The General Concept and Structure of Carbocations Based on Differentiation of Trivalent ("Classical") Carbenium Ions from Three-Center Bound Penta- or Tetracoordinated ("Nonclassical") Carbonium Ions. The Role of Carbocations in Electrophilic Reactions[1a–c]

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Abstract: The general concept of carbocations (the suggested generic name for all cations of carbon compounds, in accordance with carbanion for negative ions) is defined based on the differentiation of *trivalent* ("classical") *carbenium ions* from three-center bound *penta-* or *tetracoordinated* ("nonclassical") *carbonium* ions. Carbenium ions usually have a planar or nearly planar sp^2 hybridized electron-deficient carbenium center, although linear vinyl and acyl cations are also known. The carbocation centers in carbonium ions are substantially less electron deficient penta- or tetracoordinated carbon atoms bound by three single bonds and a two-electron three-center bond (either to two additional bonding atoms or involving a carbon atom to which they are also bound by a single bond). Thus, in a carbonium ion the two electrons from the original π or σ bond are delocalized over three centers. Long-lived carbenium and carbonium ions can be experimentally differentiated from each other showing marked differences, for example, in their nmr and core photoelectron spectra. The structures of typical carbenium and carbonium ions, like alkenium ions, alkonium ions, alkenonium ions, cycloproponium ions, norbornonium ions, cyclopropylcarbonium ions, ethenebenzenium ions [bicyclo[2.5]octadienyl cations], are discussed in the context of the general carbocation concept. It is emphasized that division of carbocations into limiting trivalent ("classical") and penta- or tetracoordinated ("nonclassical") categories is frequently arbitrary. In many carbocation systems an intermediate range of delocalization (partial carbonium ion character) must be considered, as is the case in the 2-methylnorbornyl cation. Both carbenium and carbonium ions play important roles in electrophilic reactions involving not only n- and π- but also σ-donor systems. The recently discovered general reactivity of single bonds (σ donors) in electrophilic reactions is due to their ability to form carbonium ions *via* electron-pair sharing with the electrophile in two-electron, three-center bond formation. Subsequent cleavage to trivalent carbenium ions is followed by typical carbenium ion reactivity.

The concept of carbocations[2] (the logical name for all cationic carbon compounds, since the negative ions are called carbanions) had its origin and grew to maturity through kinetic, stereochemical, and product studies of varied reactions, especially unimolecular nucleophilic substitutions and eliminations.[3] Leading investigators, such as Meerwein, Ingold, Hughes, Whitmore, Bartlett, Nenitzescu, Winstein, and others, have contributed fundamentally to the development of modern carbocation theory, *e.g.*, the concept of cationic carbon intermediates. Although certain highly stabilized triarylcarbenium salts were isolated as early as the 1900's, direct observation of stable, long-lived carbocations usually in highly acidic (superacid) solvent systems has become possible only in recent years.[3,4]

Definition and Differentiation of Trivalent Carbenium Ions from Penta-or Tetracoordinated Carbonium Ions. In our continuing study of carbocations based on direct observation (by nmr, ir, Raman, X-ray induced electron spectroscopy, and crystallography) of long-lived stable ions, we were able in recent years to observe a substantial number of trivalent ions containing electron-deficient, generally planar (or nearly planar) sp^2-hybridized carbocation centers.[5a] Very characteristic are the highly deshielded ^1H and ^{13}C nmr shifts and coupling constants typical of sp^2 carbon. At the same time, in connection with the study of structural problems related to the so-called "nonclassical" nature of ions such as norbornyl[6a] (**1**), 7-norbornenyl[6a] (**2**), 7-norbornadienyl (**3**),[6a] cyclopropylcarbinyl (**4**), and cyclobutyl cations **5**,[6b] we observed different, substantially less electron-deficient penta- or tetracoordinated carbonium centers bound by three, two-electron single bonds and a two-electron three-center bond. (The only previously observed pentacoordinated carbocations, *e.g.*, CH_5^+ (**6**) and its homologs, were gaseous ions observed only by mass spectrometry.) Table I sum-

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(1) (a) Stable Carbocations. CXVIII. Note the change of the title of the series to "Carbocations" from the previously used "Carbonium Ions," as the name carbonium ion will be used, as discussed in this paper, from here on out to denote pentacoordinated ions. (b) Part CXVII: G. A. Olah, A. T. Ku, and J. A. Olah, *J. Org. Chem.*, **35**, 3929 (1970). (c) Presented in part at the 13th Conference on Reaction Mechanisms, University of California, Santa Cruz, Calif., June 1970, and at the Symposium on the Transition State of the French Physical Chemical Society, Paris, Sept 1970.

(2) Rule C-83 of IUPAC rules on nomenclature of organic compounds (*Pure Appl. Chem.*, **11**, 63 (1965) states "...When the charge is on carbon, such cations are known generically as carbanions." Obviously this is a misprint and replacement of carbanions with carbocations is suggested.

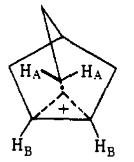
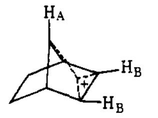
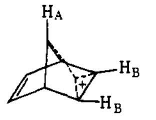
(3) For reviews see (a) G. A. Olah and P. v. R. Schleyer, Ed., "Carbonium Ions," Vol. I, Wiley-Interscience, New York, N. Y., 1968; Vol. II, 1970; Vol. III and IV, in preparation; (b) D. Bethell and V. Gold, "Carbonium Ions, An Introduction," Academic Press, New York, N. Y., 1967.

(4) For reviews, see: G. A. Olah, *Chem. Eng. News*, **45**, 76 (March 27, 1967); *Science*, **168**, 1298 (1970).

(5) (a) For a summary, see: G. A. Olah and J. A. Olah in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 715; (b) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969); (c) G. A. Olah, G. D. Mateescu, L. A. Wilson, and M. H. Gross, *ibid.*, **92**, 7231 (1970); (d) G. A. Olah, G. D. Mateescu, and J. L. Riemenschneider, *ibid.*, in press.

(6) (a) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970), and references given therein; (b) G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *ibid.*, **92**, 2544 (1970).

Table I. Comparison of Nmr Parameters of Carbocation Centers in Representative Carbenium and Carbonium Ions[a]

Carbenium ions					Carbonium ions			
Ion	$\delta_{\alpha H}$	J_{CH}, Hz	% s character	$\delta_{^{13}C^+}$	Ion	δ	J_{CH}, Hz	$\delta_{^{13}C}$[b]
7, $(CH_3)_2\overset{+}{C}H$	13	169	33.8	−125	 **1**	H_A, 3.05	H_{A+B}, 320[c]	C_A, 173
8, $CH_3(C_6H_5)\overset{+}{C}H$	10.5			−40		H_B, 6.59		C_B, 70
9, $(C_6H_5)_2\overset{+}{C}H$	9.7	164	32.8	−5.6	 **2**	H_A, 3.25		C_A, 162.2
10, $CH_3(C_3H_5)\overset{+}{C}H$	9.6			−59.1		H_B, 7.04	H_B, 194	C_B, 68.7
11, $(C_3H_5)_2\overset{+}{C}H$	8.1				 **3**	H_A, 3.24	H_A, 220	C_A, 152.7
12, 2,6-$(CH_3)_2$-4-$(CH_3)_3CC_6H_3\overset{+}{C}H_2$	8.7	169	33.8	19.5		H_B, 7.48	H_B, 200	C_B, 75.8

[a] In SbF_5–SO_2ClF solution at −70°, in case of the norbornonium ion in SbF_5–SO_2ClF–SO_2F_2 at −156°. [b] From external $^{13}CS_2$ as reference. [c] In equilibrating ion at −78° J_{H_A-C} and J_{H_B-C} are not directly observable.

marizes pmr and cmr data for selected carbenium and carbonium ions. The carbenium centers are electron-deficient trivalent carbons. In the carbonium ions C_A refers to the pentacoordinated carbon, whereas C_B is tetracoordinated (see subsequent discussion).

Recently with Mateescu we found it possible to apply X-ray photoelectron spectroscopy (ESCA or IEE) to the study of carbocations in frozen superacid solutions and as isolated salts.[5c] This method allows direct measurement of carbon 1s electron binding energies. As the charge distribution within carbocations causes increasing binding energies with increasing positive charge localization, highly electron-deficient classical alkyl and cycloalkyl carbenium centers (*e.g.*, *tert*-butyl **5c** and adamantyl **5d** cations) show about 4-eV 1s binding energy differences from the remaining less electropositive carbon atoms. In nonclassical carbonium ions (*e.g.*, the norbornonium ion) there is no such highly electron deficient carbon center and the photoelectron spectrum indicates only two modestly electropositive carbon atoms (the tetracoordinated methine atoms, see subsequent discussion) separated by about 1.5 eV from the remaining carbon atoms, with the bridging methylene carbon indicating no detectable electron deficient "shift."[5d]

Indisputable experimental evidence has thus been obtained from independent physical methods (Raman and ir, nmr (with particular emphasis on cmr), and photoelectron spectroscopy) for the differentiation of classical from nonclassical ions.

The General Concept of Carbocations

It became increasingly apparent from our studies that the concept of carbocations is much wider than previously realized and necessitates general definition. Therefore such a definition is now offered based on the realization that two distinct classes of carbocations exist.[7] (1) One class consists of trivalent ("classical") carbenium ions, of which CH_3^+ (**15**) is a parent. They usually contain a planar or close to planar sp^2-hybridized electron-deficient[8a] carbenium center (if no skeletal rigidity or steric hindrance prevents planarity). There are, however, also known examples of trivalent ions which contain a linear (or close to linear) sp-hybridized carbonium center as in vinyl cations and acyl cations. (2) A second class consists of three-center bound penta- or tetracoordinated ("nonclassical") carbonium ions of which CH_5^+ is the parent. They contain a penta- or tetracoordinated less electron-deficient[8b] carbon atom bound by three single bonds and a two-electron, three-center bond (to either two additional bonding atoms or to a carbon atom to which there is also a single bond.

$$\begin{tikzcd}
 & \text{carbocations} \arrow[dl] \arrow[dr] & \\
\text{carbenium ions} \\ \text{trivalent} \\ \text{"classical ions"} & & \text{carbonium ions} \\ \text{penta- or tetracoordinated} \\ \text{"nonclassical ions"}
\end{tikzcd}$$

The Naming of Carbocations

Concerning the carbocation ion concept, it is regrettable that general usage names the trivalent carbocations as "carbonium ions."[9] If the name is considered analogous to other onium ions (ammonium, sulfonium, phosphonium ions, etc.), then it should relate to the highest valency state carbocation. The highest valency state carbocations, however, clearly are not the trivalent carbenium ions but the penta- or tetracoordinated cations of the CH_5^+ type.

The term "carbonium," as pointed out, suggests that these ions are analogs of other onium ions and was introduced by Baeyer in 1902 with such an analogy in mind.[10] However, the analogy does not extend beyond the cationic charge of the species. Ammonium (as well

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[7] Existence is defined by Webster (Third New International Dictionary, unabridged edition, Merriam Co., 1961, p 796) as: "The state or fact of having being, especially as considered independently of human consciousness."

[8] (a) An electron-deficient atom is defined as one which has more bonding orbitals than electrons in its valence shell (R. E. Rundle, *J. Amer. Chem. Soc.*, **69**, 1327 (1947); *J. Chem. Phys.*, **17**, 671 (1949). (b) In a carbonium ion the two electrons from the original π or σ orbital are delocalized over three centers.

[9] For reviews, see D. Bethell and V. Gold, "Carbonium Ions, An Introduction," Academic Press, New York, N. Y., 1967; ref 3.

[10] A. v. Baeyer and V. Villiger, *Ber.*, **35**, 1189 (1902).

as other onium ions) are generally formed by combination of an unshared electron pair donor (Lewis base) with an electron pair acceptor (*e.g.*, proton or other electrophile). In this way, the donor atom (nitrogen, oxygen, phosphorus, etc.) increases its covalency by one unit and the onium ion acquires positive charge. The carbon atom in covalent compounds of ordinary valence does not possess a lone pair of electrons and a carbocation center was considered to exhibit a covalency of three, *i.e.*, one unit less than the normal quadrivalency. It was Gomberg[11] who immediately objected to the term "carbonium" and suggested instead the name "carbyl salts" which, however, never gained acceptance.

Dilthey and Dinklage suggested in 1929 that the term "carbenium ion" is more correctly applied to these ions.[12] Arndt and Lorenz agreed with this naming and pointed out that these ions are electron deficient, whereas an onium ion should be [CH_5^+], which they thought impossible.[13]

Jennen, discussing in 1966 the naming of ions, pointed out that the carbenium ion (methyl cation) can be looked at as protonated carbene[14] (*i.e.*, singlet carbene). Similarly, diphenylcarbene gives the diphenylcarbenium ion (**9**). Thus, there is a logical relationship between

$$\uparrow\downarrow CH_2 + H^+ \rightleftharpoons CH_3^+ \text{ or } (C_6H_5)_2C\uparrow\downarrow + H^+ \longrightarrow \underset{\mathbf{9}}{(C_6H_5)_2\overset{+}{C}H}$$

carbene and carbenium ion. It can be further pointed out that C_2 and higher carbenium ions can be derived by protonation of alkenes. Thus, in accordance with IUPAC rules, their name, indeed, is alkenium ions[15] (or in a generalized way carbenium ions).

$$\underset{\text{alkene}}{RCH{=}CHR} + H^+ \rightleftharpoons \underset{\text{alkenium ion}}{R\overset{+}{C}HCH_2R}$$

The carbenium ion naming indeed is widely used in the German (and French) literature. It should be pointed out, however, that "carbenium" should be used only for the trivalent ions and not as a generic name for *all* carbocations (for systematic naming of carbocations see the Appendix).

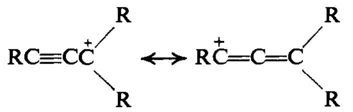
The Structure of Carbocations

A. Carbenium Ions. Experimental evidence for planarity or near planarity of the trivalent alkylcarbenium ion center comes from nmr (^1H and ^{13}C), ir, and Raman spectroscopic studies.[5] As seen from the ^1H and ^{13}C nmr parameters for the carbenium ion center in a series of selected secondary carbenium ions in Table I the data are characterized by very substantially deshielded chemical shifts with coupling constants (J_{CH}) indicating sp^2 hybridization.

Neighboring group interactions with the vacant p orbital of the carbonium center can contribute to ion stabilization *via* charge delocalization. This can involve atoms having unshared electron pairs (n donors), C–H and C–C hyperconjugation (σ donors), conjugation with bent σ bonds (as in cyclopropylcarbenium ions), and π electron systems (direct conjugative or allylic stabilization). Thus, trivalent carbenium ions can show varying degrees of delocalization. The two limiting classes defined clearly do not exclude varying degrees of delocalization, but in fact imply a spectrum of carbocation structures. There also are known a number of trivalent carbocations in which the sp-type carbocation center is linear (or close to linear) and has a coordination number of 2. Vinyl cations and acyl cations belong, among others, in this category. Vinyl cations can be derived by protonation of acetylenes (alkynes) or arynes and consequently can be called carbynium (alkynium, arynium) ions.[16] (For example, ethynium ($CH_2{=}CH^+$) and benzynium ion ($C_6H_5^+$)).

$$\underset{\text{alkyne}}{RC{\equiv}C{-}R} + H^+ \rightleftharpoons \underset{\text{alkynium ion}}{RCH{=}\overset{+}{C}R}$$

Vinyl cations have not yet been observed under long-lived ion conditions. As studied, however, by Olah[17] and Richey[18] alkynylcarbenium ions (propargylic cations) show mesomerism with the corresponding



allenyl cations. Linear sp-type carbon atoms are also found in Meerwein's nitrilium ions[19] and in protonated nitriles, which show the mesomerism indicated by Olah and Kiovsky's ^1H and ^{13}C nmr studies.[20]

$$RC{\equiv}N \underset{}{\xrightleftharpoons{H^+ \text{ or } R^+}} RC{\equiv}\overset{+}{N}H(R) \longleftrightarrow R\overset{+}{C}{=}NH\ (R)$$

Acyl cations (acylium ions) are further examples of linear trivalent carbocations involving mesomerism of oxocarbenium ions with oxonium ions. ^1H and ^{13}C

$$RC{\equiv}\overset{+}{O} \longleftrightarrow R\overset{+}{C}{=}O$$

nmr studies[21] and X-ray crystallography[22] showed the linear structure of these ions. The ethynylium ions $HC{\equiv}C^+$ which can be derived by hydride abstraction from acetylene and the cyanyl cation, CN^+, are only known in the gas phase. They are, of course, also linear with a coordination number of 1, but their existence as long-lived species in solution is highly questionable as they obviously are of high-energy nature (heats of formation of the gaseous ions[23] are 399 and 430 kcal/mol, respectively). They are considered of little importance in solution chemistry. However, cyanogen halide–Lewis acid halide complexes (not necessarily of the free CN^+ type) were reported.[24]

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(11) M. Gomberg, *Ber.*, **35**, 2397 (1902).

(12) W. Dilthey and R. Dinklage, *ibid.*, **62**, 1834 (1929).

(13) F. Arndt and L. Lorenz, *ibid.*, **63**, 3124 (1930).

(14) J. J. Jennen, *Chimia*, 20, 309 (1966).

(15) IUPAC Definitive Rules for Nomenclature of Organic Chemistry, Section C, No. 82.4: an organic cation formed by addition of a proton to an unsaturated hydrocarbon is named by adding "ium" to the name of the hydrocarbon, with elision of terminal "e" if present; examples, ethenium $CH_3CH_2^+$, benzenium $C_6H_7^+$.

(16) The name "alkinium" was suggested by Jennen.[14] In view of the general naming of alkynes, we adapt the name alkynium ions in accordance with IUPAC rule 82.4;[12] examples: ethynium, $CH_2{=}CH^+$; benzynium, $C_6H_5^+$.

(17) C. U. Pittman, Jr., and G. A. Olah, *J. Amer. Chem. Soc.*, 87, 5632 (1965).

(18) H. G. Richey, Jr., J. C. Philips, and L. E. Remnick, *ibid.*, 87, 1381 (1965); H. G. Richey, Jr., L. E. Remnick, A. S. Kushner, J. M. Richey, and J. C. Philips, *ibid.*, 87, 4017 (1965).

(19) H. Meerwein, *Chem. Ber.*, 89, 209 (1956).

(20) G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, 90, 4666 (1968).

(21) G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *ibid.*, **84**, 2733 (1962); G. A. Olah, *Rev. Chim. Acad. Repub. Pop. Roum.*, 7, 1139 (1962); W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Amer. Chem. Soc.*, 85, 1328 (1963); G. A. Olah and A. M. White, *ibid.*, **89**, 7072 (1967).

(22) F. P. Boer, *ibid.*, 88, 1572 (1966); 90, 6706 (1968).

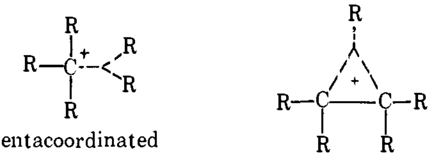
(23) J. L. Franklin, *et al.*, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 26 (1969).

The structural aspects of carbenium ions are widely studied and well reviewed.[3,4] It is thus not considered necessary to discuss them further here.

B. Carbonium Ions. There can be only eight valence electrons in the outer shell of carbon since expansion of the outer octet *via* 3d orbital participation does not seem possible.[25] Thus, the covalency of carbon cannot exceed four. Penta- or tetracoordination describes a species with five or four ligands, respectively, being within reasonable bonding distance from the central atom,[26] a definition well adaptable to the carbon atom in carbonium ions. Indeed, the transition states suggested for SN2 and SE2 reactions[27] as well for 1,2-alkyl or hydrogen shifts in saturated hydrocarbons[28] represent such cases. However, the observation of such penta- or tetracoordinated species in solution had never been reported until recent studies relating to long-lived "nonclassical ions" in superacid solvent systems. Moreover, aliphatic SE2 substitution reactions have been restricted in the past primarily to organometallic compounds, like organomercurials.[29] No example of "pure" aliphatic electrophilic substitution had been reported until the recent hydrogen–deuterium exchange studies of alkanes in superacid media[30] and discovery of the general concept of electrophilic reactions at single bonds. In contrast to the rather well-defined trivalent ("classical") carbocations, "nonclassical" ions[31] have been more loosely defined. In recent years, a lively controversy has centered on the "classical–nonclassical carbonium ion" problem.[32a,c] The literature contains numerous contributions to the topic. A frequently used definition of nonclassical ions is that of Bartlett: "an ion is nonclassical if its ground state has delocalized σ-bonding electrons."[32a] Sargent gave a similar but more elaborate definition.[32b] The extensive and indiscriminate use of "dotted lines" in writing nonclassical carbonium ion structures has been (rightly) strongly criticized by Brown[32d] who carried, however, the criticism to questioning the existence of any σ-delocalized (nonclassical) ion. For these ions, if they exist, he stated ". . . a new bonding concept not yet established in carbon structures is required." Unequivocal experimental evidence has been obtained since, based on direct spectroscopic observation, for nonclassical ions such as **1–5**.

a. The Methonium Ion, CH_5^+.

The bonding concept required for "nonclassical ions" is to define them as penta- or tetracoordinated carbonium ions of which CH_5^+ (methonium ion **6**)[33] is the parent, as CH_3^+ (methenium ion) is the parent for trivalent carbenium ions. The bonding involves three, two-electron covalent bonds with the fourth bond being a two-electron, three-center bond. The latter can be bound either to two additional atoms (pentacoordinated) or involve a carbon atom to which there is already a single bond (tetracoordinated).

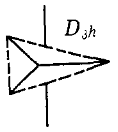


pentacoordinated

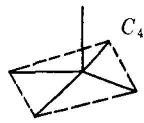
tetracoordinated

carbonium ions , R = H or alkyl

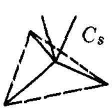
Of the possible structures for the methonium ion **6** with D_{3h} (**6a**), C_{4v} (**6b**), C_s (**6c**), D_{2h} (**6d**), or C_{3v} (**6e**) symmetry, Olah, Klopman, and Schlosberg[34a] suggested preference for the C_s front-side protonated form, **6c**, based on consideration of the observed chemistry of methane in superacids (hydrogen–deuterium exchange and more significantly polycondensation indicating the ease of cleavage to CH_3^+ and H_2) and also on the basis of self-consistent field calculations.



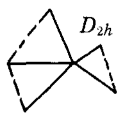
6a



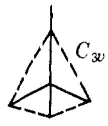
6b



6c



6d



6e

Gamba, Korosi, and Simonetta,[34b] Kollmar and Smith,[34e] and Mulder and Wright[34d] in independent nonempirical calculations came to similar conclusions. Lugt and Ros,[34c] Dyczmons, Staemmler, and Kutzelnigg,[34f] Veillard,[34g] and Pople[34h] also found in *ab initio* calculations, in the latter case by utilizing an "all-geometry" parameter search, the C_s symmetry structure to be favored. This structure is about 2 kcal/mol below

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(24) G. Fodor, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, ORGN 117.

(25) R. J. Gillespie, *J. Chem. Soc.*, 1002 (1952), and for rebuttals, H. J. S. Dewar, *ibid.*, 2885 (1953); H. H. Jaffe, *ibid.*, 21, 1893 (1963), and also R. J. Gillespie, *ibid.*, 21, 1893 (1963).

(26) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, 20, 245 (1966).

(27) For a general discussion see, for example, J. March, "Advanced Organic Chemistry Reactions, Mechanisms and Structure," McGraw-Hill, New York, N. Y., 1968.

(28) M. Stiles and R. P. Mayer, *J. Amer. Chem. Soc.*, 81, 1497 (1959).

(29) S. Winstein and T. G. Traylor, *ibid.*, **78**, 2597 (1956), and earlier papers. For a review and critical discussion, see F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968.

(30) (a) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227, 4739 (1967); **90**, 933 (1968); (b) H. Hogeveen and A. F. Bickel, *Chem. Commun.*, 635 (1967); H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, 87, 319 (1968); H. Hogeveen, C. J. Gaasbeek, and A. F. Bickel, *ibid.*, 88, 703 (1969).

(31) Roberts seems to have first used the term "nonclassical ion" when he proposed the tricyclobutonium structure for the cyclopropylcarbinyl cation [J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, 73, 3542 (1951)] and Winstein who referred to the "nonclassical structures of norbornyl, cholesteryl, and 3-phenyl-2-butyl cations" (S. Winstein and D. Trifan, *ibid.*, 74, 1154 (1952)).

(32) For leading references, see: (a) P. D. Bartlett, "Nonclassical Ions," reprints and commentary, W. A. Benjamin, New York, N. Y., 1965; (b) G. D. Sargent, *Quart. Rev., Chem. Soc.*, 20, 301 (1966); (c) S. Winstein, *ibid.*, 23, 141 (1969), and for an opposing view, (d) H. C. Brown, *Chem. Eng. News*, 86 (Feb 13, 1967), and references given therein.

(33) The methonium ion, until the recent superacid chemistry work of methane,[30] was only known from mass spectrometric studies (of the gaseous ion): V. L. Talrose and A. K. Lyubimova, *Dokl. Akad. Nauk SSSR*, 86, 909 (1952); F. H. Field and M. S. B. Munson, *J. Amer. Chem. Soc.*, 87, 3289 (1965), and references therein.

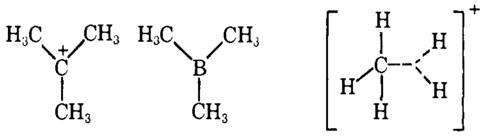
(34) (a) G. A. Olah, G. Klopman, and R. H. Schlosberg, *ibid.*, **91**, 3261 (1969); (b) A. Gamba, G. Korosi, and M. Simonetta, *Chem. Phys. Lett.*, 3, 20 (1969); (c) W. Th. A. M. Van Der Lugt and P. Ros, *ibid.*, 4, 389 (1969); (d) J. J. C. Mulder and J. S. Wright, *ibid.*, **5**, 445 (1970); (e) H. Kollmar and H. O. Smith, *ibid.*, **5**, 7 (1970); (f) V. Dyczmons, V. Staemmler, and W. Kutzelnigg, *ibid.*, **5**, 361 (1970); (g) A. Dedieu and A. Veillard, presented at the 21st Annual Meeting of the French Physical Chemical Society, Paris, Sept 1970; A. Veillard, personal communication; (h) W. A. Lathan, W. J. Hehre, and J. A. Pople, *Tetrahedron*, 2699 (1970); *J. Amer. Chem. Soc.*, **93**, 808 (1971).

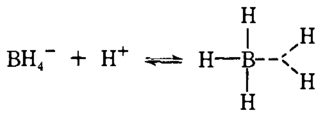
the energy level of the C_{4v} symmetry structure, which in turn is about 8 kcal/mol favored over the trigonal-bipyramidal D_{3h} symmetry structure. Until the superacid solution chemistry of CH_5^+ was published[30,34a] and the suggestion for the "front-side" protonated C_s symmetry form was made, all available theoretical calculations on CH_5^+ (see references cited in ref 30a) considered it as the trigonal-bipyramidal D_{3h} symmetry species. (The only experimental evidence at that time was the mass spectrometric observation of CH_5^+). As it turned out, however, from chemical evidence and results of more sophisticated calculations, the trigonal-bipyramidal form is the least favorable.

All theoretical energy calculations relating to the equilibrium geometry of CH_5^+, of course, apply only to the gaseous ion. In solution, solvent effects may possibly change the relative order of calculated stability and modify numerical values of bond lengths and angles, but overall conclusions are not expected to be changed significantly (solvation, for example, may well affect all CH_5^+ forms).

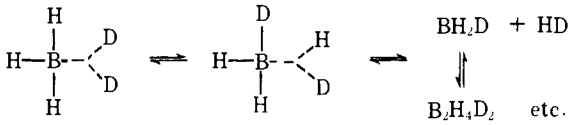
It is indicated, from the extensive amount of recent theoretical work on the methonium ion, that our conclusions[34a] concerning the preferred geometry of CH_5^+ reached from observed chemical reactivity in superacids and calculated by an SCF approximation were correct. At the same time it should also be recognized that ready interconversion of stereoisomeric forms of CH_5^+ is possible by a pseudorotational type process, or as Muetterties recently suggested[35] naming stereoisomerization processes of this type by "polytopal rearrangements" (also called sometimes "polyhedral rearrangements"). We prefer to call intramolecular carbonium ion rearrangements "bond to bond rearrangements" (see subsequent discussion). Hydrogen–deuterium scrambling observed in superacid solutions of deuterated methane[30,34a] strongly indicates such processes.

It is of interest to note that isoelectronic boron compounds can be used as model compounds for both carbenium and carbonium ions. Trimethylboron was used for comparison with the trimethylcarbenium ion[36a] and it is suggested that BH_5 similarly is a suitable model for CH_5^+. BH_5 is indicated in the acid hydrolysis of borohydrides. When the hydrolysis is carried out with deuterated acid not only HD but also H_2 is formed.[36b] This indicates that the attack of D^+ is on the B–H bond, followed by polytopal (bond–bond) rearrangement, before cleavage takes place. The ease with which diborane exchanges hydrogen to deuterium when treated with deuterium gas[36c] also indicates the formation of the three-center bound analog, BH_3D_2.



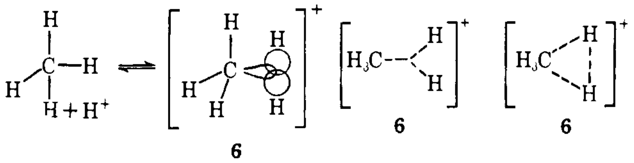


$B_2H_6 \rightleftharpoons 2BH_3 \quad BH_3 + D_2 \rightleftharpoons$



b. Alkonium Ions.

Considering the mechanism of protolytic (and, in general, electrophilic) attack on saturated hydrocarbons, we expressed the view that such reactions will usually take place on the C-H or C-C bonds.[37a-c] The electrophilic reagent will seek out the region of highest electron density. Thus, attack generally will occur, if not otherwise hindered, on the main lobes of the bonds and not on the relatively unimportant back lobes (which usually contain less than 10% of the overall electron density). Protonation of methane can be depicted as the proton coming in onto the C–H bond, forcing the single bond into sharing its electron pair with the electron-deficient reagent. For simplicity it is suggested that, instead of drawing the orbitals, dotted branched lines joining the three atoms should be used to depict the three-center bonds. In the general usage straight lines represent two-center bonds (full lines usually meaning two-electron bonds and dotted lines one-electron bonds). Alternatively, the three-center bonds can also be written by a triangle of dotted lines joining all three atoms. This notion may avoid misunderstandings assuming an atom at the "junction" of the branched dotted line symbols. As, however, by definition a three-center bond joins three atoms and does not usually represent equal bonding character between them (in CH_5^+ the "long bond" indeed indicates CH_3^+ bound to H_2), the former symbol is adopted and its usage may become useful.



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The preferred direction of attack by the electrophile should not be dogmatically considered always to be the same and may well vary from compound to compound (depending on the reaction conditions involved). As the various forms of pentacoordinate carbon do not differ very much in stability (as in CH_5^+, with the "back-side" substitute trigonal-bipyramidal form considered least favorable), it is unlikely that there is any "inherently" preferred pathway; it will depend on the individual reaction conditions. Carrying out electrophilic reactions on optically active hydrocarbons thus may not necessarily always lead to retention of optical configuration, and other stereochemical behavior should also be possible. Such reactions are presently being studied in our laboratories and will be reported.

It should be emphasized that if steric interference (as is the case in the interaction of tertiary C–H bonds in

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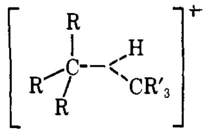
(35) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969).

(36) (a) G. A. Olah, J. R. DeMember, A. Commeyras, and J. L. Bribes, *ibid.*, **93**, 459 (1971), and references given therein; (b) R. E. Mesmer and W. L. Jolly, *Inorg. Chem.*, **1**, 608 (1962); G. A. Olah, P. Westerman, Y. K. Mo, and G. Klopman, *J. Amer. Chem. Soc.*, in press; (c) A. N. Webb, J. T. Neu, and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1007 (1949).

(37) (a) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Amer. Chem. Soc.*, **93**, 1251 (1971); (b) G. A. Olah and J. A. Olah, *ibid.*, **93**, 1256 (1971); (c) G. A. Olah and H. C. Lin, *ibid.*, **93**, 1259 (1971).

isoalkanes with tertiary carbonium ions) is substantial, the formation of the three-center bond from the front side can only be highly unsymmetrical (A), but still is not necessarily considered to be linear, (B), *i.e.*, to lie along an extension of the interacting bond.[37b]



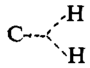
A

$[R_3C\text{--}H\text{--}CR'_3]^+$

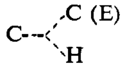
B

It should be noted that if we are dealing with carbonium ion type transition states leading to products (alkanes and alkylcarbenium ions) and not with stable carbonium ion intermediates, the transition states of course never can be completely symmetrical. Throughout this paper carbonium ions will be put in brackets when at the present time they have not been directly observed and therefore can be considered only as transition states or relatively unstable ions. This does not exclude, however, the possibility that in some cases such intermediate carbonium ions could not exist (under favorable conditions). Future work will help to decide whether improved experimental methods can be found to observe carbonium ions of lesser stability.

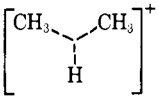
When a C–H bond is protonated a two-electron three-center bond



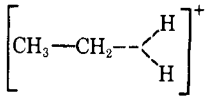
is formed in which two of the ligands are hydrogen (in CH_5^+, etc.).



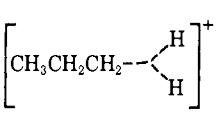
(E depicting a general electrophile) bonded carbonium ions are formed by electron sharing of C–C bonds with protons or electrophiles like carbenium ions,[37b] nitronium ions,[37c] halogen cations,[1c] etc. Ethane can be protonated either on the C–C or C–H bonds.[36a] Thus, the isomers of $C_2H_7^+$ are the C- and H-ethonium ions (**16a,b**). (See Appendix for systematic naming of carbocations; as one of the bonding atoms in hydrocarbons is always a carbon atom, C or H denotes C–C or C–H bond coordination.) Propane can be protonated on the secondary or primary C–H bonds or on the C–C bonds. The possible isomers thus are H-1- and H-2-proponium and C-proponium ions (**17a–c**).



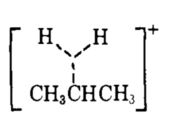
C-ethonium ion
16a



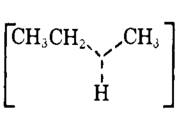
H-ethonium ion
16b



H-1-proponium ion
17a

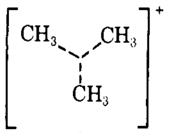


H-2-proponium ion
17b



C-proponium ion
17c

Another isomeric proponium ion, indicated by methylation of ethane with $CD_3F\text{–}SbF_5$ giving in the alkylation products some 1,1,1-trideuterioethane, is the symmetrical C-ethanemethonium ion[38a] (**18**) with a three-center carbon bond. Similar three-center bonds



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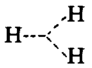
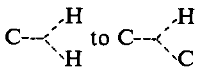
are also indicated in alkyl-bridging processes and in the recently observed C–C bond alkylation of alkanes by alkylcarbenium ions (alkylolysis). H_3^+ observed in mass spectrometry and indicated in our previous work on H–D exchange of H_2 and D_2 in superacids[38b] is, of course



the three-center, two-electron bond case.

We discussed previously bond–bond rearrangement of the isomeric methonium ions. It should be pointed out that the higher isomeric alkonium ions also can undergo similar interconversions. These can, however, involve more deeply seated reorganization of nonequal bonds



Thus, the question of whether primary protonation or electrophilic attack involves a specific C–H (tertiary, secondary, or primary) or C–C bond becomes less important. No formalistic differentiation between energetically quite similar possibilities is necessary. Products obtained in carbocation processes can be well explained by assuming ready intramolecular rearrangement processes (bond–bond rearrangements) between energetically close carbonium ion forms, supplementing well-known rearrangements of trivalent carbenium ions.

c. Cycloproponium Ions.

Cyclopropane, based on the foregoing concepts, can be considered protonated (for reviews see ref 39) either on the electron-rich bent C–C bond or, less probably, on the C–H bond. The resulting protonated cyclopropanes would be the C-cycloproponium (**19a**) and H-cycloproponium ions (**19b**). The methyl-bridged form, **20**, of protonated cyclopropane processes is not considered to be directly formed in the protonation of cyclopropane, but results from rearrangements. It contains a three-center carbon bond, formed by methyl bridging from the 1-propenium ion (**21**) involving C–C bond delocalization. It also can be considered as the ethenemethonium ion. The bridging methyl group is pentacoordinated and the methylene carbons are tetracoordinated (see subsequent discussion).

Protonated cyclopropane equilibration can thus be depicted to involve equilibration through C-cycloproponium ion followed by proton shift to H-cyclopropo-

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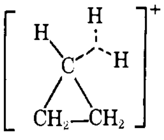
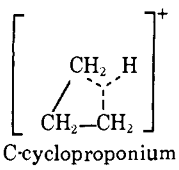
(38) (a) G. A. Olah, J. R. DeMember, and R. Schlosberg, to be published; (b) G. A. Olah, J. Shen, and R. Schlosberg, *J. Amer. Chem. Soc.*, **92**, 3831 (1970).

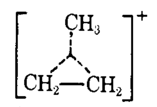
(39) C. C. Lee, *Progr. Phys. Org. Chem.*, 7, 129 (1970); J. L. Fry and G. J. Karabatsos in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 521–571.



H-cycloproponium ion, **19b** (corner-protonated cyclopropane)

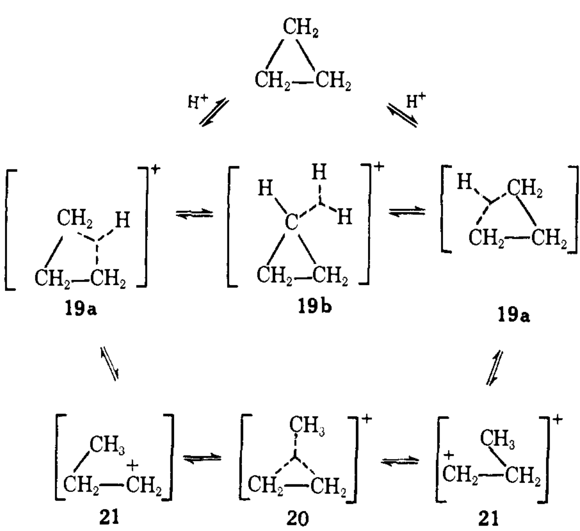


C-cycloproponium ion, **19a** (edge-protonated cyclopropane)



C-ethenemethonium ion, **20** (methyl bridged)

nium ion and again to C-cycloproponium ion (on the other edge), or the methyl-bridged species (ethylenemethonium ion).

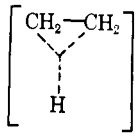


It should be mentioned that no direct interconversion of cycloproponium ions (**19a,b**) with the methyl-bridged ion **20** seems likely, without going through some form of the 1-propenium ion. Pople and Schleyer calculated[40] possible forms of the $C_3H_7{}^+$ ions by an *ab initio* method and found besides the isopropyl cation an energy minimum for a partially methyl-bridged ion with a CCC bond angle of 83°. Primary carbenium ions clearly (even more than secondary or tertiary ones) try to stabilize by delocalization. Whenever possible such delocalization will lead to bridged or partially bridged forms representing energy minima. The low-activation energies of overall protonated cyclopropane equilibration processes indicate that the energies of the different forms involved cannot be too far from each other. As H-cycloproponium ion **19b** in all probability would represent a rather high-lying transition state,[40] it is possible to visualize one edge-protonated form **19a** converting into another not going through the corner-protonated form (H-cycloproponium ion), but instead through the methyl-bridged form **20** (which, however, necessitates involvement of a form of 1-propenium ion **21**). "Face"-protonated cyclopropane seems to have little physical reality.

Similar considerations can be applied to the question of protonated notricyclenes and bicyclobutanes.

d. Alkenonium Ions.

The discussed ethenemethonium ion **20** calls attention to an important class of carbonium ions, in which *tetracoordinated carbonium* atoms are present. We encounter this type of ion when the carbonium atoms are bound to four atoms (at least one of which is carbon) by three two-electron σ bonds and a two-electron, three-center bond, which involves bonding to the same carbon atom to which there is also single bonding. The parent of this type of tetracoordinated carbonium ions can be considered the etheneprotonium ion (C-ethenonium ion, **22**). The etheneprotonium ion, as a transition state, must be considered involved in the protonation of ethylene,[41] with the π-electron pair acting as the electron donor. Ions of this type are considered to play an important role in usual electrophilic reactions of π-donor systems (alkenes, alkynes, and π-aromatic systems) and also in bridged "nonclassical" ions.



22

Recent spectroscopic studies[42a] and theoretical calculations[42b] indicate that the C-etheneprotonium ion **22** and related alkenonium ions are not intermediates, but should be considered only as transition states in the alkene–proton interactions leading to trivalent alkylcarbenium ion intermediates (see subsequent discussion).

The well-known Ag^+ complexes of olefins[43a] and recently observed alkenemercurinium ions[43b] may have a somewhat similar bonding nature. With the heavier metal atoms, however, the nature of overlap is quite different and d electrons can also be involved in additional bond formations with the antibonding MO of the olefin. Therefore, these ions are generally stable and can be directly studied by spectroscopic methods (for example, nmr) or even isolated in many instances.

e. Norbornyl Cations.

The aliphatic carbonium ions discussed so far are indicated by the superacid chemistry of their relevant hydrocarbons (σ donors) and by the extensive literature of electrophilic reactions of cyclopropane and olefins (as well as other π-donor systems). Alkonium ions are observed in mass spectrometry as some of the most abundant ions of alkanes and they are known in certain molecule–ion reactions in the gas phase, but no direct observation in solution was so far achieved.

More rigid cycloaliphatic, particularly bicyclic systems, provide examples of directly observable, stable carbonium ions.[44,45]

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(40) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 1813 (1971).

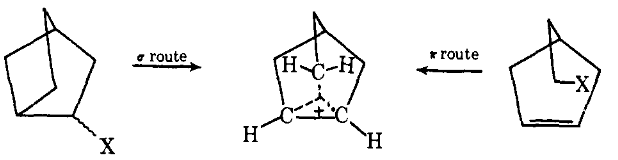
(41) R. W. Taft, Jr. (*ibid.*, 74, 5372 (1952)), seems to be the first to have suggested the initial formation in the acid-catalyzed hydration of isobutylene of a proton π complex, of the type described originally by M. J. S. Dewar (*J. Chem. Soc.*, 406 (1946); *Bull. Soc. Chim. Fr.*, C75 (1951)) in which "...the proton is embedded in the π-orbitals which extend above (or below) the plane of the C–C double bond."

(42) (a) G. A. Olah, J. R. DeMember, A. Commeyras, and J. L. Bribes, *J. Amer. Chem. Soc.*, **93**, 459 (1971); (b) J. E. Williams, Jr., V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **92**, 2141 (1970); G. V. Pfeiffer and J. G. Jewett, *ibid.*, **92**, 2143 (1970).

(43) (a) For reviews, see L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964; M. Cais in "The Chemistry of Alkenes," Vol. I, S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1964, pp 335–385; (b) G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, **93**, 1261, 2320 (1971).

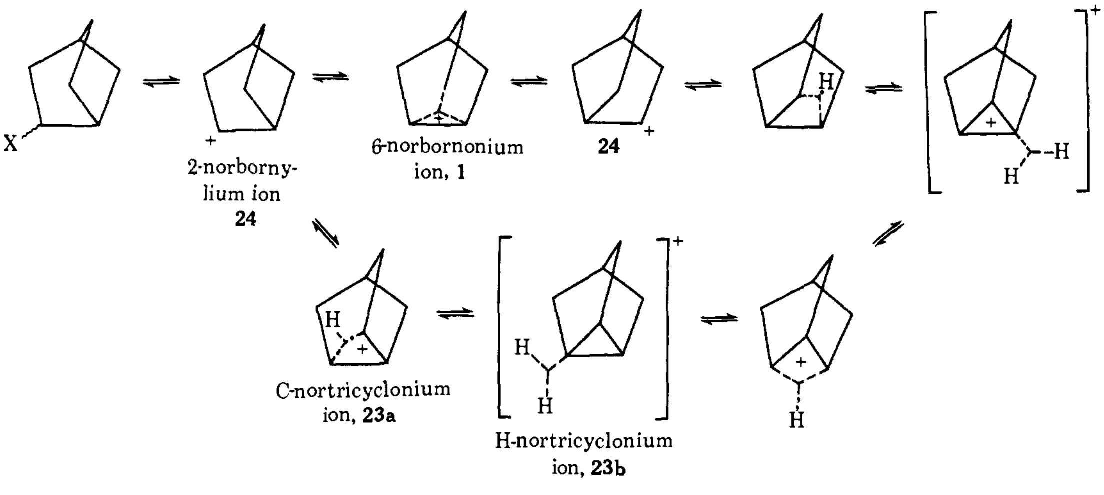
(44) (a) See lectures by S. Winstein and G. A. Olah, 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June, 1969; (b) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 6883 (1969); (c) P. R. Story and M. Saunders, *ibid.*, 84, 4876 (1962); L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. L. Kornegar, *ibid.*, **85**, 3630 (1963); (d) R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **89**, 6350, 6352, 6354 (1967); (e) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966); (f) H. G. Richey, Jr., and R. K. Lustgarten, *ibid.*, **88**, 3136 (1966).

The most disputed of nonclassical carbonium ions, the 2-norbornyl cation **1** (6-norbornonium ion, see Appendix for naming of carbocations), can be generated under long-lived ion conditions and at low temperature.[6a] At −150° it exists in a nonrearranging and nonexchanging static form. ^{1}H and ^{13}C nmr spectroscopy (Table I) indicate that the bridging pentacoordinated methylene carbon atom is tetrahedral in nature and carries little charge. The methine carbons, to which bridging takes place, are tetracoordinated, the charge delocalized mostly into the methine bonds. The nmr spectrum (−156°) is the first experimental observation of a nonclassical carbonium ion formed by C–C σ-bond delocalization, *i.e.*, the σ route to the symmetrically delocalized ion. It should also be emphasized that the same ion is observed when generated by the alternate π route from β-Δ^3-cyclopentenylethyl halides.



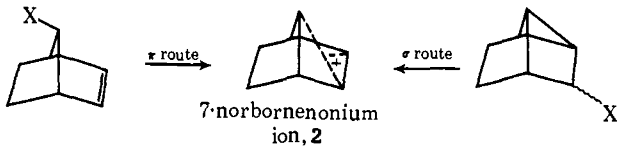
Superacid solutions of the norbornyl cation above −130° show equilibration assumed to involve a protonated nortricyclene-like system[6a] **23**. By cooling the solution below −150° the static, nonclassical norbornyl cation ($C_{1,2}$-norborn-6-onium ion, **1**) can be frozen out. Its methylene-bridged structure contains, similarly to the C-ethenemethonium ion, a three-center carbon bond and was unequivocally established by ^{1}H and ^{13}C nmr and Raman spectroscopy. X-Ray-induced photoelectron spectroscopy, with no time scale problem in the chemical sense, also gave clear indication for the nonclassical carbonium ion nature. No high binding energy, electron-deficient carbenium center is observed in the 1s core electron spectrum, ruling out any possibility of a classical ion system.

The formation of protonated nortricyclenes **23a,b** in a superacid solution of a 2-norbornyl system (and related precursors) must first go through a trivalent 2-norbornylium ion **24** similar to 1-propenium ion **21** involvement in protonated cyclopropane equilibrations.

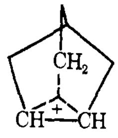


6,2,1-Hydride shifts can take place through the nortricyclonium ions, but the Wagner–Meerwein shift takes place only through C–C bond delocalization, *i.e.*, the norbornonium ion. Other examples of directly observed long-lived carbonium ions in which the tetra- and/or pentacoordinated carbons were identified by ^{13}C and ^{1}H nmr spectroscopy are the 7-norbornenyl cation **2** and 7-norbornadienyl cation[44] **3**.

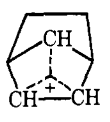
Winstein[44e] and Richey[44f] showed that the 7-norbornenyl cation **2** can be obtained through both the σ and π routes.



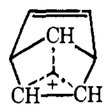
The carbonium carbon in the norbornyl ion **1**, 7-norbornenyl ion **2**, and 7-norbornadienyl ion **3** are similar and related to the ethylenemethonium ion **20**, although strain differences in the ions are obviously significant.



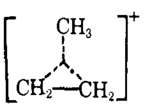
1



2



3



20

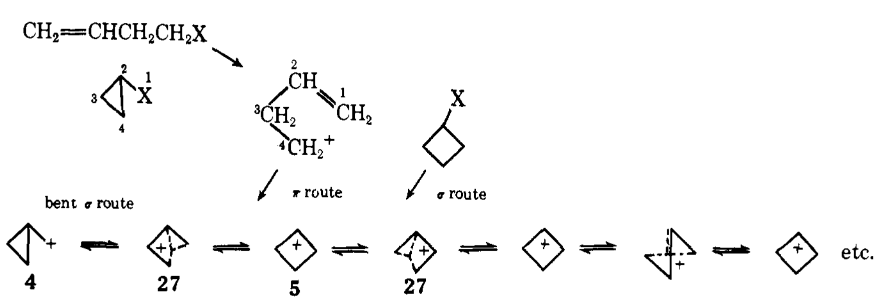
It is now clear that the original views of Winstein[45] on the nonclassical nature of the norbornyl cation, based on kinetic and stereochemical results, were fully substantiated through the direct spectroscopic studies of the long-lived norbornonium ion.[6a]

Study of long-lived 2-alkylnorbornyl cations (methyl, **25**, and ethyl, **26**) by ^{1}H and ^{13}C nmr and photoelectron spectroscopy gave evidence for the partially delocalized (nonclassical) nature of these ions. As stated, trivalent "classical" and tetra- or pentacoordinated "nonclassical" carbocations are only limiting and division of ions into these categories is frequently arbitrary. Intermediate degrees of delocalization of trivalent carbenium ions into partially delocalized carbonium ions indeed can frequently be encountered, and the 2-methylnorbornyl cation **25** is an example of direct spectroscopic observation of such an ion.

f. Cyclopropylcarbinyl and Cyclobutyl Cations.

In the cyclopropylcarbinyl–cyclobutyl–allylcarbinyl

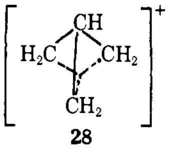
(45) S. Winstein, *et al.*, *J. Amer. Chem. Soc.*, 71, 2953 (1949); 74, 1154 (1952); 87, 381 (1965), and intervening papers. Also for a summary, S. Winstein, *Quart. Rev., Chem. Soc.*, 23, 141 (1969).



system, extensive study of solvolytic reactions by Roberts,[46] Wiberg,[47] and others, as well as recent spectroscopic investigation of the long-lived ions in super acids,[6b,48a] established the nonclassical nature of the common ions. Rapid equilibration between the so-called unsymmetrical bicyclobutonium ions **27** is in agreement with all data.

Allylcarbinyl precursors represent the π route (as the cyclopentenylethyl precursors do in the case of the norbornyl cation) compared to the cyclobutyl and cyclopropylcarbinyl σ (or bent σ) route.

As in the case of the 1-propenium ion–cycloproponium ion–ethylenemethonium ion systems, the cyclopropylcarbinyl–cyclobutyl cation system also could be considered to undergo C–H as well as C–C bond delocalization. This process, however, would equilibrate all protons (and carbons) if the bridgehead bicyclobutane methine group could be involved in H- as well as 1,3-C-bicyclobutonium ion formation. Experimental facts are to the contrary. Considering also the orbital symmetry of the system it is concluded that the electron-rich and well-oriented C_2–C_3 and C_2–C_4 bonds and not the C–H bonds are involved in carbonium ion type three-center bond formation. Whereas (sp) overlap with the C_3–C_4 bond may be symmetry allowed, the tetrahedrene-like geometry which would develop would be too strained and prevents the C_3–C_4 bond from participating (as evidenced by the methine group not taking part in the equilibration processes). This explains why the symmetrical tricyclobutonium ion **28** is not formed.

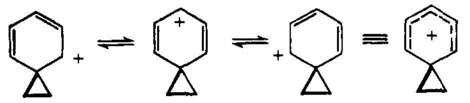


28

In the rapidly equilibrating cyclopropylcarbonium ion system the three-center bonding always involves a pentacoordinated and two tetracoordinated carbonium carbon atoms, similar to the previously discussed norbornium **1** ion and norbornenonium **2** or **3** ions.

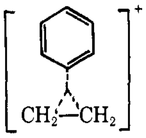
g. Ethenebenzenium Ions.

The classical–nonclassical ion controversy[32] also frequently included the question of the so-called ethylenephenonium ions. Cram's extensive original studies[49] established, based on kinetic and stereochemical evidence, the symmetrically bridged ionic nature of β-phenylethyl cations in solvolytic systems. Spectroscopic studies (particularly pmr and cmr) of the stable long-lived ions proved the symmetrically bridged structure[50] **29**, and at the same time showed that these ions do *not* contain a pentacoordinated carbonium ion center (thus are not "nonclassical ions"). They are ethenebenzenium ions or spiro[2.5]octadienyl cations (spirocyclopropylbenzenium ions), or in other words, cyclopropylcarbinyl cations in which the carbenium center belongs to a cyclohexadienyl cation (benzenium ion).



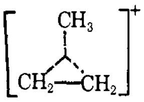
29

The nature of the spiro carbon atom is of particular importance in defining the carbocation nature of the ions. Cmr spectroscopic studies clearly established the aliphatic tetrahedral nature of this carbon, thus ruling out a "nonclassical" pentacoordinated carbonium ion. If such an atom would indeed be present in a nonclassical ethylenephenonium ion **30**, it should be involved in three-center carbon bond formation similar to the previously discussed ethenemethonium ion **20**. In the ethenephenonium ion an aromatic type sp^2-hybridized carbon would be involved in bridging (probably with a less favorable overall geometry).



30

ethylenephenonium ion
(bridging carbon sp^2 hybridized)



20

ethylenemethonium ion
(bridging carbon sp^3 hybridized)

The formation of the ethenebenzenium ion **29** from β-phenylethyl precursors thus simply can be depicted as cycloalkylation of the aromatic π system and not of the C_{Ar}–C_α bond which would give the tetracoordinated ethylenephenonium ion. Rearrangement of β-

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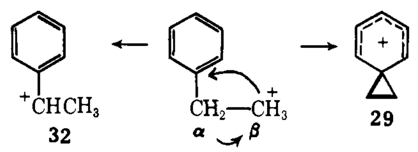
(46) J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, 73, 3542 (1951); R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

(47) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968); K. B. Wiberg and G. Szemies, *J. Amer. Chem. Soc.*, 90, 4195 (1968), and for a review see K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, in "Carbonium Ions," Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., in press.

(48) J. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, **94**, 146 (1972).

(49) D. J. Cram, *ibid.*, 71, 3863 (1949), and subsequent publications; for a critical review, D. J. Cram, *ibid.*, **86**, 3767 (1964).

(50) (a) G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsay, *ibid.*, 89, 5259 (1967); (b) G. A. Olah, M. B. Comisarow, and C. J. Kim, *ibid.*, **91**, 1458 (1969); (c) G. A. Olah and R. D. Porter, *ibid.*, 92, 7267 (1970); **93**, 6877 (1971).

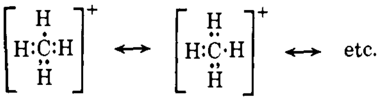


32 31 29

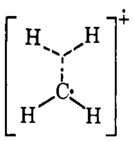
phenylethyl **31** to α-phenylethyl (styryl **32** ions on the other hand is a regular 1,2-hydrogen shift involving the C_α-H bond.

h. Alkanium Ions.

To complete the discussion of carbonium ions it should be mentioned that carbon radical cations, of which the methanium ion, $CH_4\cdot^+$ (**33**), is parent (well known in mass spectrometry and in radiation chemistry[51]), can be considered as carbocations with a coordination number of 4, and have a one-electron bond resonance structure. The methanium ion, as indicated by theoretical calculations,[52] has a distorted (by Jahn–Teller effect) tetragonal configuration with two energy minima in the potential energy surface. An additional energy minimum configuration for the ion can be suggested, based on the calculations of Olah and Klopman,[53] by considering it distorted all the way into a tetracoordinated radical cation **34**. This configuration will have two single C–H bonds, a two-electron three-center bond with the two hydrogens involved in this bond freely rotating around the sp^2 carbon orbital, with the remaining lone electron located in the p_z carbon orbital. The hydrogen atom abstracting ability of $[CH_4\cdot^+]$ in ion–molecule reactions like $[CD_4\cdot^+] + C_3H_8 \rightarrow [CD_4H^+] + C_3H_7\cdot$ and the ease and extent of the formation of $[CH_2\cdot^+]$ from $[CH_4\cdot^+]$ under mass spectrometric conditions also indicate contribution of the three-center bound, lone-electron structures.



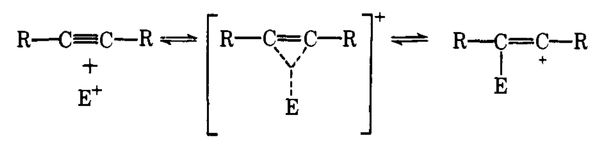
33



34

i. Alkynonium Ions.

Finally, it can be pointed out that tricoordinated carbonium ions could also exist. Electrophilic reactions of alkynes (acetylenes) can be considered to involve π-electron pair donation into the vacant orbital of the electrophile leading to tricoordinated carbonium ion (alkynonium ions) (the two-carbon atoms involved in the three-center bond are also bound by a double bond). No examples of long-lived alkynonium ions are known at present and substantial ring strain makes it improbable that they will be stable. A somewhat related complex, the ethynemercurinium ion, was suggested (but not observed) in the Hg^{2+} catalyzed hydration of acetylene.[54]



R = H or alkyl
E = electrophile

Conclusions and the Role of Carbocations in Electrophilic Reactions

The differentiation of trivalent ("classical") carbenium ions from penta- or tetracoordinated ("nonclassical") carbonium ions, based on spectroscopic observation of long-lived ions showing marked differences, for example in their nmr spectra, should put an end to much of the controversy surrounding the structure of carbocations, *i.e.*, the so-called "classical–nonclassical ion controversy."[32] In defining limiting categories of carbocations of course it must be clearly understood that there exists the possibility of a whole spectrum of ions of intermediate degrees of delocalization (or partial "nonclassical" nature) and therefore division in strictly limiting categories frequently is arbitrary. Whereas the norbornyl cation itself, for example, is a completely symmetrically delocalized nonclassical carbonium ion, the 2-methylnorbornyl cation shows partial delocalization. The definition of the general carbocation concept also allows an understanding of electrophilic reactions involving not only π- or σ-donor substrates (nucleophiles) but also σ-donor systems.

Electrophilic reactions of hydrocarbons generally should be considered taking place at the respective bonds and not at individual atoms. It is in the bonds (σ C–C or C–H bonds or π C═C or C≡C bonds) where the major electron densities reside. This does not necessarily indicate a single preferred direction of attack, as specific conditions, including steric effects, of individual systems will define the exact mode of interaction.

Although π bonds are obviously stronger electron donors than σ bonds there is no fundamental difference in the nucleophilic donor reactivity of π and σ bonds. They both act as electron donors forming initially, *via* overlapping with the empty orbital of the electrophiles, two-electron three-center bonds characteristic of carbonium ions. One significant difference besides the easier availability of the π-electron pair is, that when a σ bond is the electron donor, there is no unaffected covalent bonding left between the two atoms of the original bond. Consequently cleavage of the three-center bond, in the latter case, also means cleavage of the original σ bond. Not only C–H but also C–C bond substitutions can take place, the latter with cleavage of the original C–C bond. In the case of a π bond acting as electron donor, the σ bond binding the same two atoms is maintained and consequently cleavage of the three-center bond only results in substitution or addition products, although subsequent intramolecular reaction of another σ bond (preferentially in the β-position) with the formed carbenium ion center can result in σ bond cleavage.

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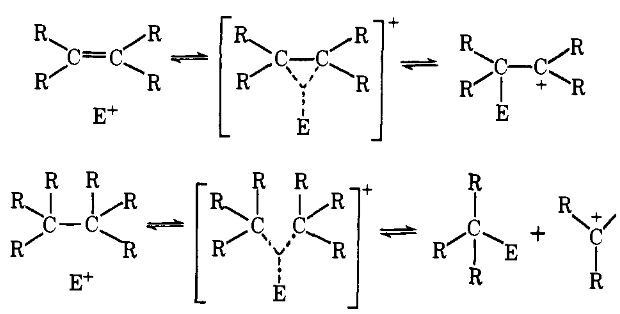
(51) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press, New York, N. Y., 1963.

(52) (a) C. A. Coulson and H. L. Strauss, *Proc. Roy. Soc., Ser. A*, **269**, 443 (1962); (b) J. Arents and L. C. Allen, *J. Chem. Phys.*, **53**, 73 (1970); (c) F. A. Grimm and J. Godoy, *Chem. Phys. Lett.*, **6**, 36 (1970); (d) R. N. Dixon, *Mol. Phys.*, 20, 113 (1971); (e) W. A. Lathan, W. J. Hehre, and J. A. Pople, **93**, 808 (1971).

(53) G. A. Olah and G. Klopman, *Chem. Phys. Lett.*, **11**, 604 (1971).

(54) J. March, "Advanced Organic Chemistry," McGraw-Hill New York, N. Y., 1968, p 583.



R = H or alkyl

If the involved bonds are not symmetrically substituted, formation of the two-electron three-center bond will be more unsymmetrical, oriented according to electronic (and/or steric) effects of the substituents. Direction of cleavage of the three-center bond is thus also predetermined, not only in π-donor systems (in accordance with the empirically long recognized Markovnikov rule) but also in σ-donor systems and can be predicted.

In the limiting case we approach the interaction with lone-pair donors which react with electrophiles at individual atoms and not at the bonds.

The ability of π and σ bonds to participate in intramolecular carbonium ion formations through forming two-electron three-center bonds is usually much dependent on overall geometry and orientation of the involved bonding orbitals in relationship to the vacant p orbital on the carbenium ion center. Only suitably oriented bonds within reasonable bonding distance can overlap. Increased p character of the carbon atomic orbitals involved generally facilitates delocalization, showing the continuum going from π to bent σ to σ bonds. In intermolecular carbonium ion formation reactions orbital orientation obviously plays a lesser role (assuming relatively free rotation) and steric considerations become increasingly important.

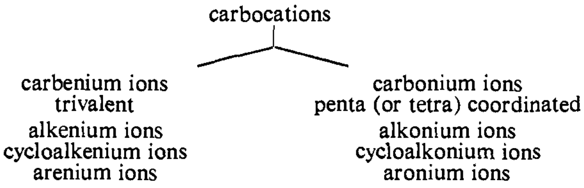
The mechanistic concepts of electrophilic hydrocarbon reactions, realizing the importance of trivalent carbeium ions, were laid down by the pioneering work of Meerwein, Ingold and Hughes, Whitmore, Winstein, Bartlett, Nenitzescu, and many other investigators. These concepts can now be substantially extended with the realization of the importance of penta- and tetracoordinated, three-center bound carbonium ions.

The realization of the electron donor ability of shared (bonding) electron pairs, including those of single bonds, should rank one day equal in importance with that of unshared (nonbonding) electron pairs recognized by Lewis.[55] We can now not only explain the reactivity of saturated hydrocarbons and in general of single bonds in electrophilic reactions, but indeed use this understanding to explore new areas of carbocation chemistry.[1c,36]

Acknowledgment. Our work on carbocations was possible through grants by the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the National Institutes of Health, and the C. F. Mabery Fund of Case Western Reserve University. Stimulating discussions with many colleagues, particularly with Professors Paul von R. Schleyer and Gilles Klopman, are gratefully acknowledged. My particular thanks go to all members of my research group (past and present) whose enthusiastic hard work really made our work possible. Individual references give credit to their work.

Appendix

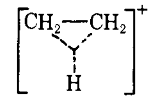
Suggested Systematic Naming of Carbocations (In Accordance with IUPAC Rules of Nomenclature).[56] As discussed in the foregoing paper on the general concept of carbocations (the logical and systematic name for all cations of carbon compounds[2]), we differentiate trivalent carbenium ions from penta- or tetracoordinated carbonium ions. The systematic name for trivalent alkyl (cycloalkyl) cations is alkenium (cycloalkenium, arenium) ion, while that for penta- or tetracoordinated alkyl cations is alkonium (cycloalkonium, aronium) ion.


carbocations

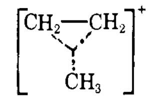
carbenium ions	carbonium ions
trivalent	penta (or tetra) coordinated
alkenium ions	alkonium ions
cycloalkenium ions	cycloalkonium ions
arenium ions	aronium ions

In the systematic naming of carbocations it is necessary to identify, by the usual convention of numbering, the carbocation centers. Trivalent carbenium ions generally cause no difficulty as the position of the carbenium carbon atom can be specified, if needed, by placing the appropriate locant before the ending "ium." In the case of carbonium ions, however, the three-center bond can be formed either by C–H or C–C bond coordination with an electrophile. Accordingly, the prefix H or C is used to denote the participating bond (one of the atoms of the bond is always carbon and must, therefore, not be indicated).

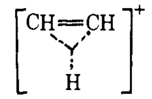
The following examples are typical (Table II). Bridged alkene carbonium ions are the alkenonium ions. Hydrogen-bridged carbonium ions contain tetracoordinated carbonium atoms and can be considered the parent alkenonium ions or alkeneprotonium ions. Carbon-bridged carbonium ions similarly are alkenalkonium ions (alkenaronium). There also exists the tricoordinated bridged ion, alkynonium ion. Carbon-



C-etheneprotonium ion
C-ethenonium ion



C-ethenemethonium



C-ethynonium ion

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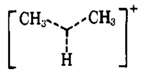
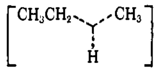
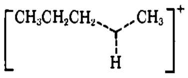
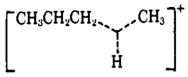
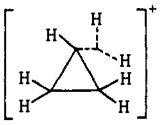
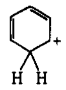
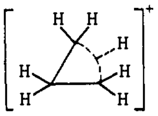
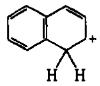
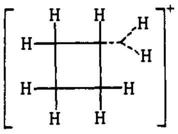
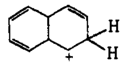
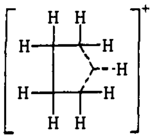
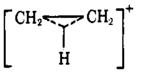
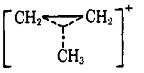
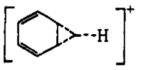
(55) G. N. Lewis, *J. Amer. Chem. Soc.*, 38, 762 (1916); G. N. Lewis, "Valence and Structure of Atoms and Molecules," Chemical Catalog Corp., New York, N. Y., 1923.

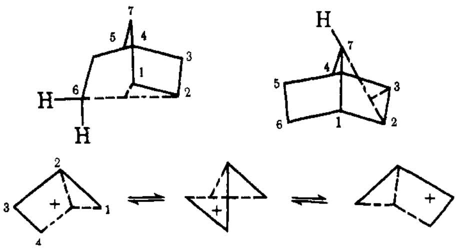
(56) The suggested nomenclature is that of the author and publication does not represent approval by the journal, nor acceptance by the nomenclature comittees of the American Chemical Society or IUPAC. It is the author's hope that these committees will review the suggested nomenclature of carbocations.

Table II

Alkenium ions		Alkanium ions	Alkonium ions	
CH_3^+	methenium	CH_4^+ methanium	$[CH_5]^+$	methonium
$CH_3CH_2^+$	ethenium	$C_2H_6^+$ ethanium	$[CH_3CH_4]^+$	H-ethonium
				C-ethonium
$CH_3CH_2CH_2^+$	1-propenium			
$CH_3\overset{+}{C}HCH_3$	2-propenium		$[CH_3CH_2CH_4]^+$	1-H-proponium
$CH_3CH_2CH_2CH_2^+$	1-butenium		$[CH_3\overset{+}{C}H_3CH_3]$	2-H-proponium
$CH_3CH_2\overset{+}{C}HCH_3$	2-butenium			C-proponium
$(CH_3)_2CHCH_2^+$	2-methyl-1-propenium		$[CH_3CH_2CH_2CH_4]^+$	1-H-butonium
$(CH_3)_3C^+$	2-methyl-2-propenium		$[CH_3CH_2\overset{+}{C}H_3CH_3]$	2-H-butonium
				1-C-butonium
				2-C-butonium

Cycloalkenium ions		Cycloalkonium ions	
	cyclopropenium		H-cycloproponium
	cyclobutenium		
	cyclopentenium		
	benzenium		C-cycloproponium
	2-naphthalenium		H-cyclobutonium
	1-naphthalenium		C-cyclobutonium
			C-ethenonium (C-etheneprotonium)
			C-ethenemethonium
			C-benzonium (C-benzenonium)

bridged alicyclic carbonium ions (the most studied "nonclassical" ions) represent a more severe naming problem. It is suggested that the bridging carbon with highest coordination number (*i.e.*, pentacoordinated) should be depicted with the onium suffix, the carbons to which bridging takes place (generally tetracoordinated) indicated by the usual numbering system employed in identifying specific bonds, for example in unsaturated systems. For example, see below.



Due to the present wide acceptance of naming all carbocations as "carbonium ions," an interim period of nomenclature seems inevitable. We find, however, the use of at least "trivalent" and "penta-" or "tetracoordinated" prefixes necessary. When using only the suffix "cation" we should also differentiate, when necessary, trivalent and penta(tetra)coordinated cations. In the systematic naming of carbocations we urge the adoption of the classification of belonging either to carbenium or carbonium ions and their naming in accordance with the general rules of the IUPAC system of naming organic compounds.

The Acidities of Polyfluorinated Hydrocarbons. I. Aryl-Substituted 2-Hydro-2-phenylhexafluoropropanes. Intermediate Carbanion Stability and Geometry

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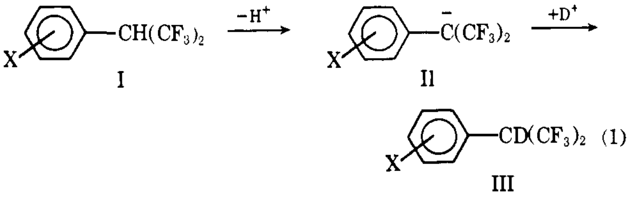
Abstract: Fluorinated hydrocarbon acidities have been studied by base-catalyzed hydrogen, deuterium, and tritium isotope exchange kinetics with a series of phenyl-substituted 2-hydro-2-phenylhexafluoropropanes. A 50:50 mol% solution of dimethyl sulfoxide (DMSO-d_6) and methanol-*O-d* was used as solvent, and triethylamine served as base catalyst. Methoxide ion formed *in situ* probably acts as the true active catalyst, however. Data interpretation indicates several things: (a) fluorine hyperconjugation is not important as a stabilization mechanism for the intermediate fluorocarbanions, (b) polarizability and induction are most important, and (c) a $^+$R carbanion destabilizing mechanism is important for nearly all substituents, especially fluoro and methoxy. The geometries of the intermediate carbanions are also considered.

Quantitative studies of carbanions normally are carried out by kinetic analysis of hydrogen isotope exchange of the "carbon acids." The intermediate carbanion stabilities frequently are proportional to the acidities determined.[2] In fluoroorganic chemistry carbanions are quite common as reaction intermediates, and so fluorocarbons have received close attention. Additionally, fluorocarbanion stabilities increase or decrease depending on the relative positions of fluorine and negative charge. In light of the high electronegativity of fluorine, the latter effect seems quite unique. Thus, perfluoroalkyl groups are very capable of carbanion stabilization,[3] while fluorine α to a carbanion site can destabilize the site over and above that of hydrogen itself.[4] Still, many aspects of fluorocarbanion stabilization are unclear for several reasons. First, there have been so many carbanion stabilization mechanisms proposed[2,5,6] that it is difficult to choose the most important ones. Second, carbanion geometries, steric effects, and β-fluoride ion elimination reactions have been little studied. Also, a clear picture of the destabilization mechanism has not been obtained.

Our system, I, was chosen for study so that complications of steric factors in the formation of II could be eliminated, and the geometry of II would, for the most part, remain the same. Isotope effects were determined by examination of the reverse exchange (III → I). The solvent–catalyst system employed allowed interconversion between I and III without fluoride ion eliminations and other complications from II.



a, X = H
b, X = m-Br
c, X = p-Br
d, X = m-Cl
e, X = p-Cl
f, X = m-CN
g, X = p-CN
h, X = p-N(CH$_3$)$_2$
i, X = m-F
j, X = p-F
k, X = m-CF(CF$_3$)$_2$
l, X = p-CF(CF$_3$)$_2$
m, X = m-I
n, X = p-I
o, X = p-CH$_3$
p, X = m-OCH$_3$
q, X = p-OCH$_3$
r, X = m-NO$_2$
s, X = m-CCl$_3$
t, X = p-CCl$_3$
u, X = m-CF$_3$
v, X = p-CF$_3$

Method and Results

Solvent System. The solvent employed in these investigations was a 50:50 mol % mixture of dimethyl sulfoxide (DMSO-d_6) and methanol-O-*d*. The corresponding protio system was employed for the reverse isotope exchanges. In the absence of triethylamine catalyst isotope exchange did not occur to any significant extent. Substrate (protio plus deuterio) did not disappear with time even for "infinite" exchange studies, as determined by glpc. The catalyst did not disappear with time either, and so the rate of exchange did not cease or decrease with time more than would be predicted by the rate law.

Kinetics of Exchange. The rates of hydrogen and deuterium exchange were determined by ^{19}F nmr. Fig-

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[1] NSF Trainee, 1965–1968, and Phillips Petroleum Fellow, 1968–1969. This work was taken from the Ph.D. Thesis of K. J. K., 1969.

[2] For an excellent review, see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, London, 1965.

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[5] J. Hine, R. W. Burske, M. Hine, and P. B. Langford, *ibid.*, **79**, 1406 (1957).

[6] K. J. Klabunde, Ph.D. Thesis, The University of Iowa, 1969.