My Search for Carbocations and Their Role in Chemistry (Nobel Lecture)**

George A. Olah*

> *Every generation of scientific men (i.e., scientists) starts where the previous generation left off, and the most advanced discoveries of one age constitute elementary axioms of the next.*
>
> Aldous Huxley

Introduction

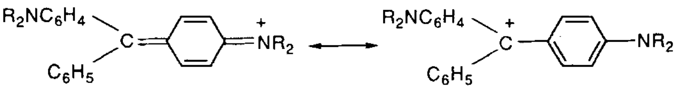
Hydrocarbons are compounds of the elements carbon and hydrogen. They make up natural gas and oil and thus are essential for our modern life. Burning of hydrocarbons generates energy in our power plants and heats our homes. Derived gasoline and diesel oil propel our cars, trucks, airplanes. Hydrocarbons are also the feedstock for practically every synthetic material from plastics to pharmaceuticals. What nature gives us needs, however, to be processed and modified. We will eventually also need to make hydrocarbons ourselves, as our natural resources are depleted. Many of the processes used are acid-catalyzed, and the chemical reactions involved proceed through positive ion intermediates. Consequently, the knowledge of these intermediates and their chemistry is of substantial significance in both fundamental research and practical science.

Carbocations are the positive ions of carbon compounds. In 1901 Norris[1a] and Kehrmann and Wentzel[1b] 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. Adolf von Baeyer (Nobel laureate, 1905) should be credited for having recognized in 1902 the saltlike character of the products [Eq. (1)].[1c]

$$Ar_3C{-}X \rightleftharpoons Ar_3C^+ + X^- \qquad (1)$$

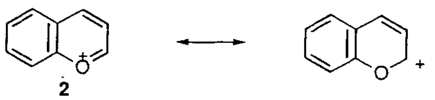
He then suggested a correlation between the appearance of color and salt formation—the so-called "halochromy". Gomberg[1d] (who had shortly before discovered the stable triphenylmethyl radical) as well as Walden[1e] contributed to the evolving understanding of the structure of related cationic dyes, such as malachite green **1**.

Stable carbocationic dyes were soon found to be present even in nature. The color of red wine as well as of many flowers, fruits, leaves, etc. is due in part to flavylium and anthocyanin compounds formed upon cleavage of their respective glycosides.

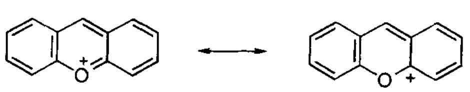


1

The elucidation of the constitution of flavylium and anthocyanin compounds developed from Robinson's and Willstätter's pioneering studies. Werner[1f] formulated the parent benzopyrilium or xanthylium salts **2** and **3** as oxonium salts, while Baeyer[1g] emphasized their great similarity to triarylmethylium salts and considered them carbenium salts. Time has indeed justified both points of view with the realization of the significance of the contribution of both oxonium and carbenium ion resonance forms.



2



3

Whereas the existence of ionic triarylmethyl and related dyes was established at around the turn of the 20th century, the more general significance of carbocations in chemistry was long unrecognized. Triarylmethyl cations were considered as an isolated curiosity of chemistry, not unlike Gomberg's triarylmethyl radicals. Not only were simple hydrocarbon cations believed to be unstable, their fleeting existence was even doubted.

One of the most original and significant ideas in organic chemistry was the suggestion that carbocations (as we now call all the positive ions of carbon compounds) might be intermediates in the course of reactions that start from nonionic reactants and lead to nonionic covalent products.

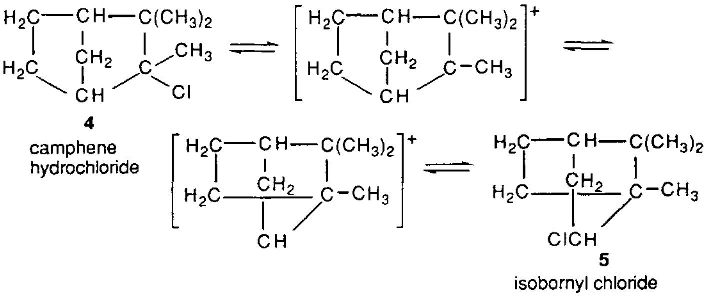
It was Hans Meerwein[2] who, while studying the Wagner rearrangement of camphene hydrochloride to isobornyl chloride together with van Emster in 1922, found that the rate of the reaction increased with the dielectric constant of the solvent. Further, he found that certain Lewis acid chlorides such as $SbCl_5$, $SnCl_4$, $FeCl_3$, $AlCl_3$, and $SbCl_3$ (but not BCl_3 or $SiCl_4$)

---

[*] Prof. Dr. G. A. Olah
Loker Hydrocarbon Research Institute and Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661 (USA)
Telefax: Int. code +(213) 740-6679

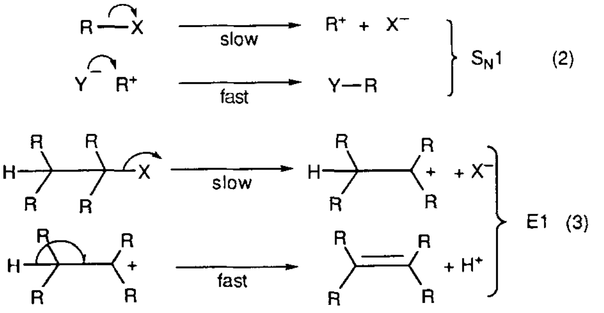
[**] Copyright © The Nobel Foundation 1995. We thank the Nobel Foundation, Stockholm, for permission to print this lecture.

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 (**4**) to isobornyl chloride (**5**). 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, and he was discouraged from following up on these studies.


4 camphene hydrochloride

5 isobornyl chloride

C. K. Ingold, E. H. Hughes, and their collaborators in England started in the late 1920s to carry out detailed kinetic and stereochemical investigations on what became known as nucleophilic substitution at saturated carbon and as polar elimination reactions.[3] Their work relating to unimolecular nucleophilic substitution and elimination called S_N1 and E1 reactions [Eq. (2) and (3)] laid the foundation for the role of electron-deficient carbocationic intermediates in organic reactions.



(2)

(3)

F. C. Whitmore[4] in the US in the thirties generalized these concepts to include many other organic reactions in a series of papers. Carbocations, however, were generally considered to be unstable and transient (short-lived), as they could not be directly observed. Many leading chemists, including Roger Adams, determinedly doubted their existence as real intermediates and strongly opposed even mentioning them. Whitmore consequently never was able in any of his publications in the prestigeous Journal of the American Chemical Society to use the notation of ionic R_3C^+. The concept of carbocations, however, 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 have contributed fundamentally to the development of modern carbocation chemistry. The role of carbocations as one of the basic concepts of modern chemistry was firmly established and is well reviewed.[5–7] With the advancement of mass spectrometry the existence of gaseous cations was proven, but this could give no indication of their structure or allow extrapolation to solution chemistry. Direct observation and study of stable, long-lived carbocations, such as of alkyl cations in the condensed state remained an elusive goal.

My involvement with the study of carbocations dates back to the fifties and resulted in the first direct observation of alkyl cations and subsequently the whole spectrum of carbocations as long-lived species in highly acidic (superacidic) solutions.[5, 8, 9] The low nucleophilicity of the counteranions (SbF_6^-, $Sb_2F_{11}^-$ etc.) greatly contributed to the stability of the carbocationic salts, which could in some instances even be isolated as crystalline salts. The techniques we developed with superacids to generate stable ions also gained wide application in the preparation of other ionic intermediates (nitronium, halonium, oxonium ions, etc.). At the same time the preparation and study of an ever increasing number of carbocations allowed a general concept of carbocations, which I suggested in a 1972 paper, to evolve. In the same paper I suggested that the cations of carbon compounds be termed "carbocations".[10] "Carbocations" is now the approved[11] (IUPAC) generic name for all cationic carbon compounds. Similarly, the anionic compounds are called "carbanions".

George A. Olah was born in 1927 and educated in Budapest, Hungary. He moved in 1957 first to Canada and then to the USA with the Dow Chemical Company. Since 1977 he has been Director of the Loker Hydrocarbon Research Institute and Distinguished Professor of Organic Chemistry at the University of Southern California, Los Angeles. He is a member of the US National Academy of Sciences, a Foreign Member of the Italian Academia dei Lincei, and an Honorary Member of the Hungarian Academy of Sciences. He received Honorary Doctorates from the University of Durham (England), the University of Munich, the University of Crete (Greece), and his alma mater, the Technical University of Budapest. He is the recipient of many awards including the American Chemical Society Awards in Petroleum Chemistry, Creative Work in Synthetic Organic Chemistry, the Roger Adams Award, and the Nobel Prize in Chemistry, 1994. His research interests are in the area of synthetic and mechanistic organic chemistry, reactive intermediates (carbocations), superacids, and hydrocarbon chemistry. He has published more than 1000 scientific papers, holds 100 patents, and authored or co-authored 15 monographs.

From Acyl Cations to Alkyl Cations

The transient nature of carbocations arises from their high reactivity towards reactive nucleophiles present in the system. The use of counterions with relatively low nucleophilicity, particularly tetrafluoroborate (BF_4^-), enabled Meerwein in the forties to prepare a series of oxonium and carboxonium ion salts, like $R_3O^+BF_4^-$ and $HC(OR)_2^+BF_4^-$, respectively.[12] These Meerwein salts are efficient alkylating agents; they transfer alkyl groups in S_N2-type reactions. However, no acyl ($RCO^+BF_4^-$) or alkyl cation salts ($R^+BF_4^-$) were obtained in Meerwein's studies.

Acetic acid and acetic anhydride were shown to form complexes with Lewis acids such as boron trifluoride. The behavior of acetic acid and acetic anhydride in strong protic acids (sulfuric acid, oleum, perchloric acid, etc.) was also extensively studied. None of these resulted, however, in the isolation or unequivocal characterization of the acetyl cation (or other related homologous acyl cations). F. Seel prepared acetylium tetrafluoroborate[13] for the first time in 1943 by treating acetyl fluoride with boron trifluoride [Eq. (4)].

$$CH_3COF + BF_3 \rightleftharpoons CH_3CO^+BF_4^- \tag{4}$$

In the early fifties, I became interested in organic fluorine compounds while working at the Organic Chemical Institute of the Technical University in Budapest led by the late Professor G. Zemplén, a noted carbohydrate chemist and former student of Emil Fischer (Nobel laureate, 1902) whose "scientific grandson" I can thus consider myself. Zemplén was not very impressed by my ideas, as he thought attempts to study fluorine compounds which necessitated "outrageous" reagents such as hydrogen fluoride to be extremely foolish. Eventually, however, I prevailed and was allowed to convert an open balcony at the rear of the top floor of the chemistry building into a small laboratory, where together with some of my early dedicated associates, A. Pavlath, S. Kuhn, we started up the study of organic fluorides as reagents. Seel's previous work particularly fascinated me. As Zemplén's interest was in glycoside synthesis and related carbohydrate chemistry, I thought that selective α- or β-glycoside synthesis could be achieved by treating either acetofluoroglucose (and other fluorinated carbohydrates) or their relatively stable, deacetylated fluorohydrins with the appropriate aglucons. In the course of the project –COF compounds were needed. As Seel did not seem to have followed up his earlier study, I became interested in exploring acylation with acyl fluorides in general. The work was subsequently extended to alkylation with alkyl fluorides with boron trifluoride as catalyst for Friedel–Crafts type reactions. These studies also aroused my interest in the mechanistic aspects of the reactions, including the complexes of RCOF and RF with BF_3 and subsequently with other Lewis acid fluorides [Eq. (5) and (6)]. Thus, my long fascination with the chemistry of carbocationic complexes began.

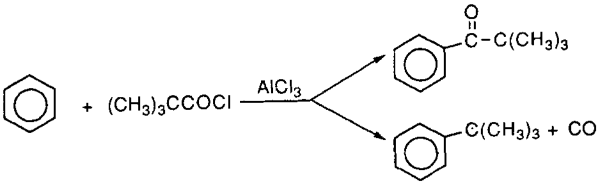
$$ArH + RCOF \overset{BF_3}{\rightleftharpoons} ArCOR + HF \tag{5}$$

$$ArH + RF \overset{BF_3}{\rightleftharpoons} ArR + HF \tag{6}$$

Carrying out such research in post-war Hungary was not easy. There was no access to such 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 reagents and performing this chemistry in a laboratory equipped with the barest of necessities was indeed a challenge. It was only around 1955 through Meerwein, who read some of my early publications, started corresponding with me, and offered his help, that we received a cyclinder of BF_3 gas. What a precious gift it was![14]

My early work with acyl fluorides also involved formyl fluoride, HCOF,[15] which was first prepared by Nesmejanov and Kahn in the thirties,[16] but they did not pursue its use in synthesis. We also prepared a series of higher homologous acyl fluorides and studied their chemistry.[15]

In Friedel–Crafts chemistry when pivaloyl chloride is treated with aromatics in the presence of aluminum chloride, *tert*-butylated products were obtained besides the expected ketones [Eq. (7)].[17]



(7)

These were assumed to be formed by decarbonylation of the intermediate pivaloyl complex or cation. In the late fifties, now working at the Dow Chemical Company laboratory in Sarnia, Ontario (Canada), I was able to return to my investigations and extend them by using IR and NMR spectroscopy to study isolable complexes between acyl fluoride and Lewis acid fluoride, including those higher valency Lewis acid fluorides such as SbF_5, AsF_5, PF_5. Consequently, it was not unexpected that the $(CH_3)_3CCOF$–SbF_5 complex we generated showed substantial tendency toward decarbonylation.[18] What was exciting, however, was that we could follow this process by NMR spectroscopy and observe what turned out to be the first stable, long-lived alkyl cation salt, namely, *tert*-butyl hexafluoroantimonate.[18–20]

$$(CH_3)_3CCOF + SbF_5 \longrightarrow (CH_3)_3CCO^+SbF_6^- \xrightarrow{-CO} (CH_3)_3C^+SbF_6^- \tag{8}$$

This breakthrough was first reported in my 1962 papers[18–19] and was followed by studies that led to methods yielding long-lived alkyl cations in solution.[20] Before recollecting some of this exciting development, however, a brief review of the long quest for these elusive alkyl cations is in order.

Earlier Unsuccessful Attempts To Observe Alkyl Cations in Solution

Until the early sixties alkyl cations were considered only as transient species. Their existence had been indirectly inferred from kinetic and stereochemical studies.[3] No reliable spectroscopic or other physical measurements of simple alkyl cations in solution or in the solid state were reported despite decades of extensive studies (including conductivity and cryoscopic measurements). Gaseous alkyl cations had been investigated since the fifties by electron bombardment of alkanes, haloalkanes, and other precursors in mass spectrometric studies, but these investigations, of course, did not provide structural information.[21]

The existence of complexes between Friedel–Crafts alkyl halides and Lewis acid halides had been established from observations, such as Brown's study of the vapor pressure depression of CH_3Cl and C_2H_5Cl in the presence of gallium chloride.[22] The conductivity of aluminum chloride in alkyl chlorides[23] and of alkyl fluorides in boron trifluoride was measured,[24] and the effect of ethyl bromide on the dipole moment of aluminum bromide was studied.[25] However, in no case could well-defined, stable alkyl cation complexes be detected, even at very low temperatures.

Electronic spectra of alcohols and olefins in strong protic acids such as sulfuric acid were obtained by Rosenbaum and Symons.[26] They observed that several simple aliphatic alcohols and olefins give an absorption maximum around 290 nm and ascribed this characteristic absorption to the corresponding alkyl cations. Finch and Symons,[27a] on reinvestigation, however, showed that condensation products, formed with acetic acid (used as solvent for the precursor alcohols and olefins), were responsible for the spectra and not the simple alkyl cations. Moreover, protonated mesityl oxide was also identified as the absorbing species in the isobutylene/acetic acid/sulfuric acid system.

Deno and his coworkers[27b] carried out an extensive study of the fate of alkyl cations formed from alcohols or olefins in undiluted H_2SO_4 and oleum, and showed that equal amounts of a saturated hydrocarbon mixture (C_4 to C_{18}) insoluble in H_2SO_4 and a mixture of cyclopentenyl cations (C_9 to C_{20}) in the H_2SO_4 layer formed. These cations exhibit strong ultraviolet absorption around 300 nm. Olah, Pittman, and Symons subsequently reviewed and clarified the question of electronic spectra of carbocationic systems and the fate of various precursors in different acids.[27c]

At this stage it was clear that all earlier attempts to prove the existence of long-lived, well-defined alkyl cations were unsuccessful in acids such as sulfuric acid, perchloric acid, etc. and at best inconclusive in case of the interaction of alkyl halides with Lewis acid halides. Proton elimination from any alkyl cation formed as intermediate gives an olefin, which then reacts further and can lead to complex systems affecting conductivity, as well as other chemical and physical studies.

It was not realized till the breakthrough in superacid chemistry (see below) that in order to suppress the deprotonation of alkyl cations to olefins [Eq. (9)] and the subsequent formation of very complex systems by reactions such as alkylation, oligomerization, polymerization, and cyclization of olefins with alkyl cations, acids much stronger than those known and used at the time were needed.

$$(CH_3)_3C^+ \rightleftharpoons H^+ + (CH_3)_2C{=}CH_2 \qquad (9)$$

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

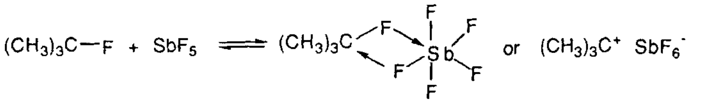
Long-Lived Alkyl Cations from Alkyl Fluorides in Antimony Pentafluoride and Related Conjugate Superacids

The idea that ionization of alkyl fluorides to stable alkyl cations could be possible with an excess of strong Lewis acid fluorides that serve as solvents first came to me while I was working in Hungary in the early fifties and 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 to find suitable solvents that would allow ionization but at the same not react with developing, potentially highly reactive alkyl cations, we condensed neat alkyl fluorides with boron trifluoride at low temperatures. At the time I had no access to spectroscopic methods such as IR or NMR, which were still in their infancy. I remember a visit by Costin Nenitzescu (an outstanding but never fully recognized Rumanian chemist, who carried out much pioneering research on acid-catalyzed reactions). We commiserated our lack of access even to an IR spectrometer. (Nenitzescu later recalled sending a cyclobutadiene–Ag^+ complex on the Orient Express to a colleague in Vienna for IR studies, but it decomposed en route.) All we could do at the time on our $RF-BF_3$ systems were conductivity measurements. The results showed that methyl fluoride and ethyl fluoride gave only low conductivity complexes, whereas the isopropyl fluoride and *tert*-butyl fluoride complexes were highly conducting [Eq. (10)]. The latter systems, however, also showed some polymerization (from deprotonation of the involved carbocations to give olefins). Thus, the conductivity data must have been affected by acid formation.[24]

$$R{-}F + BF_3 \rightleftharpoons \overset{\delta+}{R}{-}F \rightarrow \overset{\delta-}{B}F_3 \rightleftharpoons R^+BF_4^- \qquad (10)$$

After the defeat of the 1956 Hungarian revolution I escaped with my family and spent some months in London before moving to Canada, where I was able to continue my research at the Dow Chemical Company Research Laboratory in Sarnia, Ontario. After a prolonged, comprehensive search of many Lewis acid halides I finally hit on antimony pentafluoride.[18–20] It turned out to be an extremely strong Lewis acid and for the first time enabled the ionization of alkyl fluorides in solution to stable, long-lived alkyl cations. Neat SbF_5 solutions of alkyl fluorides are viscous, but 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 much lower temperatures. As sequel to 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.[28, 29]

In the late fifties the research director of the Canadian Dow laboratories was not yet convinced about the usefulness of NMR spectroscopy. Consequently we had no such instrumentation of our own. Fortunately the Dow laboratories in Midland (Michigan) just 100 miles across the border 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 with our samples in the early morning to Midland and watched Ned Baker obtain their NMR spectra. *tert*-Butyl fluoride itself shows a characteristic doublet in its ^1H NMR spectrum due to the fluorine-hydrogen coupling of $J_{H,F} = 20$ Hz. In SbF_5 solution the doublet disappeared and the methyl protons became significantly deshielded from about $\delta = 1.5$ to $\delta = 4.3$. This was very encouraging but not yet entirely conclusive to prove 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 still a significant deshielding of the methyl protons would be expected. The differentiation of a rapidly exchanging, polarized donor-acceptor complex from the long sought-after, really ionic t-$C_4H_9^+ SbF_6^-$ thus became a major challenge [Eq. (11)].



(11)

Ned Baker, despite being himself a physicist, showed great interest in our chemical problem. To solve it, he devised a means to obtain the ^{13}C NMR spectra of our dilute solutions, an extremely difficult task before the advent of Fourier transform NMR techniques. Labeling with carbon-13 was generally possible at the time only to about 50% level (from $Ba^{13}CO_3$). When we prepared 50% ^{13}C-labeled *tert*-butyl fluoride, we could obtain at best only 5% solutions in SbF_5. Thus, the ^{13}C content of the solution was highly diluted. Baker, however, undaunted devised an INDOR (INDOR = internuclear double resonance) method. Using the high sensitivity of the proton signal, he was able by the double resonance technique to observe the ^{13}C shifts of our dilute solutions—a remarkable achievement around 1960! To our great joy the tertiary carbon atom [$\delta(^{13}C) = 335.2$] in $(CH_3)_3CF-SbF_5$ turned out to be more than $\Delta\delta = 300$ 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. For simplicity I am not discussing here the nature of the counterion, which can be a dimer ($Sb_2F_{11}^-$) or even an oligomer, or questions of ion-pairing and separation (concepts developed by Winstein).

Besides the *tert*-butyl cation we also succeeded in preparing and studying the related *sec*-isopropyl and the *tert*-amyl cations [Eq. (12) and (13)]. The isopropyl cation was of particular interest.

$$(CH_3)_2CHF + SbF_5 \longrightarrow (CH_3)_2CH^+ SbF_6^- \qquad (12)$$

$$(CH_3)_2CFCH_2CH_3 + SbF_5 \longrightarrow (CH_3)_2\overset{+}{C}CH_2CH_3 SbF_6^- \qquad (13)$$

Whereas in the *tert*-butyl cation the methyl protons are attached to carbons that are adjacent only to the carbocationic center, in the isopropyl cation a proton is directly attached to it. When we obtained the proton NMR spectrum of the i-$C_3H_7F-SbF_5$ system, the CH proton showed up as an enormously deshielded septet at $\delta = 13.5$, ruling out the possibility of a polarized donor-acceptor complex and indicating the formation of $(CH_3)_2CH^+$ ion. The ^{13}C NMR spectrum was also conclusive showing a very highly deshielded (by $\Delta\delta > 300$) ^+C atom (chemical shift: $\delta(^{13}C) = 320.6$). The spectrum of the *tert*-amyl cation showed an additional interesting feature in 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 (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 ^1H NMR spectra of the *tert*-butyl, *tert*-amyl, and isopropyl cations. These original spectra are framed and hung in my office as a momento, as is the ESCA spectrum of the norbornyl cation (see below).

Our studies also included an IR spectroscopic investigation of the observed ions (Fig. 2).[29] John Evans, 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 to see that some thirty years later FTIR spectra obtained by Denis Sunko and his colleagues in Zagreb with low-temperature matrix-deposition techniques and Schleyer's calculations of the spectra show good agreement with

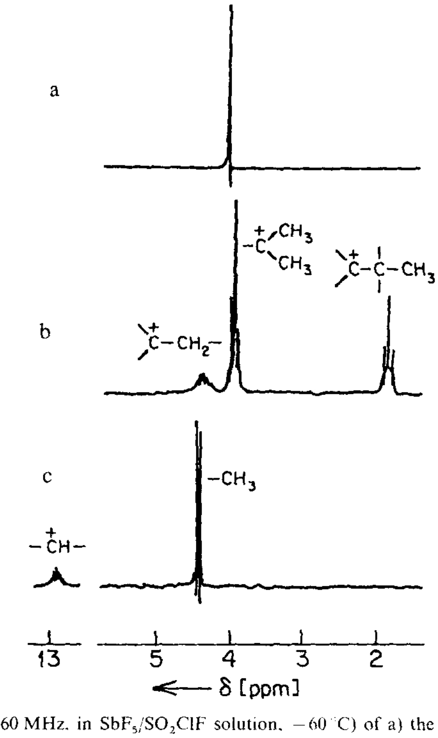


Fig. 1. ^1H NMR spectra (60 MHz, in SbF_5/SO_2ClF solution, −60 °C) of a) the *tert*-butyl cation [trimethylcarbenium ion, $(CH_3)_3C^+$], b) the *tert*-amyl cation [ethyldimethylcarbenium ion, $(CH_3)_2C^+-C_2H_5$], and c) the isopropyl cation [dimethylcarbenium ion, $(CH_3)_2C^+-H$].

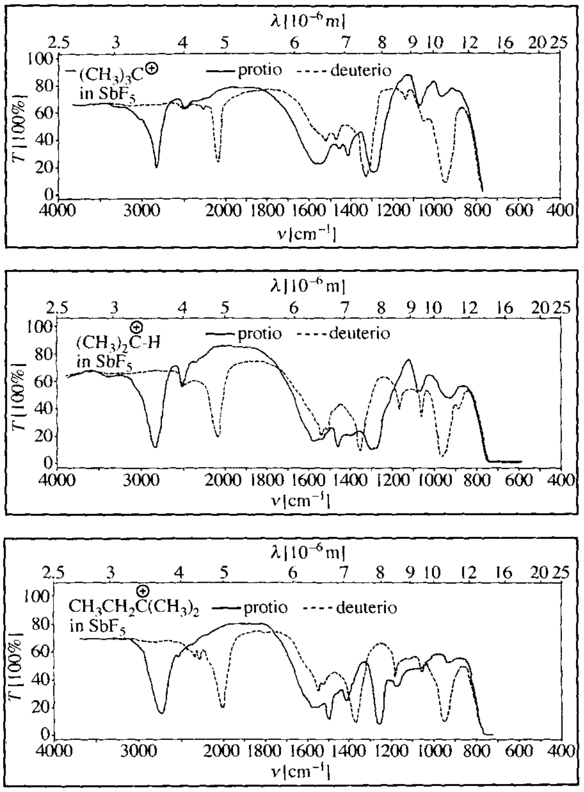
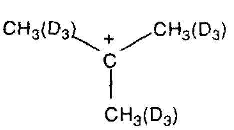


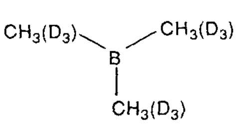
Fig. 2. IR spectra of *tert*-butyl (top), isopropyl (center), and *tert*-amyl (bottom) cations. T = transmission.

our early work, even though our work was carried out in neat SbF_5 at room temperature long before the advent of the FTIR methods.[30]

Subsequently in 1968–1970 with Jack DeMember and August Commeyras[31] we were able to carry out more detailed IR and laser Raman spectroscopic studies of alkyl cations. Comparison of the data of unlabeled and deuterium-labeled *tert*-butyl cations (**6**) with those of isoelectronic trimethylboron (**7**) proved the planar structure of carbocation **6** (Table 1).



6 / [D₉]-6



7 / [D₉]-7

This was also an early example of the realization that for nearly all carbocations there exist neutral isoelectronic isostruc tural boron analogues, which later in the hands of R. E. Williams and others proved so useful.

When in the summer of 1962 I was able for the first time to present our work in public at the Brookhaven Organic Reaction Mechanism Conference[28a] and subsequently in a number of other presentations and publications,[28b–e, 29] I had convincing evidence to substantiate that after a long and frequently frustrating search stable, long-lived alkyl cations had finally been obtained in superacidic solutions.

The chemistry of stable, long-lived carbocations as they became known, began and its progress became fast and wide spread. In an industrial laboratory, publication of research is not always easy. I would therefore like to thank the Dow Chemical Company for allowing me not only to carry out the work, but also to publish the results.

After successful preparation of long-lived, stable carbocations in antimony pentafluoride solutions, the work was 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 to ionize precursors, including alcohols. Superacids based on 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 J. Lukas, a German post-doctoral fellow working with me in Cleveland in the sixties, who after a laboratory party put remainders of a Christmas candle into the acid. The candle dissolved and the resulting solution gave an excellent NMR spectrum of the *tert*-butyl cation. This observation understandably evoked much interest, and hence he termed the acid "Magic". The name stuck in our laboratory. I think it was Ned Arnett who subsequently introduced the name into the literature where it increasingly became used. When a former graduate student of mine, J. Svoboda, started a small company (Cationics) to make some of our ionic reagents commercially, he obtained trade name protection for Magic Acid, and it has been marketed as such since.

Many contributed to the study of long-lived carbocations. The field rapidly expanded and allowed successful study of practically any carbocationic system. Time does not allow crediting here all my former associates and the many researchers around the world who contributed so much to the development of the field. Their work can be found in the extensive literature. I would like, however, to specifically mention the pioneering work of D. M. Brouwer and H. Hogeveen, as well as their colleagues at the Shell Laboratories in Amsterdam in the sixties and seventies. 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 *Chemical Communications* in 1964,[32] following closely my initial reports of 1962–1964. Similarly,

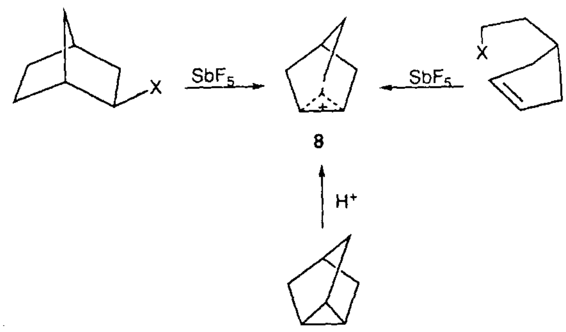
Table 1. Raman and IR frequencies $\tilde{\nu}$ [cm⁻¹] of **6**/[D₉]-**6** and **7**/[D₉]-**7**.

Species	$\nu_1,\nu_{12},\nu_7,\nu_{19}$	ν_2,ν_{13}	ν_{21}	ν_{14}	ν_{15}	ν_{17}	ν_5	ν_{16}	ν_6	ν_9	ν_{10}	ν_{18}
$(CH_3)_3C^+$ **6**	2947	2850		1450		1295			667		347	306
$(CH_3)_3B$ **7**	2975	2875	1060	1440	1300	1150	906	866	675	973 (486?)	336 [a]	320
$(CD_3)_3C^+$ [D₉]-**6**	2187	2090		1075		980			720		347	300
$(CD_3)_3B$ [D₉]-**7**	2230	2185		1033	1018	1205			620	870	(289) [b]	(276) [b]

[a] IR frequency. [b] Calculated.

I would like to emphasize the fundamental contributions of R. J. Gillespie to strong acid (superacid) chemistry[33] and also his generous help while I was working at the Dow Laboratories in Canada. I reestablished contact with him during this time after we first met in the winter of 1956 at University College in London where he worked with C. K. Ingold. Subsequently, he moved to McMaster University in Hamilton, Ontario. In the late fifties he already had an NMR spectrometer and in our study of SbF_5 containing highly acidic systems of carbocations we were gratified by his help to run some of our spectra on his instrument. His long-standing interest in fluorosulfuric acid and our studies in SbF_5-containing systems found common ground in studies of FSO_3H-SbF_5 systems.[34] It was also Gillespie who suggested calling protic acids stronger than 100% sulfuric acid as superacids.[33] This arbitrary, but most useful definition is now generally used. It should be pointed out, however, that the name "superacid" goes back to J. B. Conant of Harvard who used it in 1927 to denote acids such as perchloric acid, which he found stronger than conventional mineral acids and capable of protonating even such weak bases as carbonyl compounds.[35] Our book "Superacids" published in 1985 with Surya Prakash and Jean Sommer[33c] was appropriately dedicated to the memory of Conant. Few of today's chemists are aware of his contributions to this field.

My memories of the already mentioned 1962 Brookhaven Mechanism Conference,[28a] where I first reported on long-lived carbocations in public, are still clear in my mind. The scheduled "main event" of the meeting was the continuing debate between Saul Winstein and Herbert C. Brown (the pioneer of hydroboration chemistry, Nobel laureate, 1979) on the classical or nonclassical nature of some carbocations (or carbonium ions as they were still called at the time).[36] It must have come to them and others in the audience as quite a surprise that a young chemist from an unknown industrial laboratory was invited to give a major lecture and claimed to have obtained and studied stable, long-lived "carbonium" ions (i.e., carbocations) by the simple new method of using a highly acidic (superacidic) system. I remember being called aside separately by both Winstein and Brown during the conference and cautioned that a young chemist should be exceedingly careful making such claims. Each pointed out that most probably I was mistaken and could not have obtained long-lived carbonium ions. Just in case, however, my method should turn out to be real, I certainly would obtain evidence for the "nonclassical" or "classical" nature, of the much disputed 2-norbornyl cation (**8**, see Scheme 1). Their much heralded controversy[36b, c] centered around the question whether the experimentally observed, significant rate enhancement of the hydrolysis of 2-*exo*- over 2-*endo*-norbornyl esters and high *exo* selectivity in the system were caused, as suggested by Winstein, by σ participation of the C_1-C_6 single bond with delocalization to a bridged nonclassical ion or only by steric hindrance in the *endo* system and involving equilibrating classical trivalent ions. Nonclassical ions, a term first used by J. D. Roberts,[37] were suggested by P. D. Bartlett to contain too few electrons to allow a pair for each "bond", that is, in the ground state they must contain delocalized σ electrons.[36a] As my method allowed us to prepare carbocations as long-lived species, clearly the opportunity was given to decide the question experimentally through direct observation of the ion. At the time I had obtained only the proton spectrum of 2-norbornyl fluoride in SbF_5 at room temperature, which displayed a single, broad peak indicating complete equilibration through hydride shifts and Wagner–Meerwein rearrangement (well-known in solvolysis reactions and related transformations of 2-norbornyl systems). However, my curiosity was aroused and subsequently when in 1964 I transferred to Dow's Eastern Research Laboratory (established under Fred McLafferty as laboratory director first in Framingham, MA, and then moved to Weyland, MA), the work was further pursued in cooperation with Paul Schleyer from Princeton University and Marty Saunders from Yale University.[38a] Paul, who became a life-long friend, had, even at that time, a knack of acting as the catalyst to initiate cooperative efforts. Using SO_2 as solvent, we were able to lower the temperature of our solution to −78 °C and also prepared the ion by ionization of cyclopentenylethyl fluorides or by protonation of nortricyclene in $FSO_3H/SbF_5/SO_2ClF$ (Scheme 1).



Scheme 1.

I still did not have access to suitable low temperature instrumentation to carry out needed NMR studies, but Marty Saunders did. Thus, our samples now traveled the Massachusetts turnpike to New Haven, where Saunders was able to study solutions of the norbornyl cation at increasingly low temperatures using his own home-built NMR instrumentation housed in the basement of the Yale chemistry building. We were able to obtain NMR spectra of the ion at −70 °C, where the 3,2-hydride shift was frozen out. It took, however, till 1969 following my move to Cleveland to Case Western Reserve University to develop efficient low-temperature techniques with solvents such as SO_2ClF and SO_2F_2, to obtain high resolution ^1H and ^{13}C NMR spectra of the 2-norbornyl cation eventually down to −159 °C in supercooled solutions.[38b, c] Both 1,2,6-hydride shifts and the Wagner–Meerwein rearrangement could be frozen out at such a low temperature and the static, bridged ion was observed (Figs. 3a and 3b).[38c]

The differentiation of bridged, nonclassical from rapidly equilibrating classical carbocations based on NMR spectroscopy is difficult, since NMR is a relatively slow physical method with a limited time scale. We addressed this question in some detail in our work by comparing estimated shifts of the two systems with model systems.[38b, c] Of course these days this task is greatly simplified by highly efficient theoretical methods such as IGLO and GIAO to calculate NMR shifts of ions and comparing them with the experimental data.[38d] It is rewarding

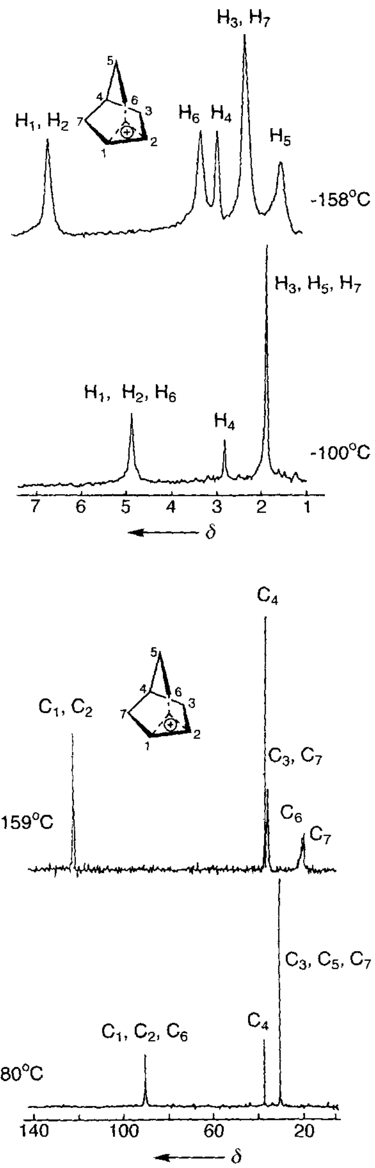


Fig. 3. Top: 395 MHz ^{1}H NMR spectra of the 2-norbornyl cation in SbF$_5$/SO$_2$ClF/SO$_2$F$_2$ solution. Bottom: 50 MHz, proton-decoupled ^{13}C NMR spectra of 2-norbornyl cation (^{13}C enriched) in SbF$_5$/SO$_2$ClF/SO$_2$F$_2$ solution.

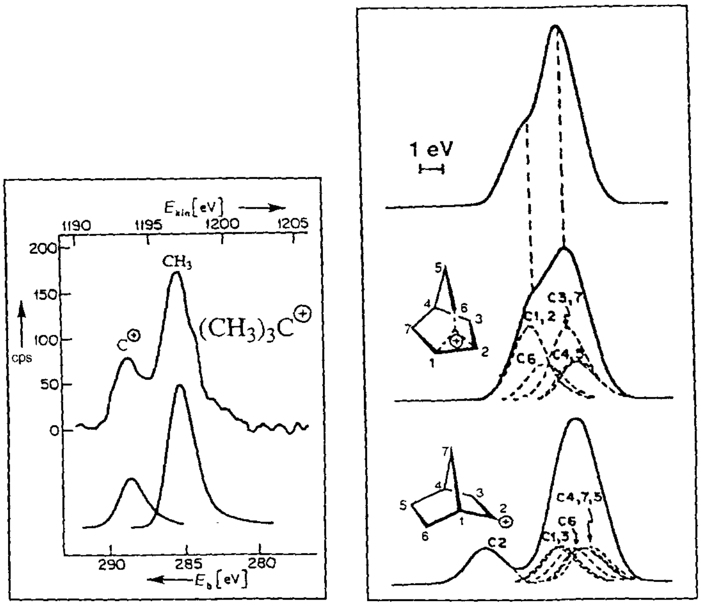


Fig. 4. Left: Carbon 1s photoelectron spectrum of the *tert*-butyl cation (top curve from experiment; bottom curve calculated). Right: 1s core-hole-state spectra for the 2-norbornyl cation (top), and Clark's simulated spectra for the classical (center) and nonclassical ions (bottom).

to see that our results and conclusions stood up well to comparison with all the more recent studies.

As mentioned, we carried out IR studies (using fast vibrational spectroscopy) early in our work on carbocations. In our studies of the norbornyl cation we also obtained Raman spectra,[38b] and although at the time it was not possible to calculate the spectra theoretically, comparison with model compounds (2-norbornyl system and notricyclene) indicated the symmetrical, bridged nature of the ion. Sunko and Schleyer recently were able to obtain the FTIR spectrum in elegant studies and compare it with theoretical calculations.[30]

Kai Siegbahn's (Nobel laureate in Physics, 1981) core electron spectroscopy (ESCA) was another fast physical method we applied to resolve the question of bridged vs. rapidly equilibrating ions. We were able to study carbocations in the late sixties by this method, adapting it to superacidic matrixes. George Mateescu and Louise Riemenschneider in my Cleveland laboratory established ESCA instrumentation and the needed 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 (Fig. 4).[39] These studies again convincingly showed the nonclassical nature of the 2-norbornyl cation, because no trivalent carbenium ion center was observed in the ESCA spectrum characteristic of a classical ion, such as is the case for the *tert*-butyl cation. Although again some criticism was leveled at our work by proponents of the equilibrating classical-ion concept, subsequent studies by Dave Clark fully justified our results and conclusions.[39c] So did a comparison of theoretical calculations with the experimental data.

It is proper to mention here some significant, more recent studies. Saunders's studies showed the absence of deuterium isotopic perturbation, as anticipated for a classical equilibrating system.[40] Myhre and Yannoni[41] at very low (5 K!) temperatures were able to obtain solid state ^{13}C NMR spectra that showed no indication of freezing out any equilibrating classical ions; the barriers at this temperature should be as low as 200 cal mol^{-1} (the energy of a vibrational transition). Laube was able to carry out single crystal X-ray structural studies on substituted 2-norbornyl cations.[42] Schleyer's theoretical studies,[38d] includng IGLO and related calculation of NMR shifts and their comparison with experimental data, contributed further to the understanding of σ-bridged carbonium ion nature of the 2-norbornyl cation. (The classical 2-norbornyl cation was not even found to be an energetically high-lying intermediate!) So did Arnett's calorimetric studies.[43] In a 1983 paper entitled "Conclusion of the Norbornyl Ion Controversy" with Prakash and Saunders we were able to state[44] that "all these studies unequivocally ended the so-called nonclassical-ion controversy". Winstein's original views were fully justified by the extensive structural studies made possible through my "stable ion" chemistry.

Although many believe that too much effort was expended on this problem, in my view the norbornyl ion controversy had significant consequences for chemistry. It not only helped to extend the limits of available techniques for structural studies and theoretical calculations, but also laid the foundation for the chemistry of C-H and C-C single bonds with electrophiles and thus of saturated hydrocarbons (see below).

Intensive, critical studies of a controversial topic always help to eliminate the possibility of any errors. One of my favorite quotations is that by Georg von Békésy (Nobel laureate in Physiology and Medicine, 1961).[45]

> "[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. 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. 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 controversy. It is to their credit that we know probably more today about the structure of carbocations such as the norbornyl cation than of any other chemical species. Their efforts resulted in the most rigorous studies and the development or improvement of many techniques.

To me the most significant consequence of the norbornyl cation studies was the realization that C–H and C–C single bonds can act as two-electron σ donors not only in intramolecular but also in intermolecular transformations and electrophilic reactions. Two-electron, three-center (2e–3c) bonding (familiar in boron and organometallic chemistry) is the key for these reactions. Much new chemistry rapidly evolved, and the broad scope and significance of the chemistry of hypercoordinated carbon compounds (in short hypercarbon) was recognized.[46]

The General Concept of Carbocations

The study of carbocations by direct observation of long-lived species and related superacid chemistry made it apparent that the carbocation concept is wider than previously thought and needed a more general definition, which I offered in a 1972 paper.[10] The definition takes into account the existence of two major limiting classes of carbocations with a continuum of species with different degrees of delocalization bridging them.

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. (It should be noted that sp-hybridized, linear oxocarbonium ions and vinyl cations also show substantial electron deficiency on carbon). The carbenium carbon center contains six valence electrons and is thus 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 trivalent ion.

b) Pentacoordinated (or higher coordinated) "nonclassical" carbonium ions, which contain five (or more coordinated 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 is always surrounded by eight electrons, but overall the carbonium ions are electron-deficient because two electrons are shared between three (or more) atoms. CH_5^+ can be considered the parent for carbonium ions.

Subsequently in 1977 Brown and Schleyer offered a related definition:[36c]

> "A nonclassical carbonium ion is a positively charged species which cannot be represented adequately by a single Lewis structure. Such a cation contains one or more carbon or hydrogen bridges joining the two electron-deficient centers. The bridging atoms have coordination numbers higher than usual, typically five or more for carbon and two or more for hydrogen. Such ions contain two-electron, three- (or multiple-) center bonds including a carbon or hydrogen bridge."

Lewis's concept that a covalent chemical bond consists of a pair of electrons shared between the two atoms became a cornerstone of structural chemistry. Chemists tend to brand compounds as anomalous if their structures cannot be depicted in terms of such bonds alone. Carbocations with too few electrons to allow a pair for each "bond" came to be referred to as nonclassical, a name first used by J. D. Roberts[37] for the cyclopropylcarbinyl cation and adapted by Winstein to the norbornyl cation.[47] 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, two- or three- (even multi-) center bonding (not unlike the bonding principles for boron compounds established by Lipscomb, Nobel laureate, 1976). The terms classical and nonclassical are expected, however, to fade away gradually as the general nature of bonding becomes recognized.

Whereas the differentiation of trivalent carbenium, and pentacoordinated carbonium ions serves a useful purpose to define them as limiting ions, it should be clear that in carbocationic systems varying degrees of delocalization always exist. This can involve participation by neighboring n-donor atoms, π-donor groups, or σ-donor C–H or C–C bonds.

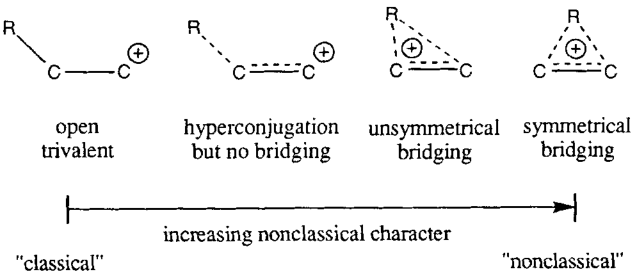
Carbocations
↙ ↘

trivalent "classical" ions (carbenium ions) CH_3^+ is parent	pentacoordinated (or higher) "nonclassical" ions (carbonium ions) CH_5^+ is parent

Trivalent carbenium ions are the key intermediates in reactions of unsaturated π-donor hydrocarbons with electrophiles. At the same time pentacoordinated carbonium ions are the key to reactions of saturated σ-donor hydrocarbons with electrophiles. The ability of single bonds to act as electron donors lies in their ability to form carbonium ions by two-electron, three-center (2e–3c) bond formation.

Expansion of the carbon octet through 3d orbital participation does not seem possible; there can be only eight valence electrons in the outer shell of carbon, a small, first row element.[46] The valency of carbon cannot exceed four. Kekulé's concept of the tetravalency of carbon in bonding terms represents attachment of four atoms (or groups) involving 2e–2c Lewis-type bonding. There is, however, nothing that prevents carbon from also participating in multicenter bonding. Pentacoordination (or higher) of carbon implies five (or more) atoms or ligands simultaneously attached to it within reasonable bonding distance.[46]

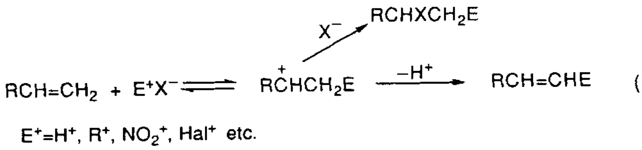
Neighboring group participation with the vacant p orbital of a carbenium ion center contribute to its stabilization through delocalization, which can involve atoms with unshared electron pairs (n-donors), π-electron systems (direct conjugative or allylic stabilization), bent σ-bonds (as in cyclopropylcarbinyl cations), and C–H and C–C σ-bond hyperconjugation. Trivalent carbenium ions, with the exception of the parent CH_3^+, therefore always show varying degrees of delocalization without becoming pentacoordinated carbonium ions. The limiting cases define the extremes of the spectrum of carbocations (Scheme 2).



Scheme 2.

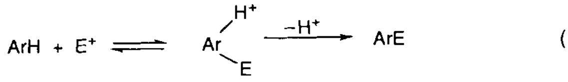
The Role of Carbocations in Electrophilic Reactions

Acid-catalyzed electrophilic reactions and transformations such as isomerization, alkylation, substitution, addition, elimination, rearrangements, etc. involve carbocationic intermediates. Many of these reactions also gained significance in industrial applications. Aromatic hydrocarbon chemistry and that based on acetylene laid the foundation for industrial organic chemistry a century ago. Subsequently olefin-based chemistry took on great significance. In all this chemistry reactive π-bonded systems are the electron donor substrates. In electrophilic reactions they readily form trivalent carbocationic intermediates [Eq. (14) and (15)].

 (14)

$$RCH{=}CH_2 + E^+X^- \rightleftharpoons R\overset{+}{C}HCH_2E \xrightarrow{-H^+} RCH{=}CHE \quad (X^- \rightarrow RCHXCH_2E)$$

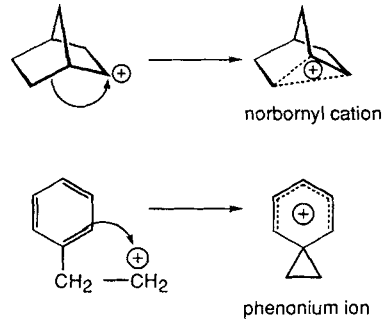
$E^+ = H^+, R^+, NO_2^+, Hal^+$ etc.

 (15)

$$ArH + E^+ \rightleftharpoons Ar\!\begin{smallmatrix}H^+\\E\end{smallmatrix} \xrightarrow{-H^+} ArE$$

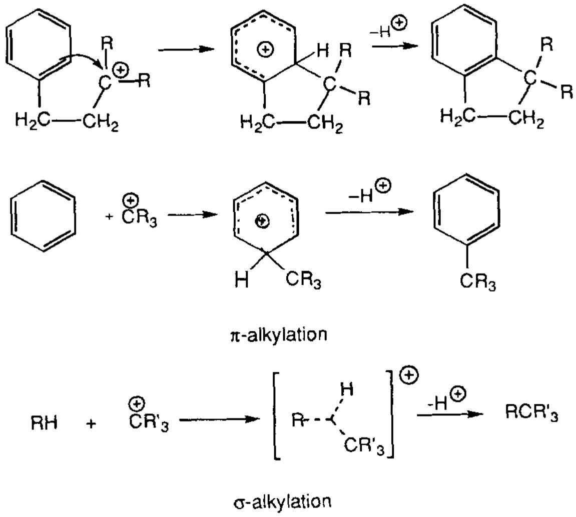
The discovery of pentacoordinate carbonium ions discussed previously led to the realization that they play an important role not only in understanding the structure of nonclassical ions, but more importantly as the key to electrophilic reactions at single bonds, for example, of saturated aliphatic hydrocarbons (alkanes and cycloalkanes). Such reactions include not only acid-catalyzed hydrocarbon isomerizations, fragmentations, cyclizations, but also substitutions and related electrophilic reactions and transformations.

In ionization of β-phenylethyl systems, neighboring π-orbital participation with the carbocationic center occurs, which can be considered as intramolecular π-alkylation giving Cram's phenonium ions. The corresponding ionization of 2-norbornyl systems involves participation of a properly oriented C–C single bond (that is, intramolecular σ-alkylation) giving the bridged ion (Scheme 3).



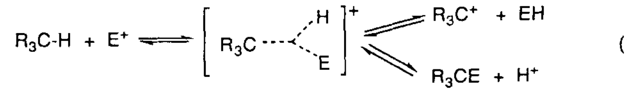
Scheme 3.

Alkylation of π systems in Friedel–Crafts type reactions (either by an inter- or intramolecular route) has long been widely known and well studied. To extend these relationships it was logical to ask why intermolecular alkylation (and other electrophilic reactions) of σ-donor hydrocarbons could not be affected (Scheme 4).

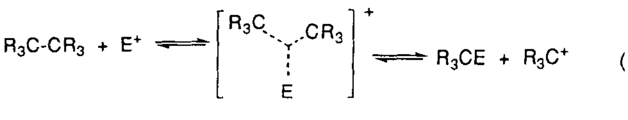


Scheme 4.

Our studies in the late sixties and early seventies for the first time provided evidence for the general reactivity of covalent C–H and C–C single bonds of alkanes and cycloalkanes in various protolytic processes as well as in hydrogen–deuterium exchange, alkylation, nitration, halogenation, etc. [Eq. (16) and (17)]. This reactivity is due to the σ-donor ability (σ basicity) of single bonds, which allows bonds to share their bonded electron pairs with an electron-deficient reagent in two-electron, three-center bond formation. The reactivity of single bonds thus stems from their ability to participate in the formation of pentacoordinate carbonium ions. Subsequent cleavage of the three-center

 (16)

$$R_3C\text{-}H + E^+ \rightleftharpoons \left[R_3C\cdots\begin{smallmatrix}H\\E\end{smallmatrix}\right]^+ \rightleftharpoons R_3C^+ + EH \;/\; \rightarrow R_3CE + H^+$$

 (17)

$$R_3C\text{-}CR_3 + E^+ \rightleftharpoons \left[\begin{smallmatrix}R_3C & & CR_3\\ & E & \end{smallmatrix}\right]^+ \rightleftharpoons R_3CE + R_3C^+$$

$E^+ = D^+, H^+, R^+, NO_2^+, Hal^+$ etc.

bond in a C–H reaction results in formation of substitution products, whereas C–C reaction results in bond cleavage and formation of a fragment carbenium ion, which then can react further.

As bond-to-bond shifts can readily take place through the low barriers within five coordinate carbonium ions, the intermediates can be more complex but always involve interconverting carbonium ions.

Superacidic hydrocarbon chemistry under conditions favoring carbocationic intermediates is also gaining in significance in practical applications. Isomerization of alkanes at relatively low temperature, a much improved and environmentally adaptable alkylation, new approaches to the functionalization of methane and possibilities in its utilization as a building block for higher hydrocarbons and their derivatives, as well as moderate conditions for coal liquefaction are just a few examples to be mentioned here.[48]

Protosolvolytic Activation of Carbocationic Systems

Carbocations are electrophiles, that is, electron-deficient compounds. In electrophilic reactions of unsaturated, π-donor hydrocarbons and their derivatives (such as acetylenes, olefins, aromatics) the reaction with the electrophilic reagents is facilitated by the nucleophilic assistance of the substrates. In reactions with increasingly weaker (deactivated) π-donors and even more so with only weakly electron-donating saturated hydrocarbons (σ-donors), the electrophile itself must provide the driving force for the reactions. Hence the need for very strongly electron-demanding electrophiles and comparably low nucleophilicity reaction media (such as superacidic systems).

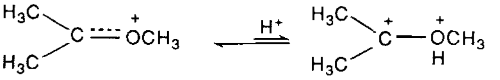
It was only more recently realized[49] that electrophiles capable of further interaction (coordination, solvation) with strong Brønsted or Lewis acids can be greatly activated. The resulting enhancement of reactivity can be very significant compared to that of the parent electrophiles under conventional conditions and indicates *superelectrophile* formation, that is, electrophiles with greatly enhanced electron deficiency (frequently of dipositive nature). I have reviewed[49] elsewhere the superelectrophilic activation of various electrophiles and will not discuss it here, except for some superelectrophilic activation which can also affect the reactivity of carbocations.

In carboxonium ions, originally studied by Meerwein, alkyl groups of an alkyl cation, such as the *tert*-butyl cation, are replaced by alkoxy, such as methoxy groups. The methoxy groups delocalize charge (by neighboring oxygen participation) and thus make these ions increasingly more stable:

$$(CH_3)_3C^+ < (CH_3)_2\overset{+}{C}OCH_3 < CH_3\overset{+}{C}(OCH_3)_2 < {}^+C(OCH_3)_3$$

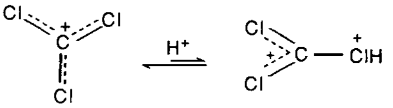
At the same time their reactivity as carbon electrophiles decreases. For example, they do not alkylate aromatics or other hydrocarbons. Strong oxygen participation thus greatly diminishes the carbocationic nature.

Neighboring oxygen participation, however, can be decreased if a strong acid protosolvates (or protonates) the nonbonded oxygen electron pairs [Eq. (18)]. Consequently, carboxonium ions (and related ions such as acyl cations) in superacidic media show greatly enhanced carbon electrophilic reactivity indicative of dicationic nature.



(18)

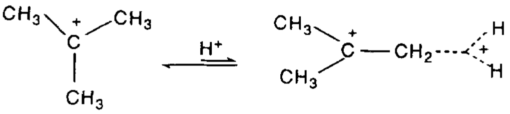
Similarly halogen-substituted carbocations, such as the trichloromethyl cation Cl_3C^+,[50] are greatly stabilized by n–p back donation (not unlike BCl_3). They can also be greatly activated by superacidic media, which protosolvate (protonate) the nonbonded halogen electron pairs, thus diminishing neighboring halogen participation [Eq. (19)].



(19)

This explains for example why carbon tetrachloride highly enhances the reactivity of protic superacids for alkane transformations. Lewis acids have similar activating effect.[49]

Alkyl cations themselves, in which only hyperconjugative C–H or C–C single bond interactions stabilize the electron-deficient center, are activated by superacidic solvation. Results of theoretical calculations and hydrogen–deuterium exchange of long-lived alkyl cations in deuterated superacids, under conditions where no deprotonation–reprotonation can take place substantiate the existence of these protoalkyl dications as real intermediates [Eq. (20)].[51]



(20)

The widely recognized high reactivity of alkanes for isomerization alkylation reactions in strongly acidic media is very probably assisted by protosolvation of the intermediate alkyl cations. Similar activation can be involved in other acid-catalyzed hydrocarbon transformations, which are preferentially carried out in solutions containing excess acid.

Activation by Solid Superacids and Possible Relevance to Enzymatic Systems

The chemistry of carbocations and their activation was discussed so far in superacidic solutions. However, superacidic systems are not limited to solution chemistry. Solid superacids, possessing both Brønsted and Lewis acid sites, are of increasing significance. They range from supported or intercalated systems, to highly acidic perfluorinated resinsulfonic acids (such as Nafion-H and its analogues) to certain zeolites (such as H-ZSM-5).

To explain why their remarkable activity, for example in catalytic transformations of alkanes (even methane), an appraisal of the de facto activity at the acid sites of such solid acids is called for.[49]

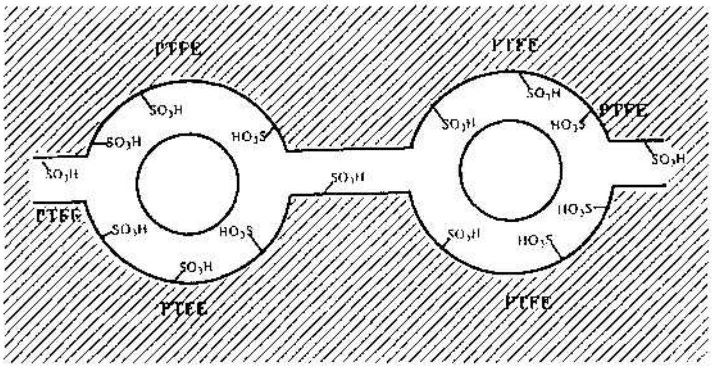


Fig. 5. Clustered SO_3H acid sites in a perfluorinated resinsulfonic acid.

Nafion-H is known to contain acidic SO_3H groups clustered together (Fig. 5).

H-ZSM-5, which also displays superacidic activity, was found by Haag et al.[52] to isomerize and alkylate alkanes readily (H_2 was observed as the protolytic by-product in stoichiometric amounts). In this zeolite, active Brønsted and Lewis acid sites are again in close proximity, approximately 2.5 Å apart (Fig. 6).

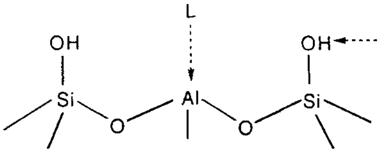


Fig. 6. Brønsted (B) and Lewis acid sites (L) in zeolites.

It is reasonable that in these (and other) solid superacid catalyst systems, bi- or multidentate interactions forming highly reactive intermediates is possible. This amounts to the solid-state equivalent of protosolvation (protonation).[49]

Nature is able to perform its own transformations in ways which chemists have only begun to understand and cannot yet come close to duplicating. At enzymatic sites many significant transformations take place which are acid-catalyzed (including electron-deficient metal-ion-catalyzed processes). Because of the unique structure at enzymatic sites bi- and multidentate interactions must be possible; the concepts discussed here thus may also have relevance to our understanding of some enzymatic processes.[49]

Conclusions

The chemistry of long-lived carbocations became a very active and fast developing field with contributions by researchers from all around the world. It is with understandable satisfaction that I look back at the progress achieved and the possibilities ahead. What started out as a for one of the most significant class of chemical reaction intermediates, the carbocations, as long-lived species and a study of their structure, led subsequently to the development of the general concept of the reactivity of single bonds, such as C–H and C–C bonds, with electrophiles and related superacidic hydrocarbon chemistry.

Despite all the progress that has been made I believe that most exciting chemistry in the field still lies ahead for future generations to explore. I wish them as much excitement and satisfaction in their work as I had.

The concept of the tetravalency of carbon stated by Kekulé well over a century ago remains an essential foundation of organic chemistry. Carbon, as a small first row element, cannot extend its valance shell, and the octet rule allows formation of only four two-electron, two-center (2e–2c) Lewis-type bonds (or their equivalent multiple bonds). It is, however, possible for one (or more) electron pair of carbon to be involved in two-electron, three-center (2e–3c) bonding.[46] This allows carbon to simultaneously bond five (or even six) atoms or groups. This is the case in carbonium ions which contain hypercarbon (hypercoordinate carbon). It also provides the key to understanding the rapidly emerging chemistry of saturated hydrocarbons with electrophiles, including that of the parent methane and of C–H and C–C bonds in general. Whereas hypercoordinate carbocations are 8e carbon systems that do not violate the octet rule, carbanionic S_N2 transition states $[Y\cdots CR_3\cdots X]^-$ are 10e systems and thus cannot be intermediates.

I wrote more than twenty years ago[9] "The realization of the electron donor ability of shared (bonded) electron pairs (single bonds) could one day rank equal in importance with G. N. Lewis' realization of the electron donor unshared (nonbonded) electron pairs (or for this reason I could add the electron pairs involved in multiple bonding). We can now not only explain the reactivity of saturated hydrocarbons and single bonds in general electrophilic reactions, but indeed use this understanding to explore new areas and reactions of carbocation chemistry." It is with some satisfaction that I feel this promise is being fulfilled.

I was fortunate to be able to build on the foundations laid by many. I would like to acknowledge particularly the fundamental contributions of Hans Meerwein (1879–1965) and Christopher Kelk Ingold (1893–1970), who recognized the role of carbocations in some chemical reactions, and Frank Whitmore (1887–1947), who generalized it to many others. I am also greatly indebted to all my former students and associates, whose dedication, hard work, and major scientific contributions made our joint effort possible. My wife Judy till her retirement was not only an integral part of our scientific effort. All those who ever worked in the Olah group appreciated greatly her warmth, caring, and concern for our "scientific family". In our 20 years of association from brilliant graduate student to trusted friend and colleague, G. K. Surya Prakash made invaluable contributions. The Loker Hydrocarbon Research Institute of the University of Southern California provided a wonderful home and support for our work in the last 15 years. The board of the Institute, particularly Mrs. Katherine Loker, Harold Moulton, and Carl Franklin are thanked for their support and friendship over the years. I also cherish close association with such wonderful colleagues and friends as Ned Arnett, Joseph Casanova, Paul Schleyer, Jean Sommer, Peter Stang, Ken Wade, and Robert Williams, who are senior distinguished fellows of the Loker Institute. The National Institutes of Health and the National Science Foundation gave support over the years to our studies of carbocations, and the Loker Institute mainly supported the work on hydrocarbon chemistry.

Received: December 5, 1994 [A 97 IE]
German version: *Angew. Chem.* **1995**, *107*, 1517

Keywords: carbocations · hydrocarbons · Nobel lecture · reactive intermediates

[1] a) J. F. Norris, *Am. Chem. J.* **1901**, *25*, 117; b) F. Kehrmann, F. Wentzel, *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 3815; c) A. Baeyer, V. Villiger, *ibid.* **1902**, *35*, 1189, 3013; d) M. Gomberg, *ibid.* **1902**, *35*, 2397; e) P. Walden, *ibid.* **1902**, *35*, 2018; f) A. Werner, *ibid.* **1901**, *34*, 3300; g) A. Baeyer, *ibid.* **1905**, *38*, 569.

[2] H. Meerwein, K. van Emster, *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 2500.

[3] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, NY, **1953**, and references therein, 2nd ed., **1969**.

[4] F. C. Whitmore, *J. Am. Chem. Soc.* **1932**, *54*, 3274, 3276; *Annu. Rep. Prog. Chem.* **1933**, 177; *Chem. Eng. News* **1948**, *26*, 668.

[5] *Carbonium Ions, Vols. I–V* (Eds.: G. A. Olah, P. von R. Schleyer), Wiley-Interscience, New York, **1968–1976**, and reviews cited therein.

[6] D. Bethell, V. Gold, *Carbonium Ions*, Academic Press, London, **1967**.

[7] P. Vogel, *Carbocation Chemistry*, Elsevier, Amsterdam, **1985**.

[8] G. A. Olah, *Chem. Eng. News* **1967**, *45*, 76 (March 27, 1967); *Science* **1970**, *168*, 1298.

[9] G. A. Olah, *Angew. Chem.* **1973**, *85*, 183; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 173; *Carbocations and Electrophilic Reactions*, Verlag Chemie, Weinheim, Wiley, New York, **1974**.

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

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

[12] H. Meerwein, *Methoden Org. Chem. (Houben-Weyl) 4th ed. 1952–*, Vol. VI/3, **1965**, and references therein.

[13] F. Seel, *Z. Anorg. Allg. Chem.* **1943**, *250*, 331; *ibid.* **1943**, *252*, 24.

[14] For my reminiscences, see: In Memory of H. L. Meerwein (*Top. Curr. Chem.* **1979**, *80*, 21).

[15] G. A. Olah, S. Kuhn, *Acta Chim. Acad. Sci. Hung.* **1956**, *10*, 233; *Chem. Ber.* **1956**, *89*, 866; *J. Am. Chem. Soc.* **1960**, *82*, 2380.

[16] A. N. Nesmejanov, E. J. Kahn, *Ber. Dtsch. Chem. Ges.* **1934**, *67*, 370.

[17] D. E. Pearson, *J. Am. Chem. Soc.* **1950**, *72*, 4169.

[18] G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, E. B. Baker, *J. Am. Chem. Soc.* **1962**, *84*, 2733.

[19] G. A. Olah, *Rev. Chim. (Bucharest)* **1962**, *7*, 1139 (Nenitzescu issue).

[20] G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, E. B. Baker, *J. Am. Chem. Soc.* **1963**, *85*, 1328.

[21] *Mass Spectrometry of Organic Ions* (Ed.: F. W. McLafferty), Academic Press, New York, **1963**.

[22] H. C. Brown, H. Pearsall, L. P. Eddy, *J. Am. Chem. Soc.* **1950**, *72*, 5347.

[23] E. Wertyporoch, T. Firla, *Justus Liebigs Ann. Chem.* **1933**, *500*, 287.

[24] G. A. Olah, S. J. Kuhn, J. A. Olah, *J. Chem. Soc.* **1957**, 2174.

[25] F. Fairbrother, *J. Chem. Soc.* **1945**, 503.

[26] J. Rosenbaum, M. C. R. Symons, *Proc. Chem. Soc. London* **1959**, 92; J. Rosenbaum, M. Rosenbaum, M. C. R. Symons, *Mol. Phys.* **1960**, *3*, 205; J. Rosenbaum, M. C. R. Symons, *J. Chem. Soc. London* **1961**, 1.

[27] a) A. C. M. Finch, M. C. R. Symons, *J. Chem. Soc. London* **1965**, 378. b) For a summary, see M. C. Deno, *Prog. Phys. Org. Chem.* **1964**, *2*, 129; c) G. A. Olah, C. U. Pittman, Jr., M. C. R. Symons in *Carbonium Ions, Vol. I* (Eds.: G. A. Olah, P. von R. Schleyer), Wiley Interscience, New York, **1968**, p. 153.

[28] Preliminary communications and lectures: a) G. A. Olah, Conference Lecture at 9th Reaction Mechanism Conference, Brookhaven, New York, August **1962**; b) G. A. Olah, Abstract 142nd National Meeting of the American Chemical Society, Atlantic City, NJ, September **1962**, p. 45; c) G. A. Olah, W. S. Tolgyesi, J. S. MacIntyre, I. J. Bastien, M. W. Meyer, E. B. Baker, Abstracts A, XIX International Congress of Pure and Applied Chemistry, London, June **1963**, p. 121; d) G. A. Olah, *Angew. Chem.* **1963**, *75*, 800; *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 629; e) *C. D. Nenitzescu's 60th Birthday Issue* (*Rev. Chim (Bucharest)* **1962** *7*, 1139); f) *Repr. Am. Chem. Soc. Div. Pet. Chem.* **1964**, *9(7)*, C31; g) Intermediate Complexes and Their Role in Electrophilic Aromatic Substituents, Conference Lecture at Organic Reaction Mechanism Conference, Cork, Ireland, June **1964** (*Spec. Publ. Chem. Soc.* **1965**, 19); h) G. A. Olah, C. U. Pittman, Jr., *Adv. Phys. Org. Chem.* **1966**, *4*, pp. 305.

[29] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, I. J. Bastien, *J. Am. Chem. Soc.* **1964**, *86*, 1360.

[30] a) H. Vancik, D. E. Sunko, *J. Am. Chem. Soc.* **1989**, *111*, 3742; b) S. Sieber, P. Buzek, P. von R. Schleyer, W. Koch, J. W. de M. Carneiro, *J. Am. Chem. Soc.* **1993**, *115*, 25.

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

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

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

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

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

[36] a) P. D. Bartlett, *Nonclassical Ions*, Benjamin, New York, **1965**; b) S. Winstein, *Q. Rev. Chem. Soc.* **1969**, *23*, 1411; c) H. C. Brown (with commentary by P. von R. Schleyer), *The Nonclassical Ion Problem*, Plenum, New York, **1977**.

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

[38] a) M. Saunders, P. von R. Schleyer, G. A. Olah, *J. Am. Chem. Soc.* **1964**, *86*, 5680; b) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, C. Y. Lui, *ibid.* **1970**, *92*, 4627; c) G. A. Olah, G. K. S. Prakash, M. Arvanaghi, F. A. L. Anet, *ibid.* **1982**, *104*, 7105; d) P. von R. Schleyer, S. Sieber, *Angew. Chem.* **1993**, *105*, 1676; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1606, and references therein.

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

[40] M. Saunders, M. R. Kates, *J. Am. Chem. Soc.* **1980**, *102*, 6867.

[41] C. S. Yannoni, V. Macho, P. C. Myhre, *J. Am. Chem. Soc.* **1982**, *104*, 7380.

[42] T. Laube, *Angew. Chem.* **1987**, *99*, 580; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 560.

[43] E. M. Arnett, N. Pienta, C. Petro, *J. Am. Chem. Soc.* **1980**, *102*, 398.

[44] G. A. Olah, G. K. S. Prakash, M. Saunders, *Acc. Chem. Res.* **1983**, *16*, 440.

[45] G. von Békésy, *Experiments in Hearing*, McGraw Hill, New York, **1960**, p. 8.

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

[47] S. Winstein, D. Trifan, *J. Am. Chem. Soc.* **1952**, *74*, 1154.

[48] a) G. A. Olah, A. Molnár, *Hydrocarbon Chemistry*, Wiley, New York, **1995**, and references therein; b) I. Bucsi, G. A. Olah, *Catal. Lett.* **1992**, *16*, 27; c) G. A. Olah, *Acc. Chem. Res.* **1987**, *20*, 422; d) G. A. Olah, M. Bruce, E. H. Edelson, *Fuel* **1984**, *63*, 1130.

[49] G. A. Olah, *Angew. Chem.* **1993**, *105*, 805; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 767, and references therein.

[50] G. A. Olah, L. Heiliger, G. K. S. Prakash, *J. Am. Chem. Soc.* **1989**, *111*, 8020.

[51] a) G. A. Olah, N. Hartz, G. Rasul, G. K. S. Prakash, *J. Am. Chem. Soc.* **1993**, *115*, 6985; b) G. A. Olah, N. Hartz, G. Rasul, G. K. S. Prakash, M. Burkhart, K. Lammertsma, *ibid.* **1994**, *116*, 3187.

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