cleveland years, in 1969 I organized a symposium on carbocation chemistry. It was attended by many of the major investigators in the field (Nenitzescu, Brown, Winstein, Dewar, Schleyer, Gillespie, Saunders, and others). We had lively discussion as was the case at the symposium in the fall of 1977 after my move to Los Angeles at USC and at a number of symposia I attended in different locations such as at La Grand Motte (France), Bangor (U.K.), and eventually Seattle, WA.

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(26) Olah, G. A. *Angew. Chem., Intl. Ind.* **1973**, *12*, 173; *Angew. Chem.* **1973**, *85*, 183. Olah, G. A. *Carbocations and Electrophilic Reactions*; Verlag Chemie:Weinheim, Wiley: New York, 1974.

6. The Nonclassical Ion Controversy and Its Significance

During the study of carbocations, much effort was put into studying whether certain carbocations represent rapidly equilibrating trivalent carbenium ions or static (bridged, delocalized) five-coordinate carbonium ion systems. This question became the focus of the rather headed controversy which centered around the question of the norbornyl cation and became known as the nonclassical ion controversy.[27]

The controversy in which I was inadvertently involved started over the structure of a deceptively simple seven-carbon-containing bicyclic carbocation, the 2-norbornyl (bicyclo[2.2.1]heptyl) cation. The involvement of the ion in the long-recognized rearrangement of norbornyl systems prevalent in natural terpenes was first suggested in 1922 by Meerwein. The remarkable facility of skeletal rearrangements in norbornyl systems attracted the early interest of chemists. Wagner realized first in 1899 the general nature of these rearrangements and related them to that which takes place during the dehydration of pinacolyl alcohol to tetramethylethylene. Sommer later found some tricyclanes in the products of the Wagner rearrangements of terpenes. In 1918, Ruzicka suggested a tricyclane-type mechanism without realizing the ionic nature of the process. Meerwein reconsidered the mechanism in 1922 and made the farsighted 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 in the “nonclassical ion” controversy following Wilson’s original suggestion in 1939 of a mesomeric, α-delocalized, carbocationic intermediate in the camphene hvdrochloride-isobornyl chloride rearrangement. From 1949 to 1952, Winstein and Trifan reported a solvolytic study of the *exo*- and *endo*-2-norbornyl brosylates (*p*-bromobenzenesulfonates) and postulated a σ-delocalized, symmetrically bridged norbornyl ion intermediate. The endo reactant was found to solvolyze in various solvents such as acetic acid, aqueous acetone, and aqueous dioxane to give substitution products of exclusively exo configuration. The *exo*-brosylate also 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 outstanding pioneer of hydroboration chemistry), in contrast, concluded that in solvolysis both 2-*exo*- and 2-*endo*-norbornyl esters (brosylates, etc.) undergo anchimerically unassisted ionization and that the singular rate and product characteristics of the system are attributable to steric effects, in particular, hindrance to ionization of the endo isomers. Explaining the results of the 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; 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), and he compared the process to that of a windshield wiper. However, at the same time, none of his studies ever showed that σ-participation cannot be involved.

In 1962, H. C. Brown lodged his dissent against the σ-bridged 2-norbornyl cation and, for that matter, other nonclassical carbocations. He has maintained his position virtually unchanged over the years and has continued to present his views forcefully. In arguing against carbon σ-bridging, he took the position, despite his pioneering work in structurally closely related boranes, that if carbon were to participate in bridging, novel bonding characteristics must be attributed to it.

In 1965, he stated, “On the other hand, the norbornyl cation does not possess sufficient electrons to provide a pair for all of the bonds required by the proposed bridged structures. One must propose a new bonding concept, not yet established in carbon structures” (with my emphasis added).

In 1967, he again wrote, “The second subclass consists of ions such as the bicyclobutonium and the norbornyl cation in its σ-bridging form, which do not possess sufficient electrons to provide a pair for all of the bonds required by the proposed structures. *A new bonding concept not yet established in carbon structures is required*” (emphasis added).

The Brown−Winstein nonclassical ion controversy can be summed up as differing explanations of the same experimental facts (which were obtained repeatedly and have not been questioned) of the observed significantly higher rate of the hydrolysis of the 2-*exo*- over the 2-*endo*-norbornyl esters. As suggested by Winstein, the reason for this is participation of the C_1-C_6 single bond leading to delocalization via the bridged “nonclassical” ion. In contrast, Brown maintained that the cause was only steric hindrance to the sterically hindered endo side involving rapidly equilibrating “classical” trivalent ions.

Nonclassical ions, a term first used by John Roberts,[28] were defined by Paul Bartlett as containing too few electrons to allow a pair for each “bond”; i.e., they must contain delocalized σ-electrons.[27a] This is where the question stood in the early 1960s. The structure of the intermediate 2-norbornyl ion could only be suggested indirectly from rate (kinetic) data and observation of stereochemistry; no direct observation or structural study was possible at the time.

My own involvement with the norbornyl ion controversy goes back to 1960−1962, when, as discussed, I succeeded in developing a general method of preparing and studying persistent (long-lived) alkyl cations. My interest subsequently extended to the study of various carbocations, including the controversial 2-norbornyl cation. Whereas previous investigators were able to study carbocations only indirectly (by kinetic and stereochemical studies), my newly discovered methods allowed their preparation and direct study as persistent (long-lived) species.

At the 1962 Brookhaven Mechanism Conference, where I first reported on long-lived carbocations in public, I was

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[27] (a) Bartlett, P. D. *Nonclassical Ions*; W. A. Benjamin: New York, 1965. (b) Winstein, S. *Quart. Rev. (London)* **1969**, *23*, 1411. (c) Brown, H. C. (with commentary by P. v. R. Schleyer) *The Nonclassical Ion Problem*; Plenum Press: New York, 1977; and references therein.

[28] Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 3542.

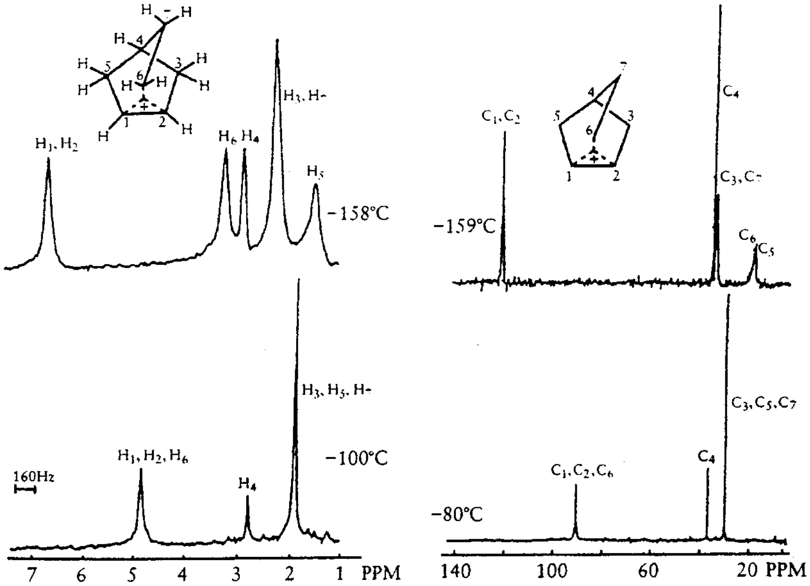
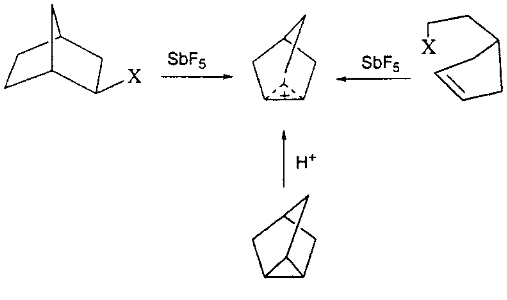


Figure 3. Left: 395 MHz ^{1}H NMR spectra of the 2-norbornyl cation in $SbF_5/SO_2ClF/SO_2F_2$ solution. Right: 50 MHz proton decoupled^{13}C NMR spectra of the 2-norbornyl cation (^{13}C enriched) in $SbF_5/SO_2ClF/SO_2F_2$ solution.

called aside separately by Winstein and Brown, both towering and dominating personalities of the time who cautioned me that a young man should be exceedingly careful in making such claims. Each pointed out that most probably I was wrong and could not have obtained long-lived carbocations. Just in case, however, my method turned out to be real, I was advised to obtain further evidence for the "nonclassical" or "classical" nature (depending on who was giving the advice) of the much-disputed 2-norbornyl cation.

Because my method indeed allowed me to prepare practically any carbocation as long-lived species, clearly the opportunity was there to experimentally decide the norbornyl ion question through direct observation of the ion. At the time of the Brookhaven conference, I had already obtained the proton NMR spectrum of 2-norbornyl fluoride in SbF_5, but only at room temperature, which displayed a single broad peak indicating complete equilibration through hydride shifts and Wagner−Meerwein rearrangement (well-known in solvolysis studies and related transformations of 2-norbornyl systems). However, my curiosity was aroused, and when I moved to Dow's Research Laboratory in the Boston area in 1964, the work was further pursued in cooperation with Paul Schleyer from Princeton (who became a lifetime friend) and Martin Saunders from Yale.[29] Using SO_2 as solvent, we were able to lower the temperature of the solution to −78 °C, and we also prepared the ion by ionization of β-cyclopentenylethyl fluoride or by protonation of nortricylene in FSO_3H; SbF_5/SO_2ClF.[30] The three separate routes (representing σ-, π-, or bent σ-participation) gave the identical ion.



As mentioned, we were able to obtain NMR spectra of the norbornyl ion at −78 °C, where the 3,2-hydride shift was frozen out. However, it took until 1969, after my move to Cleveland, to develop more efficient low-temperature techniques using solvents such as SO_2ClF and SO_2F_2. We were eventually able to obtain high-resolution ^{1}H and ^{13}C NMR spectra (using ^{13}C-enriched precursor) of the 2-norbornyl cation down to −159 °C (Figure 3).[31] Both the 1,2,6-hydride shifts and the Wagner−Meerwein rearrangement were frozen out at such a low temperature, allowing us to observe the static, bridged ion, which I first reported at the Salt Lake City Organic Symposium in 1969.

The differentiation of bridged nonclassical from rapidly equilibrating classical carbocations based on NMR spectroscopy was difficult because NMR is a relatively slow physical method. We addressed this question in our work using estimated NMR shifts of the two structurally differing ions in comparison with model systems. Later, this task became greatly simplified and more precise by highly efficient calculational methods such as IGLO and

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(29) Saunders, M.; Schleyer, P. v. R.; Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 5680.

(30) (a) Olah, G. A.; White, A. M.; DeMember, J. R.; Commeyras, A.; Lui, C. Y. *J. Am. Chem. Soc.* **1970**, *92*, 4627. (b) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1982**, *104*, 7105.

(31) (a) Olah, G. A.; Mateescu, G. D.; Wilson, L. A.; Gross, M. H. *J. Am. Chem. Soc.* **1970**, *92*, 7231. (b) Olah, G. A.; Mateescu, G. D.; Riemenschneider, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2529. (c) Johnson, S. A.; Clark, D. T. *J. Am. Chem. Soc.* **1988**, *110*, 4112.

(32) Arnett, E. M.; Pienta, N.; Petro, C. *J. Am. Chem. Soc.* **1980**, *102*, 398.

(33) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1980**, *102*, 6867.

(34) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 7380.

(35) Laube, T. *Angew. Chem.* **1987**, *99*, 580; *Angew Chem., Int. Ed. Engl.* **1987**, *26*, 560.

(36) Schleyer, P. v. R.; Sieber, S. *Angew Chem.* **1993**, *105*, 1676; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1606 and references therein.

(37) Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440.

(38) Bekesy, G. V. *Experiments in Hearing*; McGraw-Hill: New York, 1960; p 8.

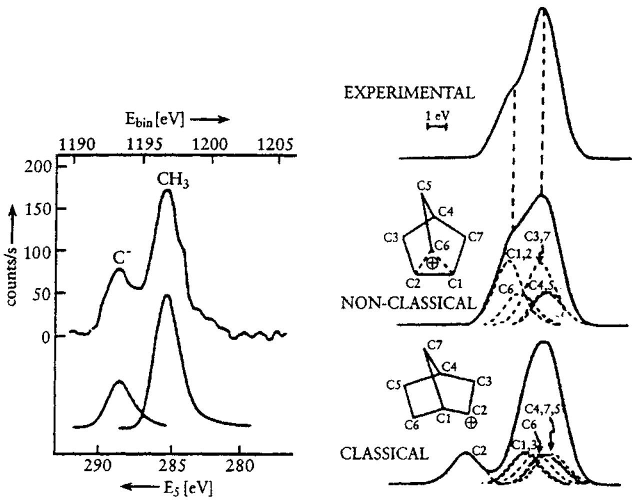


Figure 4. Left: carbon 1s photoelectron spectrum of the *tert*-butyl cation (top curve from experiment; bottom curve calculated). Right: 1s core-hole-state spectra for the 2-norbornyl cation (top), Clark's simulated spectra for the classical (center), and nonclassical ions (bottom).

GIAO, allowing the calculation of NMR shifts of differing ions and their comparison with experimental data. It is rewarding to see, however, that our earlier results and conclusions stood up well against all the more recent advanced studies.

Siegbahn's core electron spectroscopy (ESCA) was another fast physical method that we applied to further resolve the question of bridged versus rapidly equilibrating ions. We were able to study carbocations in the late 1960s by this method, adapting it to superacidic matrixes. George Mateescu and Louise Riemenschneider in my Cleveland laboratory set up the necessary instrumentation and methodology for obtaining the ESCA spectra of a number of carbocations, including the *tert*-butyl and the 2-norbornyl cation in SbF_5-based superacidic matrixes.[31] These studies again convincingly showed the nonclassical nature of the 2-norbornyl cation. No trivalent carbenium center characteristic of a "classical" ion, such as is the case for the *tert*-butyl cation, was observed in the ESCA spectrum on a time scale where no chemical equilibration process could have any effect. Subsequent ESCA studies in cooperation with Grunthaner's laboratory at Caltech's Jet Propulsion Laboratory and by Dave Clark in England fully justified our initial results and conclusions (Figure 4). So did the results of ever more advanced theoretical calculations.

Additional significant experimental studies were also carried out by other laboratories. Arnett reported fundamental calorimetric studies.[32] Saunders showed the absence of deuterium isotopic perturbation of equilibrium expected for a classical equilibrating system.[33] Myhre and Yannoni, at extremely low (5 K) temperature, were able to obtain solid-state ^{13}C NMR spectra that still showed no indication of freezing out any equilibrating classical ions. The barrier at this temperature should be as low as 0.2 kcal/mol (i.e., about the energy of a vibrational transition).[34] Laube was able to carry out single-crystal X-ray structural studies on substituted 2-norbornyl cations.[35] Schleyer's advanced theoretical studies including IGLO and related calculation of NMR shifts and their comparison with experimental data contributed further to the understanding of the σ-bridged carbonium ion nature of the 2-norbornyl cation.[36] The classical 2-norbornyl cation was not even found to be a high-lying intermediate!

As the norbornyl ion controversy evolved, it became a highly public and increasingly personal and sometimes even bitter public debate. Saul Winstein unexpectedly died in the fall of 1969, shortly after the Salt Lake City symposium. To my regret, I seemed to have inherited his role in representing the bridged nonclassical ion concept in subsequent discussions.

The 1983 Seattle American Chemical Society symposium was the de facto "closing" of the long-running debate. Although in the heat of the debates some personal remarks were made on both sides (to which I subsequently expressed my regret), the experimental evidence at the time was already so overwhelming that I concluded my presentation saying, "I do not intend to do any more research on the matter. There is nothing further to be discussed...". My lecture was subsequently published (with Prakash and Saunders) under the title "Conclusion of the Classical-Nonclassical Ion Controversy Based on the Structural Study of the 2-Norbornyl Cation" in an article in *Accounts of Chemical Research*.[37] In the same issue, Brown wrote, "The nonclassical theory is not necessarily wrong, but it has been too readily accepted" (probably an understatement concerning the enormous amount of work carried out on the topic). In any case, I kept my promise and have not done further work in the field. The chemical community seems to have accepted the closure of the debate. This is the way the much-publicized so-called nonclassical ion controversy ended. To summarize, it basically centered on the question of whether the structure of carbocations, including rapidly equilibrating "classical" ions, can be depicted adequately by using only Lewis-type two-electron two-center covalent bonding or whether there are also bridged or σ-localized ions, whose structural depiction necessitates two-electron three-center bonding of the involved higher-coordinate carbon. The outcome was a new understanding of the general bonding nature of carbon compounds and the electron-donor ability and reactivity of single bonds of saturated hydrocarbons and σ-bond in general in electrophilic reaction.

Intensive, critical studies of controversial topics also helps to eliminate the possibility of errors. One of my favorite quotations is by George Bekesy, a fellow Hungarian-born physicist who studied questions of the inner ear and hearing (Nobel Prize in medicine, 1961):[38]

> "[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 amount of time and brain power to ferreting out errors both large and small, and this without any compensation. Another trouble with enemies is that they sometimes develop into friends and lose a good deal of their zeal. It was in this way the writer lost his three best enemies. Everyone, not just scientists, need a few good enemies!"

Clearly, there was no lack of devoted adversaries (perhaps a more proper term than enemies) on both sides of the norbornyl ion controversy. It is to their credit that we today probably know more about the structure of carbocations, such as the norbornyl cation, than about most other chemical species. Their efforts also resulted not only in rigorous studies but also in the development or improvement of many techniques. Although many believe that too much effort was expended on the "futile" norbornyl ion controversy, I am convinced that it eventually resulted in significant new insights and consequences to chemistry. It affected in a fundamental way our understanding of the chemical bonding of electron-deficient carbon compounds, extending Kekule's concept of the limiting ability of carbon to associate with no more than four other atoms or groups. An equally significant consequence of the norbornyl cation studies was that I was able to realize the ability of saturated C−H and C−C single bonds to act in general as σ-electron donors toward strong electrophiles such as carbocations or other highly reactive reagents in superacidic systems, not only in intramolecular but also in intermolecular 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 of hypercoordinate, in short, hypercarbon chemistry.[39]

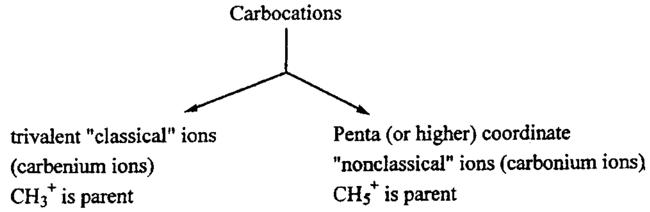
7. The General Concept of Carbocations

Once the direct observation of stable, long-lived carbocations generated in highly acidic (superacid) systems became possible, it led me to the recognition of the general concept of hydrocarbon cations, including the realization that five (and higher) coordinate carbocations 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.[40] I also suggested naming the cations of carbon compounds "carbocations" (because the corresponding anions were named "carbanions").[40] To my surprise, the name stuck and was later officially adopted by the International Union of Pure and Applied Chemistry for general use.[41]

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; thus it 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.

Pentacoordinate (or higher) ("nonclassical") carbonium ions contain five or (higher) coordinate 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 carbocation center always has eight valence electrons, but overall carbonium ions are electron deficient because of the sharing of two electrons among three (or more) atoms. CH_5^+ can be considered the parent for carbonium ions.

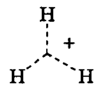
Lewis' concept that a covalent chemical bond consists of a pair of electrons shared between two atoms is a cornerstone of structural chemistry. Chemists tend to brand compounds as anomalous whose structures cannot be depicted in terms of such valence bonds alone. Carbocations with too few electrons to allow a pair for each "bond" came to be referred to as "nonclassical," a name as mentioned first used by Roberts for the cyclopropylcarbinyl cation and adapted by Winstein for the norbornyl cation.[43] The name is still used, even though it is now recognized that, like other compounds, they adopt the structures appropriate for the number of electrons they contain with two-electron three (even multi)-center bonding, not unlike the bonding principle established by Lipscomb for boron compounds.[42] The prefixes "classical" and "nonclassical," I believe, will gradually fade away as the general principles of bonding are recognized more widely.

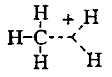


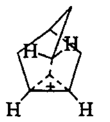
Concerning carbocations, previous usage named the trivalent, planar ions of the CH_3^+ type *carbonium ions*. If the name is considered analogous to other *onium ions* (ammonium, sulfonium, phosphonium ions), then it should relate to the higher-valency or coordination-state carbocations. These, however, clearly are not the trivalent, but the penta- or higher-coordinated, cations of the CH_5^+ type. The earlier German and French literature, indeed, frequently used the "carbenium ion" naming for trivalent cations.

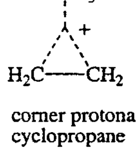
Trivalent carbenium, ions are the key intermediates in electrophilic reactions of π-donor unsaturated hydrocarbons. At the same time, pentacoordinated carbonium ions are the key to electrophilic reactions of σ-donor saturated hydrocarbons through the ability of C−H or C−C single bonds to participate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

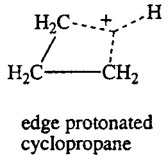
Some characteristic bonding natures in typical nonclassical ions are the following:


H_3^+


methonium ion


norbornyl ion


corner protonated cyclopropane


edge protonated cyclopropane

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[39] Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987.

[40] Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808.

[41] *Compendium of Chemical Terminology: IUPAC Recommendations*; Blackwell Scientific Publication: Oxford, 1987.

Expansion of the carbon octet via 3d orbital participation is not possible; there can be only eight valence electrons in the outer shell of carbon, a small first-row element. The valency of carbon therefore cannot exceed four. Kekulé's concept of the tetravalence of carbon in bonding terms represents attachment of four atoms (or groups) involving 2e-2c Lewis-type bonding. However, nothing prevents carbon from also participating in multicenter bonding involving 2e-3c (or multicenter) bonds.

In the 1930s, Pauling still believed that diborane had an ethane like structure and suggested this to Kharasch during a visit to Chicago (as recalled by H. C. Brown). It was Lipscomb, Pauling's student, who in the 1950s introduced the two-electron three-center (2e-3c) bonding concept into boron chemistry, while also explaining the bridged structure of diborane.

It is remarkable that chemists long resisted making the connection between boron and electron deficient carbon, which, after all, are analogues. I was lucky to be given the opportunity to be able to establish the general concept of five and higher coordination of electron-deficient carbon and thus be able to open up the field of hypercarbon chemistry.

Organic chemists who are dealing with carbon compounds (or perhaps more correctly with hydrocarbons and their derivatives) have long considered that 2e-3c bonding was limited to some "inorganic" or at best "organometallic" systems and to have no relevance to their field. The long-drawn-out and sometimes highly personal nonclassical ion controversy was accordingly limited to the structural aspects of some, to most chemists rather obscure, carbocations. Herbert Brown, one of the major participants in the debate and, besides Lipscomb, one of the great boron chemists of our time, was steadfast in his crusade against bridged nonclassical ions. He repeatedly used the argument that if such ions existed, a new, yet unknown bonding concept would need to be discovered to explain them. This, however, is certainly not the case. The close relationship of electron-deficient carbocations with their neutral boron analogues has been frequently pointed out and discussed starting with my 1971 paper with DeMember and Commeyras. In it, we pointed out the observed close spectral (IR and Raman) similarities between isoelectronic $^{+}C(CH_3)_3$ and $B(CH_3)_3$ and emphasized the point repeatedly thereafter. My colleagues Robert Williams, Surya Prakash, and Leslie Field did a fine job in carrying the carbocation, borane, and polyborane analogy much further, and we also reviewed the topic in depth in our book, *Hypercarbon Chemistry*.

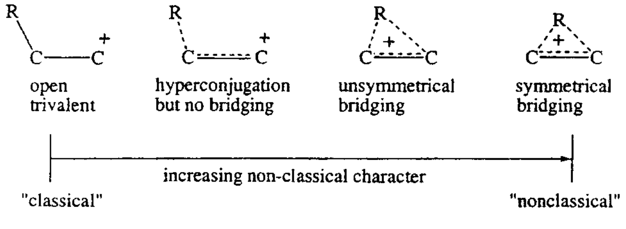
One of the cornerstones of the chemistry of carbon compounds (organic chemistry) is Kekulé's concept, proposed in 1858, of the tetravalence of carbon. Although it was independently also proposed in the same year by Couper, he however, got little recognition for it. It is generally attributed to Kekulé that carbon can bind at the same time to not more than four other atoms or groups.

Kekulé's tetravalent carbon was explained later on this basis of the atomic concept and the "rule of eight" valence electrons. From this, G. N. Lewis introduced the electron-pair concept and that of covalent shared electron-pair bonding (Lewis bond), which Langmuir further developed. It was Linus Pauling, and others following him, who subsequently applied the principles of the developing quantum theory to the questions of chemical bonding. I prefer to use "chemical bonding" instead of "chemical bond," because, after all, in a strict sense the chemists' beloved electron pairs do not exist. Electrons move individually, and it is only the probability that they are found paired in close proximity that justifies the practical term of covalent electron-pair bonding. Pauling showed that electron pairs occupying properly oriented orbitals (which are their preferred locations, but do not exist otherwise) result in the tetrahedral structure of methane (involving sp^3 hybridization). However, neither Lewis, Langmuir, nor Pauling considered that an already shared electron pair could further bind an additional atom, not just two. It was Lipscomb who revolutionalized the bonding nature of boron chemistry by introducing the concept of two electron three or multi center bonding. It was my good fortune that I was able to generalize a related concept to higher coordinate carbon compounds and their chemistry.

Whereas the differentiation of limiting trivalent and penta- or higher coordinate carbocations serves a useful purpose in establishing the significant differences between these ions, it must be emphasized that these represent only the extremes of a continuum and that there exists a continuum of charge delocalization comprising both intra- and intermolecular interactions. This can involve participation of neighboring *n*-donor atoms, π-donor groups or σ-donor C−H or C−C bonds.

Neighboring group participation (a term introduced by Winstein) with the vacant p-orbital of a carbenium ion center contributes to its stabilization via delocalization, which can involve atoms with unshared electron pairs (n-donors), π-electron systems (direct conjugate or allylic stabilization), bent σ-bonds (as in cyclopropylcarbinyl cations), and C−H and C−C σ-bonds (hyperconjugation).

Hyperconjugation is the overlap interaction of an appropriately oriented σ-bond with a carbocationic ρ-orbital to provide electron delocalization with minimal accompanying nuclear reorganization. Nuclear reorganization accompanying σ-bond delocalization can range from little or no rearrangement (hyperconjugation) to partial bridging involving some reorganization of nuclei (σ-participation) and to more extensive or complete bridging. Trivalent carbenium ions, with the exception of the parent CH_3^{+}, consequently always show varying degrees of delocalization. Eventually in the limiting case carbocations become pentacoordinated carbonium ions. The limiting cases define the extremes of the spectrum of carbocations.



Under superacidic, low nucleophilicity so-called "stable ion conditions," developing electron-deficient carbocations do not find reactive external nucleophiles to react with;

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(42) For reviews comparison and references, see: *Electron Deficient Boron and Carbon Chemistry*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley-Interscience: New York, 1991.

(43) Winstein, S.; Trifan, D. *J. Am. Chem. Soc.* **1952**, *74*, 1154.

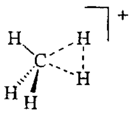
thus, they stay persistent in solution stabilized by internal neighboring group interactions.

8. Five and Higher Coordinate Carbocations and Their Chemistry

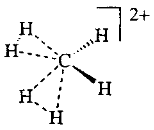
On the basis of my extensive study of stable, persistent carbocations, reported in more than 300 publications, as mentioned I was able in 1972 to develop a general concept of carbocations.[40] In higher-coordinate (hypercoordinate) carbonium ions, of which protonated methane CH_5^+ is the parent, besides two-electron two-center Lewis bonding, two-electron three-center bonding is involved.

Extensive ab initio calculations[44] reconfirmed the preferred C_s symmetrical structure for the CH_5^+ cation, as we originally suggested with Klopman in 1969.[45] 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 already pointed out with Klopman that ready bond-to-bond (isotopal) proton migration can take place through low barriers to equivalent or related structures that are energetically only slightly less favorable (which led more recently to Schleyer's suggestion of a fluxional, completely delocalized nature).[46]

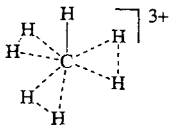
In 1982, we studied the parent six-coordinate diprotonated methane (CH_6^{2+}),[47] which has two 2e-3c bonding interactions in its minimum-energy structure (C_{2v}).[48] On the basis of ab initio calculations, with Rasul we more recently found that the seven-coordinate triprotonated methane (CH_7^{3+}) is also an energy minimum and has three 2e-3c bonding interactions in its minimum-energy structure (C_{3v}). These results further indicate the general importance of 2e-3c bonding in protonated alkanes.



CH_5^+ C_s

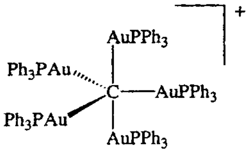


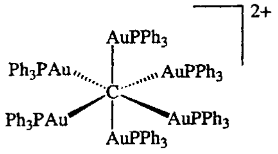
CH_6^{2+} C_{2v}



CH_7^{3+} C_{3v}

Protonated methanes and their homologues and derivatives are experimentally indicated in superacidic chemistry by hydrogen−deuterium exchange experiments, as well as by core electron (ESCA) spectroscopy of their frozen matrixes.[49] Some of their derivatives could even be isolated as crystalline compounds. In recent years, Schmidbaur has prepared gold complex analogues of CH_5^+ and CH_6^{2+} and determined their X-ray structures.[50,51] The monopositively charged trigonal bipyramidal[50] $\{[(C_6H_5)_3PAu]_5C\}^+$ and the dipositively charged octahedral[52] 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 are remarkable and greatly contributed to our knowledge of higher-coordinate carbocations.

Boron and carbon are consecutive first-row elements. Trivalent carbocations are isoelectronic with the corresponding neutral trivalent boron compounds. Similarly, pentavalent monopositively charged carbonium ions are isoelectronic with the corresponding neutral pentavalent boron compounds. BH_5, which is isoelectronic with CH_5^+, has also a C_s symmetrical structure based on high-level ab initio calculations.[52,53] Experimentally, H−D exchange was observed in our work when BH_4^- was treated with deuterated strong acids, indicating the intermediacy of isotopomeric BH_5.[54] The first direct experimental observation (by infrared spectroscopy) of BH_5 has only recently been reported.[55] The X-ray structure of the five-coordinate gold complex $[(Cy_3P^+)B(AuPPh_3)_4]$ was also reported by Schmidbaur.[56] This square-pyramidal compound represents the isolobal analogue of BH_5 and further strengthens the relationship of the bonding nature of higher-coordinate boron and carbon compounds.

As five- and six-coordinate CH_5^+ and CH_6^{2+} are isoelectronic with BH_5 and BH_6^+,[57] respectively, seven-coordinate tripositively charged CH_7^{3+}[48] is isoelectronic with the corresponding dipositively charged heptavalent boronium dication BH_7^{2+}.[57] We have also searched for a minimum-energy structure of tetraprotonated methane, CH_8^{4+}. However, CH_8^{4+} remains even computationally elusive because charge−charge repulsion appears to have reached its prohibitive limit. The isoelectronic boron analogue BH_8^{3+}, however, was calculated to be an energy minimum.[57]

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 as well as on theoretical calculations, showed that carbon hypercoordination is a general phenomenon in electron-deficient hydrocarbon

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(44) (a) Raghavachari, K.; Whitesides, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *104*, 3258. (b) Dyczmons, V.; Staemmler, V.; Kutzelnig, W. *Chem. Phys. Lett.* **1970**, *5*, 361. (c) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *Tetrahedron Lett.* **1970**, 2699. (d) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 808.

(45) Olah, G. A.; Klopman, G.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 3261.

(46) (a) Schreiner, P. R.; Jim, S.-J.; H. f. Schaefer, Schleyer, P. v. R. *J. Chem. Phys.* **1993**, *99*, 3716. (b) Scuseria, G. E. *Nature* **1993**, *366*, 512.

(47) (a) Lammertsma, K.; Olah, G. A.; Barzaghi, M.; Simonetta, M. *J. Am. Chem. Soc.* **1982**, *104*, 6851. (b) Lammertsma, K.; Barzaghi, M.; Olah, G. A.; Pople, J. A.; Schleyer, P. v. R.; Simonetta, M. *J. Am. Chem. Soc.* **1983**, *105*, 5268.

(48) Olah, G. A.; Rasul, G. *J. Am. Chem. Soc.* **1996**, *118*, 8503.

(49) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; John Wiley & Sons: New York, 1987; p 149.

(50) Scherbaum, F.; Grohmann, G.; Müller, G.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 463.

(51) Scherbaum, F.; Grohmann, G.; Huber, B.; Krüger, C.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1544.

(52) Schreiner, P. R.; Schaefer, H. F.; Schleyer, P. v. R. *J. Chem. Phys.* **1994**, *101*, 7625.

(53) Watts, J. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 825.

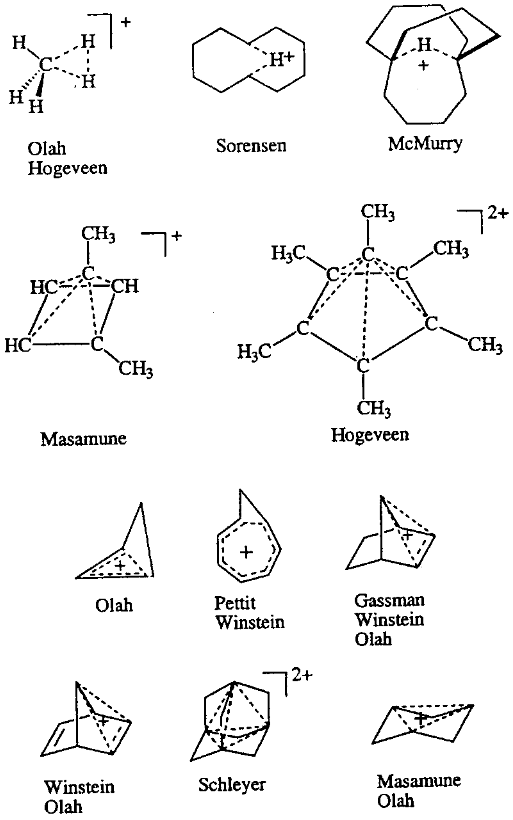
(54) Olah, G. A.; Westerman, P. W.; Mo, Y. K.; Klopman, G. *J. Am. Chem. Soc.* **1972**, *94*, 7859.

(55) Tague, T. J.; Andrews, L. *J. Am. Chem. Soc.* **1994**, *116*, 4970.

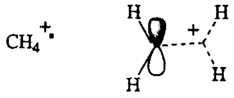
(56) Blumenthal, A.; Beruda, H.; Schmidbaur, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1005.

(57) Rasul, G.; Olah, G. A. *Inorg. Chem.* **1997**, *36*, 1278.

systems. Some characteristic nonclassical carbocations are the following.

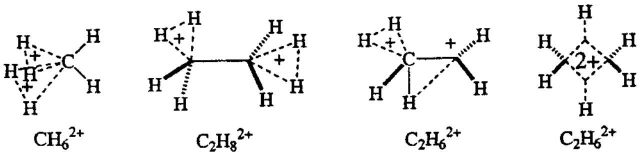


According to early theoretical calculations which Klopman and I carried[58] out in 1971, the parent molecular ions of alkanes, such as CH_4^+, observed in mass spectrometry, also can have a planar hypercarbon structure, although distortion is probable.



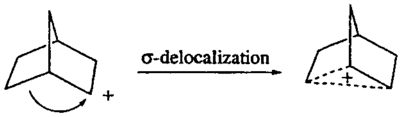
The CH_4^{2+} ion, as calculated later by Radom, however has a completely planar C_{2v} structure.[59]

Not only can carbon be involved in a single two-electron three-center bond formation, but also some carbodications simultaneously participate in two 2e-3c bonds. Diprotonated methane (CH_6^{2+})[47] and ethane ($C_2H_8^{2+}$),[47] as well as the dimer of the methyl cation ($C_2H_6^{2+}$),[47] are illustrative.

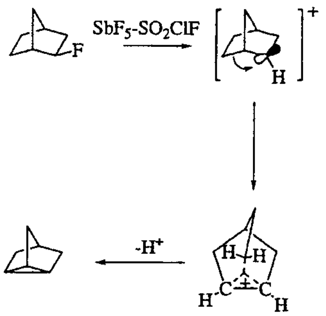


It was the study of hypercarbon-containing nonclassical carbocations that allowed us to firmly establish carbon's ability in a hydrocarbon system to bind simultaneously with five (or six or even seven) atoms or groups. It should be emphasized that carbocations represent only one class of hypercarbon compounds. A wide variety of neutral hypercarbon compounds, including alkyl (acyl)-bridged organometallics as well as carboranes, carbonyl, and carbide clusters, are now recognized and have been studied. They are reviewed in our book *Hypercarbon Chemistry* (written with Prakash, Williams, Field, and Wade).[49]

During my studies related to the nonclassical ion problem, 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).[60]



The formation of the σ-delocalized norbornyl cation via ionization of 2-norbornyl precursors in low-nucleophilicity, superacidic media can be considered an analogue of an intramolecular Friedel−Crafts alkylation in a saturated system. Indeed, deprotonation gives nortricyclane.[60]



The intramolecular σ-delocalization in the norbornyl 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 the discovery of the general electrophilic reactivity of saturated hydrocarbons and single bonds in general.

The long, drawn-out nonclassical ion controversy thus led to an unexpected new chapter of chemistry. As frequently happens in science, the drive for understanding (for whatever reason) of what appear at the time to be 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, but as Niels Bohr was frequently quoted to have said, "you must be prepared for a surprise". 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 believe it was not a waste of effort to pursue it, and eventually it greatly helped to advance chemistry to new areas of significance that are still emerging.

To illustrate the significance of higher coordinate carbocations in hydrocarbon chemistry[61] some examples are illustrative.

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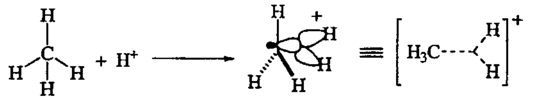
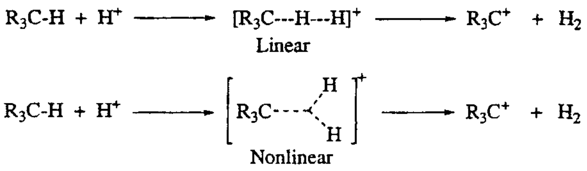
[58] Olah, G. A.; Klopman, G. *Chem. Phys. Lett.* **1971**, *11*, 604.
[59] Wong, M. W.; Radom, L. *J. Am. Chem. Soc.* **1989**, *111*, 1155.
[60] Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440.
[61] Olah, G. A.; Molnar, A. *Hydrocarbon Chemistry*; Wiley: New York **1995** and references therein.

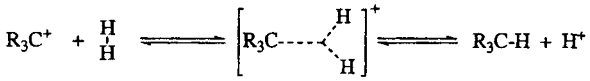
Protonation (and protolysis) of alkanes is readily achieved with superacids. The protonation of methane itself to CH_5^+, as discussed earlier, takes place readily.



Acid-catalyzed isomerization reactions of alkanes as well as their alkylation and condensation reactions are initiated by protolytic ionization. Available evidence indicates nonlinear but somewhat bent, although not triangular transition states.[62]

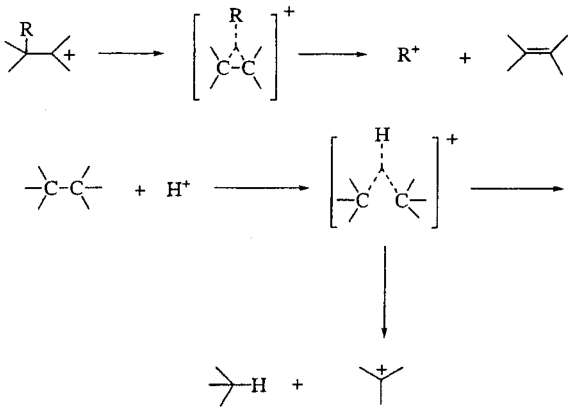


The reverse reaction of the protolytic ionization of hydrocarbons to carbocations, that is, the reaction of trivalent carbocations with molecular hydrogen giving their parent hydrocarbons, involves the same five-coordinate carbonium ions.



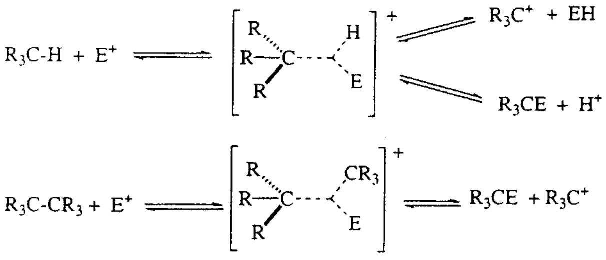
The isomerization of butane to isobutane in superacids is illustrative of a protolytic isomerization, where no intermediate olefins are present in equilibrium with carbocations.

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



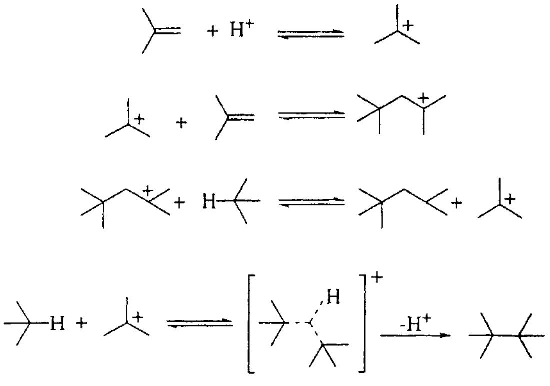
Whereas superacid (HF/BF_3, HF/SbF_5, HF/TaF_5, FSO_3H/SbF_5, etc.) catalyzed hydrocarbon transformations were first explored in the liquid phase, subsequently, solid acid catalyst systems, such as those based on Nafion-H, longer-chain perfluorinated alkanesulfonic acids, fluorinated graphite intercalates, etc. were also developed and utilized for heterogeneous reactions. The strong acidic nature of zeolite catalysts was also successfully explored in cases such as H-ZSM-5 at high temperatures.[63]

Not only protolytic reactions but also a broad range of reactions with varied electrophiles (alkylation, formylation, nitration, halogenation, oxygenation, etc.) were found to be feasible when using superacidic, low-nucleophilicity reaction conditions.[61,64]



$E = D^+, H^+, R^+, NO_2^+, Hlg^+, HCO^+$, 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 and thus 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 becomes more predominant.[61]



A fundamental difference exists between conventional acid- and superacid-catalyzed hydrocarbon chemistry. In the former, trivalent carbenium ions are always in equilibrium with olefins, which play the key role, whereas in the latter, hydrocarbon transformation can take place without the involvement of olefins through the intermediacy of five-coordinate carbocations.[61]

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 of preparing branched carboxylic acids from alkenes or alcohols. For example, in this way, isobutylene or *tert*-butyl alcohol is converted into pivalic acid. In contrast,

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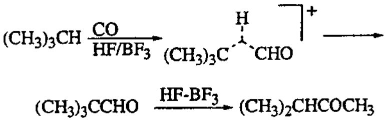
[62] Olah, G. A.; Klopman, G.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 3261.

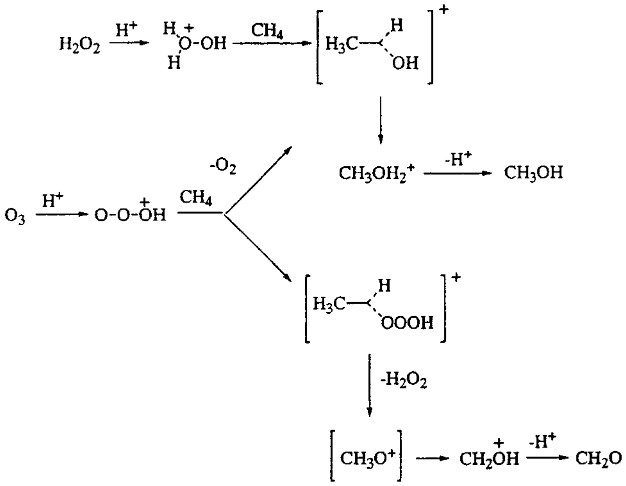
[63] Haag, W. O.; Dessau, R. H. *Int. Catal. Congr. Proc. 8th* **1984**, *II*, 105.

[64] Olah, G. A.; Prakash, G. K. S.; Mathew, T.; Marinez, E. R. *Angew. Chem., Int. Ed.* **2000**, 2647.

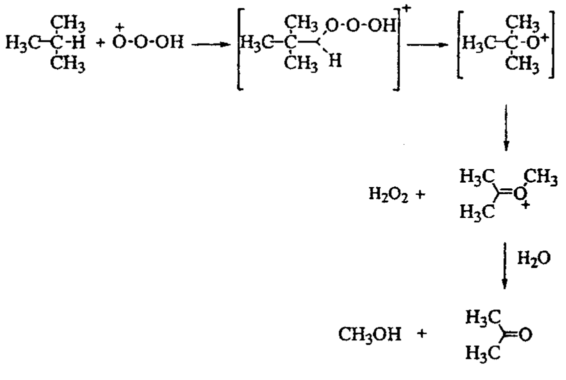
based on the superacidic activation of electrophiles leading to superelectrophiles we found it possible to formylate isoalkanes to aldehydes, which subsequently rearrange to their corresponding branched ketones.[64] These are effective high-octane gasoline additive oxygenates. The conversion of isobutane into isopropyl, methyl ketone, or isopentane into isobutyl, methyl ketone is illustrative. In this reaction, no branched carboxylic acids (Koch 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^+), allows the efficient preparation of oxygenated derivatives.[65]



Because 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. The superacid-catalyzed reaction of isobutane with ozone giving acetone and methyl alcohol, the aliphatic equivalent of the industrially significant Hock reaction of cumene, is illustrative.



Electrophilic insertion reactions into C−H (and C−C) bonds under low-nucleophilicity superacidic conditions are not unique to alkane activation processes. The C−H (and C−C) bond activation by organometallic complexes, such as Bergman's iridium complexes and other transition metal systems (rhodium, osmium, rhenium, etc.), is based on somewhat similar electrophilic insertions. These reactions, however, cannot as yet be made catalytic, although future work may change this. A wide variety of further reactions of hydrocarbons with coordinatively unsaturated metal compounds and reagents involving hypercarbon intermediates (transition states) is also recognized, ranging from hydrometalations to Ziegler−Natta polymerization.[61]

In the conclusion of my 1972 paper[40] on the general concept of carbocations I wrote, "The realization of the electron donor ability of shared (bonding) electron pairs of single bonds, should rank one day equal in importance with that of unshared (nonbonding) electron pairs recognized by Lewis. We can now 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 I ever made a prediction of the possible future significance of my chemistry. More than a quarter of a century later, I take some satisfaction that I was correct and that, indeed, hypercarbon chemistry has a significant place on the wide palette of chemistry.

Carbon can extend its bonding from Kekulé's[66] tetravalent limit to five-, and even higher-bonded (coordinate), hypercarbon systems. Higher coordinate carbocations are now well recognized. They are the key to our understanding of the electrophilic reactivity of C−H or C−C single bonds and of hypercarbon chemistry in general. Some of their derivatives, such as related gold complexes, can even be isolated as stable crystalline compounds. The chemistry of higher-coordinate carbon (i.e., hypercarbon chemistry) is rapidly expanding, with many new vistas to be explored. The road from Kekulé's tetravalent carbon to hypercarbon chemistry took more than a century to travel. Carbon also unveiled other unexpected new aspects, for example, its recently discovered fullerene-type allotropes and their chemistry. There is no reason to believe that the new century just beginning will not bring much further progress in the fascinating field of hypercarbon chemistry, to which knowledge of carbocations made essential contribution.

Acknowledgment. My work on carbocations would have not been possible without the fundamental contributions and hard work of my dedicated students, collaborators, and colleagues I was privileged to work with over the years. They became an integral part of the Olah group and my broader scientific family, many personal friends as well. Their names are to be found in the literature citations and my recently published autobiography.[1] I would like, however, to specifically thank Professor G. K. Surya Prakash who started with me a quarter century ago as a graduate student and continues as my colleague and close friend in our still continuing cooperation in search for the wonderful challenges of carbocation chemistry.

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