

# MY SEARCH FOR CARBOCATIONS AND THEIR ROLE IN CHEMISTRY

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by

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*“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

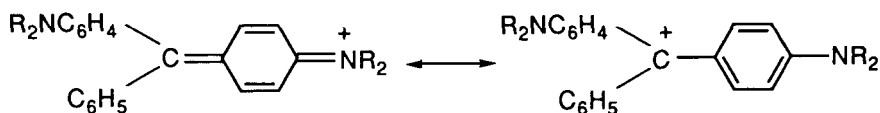
Hydrocarbons are compounds of the elements carbon and hydrogen. They make up natural gas and oil and thus are essential for our modern life. Burning of hydrocarbons is used to generate energy in our power plants and heat our homes. Derived gasoline and diesel oil propel our cars, trucks, air-planes. Hydrocarbons are also the feed-stock for practically every man-made material from plastics to pharmaceuticals. What nature is giving 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 used processes are acid catalyzed involving chemical reactions proceeding through positive ion intermediates. Consequently, the knowledge of these intermediates and their chemistry is of substantial significance both as fundamental, as well as practical science.

Carbocations are the positive ions of carbon compounds. It was in 1901 that Norris<sup>a</sup> and Kehrman<sup>b</sup> 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. von Baeyer (Nobel Prize, 1905) should be credited for having recognized in 1902 the salt like character of the compounds formed (equation 1).<sup>c</sup>



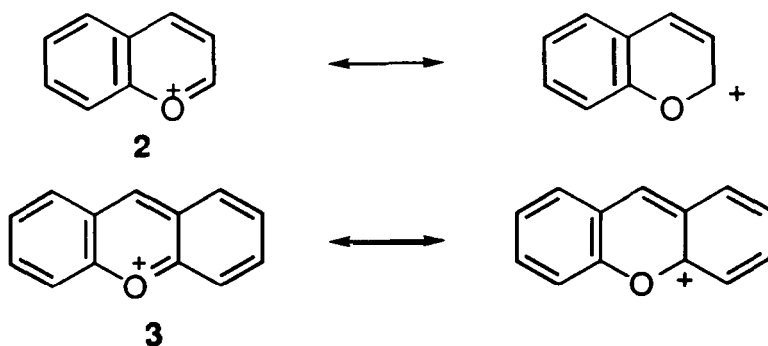
He then proceeded to suggest a correlation between the appearance of color and formation of salt - the so called “halochromy”. Gomberg<sup>d</sup> (who had just

shortly before discovered the related stable triphenylmethyl radical) as well as Walden<sup>16</sup> contributed to the evolving understanding of the structure of related dyes, such as malachite green 1.



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

The constitution of flavylum and anthocyanin compounds evolved based on Robinson's and Willstätter's pioneering studies. Werner formulated<sup>17</sup> the parent benzopyrylium or xanthylium salts 2 and 3 as oxonium salts, while Baeyer<sup>18</sup> emphasized their great similarity to triarylmethyl salts and considered them as carbenium salts. Time has indeed justified both point of view with the realization of the significance of the contribution of both oxonium and carbenium ion resonance forms.

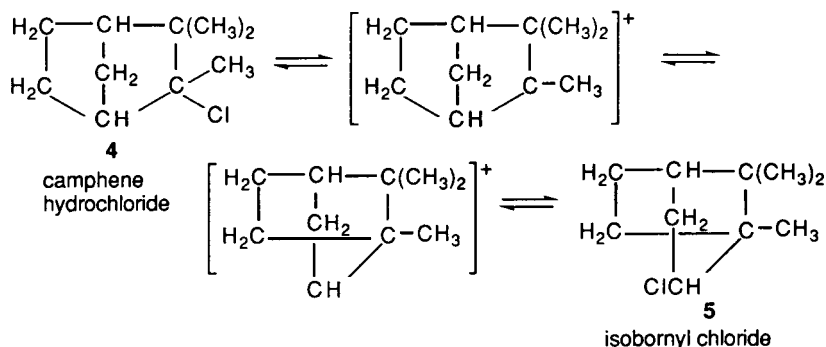


Whereas the existence of ionic triarylmethyl and related dyes was established at around the turn of the 20th century, the more general significance of carbocations in chemistry was for long unrecognized. Triarylmethyl cations were considered as an isolated curiosity of chemistry, not unlike Gomberg's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

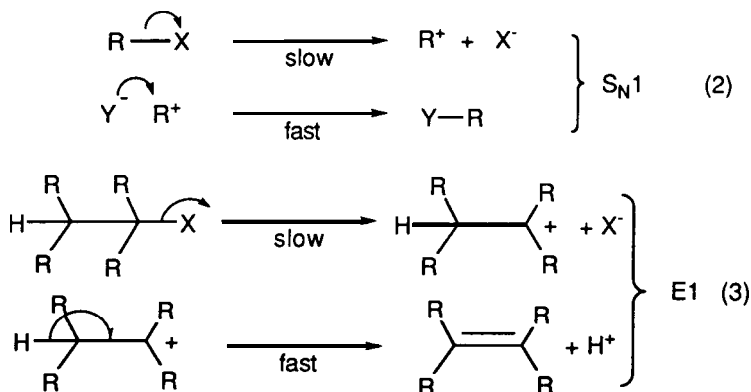
It was Hans Meerwein<sup>2</sup> who in 1922, while studying the Wagner rearrangement of camphene hydrochloride 4 to isobornyl chloride 5, found that the rate of the reaction increased with the dielectric constant of the solvent. Further, he found that certain Lewis acid chlorides - such as  $\text{SbCl}_5$ ,  $\text{SnCl}_4$ ,

$\text{FeCl}_3$ ,  $\text{AlCl}_3$ , and  $\text{SbCl}_5$  (but not  $\text{BCl}_3$  or  $\text{SiCl}_4$ ), as well as dry  $\text{HCl}$  (which promote the ionization of triphenylmethyl chloride by formation of carbocationic complexes) 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, which he formulated as



Hence, the modern concept of carbocationic intermediates was born. Meerwein's views were, however, greeted with much skepticism by his contemporary peers in Germany, discouraging him to follow up on these studies.

C. K. Ingold, E. H. 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." Their work relating to unimolecular nucleophilic substitution and elimination called  $\text{S}_\text{N}1$  and  $\text{E}1$  reactions (equations 2 and 3) laid the foundation for the role of electron deficient carbocationic intermediates in organic reactions.



F. Whitmore<sup>4</sup> in the US in a series of papers in the thirties generalized these concepts to many other organic reactions. Carbocations, however, were gene-

rally 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 prestigious Journal of the American Chemical Society use their name or 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.<sup>5,7</sup> 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.<sup>5,8,9</sup> The low nucleophilicity of the involved counter anions ( $SbF_6^-$ ,  $Sb_2F_{11}^-$ , etc.) greatly contributed to the stability of the carbocations, which were in some instances even possible to isolate as crystalline salts. The developed superacidic, "stable ion" methods 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 the evolution of a general concept of carbocations, which I suggested in a 1972 paper, as well as naming the cations of carbon compounds as "carbocations".<sup>10</sup> "Carbocations" is now the IUPAC approved<sup>11</sup> generic name for all cationic carbon compounds, similarly to the anionic compounds being called "carbanions".

#### FROM ACYL CATIONS TO ALKYL CATIONS

The transient nature of carbocations in their reactions arises from their high reactivity towards reactive nucleophiles present in the system. The use of relatively low nucleophilicity counter-ions, particularly tetrafluoroborate ( $BF_4^-$ ) enabled Meerwein in the forties to prepare a series of oxonium and carboxonium ion salts, i. e.,  $R_3O^+BF_4^-$  and  $HC(OR)_2^+$ , respectively.<sup>12</sup> These Meerwein salts are effective alkylating agents, and 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 or anhydride with Lewis acids such as boron trifluoride was shown to form complexes. The behavior of acetic acid and anhydride in strong protic acids (sulfuric acid, oleum, perchloric acid, etc.) was also exten-

sively 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 for the first time in 1943 acetylium tetrafluoroborate<sup>13</sup> by reacting acetyl fluoride with boron trifluoride (equation 4).



In the early fifties while working at the Organic Chemical Institute of the Technical University in Budapest, led by the late Professor G. Zemplen, a noted carbohydrate chemist and former student of Emil Fischer (Nobel Prize, 1902) whose "scientific grandson" I thus can consider myself, I became interested in organic fluorine compounds. Zemplen was not much impressed by this, as he thought attempts to study fluorine compounds necessitating "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 Zemplen's interest was in glycoside synthesis and related carbohydrate chemistry, I thought that selective  $\alpha$ - or  $\beta$ -glycoside synthesis could be achieved by reacting either acetofluoroglucose (as well as other fluorinated carbohydrates) or their deacetylated relatively stable fluorohydrins with the corresponding aglucons. In the course of the project -COF compounds were needed. As Seel did not seem to have followed up his earlier study, I got interested in exploring in general acylation with acyl fluorides. The work was subsequently extended to alkylation with alkyl fluorides using boron trifluoride as catalyst to achieve Friedel-Crafts type reactions. These studies also arose my interest in the mechanistic aspects of the reactions, including the complexes of RCOF and RF with  $\text{BF}_3$  and subsequently with other Lewis acid fluorides (equations 5 and 6). Thus, my long fascination with the chemistry of carbocationic complexes began.

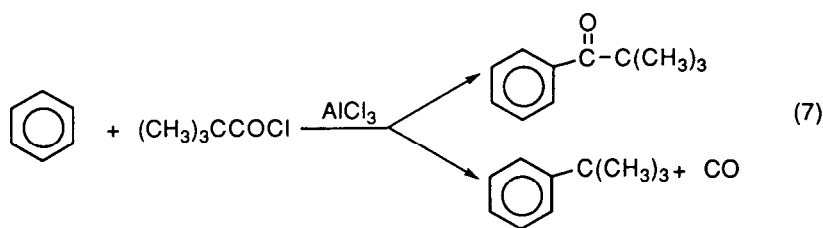


Carrying out such research in post-war Hungary was not easy. There was no access to such chemicals as anhydrous HF,  $\text{FSO}_3\text{H}$  or  $\text{BF}_3$  and we needed to prepare them ourselves. After we prepared HF from fluorspar ( $\text{CaF}_2$ ) and sulfuric acid, its reaction with SO, (generated from oleum) gave  $\text{FSO}_3\text{H}$ . By reacting boric acid with fluorosulfuric acid we made  $\text{BF}_3$ . Handling these reagents and carrying out related chemistry in a laboratory equipped with

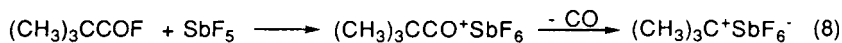
the barest of necessities was indeed a challenge. It was only around 1955 through Meerwein's kindness, who read some of my early publications, started up a correspondence and offered his help, that we received a cylinder of  $\text{BF}_3$  gas. What a precious gift it was!<sup>14</sup>

My early work with acyl fluorides also involved formyl fluoride,  $\text{HCOF}$ ,<sup>15</sup> which was first prepared by Nesmejanov in the thirties,<sup>16</sup> but did not pursue its use in synthesis. We also prepared a series of higher homologous acyl fluorides and studied their chemistry.<sup>15</sup>

In Friedel-Crafts chemistry it was known that when pivaloyl chloride was reacted with aromatics in the presence of aluminum chloride besides the expected ketones *tert*-butylated products were also obtained (equation 7).<sup>17</sup>



Formation of the latter was assumed to involve 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 studies and extend them by using IR and NMR spectroscopy in the investigation of isolable acyl fluoride - Lewis acid fluoride complexes, including those with higher valency Lewis acid fluorides such as  $\text{SbF}_5$ ,  $\text{AsF}_5$ ,  $\text{PF}_5$ . Consequently, it was not unexpected that when the  $(\text{CH}_3)_3\text{CCOF} \cdot \text{SbF}_5$  complex was obtained it showed substantial tendency for decarbonylation.<sup>18</sup> What turned out to be exciting 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, i.e., *tert*-butyl hexafluoroantimonate.<sup>18-20</sup>



This breakthrough was first reported in my 1962 papers,<sup>18-19</sup> and was followed by further studies which led to methods to obtain long lived alkyl cations in solution.<sup>20</sup> Before recollecting: some of this exciting development, however, a brief review of the long quest for these long elusive alkyl cations is in order.

## EARLIER UNSUCCESSFUL ATTEMPTS TO OBSERVE ALKYL CATIONS IN SOLUTION

Alkyl cations were considered until the early sixties only as transient species. Their existence had been indirectly inferred from kinetic and stereochemical studies.<sup>3</sup> 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 under electron bombardment of alkanes, haloalkanes, and other precursors have been investigated from the fifties in mass spectrometric studies, but these studies of course did not provide structural information.<sup>21</sup>

The existence of Friedel-Crafts alkyl halide-Lewis acid halide complexes had been established from observations, such as Brown's study of the vapor pressure depression of  $\text{CH}_3\text{Cl}$  and  $\text{C}_2\text{H}_5\text{Cl}$  in the presence of gallium chloride.<sup>22</sup> Conductivity measurements were carried out of aluminium chloride in alkyl chlorides<sup>23</sup> and of alkyl fluorides in boron trifluoride<sup>24</sup> and the effect of ethyl bromide on the dipole moment of aluminium bromide was studied.<sup>25</sup> However, in no case could well-defined, stable alkyl cation complexes be established or obtained 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.<sup>26</sup> They observed for a number of simple aliphatic alcohols and olefins to give an absorption maximum around 290 nm and ascribed this characteristic absorption to the corresponding alkyl cations. Finch and Symons,<sup>27a</sup> 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, 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<sup>27b</sup> carried out an extensive study of the fate of alkyl cations formed from alcohols or olefins in undiluted  $\text{H}_2\text{SO}_4$  and oleum and showed the formation of equal amounts of saturated hydrocarbon mixture ( $\text{C}_4$  to  $\text{C}_{18}$ ) insoluble in  $\text{H}_2\text{SO}_4$  and a mixture of cyclopentenyl cations ( $\text{C}_5$  to  $\text{C}_{20}$ ) in the  $\text{H}_2\text{SO}_4$  layer. These cations exhibit strong ultraviolet absorption around 300 nm.

Olah, Pittman and Symons subsequently reviewed and clarified the question of electronic spectra of various carbocationic systems and the fate of various precursors in different acids.<sup>27c</sup>

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 intermediately formed alkyl cation giving olefin which then react further can lead to complex systems affecting conductivity, as well as other chemical and physical studies.

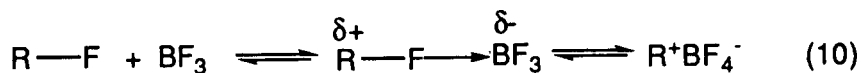
It was not realized till the breakthrough in superacid chemistry (*vide infra*) that in order to depress the deprotonation of alkyl cations to olefins (equation 9) (with subsequent formation of very complex systems via reactions such as alkylation, oligomerization, polymerization, cyclization, etc. of olefins with alkyl cations) acids much stronger than those known and used at the time were needed.



Finding such acids (called "superacids") turned out to be the key for being able to finally obtain stable, long lived alkyl cations and in general carbocations. If any deprotonation would still take place, in however, limited equilibrium, the alkyl cation (a strong acid) would immediately react with the olefin (a good  $\pi$ -base) leading to the multitude of mentioned reactions.

#### LONG LIVED ALKYL CATIONS FROM ALKYL FLUORIDES IN ANTIMONY PENTAFLUORIDE AND RELATED CONJUGATE SUPERACIDS

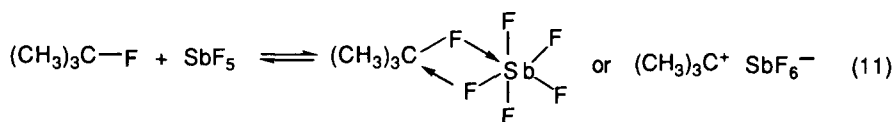
The idea that ionization of alkyl fluorides to stable alkyl cations could be possible with excess of strong Lewis acid fluorides serving themselves as solvents first came to me while still working in Hungary in the early fifties and studying the boron trifluoride catalyzed alkylation of aromatics with alkyl fluorides. In the course of these studies I attempted to isolate  $\text{RF}:\text{BF}_3$  complexes. Realizing the difficulty to find suitable solvents which would allow ionization but at the same would not react with developing potentially highly reactive alkyl cations, neat alkyl fluorides were condensed 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 on our lack of access to even an IR spectrometer: (The story of Nenitzescu's cyclobutadiene- $\text{Ag}^+$  complex travelling on the Orient Express to a colleague in Vienna for IR studies, but decomposing en route was recalled by him later.) All we could carry out at the time on our  $\text{RF}:\text{BF}_3$  systems were conductivity measurements. The results showed that methyl fluoride and ethyl fluoride gave only low conductivity complexes, whereas the isopropyl fluoride and tertiary butyl fluoride complexes were highly conducting (equation 10). The latter systems, however, also showed some polymerization (from deprotonation of the involved carbocations giving olefins) Thus, the conductivity data must have been affected by acid formation.<sup>24</sup>





After the defeat of the 1956 Hungarian revolution I escaped with my family and after spending some months in London we moved 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.<sup>18-20</sup> It turned out to be an extremely strong Lewis acid and for the first time allowed ionization of alkyl fluorides in solution to stable, long lived alkyl cations. Neat  $\text{SbF}_5$  solutions are viscous, but diluted with liquid sulfur dioxide the solutions could be cooled and studied down to  $-78^\circ\text{C}$  (subsequently, I also introduced even lower nucleophilicity solvents such as  $\text{SO}_2\text{ClF}$  or  $\text{SO}_2\text{F}_2$  which allowed studies at much lower temperatures). Following up the mentioned observation of the decarbonylation of the pivaloyl cation which 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.<sup>28-29</sup>

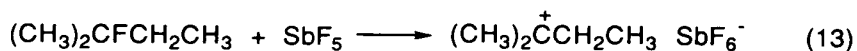
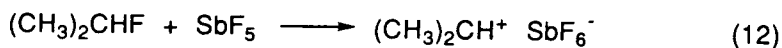
In the late fifties the research director of the Canadian Dow laboratories was not yet convinced about the usefulness of NMR spectroscopy. Consequently we had no such instrumentation of our own. Fortunately, the Dow laboratories in Midland (Michigan) just 100 miles across the border had excellent facilities run by E. B. Baker, a pioneer of NMR spectroscopy, who offered his help. To probe whether our  $\text{SbF}_5$  solutions 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 in its  $^1\text{H}$  NMR spectrum due to the fluorine-hydrogen coupling of  $J_{\text{HF}}$  20 Hz a characteristic doublet. In  $\text{SbF}_5$  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 *tert*-butyl fluoride forms with  $\text{SbF}_5$  only a polarized donor-acceptor complex which undergoes fast fluorine exchange (on the NMR time scale) then the fluorine-hydrogen coupling would be "washed out", while still a significant deshielding of the methyl protons would be expected. The differentiation of a polarized, rapidly exchanging donor-acceptor complex from the long sought-after real ionic  $\text{t-C}_4\text{H}_9^+\text{SbF}_6^-$ , thus, became a major challenge (equation 11).



Ned Baker despite being himself a physicist showed great interest in our chemical problem. In order to solve it he devised a means to obtain the carbon-13 spectra of our dilute solutions, an extremely difficult task before the advent of Fourier transform NMR techniques. Carbon-13 labeling was generally possible at the time only up to  $\sim 50\%$  level (from available  $\text{Ba}^{13}\text{CO}_3$ ).

When we prepared 50% C-13 labeled *tert*-butyl fluoride, we could obtain at best only 5% solutions in  $\text{SbF}_5$ . Thus, the C-13 content of the solution was highly diluted. Baker, however, undaunted devised an INDOR (inter nuclear double resonance) method. Using the high sensitivity of the proton signal he was able by the double resonance technique observe the C-13 shifts of our dilute solutions (a remarkable achievement around 1960!). Understandably to our great-joy the tertiary carbon shift ( $\delta^{13}\text{C}$  335.2) in  $(\text{CH}_3)_3\text{CF}\text{-SbF}_5$  turned out to be more than 300 ppm deshielded from that of the covalent starting material! Such very large chemical deshielding (the most deshielded C-13 signal at the time) could not be reconciled with only a donor-acceptor complex. It indicated rehybridization from  $\text{sp}^3$  to  $\text{sp}^2$  and at the same time showed the effect of significant positive charge on the carbocationic carbon. For simplicity I am not discussing here the nature of the counter ion (which can be dimeric  $\text{Sb}_2\text{F}_{11}^-$  or even oligomeric) 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 isopropyl and the *tert*-amyl cations (equations 12 and 13).



The isopropyl cation was of particular interest. Whereas in the *tert*-butyl cation the methyl protons are attached to carbons which are only adjacent to the carbocationic center, in the isopropyl cation a proton is directly attached to it. When we obtained the proton NMR spectrum of the  $i\text{C}_3\text{H}_7\text{F}\text{-SbF}_5$  system the CH proton showed up as an exceedingly deshielded septet at  $\delta$  13.5, ruling out the possibility of a polarized donor-acceptor complex and indicating the formation of  $(\text{CH}_3)_2\text{CH}^+$  ion. The C-13 spectrum was also conclusive showing a very highly deshielded (by >300 ppm) +C chemical shift ( $\delta^{13}\text{C}$  320.6). In case of the *tert*-amyl cation an additional interesting feature was the observation of 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 would be involved such long range coupling through an  $\text{sp}^3$  carbon would be small (1-2 Hz). Instead the observed significant coupling ( $J_{\text{H-H}}$  10 Hz) indicated that the species studied indeed had an  $\text{sp}^2$  center through which the long range H-H coupling became effective. Fig. 1 reproduces the H NMR spectra of the *tert*-butyl, *tert*-amyl and isopropyl cations. These original spectra are framed and hang in my office as a momento, as does the ESCA spectrum of the norbornyl cation (*vide infra*).

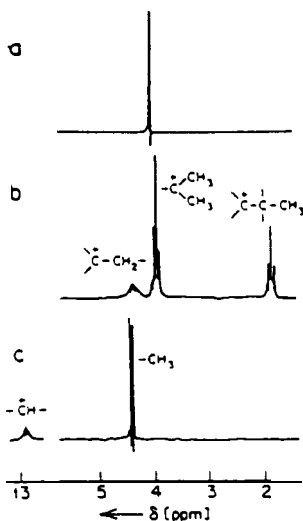


Fig. 1.  $^1\text{H-NMR}$  spectra of: a) the *tert*-butyl cation [trimethylcarbenium ion,  $(\text{CH}_3)_3\text{C}^+$ ]; b) the *tert*-amyl cation [dimethylethylcarbenium ion,  $(\text{CH}_3)_2\text{C}^+-\text{C}_2\text{H}_5$ ]; c) the isopropyl cation [dimethylcarbenium ion,  $(\text{CH}_3)_2\text{C}^+\text{H}$ ]. (60 MHz, in  $\text{SbF}_5:\text{SO}_2\text{ClF}$  solution,  $-60^\circ\text{C}$ ).

Our studies also included IR spectroscopic investigation of the observed ions (Fig. 2).<sup>29</sup> 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 30 years later FT-IR spectra obtained by Denis Sunko and his colleagues in Zagreb using low temperature matrix deposition techniques and Schleyer's calculations of the spectra show good agreement with our early work, even considering that our work was carried out in neat  $\text{SbF}_5$  at room temperature long before the advent of the FT-IR methods.<sup>30</sup>

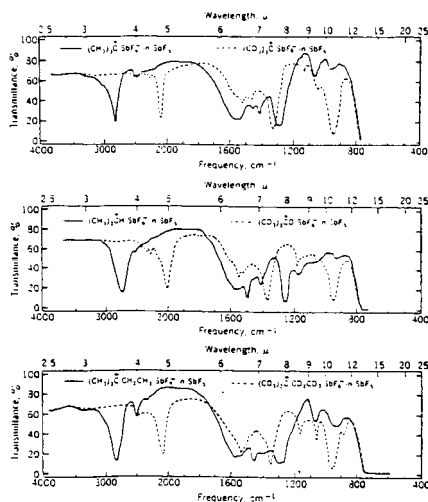
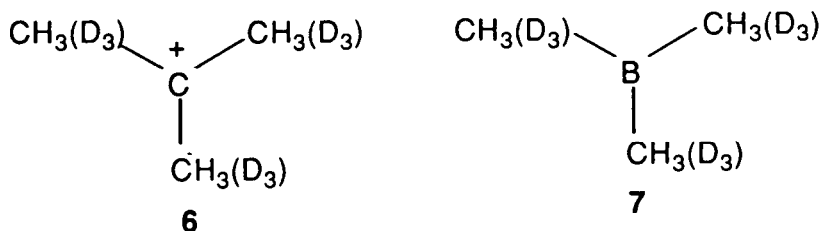


Figure 2. IR spectra of *tert*-butyl, isopropyl and *tert*-amyl cations

Fig. 2 IR spectra of *tert*-butyl, isopropyl and *tert*-amyl cation\

Subsequently in 1968-70 with Jack DeMember and August Commeyras<sup>31</sup> we were able to carry out more detailed IR and laser Raman spectroscopic studies of alkyl cations. Comparison of the data of light and deuterium labelled *tert*-butyl cations **6** with those of isoelectronic trimethylborons **7** proved the planar carbocation center of the former (Table I).



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

Table 1. Raman and IR Frequency of the *tert*-Butyl Cation and [D9]-*tert*-Butyl Cation and Their Correlation with Those of  $(\text{CH}_3)_3\text{B}$  and  $(\text{CD}_3)_3\text{B}$

Species	Frequency of Vibration [ $\text{cm}^{-1}$ ]																
	$\nu_1$	$\nu_{12}$	$\nu_7$	$\nu_{19}$	$\nu_2$	$\nu_{13}$	$\nu_{21}$	$\nu_{14}$	$\nu_{15}$	$\nu_{17}$	$\nu_5$	$\nu_{16}$	$\nu_6$	$\nu_9$	$\nu_{10}$	$\nu_{18}$	
$(\text{CH}_3)_3\text{C}^+$		2947				2850											
$(\text{CH}_3)_3\text{B}$		2975				2875	1060	1440	1300	1150	906	866	675	973(486?)	336 <sup>a</sup>		320
$(\text{CD}_3)_3\text{C}^+$		2187				2090		1075									
$(\text{CD}_3)_3\text{B}$		2230				2185		1033	1018	1205			620	870	(289) <sup>b</sup>		(276) <sup>b</sup>

a IR frequency.

b Calculated.

When in the summer of 1962, I was able for the first time to present in public our work at the Brookhaven Organic Reaction Mechanism Conference<sup>28a</sup> and subsequently in a number of other presentations and publications,<sup>28b</sup> I had convincing evidence in hand to substantiate that after a long and frequently frustrating search stable, long-lived alkyl cations were finally obtained in superacidic solutions.<sup>29</sup> Stable, long lived carbocation chemistry, as it was to be known, began and its progress became fast and wide spread. Working in an industrial laboratory, publication of research is not always easy. I would therefore like to thank again the Dow Chemical Company for allowing me not only to carry out the work but also to publish the results.

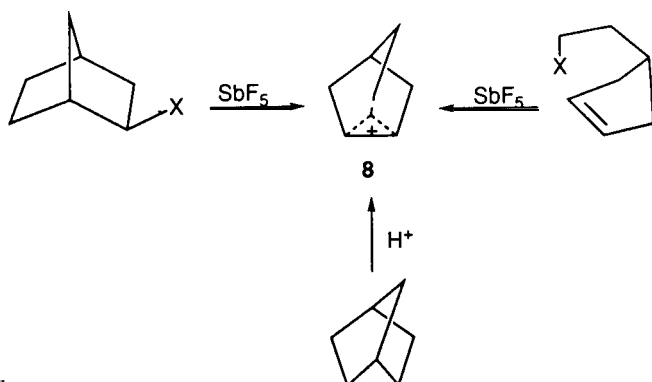
After successful preparation of long-lived, stable carbocations in antimony pentafluoride solution the work was extended to a variety of other superacids. Protic superacids such as  $\text{FSO}_3\text{H}$  (fluorosulfuric acid) and  $\text{CF}_3\text{SO}_3\text{H}$  (triflic acid) as well as conjugate acids such as  $\text{HF-SbF}_5$ ,  $\text{FSO}_3\text{HSbF}_5$  (Magic

Acid),  $\text{CF}_3\text{SO}_3\text{H-SbF}_5$ ,  $\text{CF}_3\text{SO}_3\text{H-B}(\text{O}_3\text{SCF}_3)_3$ , etc. were extensively used in ionizing varied precursors, including alcohols. Superacids based on fluorides such as  $\text{AsF}_5$ ,  $\text{TaF}_5$ ,  $\text{NbF}_5$  and other strong Lewis acids such as  $\text{B}(\text{O}_3\text{SCF}_3)_3$  were also successfully introduced. The name Magic Acid for the  $\text{FSO}_3\text{H-SbF}_5$  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 named 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 commercially make some of our ionic reagents he obtained trade name protection for Magic Acid® and it is 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 to credit here to all of 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,<sup>32</sup> following closely my initial reports of 1962-64. Similarly, I would like to emphasize the fundamental contributions of R. J. Gillespie to strong acid (superacid) chemist@ and also his generous help while I was working at the Dow Laboratories in Canada. I reestablished during this time contact with him 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 had there an NMR spectrometer and in our study of  $\text{SbF}_5$  containing highly acidic systems of carbocations we were gratified by his help allowing us to run some of our spectra on his instrument. His long standing interest in fluorosulfuric acid and our studies in  $\text{SbF}_5$  containing systems found common ground in studies of  $\text{FSO}_3\text{H-SbF}_5$  systems.<sup>34</sup> It was also Gillespie who suggested to call protic acids stronger than 100% sulfuric acid as superacids.<sup>33</sup> This arbitrary, but most useful definition is now generally used. It should be, however, pointed out that the name "superacid" goes back to J. B. Conant of Harvard who in 1927 used it 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.<sup>35</sup> Our book "Superacids" published in 1985 with Surya Prakash and Jean Sommetisc was appropriately dedicated to the memory of

Conant, although few of today's chemists are aware of his contributions to this field.

My memories of the already mentioned 1962 Brookhaven Mechanism Conference<sup>28a</sup> 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 Prize, 1979) on the classical or non-classical nature of some carbocations (or carbonium ions as they were still called at the time)<sup>36</sup> 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 highly acidic (superacidic) systems. I remember to be 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 must be wrong and could not have obtained longlived carbonium ions. Just in case, however, that my method would turn out to be real, I certainly should obtain evidence for the "non-classical" or "classical" nature, respectively, of the much disputed 2-norbornyl cation 8. Their much heralded controversy<sup>36b,c</sup> centered around the question whether experimentally observed significant rate enhancement of the hydrolysis of 2-*exo* over 2-*endo* -norbornyl esters and high *exo* selectivity in the systems were caused, as suggested by Winstein, by --participation of the C<sub>1</sub>-C<sub>2</sub> single bond with delocalization to a bridged "nonclassical" ion or only, as stated by Browns by steric hindrance in case of the *endo*-system and involving equilibrating "classical" trivalent ions. Non-classical ions, a term first used by J. D. Roberts,<sup>37</sup> were suggested by P. D. Bartlett to contain too few electrons to allow a pair for each "bond" i.e. must contain ground state delocalized  $\sigma$ -electrons.<sup>36a</sup> As my method allowed us to prepare carbocations as long lived species, clearly the opportunity was given to experimentally decide the question through direct observation of the ion. At the time I had obtained only the proton spectrum of 2-norbornyl fluoride in SbF<sub>5</sub> at room temperature, which displayed a single broad peak indicating complete equilibration through hydride shifts and WagnerMeerwein 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 and Marty Saunders from Yale.<sup>38a</sup> Paul, who became a life-long friend, even at that time had a knack to bring together cooperative efforts acting as the catalyst. Using SO<sub>2</sub> as solvent, we were able to lower the temperature of our solution to -78°C. We also prepared the ion by ionization of cyclopentenylethyl fluoride or by protonation of nortricylene in FSO<sub>3</sub>H;SbF<sub>5</sub>/SO<sub>2</sub>ClF (Scheme 1).



Scheme-1

We still did not have access to suitable low temperature instrumentation of our own 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  $-70^{\circ}\text{C}$  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 using solvents such as  $\text{SO}_2\text{ClF}$  and  $\text{SO}_2\text{F}_2$ , to be able to obtain high resolution  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the 2-norbornyl cation eventually down to  $-159^{\circ}\text{C}$  in super-cooled solutions.<sup>38b,c</sup> 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).<sup>38c</sup>

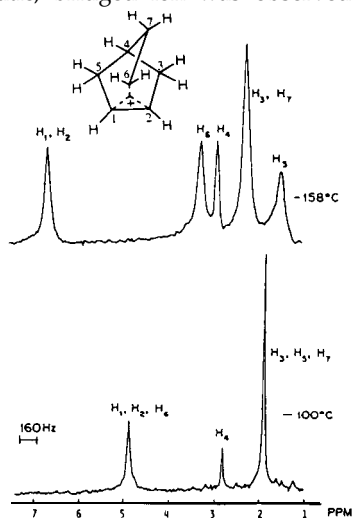


Fig. 3a: 395 MHz  $^1\text{H}$  NMR spectra of 2-norbornyl cation in  $\text{SbF}_5/\text{SO}_2\text{ClF}/\text{SO}_2\text{F}_2$  solution.

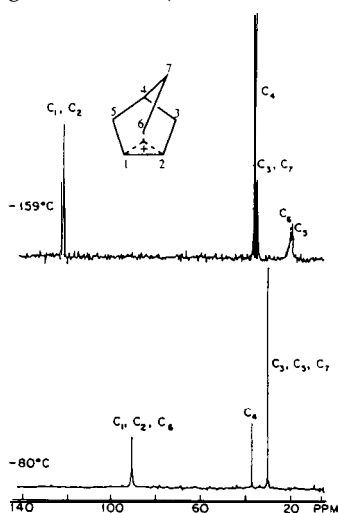


Fig. 3b: 50 MHz proton decoupled  $^{13}\text{C}$  NMR spectra of 2-norbornyl cation ( $^{13}\text{C}$  enriched) in  $\text{SbF}_5/\text{SO}_2\text{ClF}/\text{SO}_2\text{F}_2$  solution.

The differentiation of bridged non-classical 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 using estimated shifts of the two differing systems in comparison with model systems.<sup>38b,c</sup> Of course these days this task is greatly simplified by highly efficient theoretical methods, such as IGLO, GIAO, etc. to calculate NMR shifts of differing ions and comparing them with the experimental data.<sup>38d</sup> It is rewarding to see that our results and conclusions stood up well in comparison with all the more recently advanced studies.

As mentioned we also 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<sup>38b</sup> and although at the time it was not possible to theoretically calculate the spectra, comparison with model compounds (2-norbornyl system and nortricyclene, respectively) indicated the symmetrical, bridged nature of the ion. Sunko and Schleyer recently were able to obtain the FT-IR spectrum in elegant studies and compare it with theoretical calculations.<sup>30</sup>

Kai Siegbahn's (Nobel Prize 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  $\text{SbF}_5$ -based superacidic matrixes (Fig. 4).<sup>39</sup> These studies again convincingly showed the non-classical nature of the 2-norbornyl cation as 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

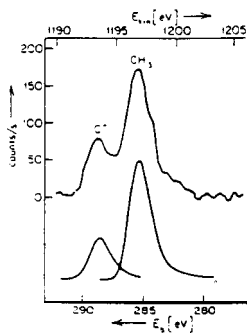


Fig. 4a. Carbon 1s photoelectron spectrum of *tert*-butyl cation.

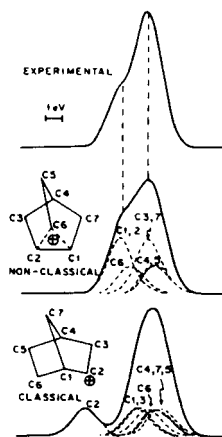


Fig. 4b. 1s core-hole-state spectra for the 2-norbornyl cation and Clark's simulated spectra for the classical and nonclassical ions.



cation. Although 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.<sup>39c</sup> So did theoretical calculations in comparison with the experimental data.

It is proper to mention here some significant some additional further studies. Saunders' studies showed the absence of deuterium isotopic perturbation of a possible classical equilibrating system.<sup>40</sup> Myhre and Yannoni<sup>41</sup> at very low (5°K!) temperatures were able to obtain solid state <sup>13</sup>C NMR spectra which showed no indication of freezing out any equilibrating classical ions; the barriers at this temperature should be as low as 200 cal/mol (the energy of a vibrational transition). Laube was able to carry out single crystal X-ray structural studies on substituted norbornyl cations.<sup>42</sup> Schleyer's theoretical studies<sup>38d</sup> including IGLO and related calculation of NMR shifts and their comparison with experimental data contributed further to the understanding of o-bridged carbonium ion nature of the 2-norbornyl cation. (The classical 2-norbornyl cation was not even found to be a high lying intermediate!) So did Arnett's calorimetric studies.<sup>43</sup> In a 1983 paper entitled "Conclusion of the Norbornyl Ion Controversy" with Prakash and Saunders we were able to state<sup>44</sup> that "all these studies unequivocally ended the so called non-classical 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 positive consequences to chemistry. It not only helped to extend the limits of available techniques for structural studies and theoretical calculations but also laid the foundation of developing the electrophilic chemistry of C-H and C-C single bonds and thus of saturated hydrocarbons (*vide infra*).

Intensive, critical studies of a controversial topic always help to eliminate the possibility of any errors. One of my favorite quotation is that by George von Bekesy (Nobel Prize in Medicine, 1961).<sup>45</sup> "[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 development or improvement of many techniques.

To me the most significant consequence of the norbornyl cation studies was the realization of the ability of C-H and C-C single bonds to act as two electron  $\sigma$ -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 allowed the recognition of the broad scope and significance of hypercoordinated carbon compounds (in short hypercarbon) chemistry.<sup>46</sup>

## THE GENERAL CONCEPT OF CARBOCATIONS

Based on the study of carbocations by direct observation of longlived species and related superacid chemistry, it became apparent that the carbocation concept is wider than previously thought and needed a more general definition which I offered in a 1972 paper.<sup>10</sup> The definition takes into account the existence of two major limiting classes of carbocations with a continuum of varied degree 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  $sp^2$ -hybridized, linear oxocarbenium ions and particularly vinyl cations also show substantial electron deficiency on carbon). The carbenium carbon contains six valence electrons, thus is highly electron deficient. The structure of trivalent carbocations can always be adequately described by using only two-electron two-center bonds (Lewis valence bond structures).  $CH_3^+$  is the parent for trivalent ions.

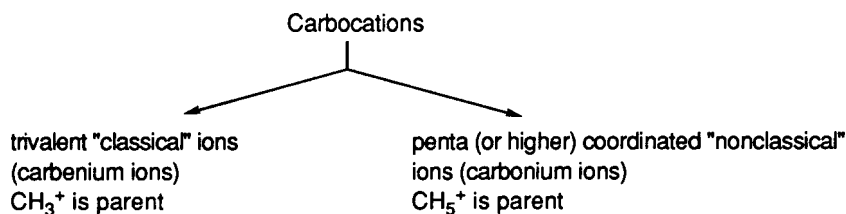
b) Penta- (or higher) coordinate ["nonclassical"] carbonium ions, which contain five or (higher) coordinated carbon atoms. They cannot be described by two-electron two-center single bonds alone, but also necessitate the use of two electron three (or multi) center bonding. The carbocation center is always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

Brown and Schleyer subsequently in 1977 offered a related definition:<sup>36c</sup> "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' 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 whose 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<sup>37</sup> for the cyclopropylcarbinyl cation and adapted by Winstein to the norbornyl cation.<sup>47</sup> 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 established by Lipscomb, Nobel Prize, 1976, for boron compounds). The prefixes "classical" and "nonclassical" are expected, however, to gradually fade away as the general nature of bonding will be 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 there always exist varying degrees of delocalization. This can involve participation by neighboring  $n$ -donor atoms,  $\pi$ -donor groups or  $\sigma$ -donor CH or C-C bonds.

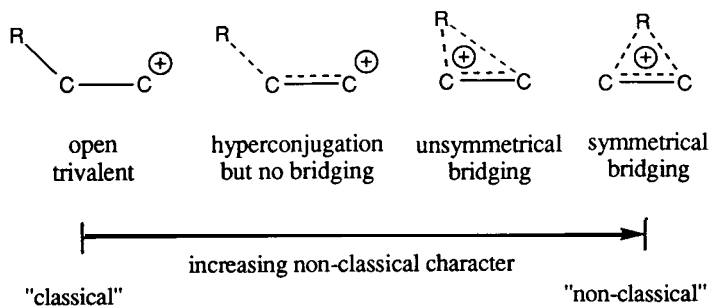


Trivalent carbenium ions are the key intermediates in electrophilic reactions of  $\pi$ -donor unsaturated hydrocarbons. At the same time pentacoordinated carbonium ions are the key to electrophilic reactions of  $\sigma$ -donor saturated hydrocarbons (C-H or C-C single bonds). The ability of single bonds to act as electron donors lies in their ability to form carbonium ions via two electron three-center ( $2e - 3c$ ) bond formation.

Expansion of the carbon octet via  $3d$ -orbital participation does not seem possible; there can be only eight valence electrons in the outer shell of carbon, a small first row element.<sup>46</sup> The valency of carbon cannot exceed four. Kekule'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 to also participate in multicenter bonding involving  $2e - 3c$  (or multicenter) bonds. Penta- (or higher) -coordination of carbon implies five (or more) atoms or ligands simultaneously attached to it within reasonable bonding distance.<sup>46</sup>

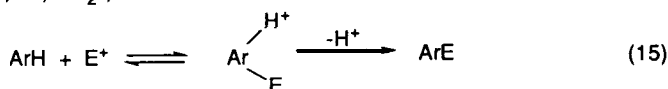
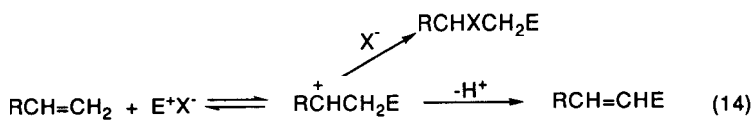
Neighboring group participation with the vacant  $p$ -orbital of a carbenium ion center contributes to its stabilization via delocalization which can involve atoms with unshared electron pairs ( $n$ -donors),  $\pi$ -electron systems (direct conjugative or allylic stabilization), bent  $\sigma$ -bonds (as in cyclopropylcarbinyl cations), and C-H or C-C  $\sigma$ -bond hyperconjugation. Trivalent carbenium ions with the exception of the parent  $\text{CH}_3^+$  therefore always show varying degrees of delocalization without becoming pentacoordinated carbonium

ions. The limiting cases define the extremes of a continuous spectrum of carbocations.



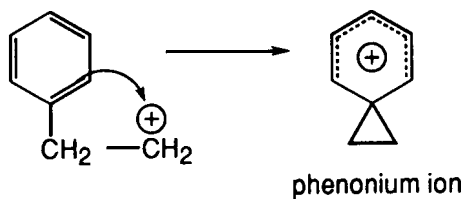
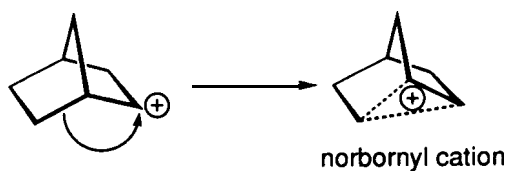
#### *The Role of Carbocations in Electrophilic Reactions*

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 organic industries a century ago. Subsequently olefin based chemistry took on great significance. In all this chemistry reactive  $\pi$ -bonded systems are the electron donor substrates. In electrophilic reactions they readily form trivalent carbocationic intermediates (equations 14 and 15).

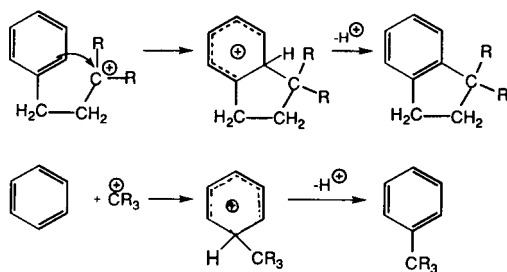


The discovery of pentacoordinate carbonium ions discussed precedingly led to the realization that they play an important role not only in understanding the structure of nonclassical ions, but more importantly represent the key to electrophilic reactions at single bonds, e.g. of saturated aliphatic hydrocarbons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

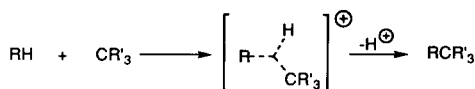
In ionization of  $\beta$ -phenylethyl systems neighboring  $\pi$ -participation into the carbocationic center occurs, which can be considered as intramolecular  $\gamma$ -alkylation giving Cram's phenonium ions. The corresponding ionization of 2-norbornyl systems involves participation of a properly oriented C-C single bond (i.e. intramolecular  $\sigma$ -alkylation) giving the bridged ion.



Alkylation of  $\pi$ -systems in Friedel-Crafts type reactions (either by an inter- or intramolecular way) is for long well known and studied. Extending these relationships it was logical to ask why intermolecular alkylation (and other electrophilic reactions) of  $\sigma$ -donor hydrocarbons could not be affected?

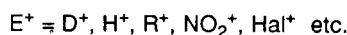
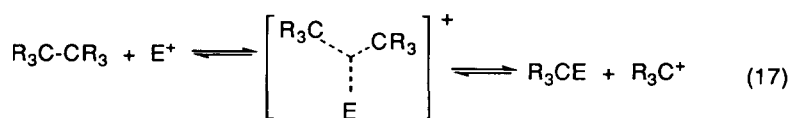
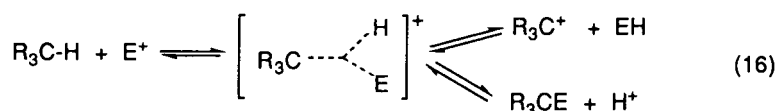


$\pi$ -alkylation



$\sigma$ -alkylation

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. (equations 16 and 17) This reactivity is due to the  $\sigma$ -donor ability (sigma basicity) of single bonds allowing bonded electron pairs to share their electron pairs with an electron deficient reagent via two-electron, three-center bond formation. The reactivity of single bonds thus stems from their ability to participate in the formation of pentacoordinated carbonium ions. Subsequent cleavage of the three-center bond in case of C-H reaction results in formation of substitution products, 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 within five coordinate carbonium ions through low barriers, the involved intermediates can be more complex but always involving interconverting carbonium ions.

Supercritical hydrocarbon chemistry involving conditions favoring carbocationic intermediates is also gaining in significance in practical applications. Relatively low temperature effective isomerization of alkanes, 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.<sup>48</sup>

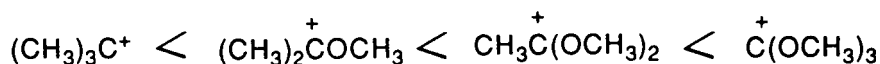
#### PROTOSOLVOLYTIC ACTIVATION OF CARBOCATIONIC SYSTEMS

Carbocations are electrophiles, i.e. electron deficient compounds. In electrophilic reactions of unsaturated,  $\pi$ -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)  $\pi$ -donors and even more so with only weakly electron donating saturated hydrocarbons ( $\sigma$ -donors) the electrophile itself must provide the driving force for the reactions. Hence the need for very strongly electron demanding electrophiles and comparable low nucleophilicity reaction media (such as superacidic systems).

It was only more recently realized<sup>49</sup> that electrophiles capable of further interaction (coordination, solvation) with strong Bronsted 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 i.e. electrophiles with greatly enhanced electron deficiency (frequently of dipositive nature). I have reviewed<sup>49</sup> elsewhere the superelectrophilic activation of varied electrophiles. and will not discuss it here with the exception of some superelectrophilic activation which can also affect the reactivity of carbocations.

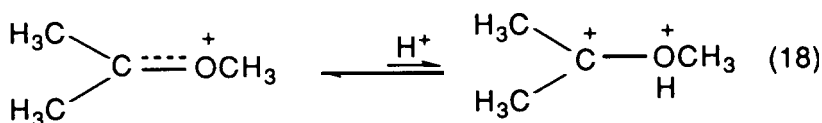
In carboxonium ions, originally studied by Meerwein, alkyl groups of an alkyl cation, such as the *tert*-butyl cation, are replaced by alkoxy, such as met-

hoxy groups. The methoxy groups delocalize charge (by neighboring oxygen participation) and thus make these ions increasingly more stable.

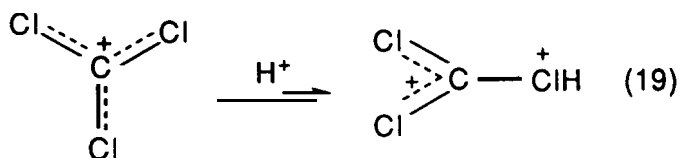


At the same time their reactivity as carbon electrophiles decreases. For example they do not alkylate aromatics or other hydrocarbons. Strong oxygen participation thus greatly diminishes the carbocationic nature.

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

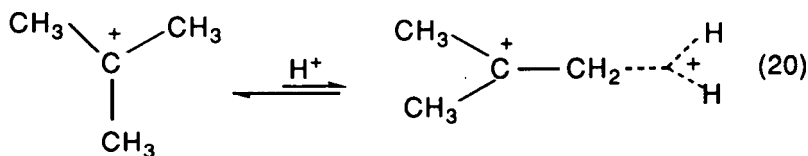


Similarly halogen substituted carbocations, such as the trichloromethyl cation  $\text{Cl}_3\text{C}^+$ ,<sup>50</sup> are strongly stabilized by n-p back donation (not unlike  $\text{BCl}_3$ ). They can also be greatly activated by superacidic media, which protosolvate (protonate) the halogen non-bonded electron pairs diminishing neighboring halogen participation (equation 19).



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

Alkyl cations themselves, in which only hyperconjugative C-H or C-C single bond interactions stabilize the electron deficient center, are also activated by superacidic solvation. 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 (equation 20).<sup>51</sup>



The well 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 excess acid solutions.

#### 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 Bronsted 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).

In order 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.<sup>49</sup>

Nafion-H is known to contain acidic  $\text{SO}_3\text{H}$  groups clustered together (Fig. 5).

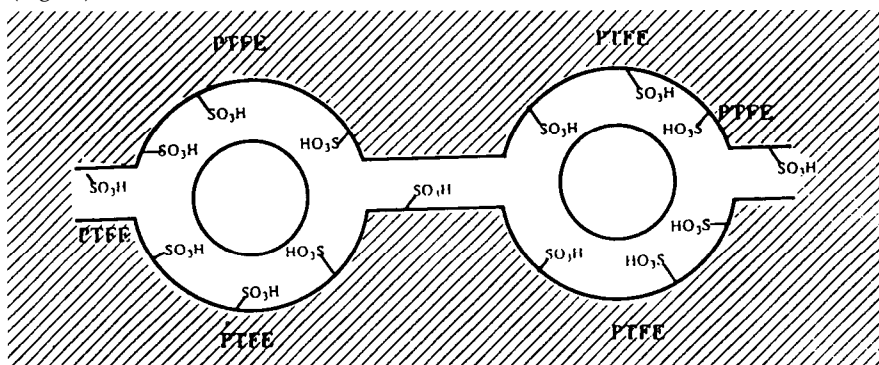


Fig. 5. Clustered  $\text{SO}_3\text{H}$  acid sites in a perfluorinated resin sulfonic acid

H-ZSM-5, which also displays superacidic activity, was found by Haag et al.<sup>52</sup> to isomerize and alkylate alkanes readily ( $\text{H}_2$  was observed as the protolytic by-product in stoichiometric amounts). In this zeolite, active Bronsted and Lewis acid sites are again in close proximity, approximately 2.5 Å apart (Fig. 6).

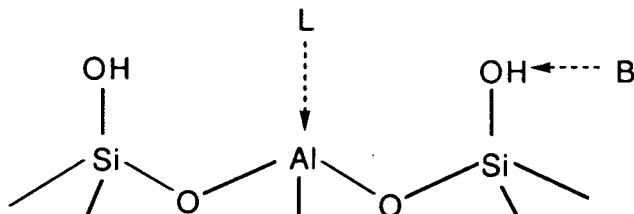


Fig. 6. Bronsted (B) and Lewis acid sites (L) in zeolites.



In comparison with solution chemistry it is reasonable that in these (and other) solid superacid catalyst systems, bi- or multidentate interactions forming highly reactive intermediates are possible. This amounts to the solid-state equivalent of protosolvation (protonation).<sup>49</sup>

Nature is able to perform its own transformations in ways which chemists have only begun to understand and can not yet come close to duplicate. At enzymatic sites many significant transformations take place which are acid catalyzed (including electron deficient metal-ion-catalyzed processes). Because of the unique geometry involved at enzymatic sites bi- and multidentate interactions must be possible and the concepts discussed previously may also have relevance to our understanding of some enzymatic processes.<sup>49</sup>

## 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 obtaining one of the most significant class of chemical reaction intermediates (i.e. carbocations) as long lived species and study of their structure, led subsequently to the development of the general concept of the electrophilic reactivity of single bonds, such as C-H and C-C bonds and related superacidic hydrocarbon chemistry.

Despite of 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 Kekule well over a century ago remains an essential foundation of organic chemistry. Carbon as a small first new element can not extend its valence 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.<sup>46</sup> 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 understand the rapidly emerging electrophilic chemistry of saturated hydrocarbons, including parent methane and that of C-H and C-C bonds in general. Whereas hypercoordinate carbocations are 8e carbon systems which do not violate the octet rule, carbanionic  $S_N2$  transition states  $[Y-CR_3-X]$  are 10e systems and thus can not be intermediates

I wrote more than twenty years ago<sup>9</sup> "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 (non-bonded) electron pairs (or for this reason I could add the electron pairs involved in multiple<sup>4</sup> bonding). We can now not only explain the reactivity of saturated hydrocarbons and single bonds in general electrophili-

lic 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.

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