Stable Carbonium Ions in Solution

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Science, New Series, Vol. 168, No. 3937. (Jun. 12, 1970), pp. 1298-1311.

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Science is currently published by American Association for the Advancement of Science.

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49. This investigation was supported by PHS grants GM-12332, GM-43002, and GM-01874 from the National Institute of General Medical Sciences. One of us (H.O.H.) is a recipient of an NIH research career professorship.

Stable Carbonium Ions in Solution

New superacid solvents and nuclear magnetic resonance spectroscopy permit direct study.

George A. Olah

In organic chemical reactions, reactive intermediates like carbonium ions, carbanions, free radicals, radical ions, carbenes, nitrenes, and arynes were for a long time considered only as transient, metastable species with very short lives. Rapid advances in experimental and spectroscopic techniques have made an increasing number of reactive intermediates available for direct observation and study (*1*). One of the most important classes of reactive organic intermediates is that of carbonium ions.

Early Studies

Less than a year after the discovery of the first stable radical, the triphenylmethyl radical, by Gomberg in 1900, Norris (*2*) in the United States and Kehrmann and Wentzel (*3*) in Germany observed that colorless derivatives of triphenylmethane, such as triphenylmethyl alcohol or chloride, give deeply colored solutions when dissolved in sulfuric acid. Similarly, triphenylmethyl chloride forms colored complexes with aluminum and tin chlorides. In 1902 von Baeyer (*4*) recognized the salt character of these compounds and named them carbonium salts.

As mentioned, the observation of the first stable carbonium ions was achieved with triphenylmethyl systems some 70 years ago. It is somewhat surprising that, despite the substantial amount of data gathered in this specific field (as a result of widespread interest in connection with dye chemistry), carbonium ion chemistry was long considered by organic chemists as a topic limited to triarylmethyl dyes. No attempt was made to extend the scope to other areas until nearly 20 years later. The analogy between the development of carbonium ion chemistry and of free radical chemistry is evident. It is also apparent that the availability of newer physical methods, like electron spin resonance spectroscopy in the free radical field and nuclear magnetic resonance spectroscopy in the carbonium ion field, helped substantially to extend our knowledge. In a brief review only selected areas of the large field can be discussed. The selection reflects my own interest as an organic chemist and in addition covers some aspects of biological interest, which may be of future importance.

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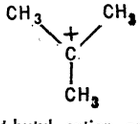
Question of Nomenclature

Baeyer originally suggested the carbonium ion nomenclature with obvious reference to "onium" ions. Gomberg objected to this nomenclature and proposed the term carbyl salt which, however, never became popular. In the late 1920's, Dilthey and Wizinger (*5*) suggested the name carbenium salts for triphenylmethyl cation complexes of the formula $R_3C^+X^-$. This nomenclature has been maintained to some degree in the German scientific literature.

It is appropriate at this point to bear in mind that in present day usage we can name organic cations by either the carbonium ion or cation nomenclature interchangeably. Although both of these naming systems are permissible, certain basic rules must be obeyed. With the carbonium ion nomenclature, the electron-deficient carbon atom is called the carbonium ion and the attached ligands are given their usual names. Accordingly with this nomenclature one refers to the trimethylcarbonium ion, while with the cation nomenclature, which is based on the naming of the parent hydrocarbon, the name tertiary-butyl (*t*-butyl) cation is employed.



t-butyl cation or trimethylcarbonium ion

$(CH_3)_3\,C-\overset{+}{C}H_2$

t-butylcarbonium ion or neopentyl cation

From the foregoing it is obvious that the *t*-butyl cation must not be named the *t*-butylcarbonium ion, as the latter is the alternative name for the neopentyl cation.

Development of Modern Carbonium Ion Theory

One of the most audacious and fruitful ideas born in organic chemistry was the suggestion that carbonium ions might be intermediates in the course of reactions that start from nonionic reactants and lead to nonionic covalent products. It was H. Meerwein (*6*) who in 1922, while studying the kinetics of the rearrangement of camphene hydrochloride to isobornyl chloride reported the important observation that the reaction rate increased in a general way with the dielectric constant of the solvent. Further he found that metallic chlorides—such as $SbCl_5$, $SnCl_4$, $FeCl_3$, $AlCl_3$, and $SbCl_3$ (but not BCl_3 or $SiCl_4$), as well as dry HCl—which promote the ionization of triphenylmethyl chloride by formation of ionized complexes, considerably accelerate the rearrangement of camphene hydrochloride. Meerwein concluded that the conversion of camphene hydrochloride to isobornyl chloride actually does not proceed by way of migration of the chlorine atom but by a rearrangement of a cationic intermediate. Thus the modern conception of carbonium ion intermediates was born.

Ingold, Hughes, and their collaborators in England, starting in the late 1920's carried out detailed kinetic investigations on what later became known as nucleophilic substitution at saturated carbon and polar elimination reactions (*7*). The well-known work relating to S_N1 and later *E*1 reactions established the carbonium concept in these reactions. Whitmore (*8*), in a series of papers which began in 1932, generalized Meerwein's rearrangement theory to many organic chemical reactions.

Stable, Long-Lived Carbonium Ions

Kinetic and sterochemical evidence helped to establish carbonium ion intermediates in organic reactions. These species, however, are generally very short lived and could not be directly observed by physical means.

The transient nature of such ions arises of course from their extreme reactivity with nucleophiles. By the use of highly acidic and very weakly nucleophilic solvents, it was possible to prevent reactions leading to covalent products; this technique made it possible to observe a wide range of carbonium ions as stable, long-lived species. The following discussion centers entirely on these stable, long-lived carbonium ions.

Alkylcarbonium Ions

Simple alklycarbonium ions were considered until very recently as transient entities only (*9, 10*). Their existence has been inferred from the study of the course of certain reactions. No reliable physical measurements other than electron impact measurements of the simple alkylcarbonium ions were known. The formation of gaseous organic cations under electron bombardment of alkanes, haloalkanes, and other precursors has been widely investigated in mass spectral studies (*11*). No similar direct observation of carbonium ions in solution was achieved.

The observation of alkylcarbonium ions (alkly cations) like that of the trimethylcarbonium ion (*t*-butyl cation) $(CH_3)_3C^+$ or the dimethylcarbonium ion (isopropyl cation) $(CH_3)_2CH^+$ thus was a challenge. The existence of alkylcarbonium ions in systems of alkyl halides and Lewis acid halides has been inferred from a variety of observations, such as vapor pressure depressions of CH_3Cl and C_2H_5Cl in the presence of gallium chloride (*12*); conductivity of aluminum chloride in alkyl chlorides (*13*) and of alkyl fluorides in boron trifluoride (*14*); as well as the effect of ethyl bromide on the dipole moment of aluminum bromide (*15*). However, in no case had well-defined, stable ionic salts or complexes been established even at very low temperatures.

Electronic spectra of alcohols and olefins in strong proton acids (H_2SO_4) were obtained by Rosenbaum and Symons (*16*). They observed, for a number of simple aliphatic alcohols and olefins, absorption maximums around 290 nanometers and ascribed this absorption to the corresponding alkylcarbonium ions.

Finch and Symons (*17*), on reinvestigation of the absorption of aliphatic alcohols and olefins in sulfuric acid solution, showed that the condensation products formed with acetic acid (used as solvent for the precursor alcohols and olefins) were responsible for the spectra, not the simple alkylcarbonium ions. Protonated mesityl oxide was identified as the absorbing species in the system of isobutylene, acetic acid, and sulfuric acid.

Deno and his co-workers (*18*) carried out an extensive study of the fate of alkyl cations in undiluted H_2SO_4, based on nuclear magnetic resonance (NMR) and analysis of the quenched products. Dissolving alcohols and olefins (such as (*t*-butyl alcohol and isobutylene) in concentrated H_2SO_4 and oleum produces 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. These cations exhibit strong ultraviolet adsorption around 300 nm.

It must therefore be concluded that earlier attempts to prove the existence of stable, well-defined alkylcarbonium ions were unsuccessful both in experiments with sulfuric acid solutions as well as in the interaction of alkyl halides with Lewis acid halides.

In 1962 my co-workers and I first

directly observed stable alkylcarbonium ions in solution (*19–21*). We obtained the trimethylcarbonium ion (*t*-butyl cation) when *t*-butyl fluoride was dissolved in excess antimony pentafluoride, which served both as Lewis acid and solvent. Later the gegen-ion was found to be, under these conditions, primarily the dimeric $Sb_2F_{11}^-$ anion; whereas in SbF_5-SO_2 or SbF_5-SO_2ClF solutions, SbF_6^- and $Sb_2F_{11}^-$ were both found.

$$(CH_3)_3CF + (SbF_5)_2 \longrightarrow (CH_3)_3C^+Sb_2F_{11}^-$$

The possibility of obtaining stable alkylcarbonium fluoroantimonate salts by interaction of alkyl fluorides with antimony pentafluoride (neat or diluted with sulfur dioxide, sulfuryl chloride fluoride, or sulfuryl fluoride) was evaluated in detail, extending the investigations to all isomeric C_3, C_4, and C_5 alkyl fluorides.

Propyl, butyl, and pentyl fluorides in excess antimony pentafluoride gave these stable carbonium ions.

$$C_3H_7F + (SbF_5)_2 \longrightarrow CH_3C^+HCH_3\ Sb_2F_{11}^-$$

$$C_4H_9F + (SbF_5)_2 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\overset{+}{C}}}}-CH_3\ Sb_2F_{11}^-$$

$$C_5H_{11}F + (SbF_5)_2 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2-CH_3}{\overset{|}{\overset{+}{C}}}}-CH_3\ Sb_2F_{11}^-$$

Generally, the most stable tertiary or secondary carbonium ions are observed from any of the isomeric alkyl fluorides in strongly acidic solvent system. Rearrangement to those more stable ions can be studied at low temperature.

One of the most powerful tools in the study of carbonium ions is nuclear magnetic proton resonance spectroscopy. The

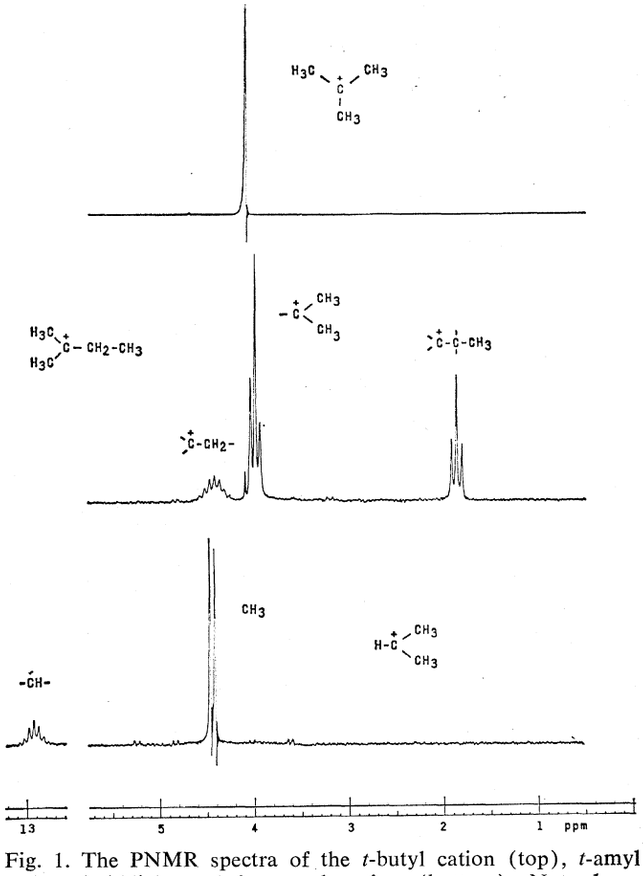
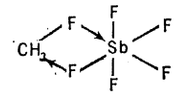


Fig. 1. The PNMR spectra of the *t*-butyl cation (top), *t*-amyl cation (middle), and isopropyl cation (bottom). Note large deshielding effects and the long-range coupling in the *t*-amyl cation indicating $sp^3 \rightarrow sp^2$ rehybridization at the potential carbonium ion center.

main feature of the proton NMR spectra of alkyl fluorides in antimony pentafluoride is the substantial deshielding of the protons in the carbonium ions as compared with the starting alkyl fluorides (Fig. 1). No H-F coupling was observed in any of the spectra of the carbonium ion complexes. This would not be expected in the ionic forms where the covalent C-F bond of the starting alkyl fluorides must be cleaved. However, this observation can be used only as supporting, but not as conclusive, evidence for the ionic dissociation. Fast exchange in a highly polarized donor-acceptor complex in the strongly acidic solvent could equally well result in the absence of observable H-F coupling. Such complexes were indeed well defined recently in the case of methyl fluoride–antimony pentafluoride and related primary alkyl fluoride–antimony pentafluoride complexes.



The ^{19}F spectra of the carbonium fluoroantimonate complexes indicated the absence of covalent C-F bonds and the presence of the ionic SbF_6^- or $Sb_2F_{11}^-$ forms. However, there is again no evidence to exclude the possibility of an exchanging, highly polarized $R-\ddot{F}:\longrightarrow SbF_5$ system.

The possibility of fluorine exchange in a highly polarized complex of the type $R-F\rightarrow SbF_5$ must be considered. In this type of complex, the C-F bond must be considerably weakened and, in the limiting case, ionized. There is also a possibility of exchange involving solvent SbF_5. Fluorine resonance probably cannot differentiate between the SbF_6^- line and the line that corresponds to an exchanging $F\rightarrow SbF_5$ system. Attempts were made to see whether, at lower temperatures, differences due to decreased exchange rates are observable, but this was not the case.

In order to prove that stable alkylcarbonium ions and not exchanging donor-acceptor complexes were obtained, we investigated the ^{13}C nuclear magnetic resonance of the potentially electropositive carbonium carbon atom in alkylcarbonium ions (*22*).

The ^{13}C shift of the *t*-butyl cation $(CH_3)_3{}^{13}C^+$ in SO_2ClF-SbF_5 solution at $-20°C$ is at -135.4 parts per million (from $^{13}CS_2$) with a long-range coupling to the methyl protons of 3.6 hertz. From the methyl ^{13}C satellites in the proton spectrum of the ion, the long-range proton coupling constant was 3.5 hertz.

The ^{13}C shift of the isopropyl cation, under identical conditions, is -125.0 ppm with a long-range coupling to the methyl protons of 3.3 hertz. The direct ^{13}C-H coupling is 169 hertz (indicating sp^2 hybridization of the carbonium carbon atom), while the long-range, proton-proton coupling constant is 6.0 hertz.

Substitution of the methyl group in the *t*-butyl cation by hydrogen thus causes an upfield shift of 10.4 ppm. The well-established relation between ^{13}C shifts and electron density leads to the conclusion that the central carbon atom in the *t*-butyl cation is slightly more positive than that in the isopropyl cation.

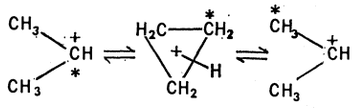
In spite of the fact that the *t*-butyl cation is calculated (*23*) to be more stable than the isopropyl cation (by 4.70 electron volts), the charge on the central carbon in the *t*-butyl cation (+0.692 electron volt) is more positive than that in the isopropyl cation (+0.611 electron volt). If we assume that the chemical shift dependence is 200 ppm per electron, this difference gives a ^{13}C chemical shift difference of 16

ppm, a value in reasonable agreement with the observed difference of 10.4 ppm. Chemical shift data thus support the assumption that the methyl group is electron-withdrawing relative to hydrogen in accordance with a negative inductive effect. At the same time, hyperconjugative stabilization in the planar carbonium ions will make the $(CH_3)_3C^+$ ion more stable than $(CH_3)_2CH^+$ relative to their precursors.

The ^{13}C shift of the *t*-amyl cation $C_2H_5C^+(CH_3)_2$ is at −139.4 ppm, only 4 ppm down field from the *t*-butyl cation. This shift difference is much smaller than the 17 ppm found in the case of the related alkanes, although the shift observed is in the same direction.

It is difficult to interpret these large deshieldings in any way other than as a direct proof that (i) the state of hybridization of the carbon atoms involved in the carbonium ion is sp^2; and (ii) at the same time, the carbon atom carries a substantial positive charge.

When the isopropyl cation was generated from 2-chloropropane with 50 percent ^{13}C enrichment of C-2 in SO_2ClF-SbF_5 at −60°C, equilibration of the ^{13}C label occurred with a half-life of 1 hour. After several hours, the ^{13}C was distributed equally among the three carbons. This observation suggests that a protonated cyclopropane is responsible for the proton scrambling mechanism.



Similar scrambling was observed in the secondary butyl (*sec*-butyl) and *t*-amyl cations.

Infrared and Raman spectra of the stable alkylcarbonium ions were also observed (*20, 24*) and are in complete agreement with the planar structure of the carbonium ions. Infrared spectra of these ions and of their deuterated analogs correspond to the spectra predicted by calculations based on molecular models and force constants. Thus, vibrational spectra can also be used in the identification of stable carbonium ions.

Laser Raman spectroscopy, particularly with helium-neon lasers, is another powerful tool in the study of carbonium ions. Because Raman spectra give valuable information on symmetry, these spectra help to establish, in detail, structures of the ions and their configurations. The Raman spectroscopic data provide strong evidence that the trimethylcarbonium ion in superacid (*25*) solution prefers a conformation leading to overall C_{3v} point group symmetry. Thus, the $+C(CH_3)_3$ ion exists in these solutions with a planar $+C(C_3)$ carbon skeleton and with one hydrogen atom of each CH_3 group above the plane parallel to the threefold axis of rotation. The other two hydrogen atoms are arranged symmetrically to the right and left of the threefold axis. Raman spectra observed for the *t*-amyl cation (dimethylethyl carbonium ion), the pentamethylethyl cation (dimethyl-*t*-butylcarbonium ion), and the dimethylisopropylcarbonium ion also show a planar, sp^2 hybridized structure. The Raman spectroscopic studies thus provide, in addition to ^{13}C NMR data, direct evidence for the planar structure of alkylcarbonium ions.

The observation of stable alkylcarbonium ions in antimony pentafluoride solutions also opened up the possibility of investigating the electronic spectra of these solutions. Waack and I reported (*26*) that solutions of alkylcarbonium ions in FSO_3H-SbF_5 solutions at −60°C showed no absorption maxima above 210 nm. In view of this observation, it is now highly probable that previous claims relating to a 290 nm absorption of alcohols and olefins in sulfuric acid solutions were due to condensation products or cyclic allylic ions and not to the simple alkylcarbonium ions (*27*).

Alkylcarbonium ions can be formed not only from halide precursors (the earlier investigation of generation from alkyl fluorides was later extended to alkyl chlorides, bromides, and even iodides) but also from olefins in superacids like HF-SbF_5 (*28, 29*).

$$RCH{=}CH_2 \xrightarrow[HF-SbF_5]{FSO_3H-SbF_5} R\overset{+}{C}H-CH_3$$

Tertiary and reactive secondary alcohols in superacids like FSO_3H-SbF_5 ("magic acid") (*30*), FSO_3H, and SbF_5-SO_2-(SO_2ClF) also ionize to the corresponding carbonium ions (*31*). The generation of alklcarbonium ions from alcohols indicates the great advantages of increasing acidity and of using acid systems with low freezing points. Deno showed that the use of sulfuric acid and oleum results in formation of cyclized allylic ions from simple aliphatic alcohols (*18*). With the use of the extremely strong acid FSO_3H-SbF_5 these alcohols can be ionized to the corresponding tertiary and secondary alkylcarbonium ions without further rearrangements.

$$(CH_3)_3C-OH \xrightarrow[-H_2O]{FSO_3H-SbF_5} (CH_3)_3C^+$$

Primary and less reactive secondary alcohols are protonated in FSO_3H-SbF_5 solution at low temperatures (−60°C) and show very slow exchange rates (*32*).

$$CH_3CH_2CH_2OH \rightleftharpoons CH_3CH_2CH_2\overset{+}{O}H_2$$

$$CH_3\underset{OH}{\underset{|}{C}}HCH_3 \rightleftharpoons CH_3\underset{+OH_2}{\underset{|}{C}}HCH_3$$

Temperature-dependence studies of the NMR spectra of protonated alcohols allow the kinetics of dehydration to be followed (*33*).

$$CH_3CH_2CH_2CH_2OH \xrightarrow[-60°C]{FSO_3H-SbF_5-SO_2} [CH_2CH_2CH_2CH_2\overset{+}{O}H_2] \xrightarrow{H^+} [CH_3CH_2CH_2\overset{+}{C}H_2] + H_3O^+$$

$$[CH_3CH_2CH_2\overset{+}{C}H_2] \xrightarrow{\text{rearrangement}} (CH_3)_3C^+$$

To overcome difficulties and achieve ionization of primary and less reactive secondary alcohols at low temperatures, we found, in some cases, that it is advantageous to transfer them with thionyl halides or carbonyl halides to the corresponding haloformates or halosulfites. These in turn ionize readily in SbF_5-SO_2 solution and lose CO_2 or SO_2 (*29*).

$$ROH \xrightarrow{COX_2} ROOCX \xrightarrow{SbF_5-SO_2} R^+SbF_5X^- + CO_2$$

$$ROH \xrightarrow{SOX_2} ROOSX \xrightarrow{SbF_5-SO_2} R^+SbF_5X^- + SO_2$$

$$X = Cl, F$$

Aliphatic ethers are protonated in strong acids, and, at low temperatures, the exchange rates of the acidic proton are low enough to permit direct observation by NMR spectroscopy (*34*). Studies of temperature-dependence of NMR spectra again allow, following the kinetics of ether, cleavage to form alkylcarbonium ions.

$$CH_3-O-CH_2CH_2CH_2CH_3 \xrightarrow[-60°C]{FSO_3H-SbF_5} CH_3-\overset{+}{\underset{H}{O}}-CH_2CH_2CH_2CH_3$$

$$\xrightarrow[H^+]{heat} CH_3\overset{+}{O}H_2 + [CH_3CH_2CH_2\overset{+}{C}H_2] \xrightarrow{\text{rearrangement}} (CH_3)_3C^+$$

Protonation and ionization of mercaptans (thiols) and sulfides were similarly studied (*35*).

Superacids such as FSO_3H-SbF_5 act as very effective hydride-abstracting agents, allowing the generation of carbonium ions from saturated hydrocarbons (*36*).

$$CH_3CH(CH_3)CH_3 \xrightarrow[SO_2ClF]{FSO_3H—SbF_5} (CH_3)_3C^+ + H_2$$

Carbonium ions can also be generated by decarbonylation of tertiary alkyloxocarbonium ions, like the *t*-butyloxocarbonium ion (pivalyl cation) (*21*).

$$(CH_3)_3CCOF + SbF_5 \rightleftharpoons (CH_3)_3CCO^+SbF_6^- \overset{heat}{\rightleftharpoons} (CH_3)_3C^+SbF_6^- + CO$$

This reaction corresponds to the reverse of the Koch-Haaf acid synthesis, which is known to involve carbonium ion intermediates. Indeed the reaction of the tertiary butyl cation with carbon monoxide gives the pivalyl cation.

Amines also can be used as precursors for the generation of alkylcarbonium ions. The classic method of deaminative formation of carbonium ions involves some type of diazotization reaction producing an equimolar amount of water.

$$R—NH_2 \xrightarrow[-H_2O]{HNO_2} [RN_2^+] \longrightarrow R^+ + N_2$$

Newer methods overcome this difficulty. The corresponding sulfinylamine or isocyanate is prepared and then reacted with stable nitrosonium salts to give the corresponding carbonium ion.

$$RNH_2 \xrightarrow{SOCl_2} RNSO + NO^+SbF_6^- \longrightarrow R^+SbF_6^- + N_2 + SO_2$$

$$RNH_2 \xrightarrow{COCl_2} RNCO + NO^+SbF_6^- \longrightarrow R^+SbF_6^- + N_2 + CO_2$$

Cyclopropylcarbonium Ions

The solvolysis studies of Roberts (*38*) and Hart (*39*) showed both the unusual stability of cyclopropylcarbonium ions and the facility with which such ions rearrange.

Cyclopropyl groups have a strong stabilizing effect on carbonium ions and effectively delocalize charge. The direct observation of cyclopropylcarbonium ions by NMR spectroscopy provides the clearest example known of delocalization of charge into a saturated system.

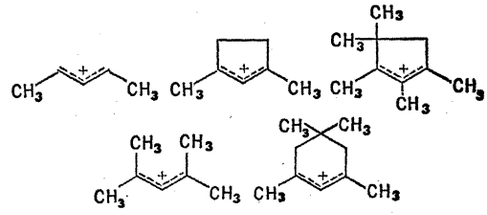
The first cyclopropylcarbonium ion directly observed was the tricyclopropylcarbonium ion (*40*). Its NMR spectrum in H_2SO_4 consists of a single sharp line at δ 2.26 (parts per million relative to trimethylsilane). In SbF_5-SO_2ClF solution at −78°C, the 100-megahertz spectrum, however, shows the methine and methylene cyclopropyl protons separately.

Pittman and I have observed several mono- and dicyclopropylcarbonium ions in FSO_3H-SbF_5-SO_2 solution at low temperatures (*41*). The cyclopropyl ring protons are resolved in the NMR spectrum of each of these ions. Most interesting of these is the dimethylcyclopropylcarbonium ion (Fig. 2). The methyl groups are not equivalent and are seperated by 0.54 ppm. In uncharged systems the hydrogens lying in the face of the cyclopropane ring experience an upfield shift of 0.3 to 0.5 ppm. This leads us to conclude that the cyclopropane ring lies in a plane perpendicular to the plane of the dimethylcarbonium ion center (bisected form).

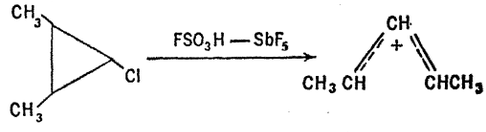
The plane of the cyclopropane ring is parallel to the axis of the vacant *p* orbital of the positive central carbon. In this configuration, one methyl group is *cis* to the cyclopropane ring and the other is *trans*. This *cis* methyl group now experiences the dimagnetic anisotrophy of the cyclopropane ring. This accounts for its observed position 0.54 ppm upfield from the *trans* methyl group. The methyl bands do not coalesce at −30°C, where the ion undergoes ring opening and subsequent decomposition reactions. This shows that the cyclopropane ring does not rotate at this temperature, corresponding to a rotational barrier of at least 10 kilocalories per mole.

Alkenyl Cations

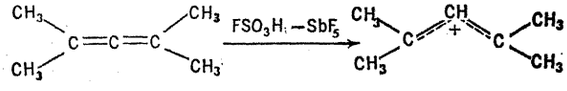
Many alkenyl cations have now been directly observed, particularly by Deno and Richey (*18, 42*), Sorensen (*43*), and Olah (*44*) and their co-workers. Deno reviewed the chemistry of these ions (*18*), and the number of examples has increased substantially since. The cations of the allylic type particularly show great stability. Representative examples are



The opening of halocyclopropane rings with the formation of allyl cations has been investigated (*45–47*).

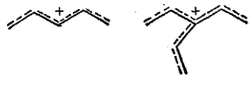


Protonation of certain allenes also leads to allyl cations which are otherwise difficult to obtain from allylic precursors (*48, 49*).

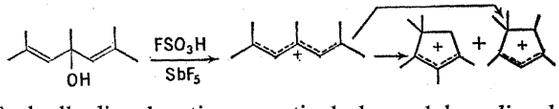


Alkadienyl and Polyenylic Cations

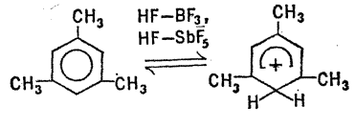
Deno, Richey, and their co-workers (*18*) observed a substantial number of alkadienyl and polyenylic cations. Sorensen (*50*) has reported the observation of the divinyl- and trivinylcarbonium ions.



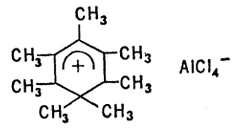
Alkenyl cations show a substantial tendency to cyclize to the more stable cyclic allylic ions. Pittman, Sorensen, and I were able to follow these cyclizations by NMR (*51*).



Cycloalkadienyl cations, particularly cyclohexadienyl cations (benzenonium ions), show remarkable stability. They can be obtained by protonation of aromatic hydrocarbons by strong acids (*52–54*).

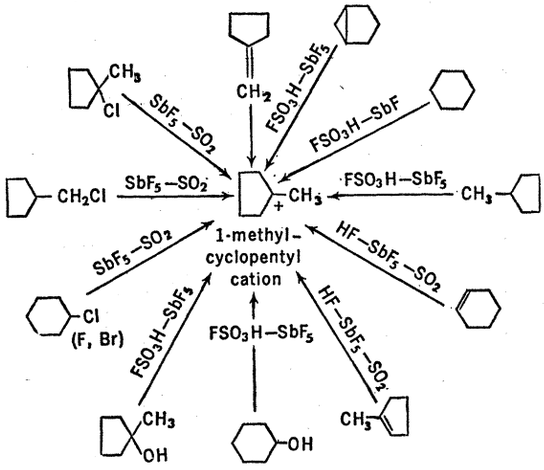


Doering and his colleagues observed the very stable heptamethylbenzenonium ion (*55*).

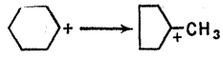


Cycloalkyl Cations

Tertiary cycloalkylcarbonium ions, like the 1-methyl-1-cyclopentyl cation, show high stability in strong acid solutions. This ion can be obtained from a variety of precursors (*55*).

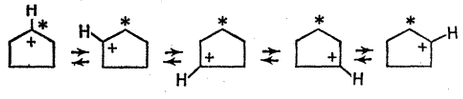


It is worthwhile to mention that not only cyclopentyl but also the cyclohexyl type of precursors gives the 1-methylcyclopentyl cation. This indicates that the cyclopentyl cation has higher stability, which causes isomerization of the secondary cyclohexyl cation to the tertiary methylcyclopentyl ion.



The mechanism of this rearrangement probably does not involve primary carbonium ions but goes through a protonated cyclopane (bicyclo[3.1.0]hexane) intermediate.

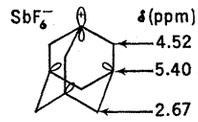
The cyclopentyl cation shows in its proton magnetic resonance spectrum in SbF_5-SO_2ClF solution, even at −70°C, only a single absorption line at δ 4.68 (*22*, *57*). This observation indicates a completely degenerate ion with a low barrier to the secondary-secondary hydride shift.



Bridgehead Carbonium Ions

Bredt's rule in its original form (*58*) excluded the possibility of carbonium ion formation at bridgehead positions of cycloalkanes. Indeed, bridgehead halides, such as apocamphyl chloride, proved extremely unreactive under hydrolysis conditions (*59*). However, 1-bromoadamantane very readily gives the bridgehead carboxylic acid under the usual conditions of the Koch-Haaf acid synthesis (*60*). 1-Fluoroadamantane is ionized in SbF_5 to give the stable bridgehead adamantyl cation (*61*).

The NMR spectrum of the adamantyl cation in SbF_5 soloution at 25°C consists of bands at 5.42, 4.50, and 2.67 in δ units with areas of 3 : 6 : 6. The γ-CH hydrogens have their bands at a lower field than the three β-CH_2 groups even though they are farther from the positive carbon. This is explained as the lobe of the empty *p*-orbital lying inside the cage overlapping with the back sides of the three sp^3 bridgehead CH orbitals. Such overlap would distribute charge preferentially to the bridgehead positions, which may account for their downfield position in the NMR spectrum.



Schleyer and I also observed a series of methyladamantyl cations. The bridgehead congressane (diamantane) cation was also recently observed (*57*) and it also shows the cation cage effect. Although the bridgehead 1-norbornyl cation was not directly observed, 1-chloronorbornane yields the stable 2-norbornyl cation in SbF_5-SO_2 solution. Thus, ionization to the bridgehead carbonium ion must be followed by a fast shift of hydrogen from C-1 to C-2, the driving force for which is obviously the tendency to relieve strain in the carbonium ion (*62*).

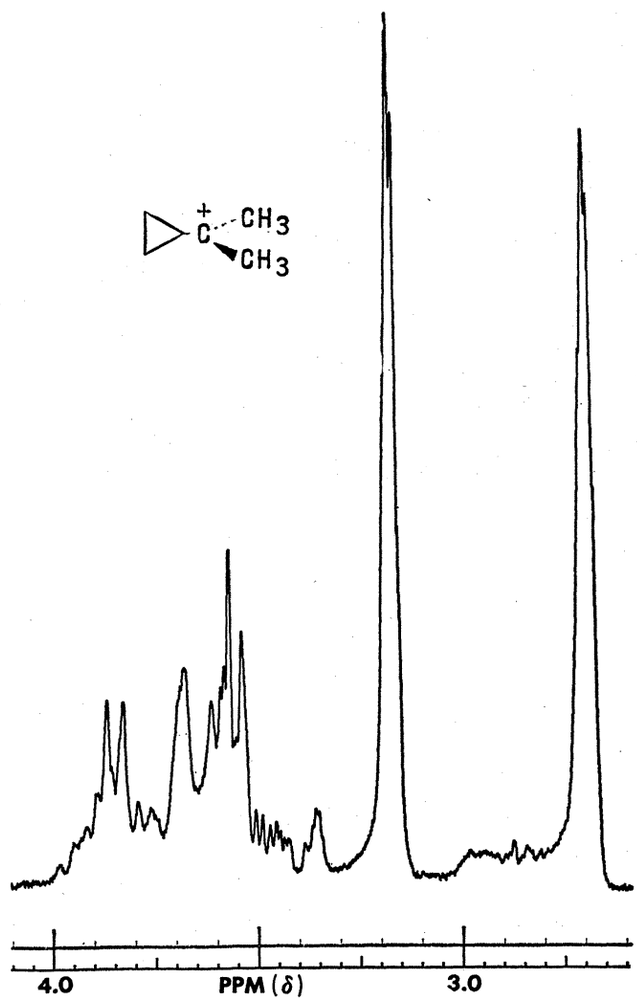
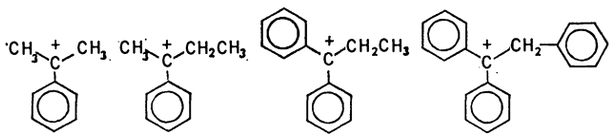


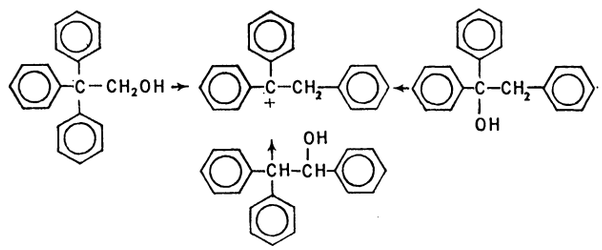
Fig. 2. The PNMR spectrum of the dimethylcyclopropyl carbonium ion shows nonequivalent methyl group proving the "bisected" structure.

Alkylarylcarbonium Ions

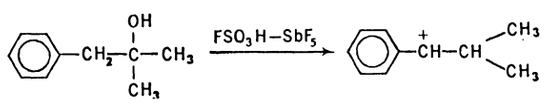
Mono- and dialkylarylcarbonium ions can be readily obtained from the corresponding alcohols, olefins, or halides in strong acid solution, such as H_2SO_4 (*63*), FSO_3H-SbF_5 (*64*), $ClSO_3H$ and FSO_3H (*65*), and oleum (*66*). Representative alkylarylcarbonium ions are:



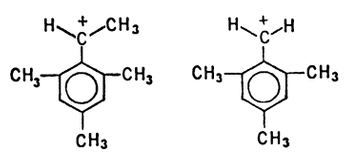
Because of the high stability of the tertiary ions, these are preferentially found in the strong acid systems from both tertiary, secondary, and even primary precursors (*67*).



If, however, the tertiary carbonium ion is not benzylic, rearrangement to a secondary, benzylic ion can be observed:

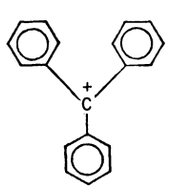


With suitable substituent groups (which also prevent transalkylations), even secondary styryl cations and primary benzyl cations were found as stable, long-lived ions (*68*, *69*).

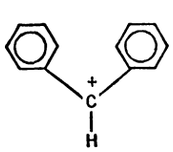


Arylcarbonium Ions

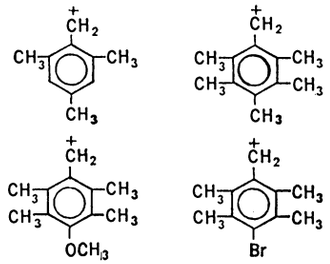
The first stable long-lived carbonium ion observed was the triphenylcarbonium ion (*2–4*).



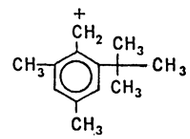
This ion is still the best-investigated carbonium ion (*10*) and its propeller-shaped structure is well proved. Diphenylcarbonium ions (benzhydryl cations) are considerably less stable than their tertiary analogs. Although ultraviolet spectra in dilute sulfuric acid solutions have been obtained (*63*), only recently has the benzhydryl ion been observed in higher concentrations in acid solutions [$ClSO_3H$ (*65*), FSO_3H, and FSO_3H-SbF_5 (*64*)].



The observation of benzyl cations in acid solutions was also recently achieved (*68*). Although the unsubstituted benzyl cation is still elusive, we have observed many substituted derivatives.



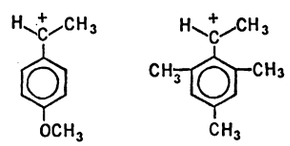
In a cation such as



2, 4-dimethyl-6-t-butyl-phenylcarbonium ion

a high rotational barrier around the sp^2-hybridized carbon atom is observed (NMR studies). This means that the methylene protons are magnetically nonequivalent (*69*). No rearrangement of benzyl cations in acid solution to tropylium ions has been found, although this rearrangement is claimed in the gas phase (mass spectroscopy).

A number of substituted styryl cations have also been observed (*70*).

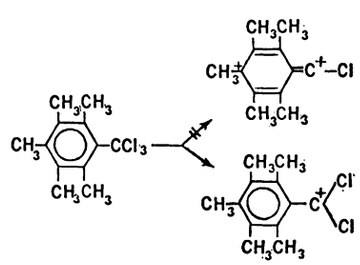


methyl p-anisyl-carbonium ion | methyl mesityl-carbonium ion

But the styryl cation (phenylmethylcarbonium ion) itself is still elusive because of its great tendency for proton elimination and subsequent polymerization.

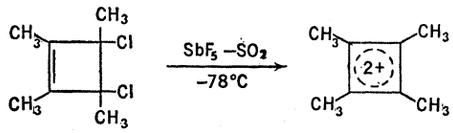
Dicarbonium Ions

Earlier reports (*71*) that a dicarbonium ion had been observed from pentamethyltrichloromethylbenzene turned out to be incorrect. The species is the benzylic dichloropentamethylphenylcarbonium ion (*72–74*).

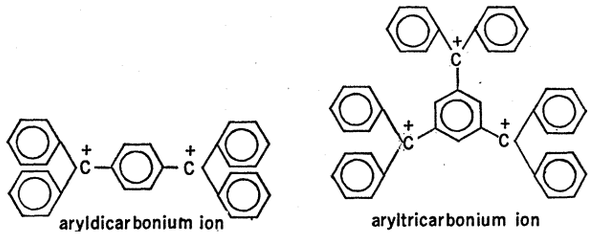


The 1,2,3,4-tetraphenylcyclobutenium di-cation has been reported (*75*). However, there is evidence that this ion was only an equilibrating cyclobutenyl mono cation. X-ray crystallographic investigation of the isolated crystalline complex confirm this conclusion (*76*). Recently Bollinger, White, and I succeeded in obtaining the 1,2,3,4-tetramethylcyclobute-

nium di-cation (*77*). ^{1}H and ^{13}C nuclear magnetic resonance studies confirmed its structure and its 2-π electron aromatic nature, which are similar to Breslow's previously observed cyclopropenium cation.

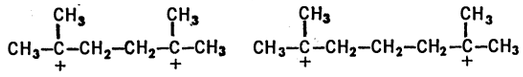


If two carbonium centers are separated by a phenyl ring, a variety of di- and tricarbonium ions can be obtained (*78, 79*).



aryldicarbonium ion aryltricarbonium ion

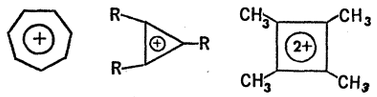
Recently, simple alkyldicarbonium ions were also observed (*80*). Separation of the two carbonium ion centers by two or three methylene groups enables these species to be present as stable entities in the strongly acidic solvent system (SbF_5-SO_2) at low temperature (−60°C).



alkyldicarbonium ions

Aromatically Stabilized Carbonium Ions

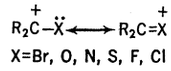
If a carbonium ion is also a Hückel-type aromatic system, resonance causes very substantial stabilization. The best known examples of aromatically stabilized carbonium ions are the cycloheptatrienyl (tropylium) cation (*81–83*), cyclopropenyl cations (*84*), and the tetramethylcyclobutenium di-cation (*85*).



Because of their aromatic character, these ions are highly stable. Numerous other examples of aromatically stabilized carbonium ions are known.

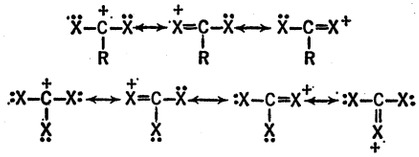
Heteroatom-Stabilized Carbonium Ions

In contrast to hydrocarbon cations, heteroatom-substituted carbonium ions are strongly stabilized by electron donation from the unshared electron pairs of the heteroatoms adjacent to the cationic carbon center:



X=Br, O, N, S, F, Cl

The stabilizing effect is enhanced when two, or even three, electron-donating heteroatoms coordinate with the electron-deficient carbon atom.

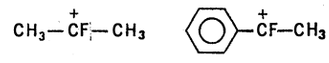


Halogen as Heteroatom

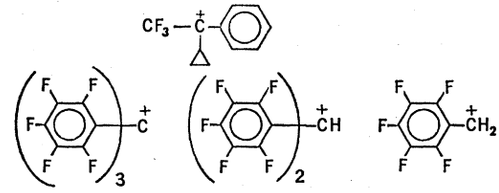
In 1965, Cupas, Comisarow, and I reported the first fluorocarbonium ions (*86*).

phenyldifluoro-carbonium ion diphenylfluoro-carbonium ion

Fluorine has a particular ability to stabilize carbonium ions via back-coordination of its unshared electron pairs into the vacant *p* orbital of the carbon atom. Because ^{19}F magnetic resonance offers an excellent possibility for structural investigations of these ions, extensive work was initiated. The dimethyl- and phenylmethylfluorocarbonium ions were obtained (*87*).

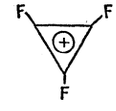


Trifluoromethylcarbonium ions (*88*) and perfluorophenylcarbonium ions were also reported (*89, 90*).

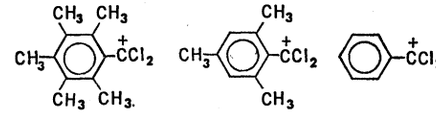


Because of the relatively large fluorine chemical shifts, anisotropy and ring current effect play a relatively much smaller role than they do in the case of proton shifts. Therefore, a better correlation of charge distribution with chemical shifts can be obtained as is also true of ^{13}C NMR spectroscopy.

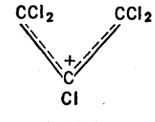
The trifluorocyclopropenium ion was also recently obtained (*91*).



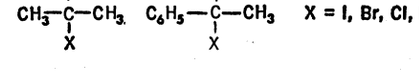
A series of chlorocarbonium ions were observed, including phenyldichlorocarbonium ions (*72–74, 92*).



West (*93*) observed the perchloroallyl cation.



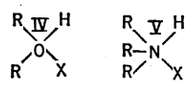
Comisarow and I observed (*94*) a series of chloro-, as well as bromo- and iodocarbonium ions and showed the general stabilizing ability of halogen attached to carbonium ion centers.



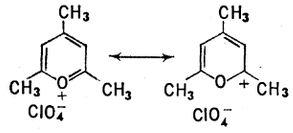
Oxygen as Heteroatom

Crystalline addition compounds of alcohols, ethers, aldehydes, and ketones with Brönsted and Lewis acids have been known since the middle of the last century. They were long

considered unstable "molecular compounds" (*95*). Collie and Tickle (*96*) were the first to assign "oxonium salt" character to the acid complexes of dimethylpyrones. They formulated the complexes as containing a tetravalent oxygen, analogous to the ammonium salts in which nitrogen at that time was assumed to be pentavalent:



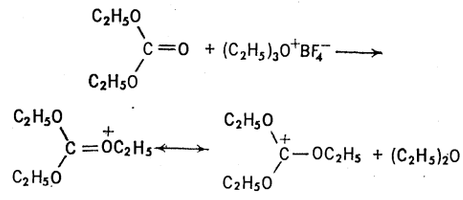
The ionic structure of the pyrylium salts was clearly stated by Hantzsch as early as 1922 (*97*).



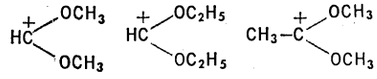
In pyrylium salts there is contribution from carbonium ion structures, a fact apparent in the behavior toward strong nucleophiles leading to phenols.

Alkoxycarbonium Ions

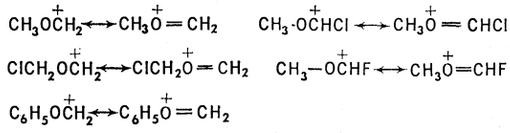
Resonance, similar to that in the pyrylium salts, was shown by Meerwein (*98*) to exist between oxonium and carbonium ions in the crystalline fluoroborates obtained by alkylation of ketones, esters, and lactones with trimethyl- or triethyloxonium fluoroborates.



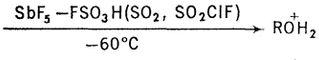
Taft and Ramsey (*99*) used NMR spectroscopy to investigate a series of secondary and tertiary alkoxycarbonium ions.



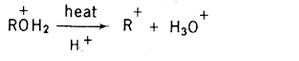
Bollinger and I (*100*) obtained primary alkoxycarbonium ions such as the methoxy- and phenoxycarbonium ions and their halogenated derivatives:



With Sommer and Namanworth (*33*) we showed that primary and secondary alcohols are protonated in FSO_3H-SbF_5(SO_2, SO_2ClF) solution at −60°C, giving well-resolved spectra of the protonated species.

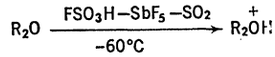


At higher temperatures they cleave to carbonium ions; the kinetics of these cleavage reactions could be followed by NMR spectroscopy.

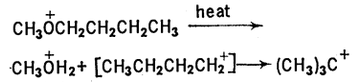


Tertiary alcohols (with the exception of the ones containing strong electron withdrawing groups like CF_3) generally dehydrate very fast in the acid media, and the intermediate protonated species cannot be observed, even at low temperature, before cleavage.

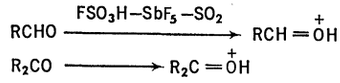
Ethers protonate in superacid media and give well-resolved spectra.



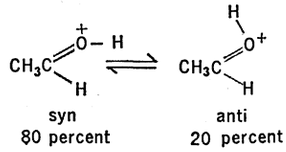
Again cleavage reactions can be followed by NMR spectroscopy as in the case of methyl *n*-butyl ether



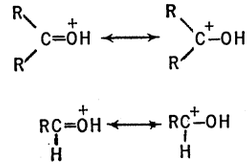
Aldehydes and ketones protonate on the carbonyl oxygen atom, and in superacid media at low temperatures the protonated species can be directly observed (*101–105*).



Even protonated formaldehyde was observed. Protonated acetaldehyde was observed in two isomeric forms, the proton on oxygen *syn* or *anti* to the aldehyde proton:

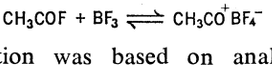


The hydroxycarbonium ion forms of protonated ketones and aldehydes (observable in strong acid solutions) contribute to the resonance hybride. Based on ^{13}C NMR studies (*106*), the degree of contribution of the hydroxycarbonium ion forms can be quite accurately estimated.

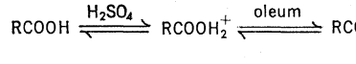


Oxocarbonium Ions (Acyl Cations)

Seel observed in 1943 the first stable acyl cation (*107*). Acetyl fluoride with boron trifluoride gave a complex (decomposition point 20°C) which was characterized as the acetyl tetrafluoroborate salt



The identification was based on analytical data and chemical behavior. Only in the 1950's were physical methods applied, infrared and NMR spectroscopy making further characterizations of the complex possible. Since 1954, a group of other acyl cations (oxocarbonium ions) has been isolated and identified (*108–110*). The hexafluoroantimonate and hexafluoroarsenate complexes were found particularly stable (*110*). Deno and his co-workers investigated solutions of carboxylic acids in sulfuric acid and oleum (*111*). They observed protonation at lower acid concentrations and dehydration, giving acyl cations at higher acidities.



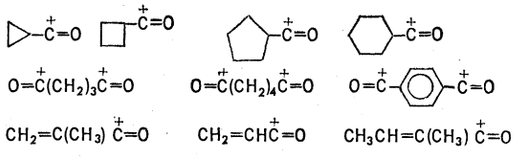
The investigation of acyl cations (oxocarbonium ions) was substantially helped by NMR. Not only ^{1}H, but also ^{2}H, ^{13}C, and ^{19}F resonance studies established the structure of these ions (*110*, *112*). These investigations, based on ^{13}C and proton resonance, showed that acyl cations, such as the CH_3CO^+ ion, are not simple oxonium ions (acylonium complexes), but are indeed oxocarbonium ions with a substantial positive charge on the carbonyl carbon atom.

$$CH_3-\overset{+}{C}O,\ CH_3CH_2\overset{+}{C}O,\ C_6H_5\overset{+}{C}O,\ (CH_3)_2CH-\overset{+}{C}O,\ (CH_3)_3C\overset{+}{C}O$$

Recent x-ray crystallography studies of the CH_3CO^+-SbF_6^- complex (*113*) substantiated this suggestion and provided convincing evidence for the linear structure of the crystalline complex.

$$CH_3-\overset{+}{C}=O$$

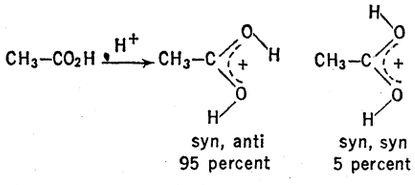
Investigation of acyl cations has been extended to the study of cycloalkyloxcarbonium ions (*114*), alkylene dioxodicarbonium ions (*115*), and alkenyl oxocarbonium ions (*116*).



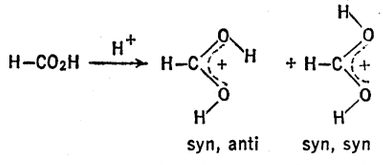
Alkylene dioxodicarbonium ions can be formed with at least three methylene groups separating the two positive charges.

Protonated Carboxylic Acids

The use of strong acid media, coupled with low temperature NMR spectroscopy, provides a convenient method of investigating the protonation of weak organic bases and subsequent reactions involving the protonated species. This approach is best illustrated by the behavior of carboxylic acids in media such as FSO_3H-SbF_5-SO_2, HF-SbF_5, or HF-BF_3 (*117*). The NMR spectrum of acetic acid in such media at low temperature shows two OH resonances indicating (i) that carbonyl protonation is favored and (ii) that hindered rotation about the resultant COH bonds is present. The predominate conformer observed is the *syn, anti,* although about 5 percent of the *syn, syn* isomer has also been observed.



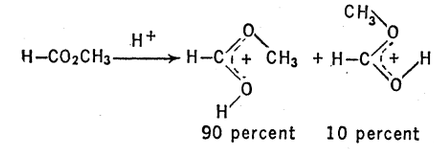
The NMR spectrum of formic acid, when protonated under the same conditions, is more complex because of the presence of proton-proton coupling and because of the fact that the two conformers are present in a ratio of 2 : 1, with the *syn, anti* isomer predominating.



These isomers can be readily identified from the magnitudes of the vicinal coupling constants; thus in the *syn, anti* isomer, the methine proton is a doublet of doublets ($J_{HH} = 15$ and 3.5 hertz) while in *syn, syn* isomer a triplet is observed ($J_{HH} = 3.5$ hertz). No evidence for the *anti, anti* isomer has been found in either protonated carboxylic acids, esters, or their thio analogs.

Protonated Esters

Esters behave in an analogous fashion, with carbonyl protonation being predominant. Thus protonated methyl formate is present in FSO_3H-SbF_5-SO_2 solution as two isomers in a ratio of 90 to 10 (*118*).



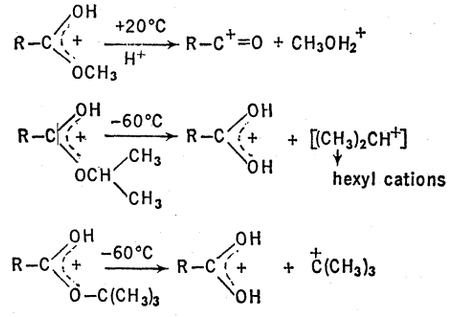
Cleavage of Protonated Acids and Esters

By raising the temperature of solutions of protonated carboxylic acids and esters, further reactions of the species involving unimolecular cleavage are observed. These reactions can be considered within the framework of the two unimolecular reaction pathways for acid-catalyzed saponification of esters, either involving alkyl- or alkyl-oxygen cleavage. The advantage of studies of these reactions in superacid media as compared to solvolytic conditions is that the cleavage step can be isolated and studied in detail because the cleavage products generally do not undergo any further reaction.

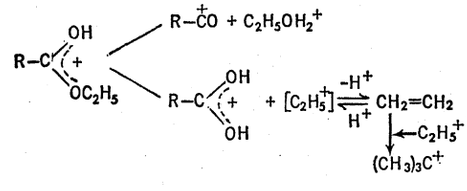
For example, in the case of protonated acetic acid in FSO_3H-SbF_5-SO_2 solution, a reaction analogous to the rate-determining step in the unimolecular cleavage of esters is observed leading to oxocarbonium ion (acyl cation) and hydronium ion formation.

$$R-CO_2H_2^+ \xrightarrow[H^+]{-20^\circ C} R-\overset{+}{C}=O + H_3O^+$$

Unimolecular cleavage in this case, of course, corresponds to dehydration of the acid, but in the case of protonated esters the cleavage pathway found depends on the nature of the alkoxy group as shown below.

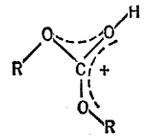


In the case of ethyl esters both pathways are observed to occur with comparable rates.

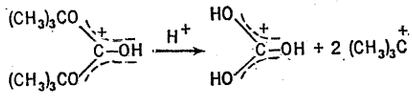


Protonated Carbonic Acid and Its Derivatives

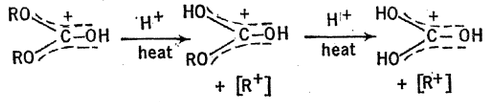
Dialkyl carbonates have been studied in FSO_3H-SbF_5 solution and have been shown to be protonated on the carbonyl group giving the dialkoxyhydroxy carbonium ion (*119*).



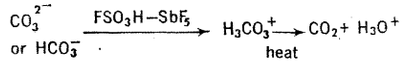
Di-*t*-butyl carbonate cleaves immediately at − 80°C with alkyl-oxygen fission, giving the *t*-butyl cation and protonated carbonic acid. The structure of the latter has been established from the C^{13} NMR spectrum of the central carbon atom which shows a 3.5 hertz quartet, being coupled to three equivalent hydroxyl protons (*118*).



Di-isopropyl and diethyl carbonate cleave at a higher temperature, also via alkyl-oxygen cleavage, with initial formation of protonated alkyl hydrogen carbonates. The alkyl hydrogen carbonates can also be formed by protonation of their sodium salts.

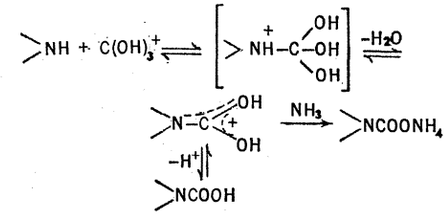


Protonated carbonic acid can also be obtained by dissolving inorganic carbonates and hydrogen carbonates in FSO_3H-SbF_5 at −80°C. It is stable in solution to about 0°C, where it decomposes to the hydronium ion and carbon dioxide. Protonated carbon dioxide (CO_2H^+) may be an intermediate.

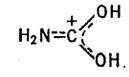


The observation of protonated carbonic acid as a stable chemical entity with substantial resonance stabilization may have major implications in our understanding of some of the more fundamental biological carboxylation processes. Our present (in vitro) observation in specific, highly acidic, solvent systems cannot be simply extrapolated to different environments (biological systems). However, it is possible that on the active receptor sites of enzyme systems (for example, those of the carbonic anhydrase type) local hydrogen ion concentration may be very high, as compared with the overall "biological *p*H." In addition, on the receptor sites a very favorable geometric configuration may help to stabilize the active species, a factor which cannot be reproduced in model systems in vitro.

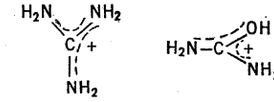
Carbon-13 magnetic resonance studies of protonated carbonic acid and comparison with data on a series of known carbonium ions indicate that the carbon atom of protonated carbonic acid is fairly electron-deficient and consequently it should be a reactive carboxylating agent. This prediction was substantiated in experiments where protonated carbonic acid and its esters were found to carboxylate ammonia to ammonium carbamate and alkylamines to alkyl carbamates. We are studying the possibility of C-carboxylations and the carboxylating ability of these compounds on biologically important systems like biotin. The "reactive form" of carbonic acid in certain systems indeed could be its protonated form which would account for its high reactivity at active sites.



The related observation of protonated carbamic acids as a stable species and its carbamylating ability (*120*)

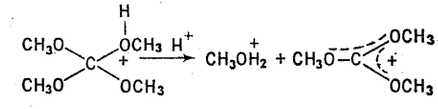


as well as the stability of mono- (and di-) protonated guanidine and urea (*121*) seem to support our contention



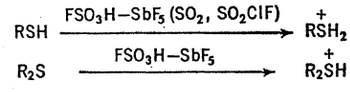
that protonated carbonic acid, like its derivatives, is a highly resonance-stabilized intermediate of substantial importance.

Orthoesters of carbonic acid cleave at −80°C in FSO_3H-SbF_5 solution giving trialkyloxocarbonium ions and protonated alcohols, analogous to the cleavage of orthoesters of carboxylic acids under the same conditions.

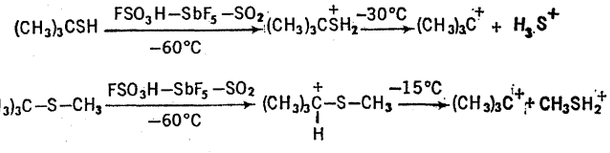


Sulfur as Heteroatom

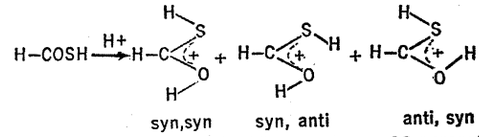
Thiols and sulfides are protonated on sulfur in superacid media, and the corresponding protonated species can be directly observed (preferentially by NMR spectroscopy).



Protonated thiols and sulfides are generally more stable than their oxygen analogs, and cleavage reactions take place only at much higher temperatures or with tertiary systems.

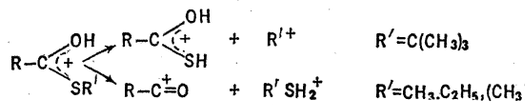


Disulfides are also protonated under similar conditions, but in this case rapid exchange (with respect to the NMR time scale) takes place between equivalent sulfur atoms. Protonated thio (*122*) and dithiocarboxylic (*123*) acids can also be easily obtained in superacid media. Protonated thioformic acid exists in three conformations, the *syn-anti* isomer being predominant. A similar type of behavior is found for other protonated thio acids.



syn,syn 30 percent | syn, anti 60 percent | anti, syn 10 percent

S-alkyl thio esters show analogous behavior to their oxygen analogs (*122*) in protonation and subsequent cleavage reactions.

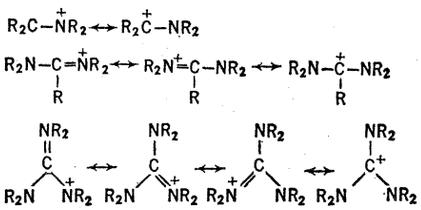


In the case of *O*-alkyl thio esters, only the *t*-butyl ester was cleaved. Esters of primary and secondary alcohols proved to be stable to higher temperatures, a reflection of stability of oxocarbonium ions as compared to their sulfur analogs.

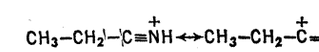
The thio analogs of protonated carbonic acid have also been prepared in FSO_3H-SbF_5-SO_2 solution (*122*). Preparation of the ions containing both OH and SH groups also lead to formation of both protonated carbonic acid and protonated trithiocarbonic acid; it was proposed that protonated carbon dioxide, carbonyl sulfide, or carbon disulfide, or all three, were intermediates in this interconversion.

Nitrogen as Heteroatom

Since nitrogen is a much stronger electron donor than oxygen, the contribution of carbonium ion structures in acid salts of imides, amidines, and guanidines is small.



Even in protonated nitriles contributions from the iminocarbonium ion resonance form can be considered.

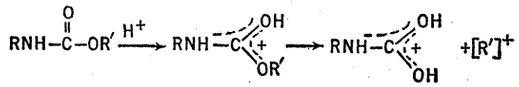


With Kiovsky we studied the protonation of hydrogen cyanide and alkyl nitriles in FSO_3H-SbF_5-SO_2 solution by ^1H, ^{13}C, and ^{15}N NMR spectroscopy (*124*). Both the protonated nitriles and *N*-alkylnitrilium ions (*125*) appear to have linear configurations involving the $-C\equiv N^+$ bond; only this form was observed in all cases studied. Iminocarbonium ion character $-{}^+C{=}N-$ would be expected to give deshielded ^{13}C NMR shifts. Carbon-13 NMR observations indicate, however, that the latter form is only a minor contributor in protonated nitriles and *N*-alkylnitrilium ions.

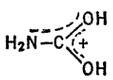
With protonated imines (*126*) NMR data indicate the predominance of immonium structures ($R_1R_2C{=}{}^+NHR_3$), with only limited contributions of aminocarbonium ion forms ($R_1R_2{}^+C{-}NHR_3$).

Amino acids are observed to undergo *N*-protonation and in superacids simultaneous *O*-protonation of the carboxylic acid group can be observed by NMR at low temperature (−70°C) (*127*). *O*-Protonation of the carboxylic acid group is conveniently observed because of its low-field chemical shift, which is usually in the range δ 14 to δ 15.5. Amino acids containing functional groups behave as might be anticipated. With the exception of those giving difficulty because of either high charge density or side reactions (serine, threonine, and cysteine), all amino acids were protonated on the carboxylic acid function. Aspartic and glutamic acids were protonated on their β and α carboxylic acid groups, respectively, as well as on the α functional groups. Aspargine and glutamine were also *O*-protonated on their amide groups; arginine was diprotonated on the nitrogen of the guanidino group, and heterocyclic amino acids gave characteristic spectra of their protonated rings.

Even protonated carbamic acid and its derivatives can be readily obtained and observed in the superacid media (*119*). Alkyl carbamates are found to be protonated on the carbonyl group, giving ions analogous to the alkyl carbonates.



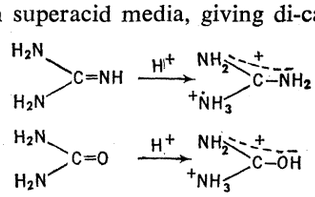
Cleavage of the alkyl-oxygen bond occurs, even in the case of carbamate esters of primary alcohols, giving protonated carbamic acids. These latter ions have high stability in strong acid media, reflecting the extensive delocalization of the positive charge.



In contrast to the usual observation of *O*-protonation of carbamate esters, *N*,*N*′-diisopropyl carbamate esters (methyl and ethyl) have been shown to be *N*-protonated in FSO_3H and 98 percent H_2SO_4 solution (*128*). It has, in this case, been possible in our related studies to observe rearrangement from *O*-protonated *N*,*N*′-diisopropyl carbamate esters to the *N*-protonated ions. Protonation of the methyl and ethyl esters in fluorosulfonic acid alone, or diluted with either sulfur dioxide or sulfuryl chlorofluoride at − 78°C, gives the *O*-protonated carbamate ester. At − 60°C, rearrangement to the *N*-protonated ester occurs, the rate being highly dependent on the solvent composition. This rearrangement is irreversible. At equilibrium a mixture of *N*- and *O*-protonated ions is observed, the mixture composition being 98 percent *N*-protonated and 10 percent *O*-protonated. This composition was independent of the solvent used. Carbonyl protonation is thus favored kinetically under these conditions, even through this leads to the thermodynamically least stable ion.

Protonated Ureas and Guanidines

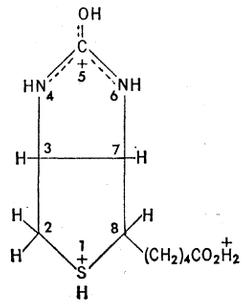
Introduction of a second and third amino group at the carbonium ion center increases the basicity enough for diprotonation to be observed. Both ureas and guanidines have been studied in superacid media, giving di-cations (*120*).



Protonation of Biotin

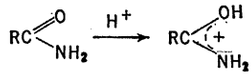
The versatility of the FSO_3H-SbF_5 ("magic acid") solvent system for structural determinations in relatively complex molecules is illustrated by the observation of biotin in FSO_3H-SbF_5-SO_2 solution (*121*). Protonation at three sites was found: at the sulfide group, the carboxyl group, and the urea carbonyl oxygen atom. Based on a detailed analysis of the NMR spectrum it was shown that protonation of the

sulfide group occurs preferentially *trans* to the valeric acid side chain. Relatively strong interaction between the sulfur in D-biotin and the protein to which it is attached has been suggested. The fact that protonation of the sulfur occurs *trans* to the valeric acid side chain suggests that binding of the sulfur with the protein should occur from the same direction. Attack from this side of the thiolane ring is particularly favorable in D-biotin in which the valeric acid side chain is *cis* to the ring junction. In L-biotin, any interaction with the sulfur would have to occur with approach from either the same side as the side chain or the same side as the ureido ring. Both of these modes of attack would be less favorable on steric grounds than in the case of D-biotin, and indeed L-biotin shows no physiological activity.



Protonated Peptides and Proteins

Amides are protonated, in superacid media at low temperatures, on the carbonyl oxygen atom, as shown first by Gillespie (*129*).



It should be kept in mind, however, that if there is contribution from the imino-form of the amides, protonation

of the latter on nitrogen will give the same result.

The possibility of observing the protonated amide linkage in strong acid media has particular relevance in the study of peptides and proteins (*127*, *130*). In superacid solutions (FSO_3H-SbF_5), Sudmeier and Schwartz (*130*) found that *O*-protonation occurs on the peptide bond in glycylglycine, triglycine, and tetraglycine. The OH proton was observed by proton magnetic resonance spectroscopy in the region δ 12 to 13.5 ppm. In our studies with Porter (*131*) we have observed similar internal *O*-protonation for L-alanine-L-leucine, L-leucine-L-leucine, and L-leucine-L-alanine dipeptides. Porcine insulin has also been studied in low concentration and at low temperature (−85°C). The time-averaged NMR spectrum (up to 525 passes), although not offering the narrow linewidths hoped for, indicates the peptide linkages to be extensively *O*-protonated (*127*).

We are currently extending the study of solutions of polypeptides and proteins in the rather unique, superacid solvent systems where complete protonation, including the peptide and carboxylic acid oxygen functions, is possible. If these protons can be directly observed under nonexchanging conditions, the studies will contribute to our knowledge of structure and interaction of reactive sites.

Conclusions

Rapid development of the preparation and direct observation of stable, long-lived carbonium ions in highly acidic solutions has occurred in less than a decade. Much of this success must be attributed to the application of new superacidic solvent systems and of NMR spectroscopy. A new field of carbonium ion chemistry has opened in which a continuously increasing number of carbonium ions can be obtained and studied as stable species. Even isolation of crystalline carbonium ion complexes has become a possibility. Structural studies extend from magnetic resonance, vibrational, Raman, and electronic spectra to x-ray crystallography. The application of the field to preparative chemistry and to the studies of natural products is just opening up. In a brief review complete coverage is not possible, and interested readers are referred to more comprehensive reviews and the original literature.

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132. Our work was supported by the National Institutes of Health (GM 14082), the National Science Foundation (GP 18098), and the Petroleum Research Fund administered by the American Chemical Society.

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