component must exist; this will be recognized as the essence of the covalent bond. An alternative to the name, "ion pair," might be "extended covalent bond." But this would tend to deemphasize too strongly the charge separation which undoubtedly exists.

We will continue to use the term ion pair, but we would hope that the organic chemical public would recognize that the situation is perhaps better described as "an extended bond with considerable ionic character."

Expressing adequately my indebtedness to and my affection for those coworkers who have contributed toward these studies I find beyond my abilities. They alone can know the extent of their contributions. The names of most of these coworkers are included among the references, but special thanks are due to Henry Weiner, John W. Larsen, Howard M. Robbins, John V. Carter, Michael A. Collins, and William A. Bradley.

Among my Purdue colleagues, H. C. Brown has been especially helpful and stimulating; above all, J. H. Brewster's talent for constructive criticism must be unmatched. Many of his ideas are inseparably tied up with my own in this manuscript. This is not to say that he necessarily agrees with all that I have written.

Evidence for Protonated Cyclopropane Intermediates from Studies of Stable Solutions of Carbonium Ions

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Most organic processes occur *via* one or more reaction intermediates. These intermediate species can be of any structural type. However, in order to *be* intermediates, they must rapidly undergo further reaction under experimental conditions.

The necessary high reactivity often results from some unusual structural feature. Anions, radicals, and cations are quite common as intermediates. Carbenes, triplet states, excited singlet states, and highly strained systems have often been proposed as reaction intermediates in recent years. The significance of the intermediates involved is so great that the study of organic reaction mechanisms is usually organized in accord with the types of intermediate proposed. There are, of course, many interesting reactions which occur *via* single-step processes without intermediates.

Many important reactions occur through intermediate cations. Some require ionic catalysts or reactants, and others occur through ionization of neutral precursors. In some of the cations the positive charge resides on carbon and in some on other elements. Cations in which the major part of the charge resides on carbon have long been called carbonium ions.

Reactions in which carbonium ion intermediates rearrange are common and have long been studied. Nevertheless, the detailed mechanisms of these rearrangements are still the subject of controversy. Among the possible intermediates and transition states considered for these rearrangements are cations containing three-membered rings with seven substituent atoms or groups, thus having structures which might arise from the addition of a proton to a cyclopropane ring. Such structures are logically invoked in considering the common Wagner-Meerwein 1,2 shift of an alkyl group in carbonium ions (Figure 1). Indeed, one is virtually required to invoke structures of this sort as either transition states or intermediates for these reactions.

There has been considerable argument concerning the bond character of the ring bonds, the possible mode of attachment of the substituents, and the charge distribution in such species, since they are electron deficient and cannot have electron-pair bonds between all connected atoms. However, the most important, and vexing, chemical question is whether these structures are only transition states in rearrangements or whether they can be intermediates in some or all cases. To discuss them without prejudging the structural and energetic uncertainties, we will use, to describe them, the name protonated cyclopropane as a neutral, catch-all term. We will draw them using solid lines for bonds indicating an apparently pentavalent carbon atom in a three-membered ring (Figure 1) even though, because of the electron deficiency, some of the bonds must be partial. Of course, many analogies to these fractional bonds may be found in the structures of electron-deficient boron and aluminum compounds as well as in CH_5^+.

Protonated cyclopropane intermediates have been proposed many times to interpret kinetic and product studies of solvolytic reactions.[1] However, the cations themselves are not stable in these reactions, and evidence for their existence and properties has only been inferred from a study of the products of reac-

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Pierre Vogel received his Ph.D. from the University of Lausanne in 1969 and spent 2 years of postdoctoral research at Yale. Edward L. Hagen and Jerrold Rosenfeld obtained their Ph.D. degrees with Professor Saunders in 1968 and 1969, respectively.

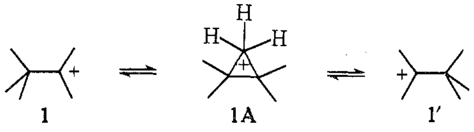

Figure 1.

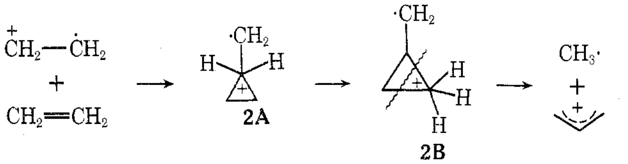

Figure 2.

tion or their rates of formation. Through such studies, one only obtains information about the transition states for the solvolytic or product-forming step. Furthermore, the solvent and/or the counterion often are highly significant factors. It is difficult, therefore, to interpret the results in terms of unambiguous structures for the ionic intermediates. The resulting uncertainty of interpretation has colored and clouded much of the discussion in the literature.

Baird and Aboderin reported the first convincing experimental evidence for the intermediacy of protonated cyclopropane.[2] They treated cyclopropane itself with D_2SO_4 and discovered: (1) exchange yielding monodeuteriocyclopropane and small amounts of dideuteriocyclopropane and (2) the formation of 1-propanol and 1-propyl hydrogen sulfate containing a deuterium atom at the C-1, C-2, or C-3 positions. It is difficult to rationalize these results without invoking a protonated cyclopropane *intermediate* which can undergo rapid intramolecular proton exchange. These findings have been confirmed using deuterated[3] and tritiated[4] acids.

Protonated cyclopropane intermediates may also be involved in reactions occuring in the gas phase.[5,6] A molecular beam study of the reaction between CD_3^+ and ethylene has been observed to yield products which are isotopically scrambled.[7] This result might be explained by proposing protonated cyclopropane as an intermediate which undergoes rapid corner-to-corner hydrogen shifts. The reaction of ethylene cation radical with ethylene[8] could be accounted for with the aid of intermediate **2A**. In this scheme, **2A** undergoes a corner-to-corner migration of a proton, yielding **2B**, which can dissociate directly to methyl radical and an observed $C_3H_5^+$ cation presumed to be the allyl cation.

Differences between a number of appearance potentials for formation of carbonium ions in the mass spectrometer have been found very similar to corresponding energy differences measured in solution.[9] All of these data imply that it would be rewarding to use a common structural and mechanistic framework in discussing data from both media. Solvation energies of ions in solution are certainly large, but *differences* between the solvation energies of different carbonium ions appear to be small.

We discuss here recent results obtained from the study of carbonium ions in solution in nonbasic media where they are stable and can be observed by nmr spectroscopy. We will consider evidence that protonated cyclopropanes are, in fact, intermediates in a number of rearrangements of simple carbonium ions. In addition, we will consider the question of their structures.

Stable Carbonium Ions in Solution

Over the past 20 years, techniques pioneered by Meerwein[10] have made accessible a series of progressively less stable organic cations. Recently, a number of solutions containing simple alkyl carbonium ions have been prepared using general methods developed mainly by Olah,[11] the group at Shell in Holland,[12] and our group at Yale.[13]

In general, tertiary acyclic carbonium ions with up to eight carbon atoms (and many cyclic ones) may be readily prepared and studied in the presence of SbF_5 in inert solvents. The secondary cations isopropyl,[14,15] secondary butyl,[16] and cyclopentyl[17,18] have been well examined. Many conjugated, unsaturated ions have been made, and a number of especially stable systems such as the norbornyl and norbornadienyl cations have been known for some time.

Attempts to prepare primary ions in the same manner have not been successful. Methyl and ethyl fluorides apparently remain un-ionized since they do not give solutions showing the strong downfield nmr shifts indicating ion formation, although they exchange halogen rapidly and the protons interchange in ethyl fluoride. All other simple primary halides give ions resulting from isomerization to more stable secondary or tertiary species.

A substantial body of evidence indicates that carbonium ions are the principal species present in these solutions. Specifically: (1) the large changes in the nmr chemical shifts of the protons and carbon-13 atoms in the ion solutions relative to those in the corresponding alkyl halides agree well with predic-

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(1) (a) C. J. Collins, *Chem. Rev.*, **69**, 543 (1969); (b) C. C. Lee, *Progr. Phys. Org. Chem.*, **7**, 129 (1970); (c) J. L. Fry and G. J. Karabastos in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 4.

(2) R. L. Baird, and A. Aboderin, *Tetrahedron Lett.*, 235 (1963); *J. Amer. Chem. Soc.*, **86**, 252 (1964).

(3) N. C. Deno, D. Lavietes, J. Mockus, and P. C. Scholl, *J. Amer. Chem. Soc.*, **90**, 6457 (1968).

(4) C. C. Lee, and L. Gruber, *J. Amer. Chem. Soc.*, **90**, 3775 (1968); C. C. Lee, L. Gruber, and K.-M. Wan, *Tetrahedron Lett.*, 2587 (1968); C. C. Lee, W. K.-Y, Chwang, and K.-M. Wan, *J. Amer. Chem. Soc.*, **90**, 3778 (1968).

(5) S. Meyerson and H. Hart, *J. Amer. Chem. Soc.* **85**, 2358 (1963); H. M. Grubb and S. Meyerson in "The Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 453.

(6) F. Cacace, A. Guarino, and P. Ausloos, *J. Amer. Chem. Soc.*, **93**, 1088 (1971).

(7) J. Weiner and G. Smith, private communication.

(8) R. Wolfgang and J. Weiner, *Chem. Phys. Lett.*, in press.

(9) F. P. Lossing, and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970); A. N. H. Yeo, and D. H. Williams, *Chem. Commun.*, 737 (1970).

(10) H. Meerwein, G. Hinz, P. Hoffmann, E. Kronig, and E. Pfeil, *J. Prakt. Chem.*, **147**, 257 (1937).

(11) G. A. Olah and J. A. Olah, in ref 1c, Chapter 17.

(12) (a) D. Brouwer, and E. Mackor, *Proc. Chem. Soc., London*, 147 (1964); (b) D. Brouwer, *Recl. Trav. Chim. Pays-Bas* **87**, 210 (1968).

(13) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968).

(14) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 6881 (1968).

(15) G. A. Olah, E. Baker, J. Evans, W. Tolgyesi, J. McIntyre, and I. Bastein, *J. Amer. Chem. Soc.*, **86**, 1360 (1964).

(16) M. Saunders, E. L. Hagen, and J. Rosenfeld, *J. Amer. Chem. Soc.*, **90**, 6882 (1968).

(17) G. A. Olah and J. Lucas, *J. Amer. Chem. Soc.*, **90**, 933 (1968); G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3954 (1969).

(18) M. Saunders and P. Vogel, *J. Amer. Chem. Soc.*, **93**, 2559 (1971).

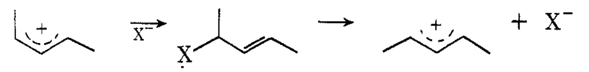


Figure 3.

tions from calculated models with a full positive charge on carbon;[15] (2) large values for long-range spin-coupling constants across the cationic center (*e.g.*, 5 Hz in the *tert*-amyl cation[13,19]) and large ^{13}C-H constants (169 Hz for H–C in the isopropyl cation[14]) can be explained in terms of a planar sp^2 hybridized carbon.

Whether the carbonium ions are or are not in equilibrium with small quantities of the corresponding alkyl halides or other neutral species in these solutions cannot ordinarily be determined from the proton, carbon, or fluorine spectra.[14,18] However, the isomerization of *cis,trans*- to *trans,trans*-dimethylallyl cation in SbF_5-SO_2ClF required an activation barrier of 24 kcal/mol.[20]

If the ion recombined with an anion to give a covalent intermediate (Figure 3), rotation and dissociation would surely follow. Thus the *minimum* barrier for recombination with an anion is 24 kcal/mol in at least this cation.[20] The nmr spectrum of $(CD_3)_2(CH)$ in SbF_5/SO_2ClF at 100° ruled out deuterium-hydrogen interchange.[21] Deprotonation to isobutylene followed by reprotonation from a pool of acid would have produced observable changes in the spectrum had it occured. A minimum energy barrier of 28 kcal/mol is thus implied for this reaction, demonstrating the extraordinary resistance of tertiary ions toward elimination in SbF_5/SO_2ClF, a consequence of the extremely low basicity of this medium.

Since the barriers to elimination and recombination with the counterion are high in these media, it is possible to study many rearrangement processes which occur with lower barriers without interference. The good agreement of the nmr spectra and rearrangement barriers of the same ions prepared in different solvent systems, with different counterions and reported by different groups, also indicates the lack of auxiliary equilibria with other species and is consistent with a nonspecific role for the anion and the solvent. Furthermore, all of the carefully measured entropies of activation have been close to zero, thus far. This is inconsistent with highly specific solvation or ion pairing. Carbonium ions may therefore be considered to be well-established entities with properties which vary little over a range of media.

Isopropyl Cation: Unsubstituted Protonated Cyclopropane

The simplest carbonium ion prepared in stable solution thus far is isopropyl cation. It was made by distilling isopropyl chloride into an SbF_5-SO_2ClF mixture at low temperature using vacuum line techniques.[14] Over the range from 0° to 40° the proton nmr spectrum changes, indicating rapid exchange of the two types of protons. Line-shape analysis demonstrated that the process was intramolecular and made it possible to obtain rate constants. The Arrhenius activation energy for the proton interchange process was found to be 16.4 ± 0.4 kcal/mol, with $\log A = 13.2 \pm 0.3$.[14]

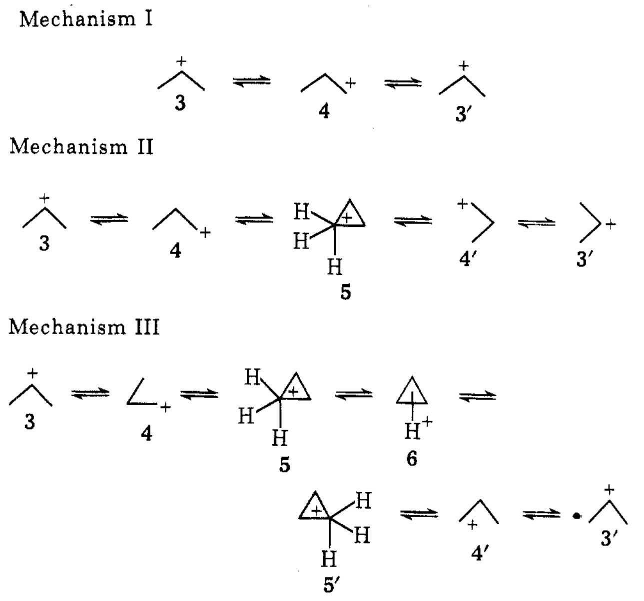
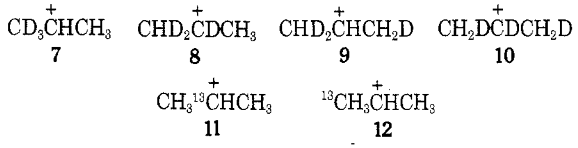


Figure 4.



$CD_3\overset{+}{C}HCH_3$ **7** $CHD_2\overset{+}{C}DCH_3$ **8** $CHD_2\overset{+}{C}HCH_2D$ **9** $CH_2D\overset{+}{C}DCH_2D$ **10**

$CH_3{}^{13}\overset{+}{C}HCH_3$ **11** $^{13}CH_3\overset{+}{C}HCH_3$ **12**

Figure 5.

The simplest mechanism for hydrogen interchange is reversible rearrangement to *n*-propyl cation (mechanism I), a process which would not interchange carbons. The observation of carbon-13 scrambling in isopropyl cation prepared from 2-chloropropane-2-^{13}C[19,21] virtually *requires* a process involving a protonated cyclopropane intermediate or transition state (mechanism II and/or III). The protonated cyclopropane **5** could be reached from the primary ion **4** or (in a more complicated step) directly from isopropyl cation by simultaneous hydrogen shift and ring closure (Figure 4).

In order to accurately measure the relative rates of hydrogen and carbon interchange (and thus assess the importance of the protonated cyclopropane), we studied a mixture of $(CD_3)(CH_3)C^+$ **7** and the undeuterated ion labeled with carbon-13 on the central atom, **11**. At −88° we observed changes in the relative areas of the methine and methylene peaks at the same time as we observed changes in the areas of the carbon-13 satellites. The kinetic dependence of the concentration of the four isomers of the deuterium-labeled ion and the two isomers of the carbon-labeled substance (Figure 5) was simulated as a function of rate constants for processes I, II, and III with the use of a computer program employing the Runge–Kutta method for integrating the kinetic differential equations.[22] The computed areas of the nmr peaks were compared with the experimental data. Several choices of rate constants were tried until a satisfactory fit with the experimental data was obtained.

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(19) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(20) P. v. R. Schleyer, T. M. Su, M. Saunders, and J. Rosenfeld, *J. Amer. Chem. Soc.*, 91, 5174 (1969).

(21) M. Saunders and E. L. Hagen, unpublished results.

(22) H. Margenau and G. M. Murphy in "The Mathematics of Physics and Chemistry," Van Nostrand, New York, N. Y., 1956, p 486.

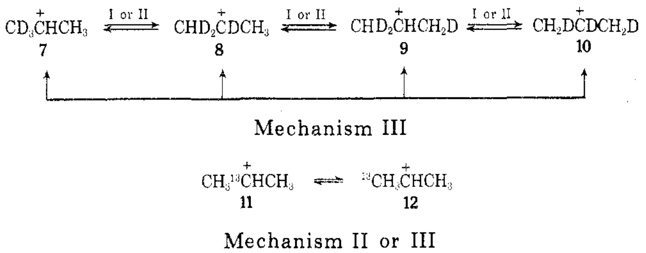

Figure 6.

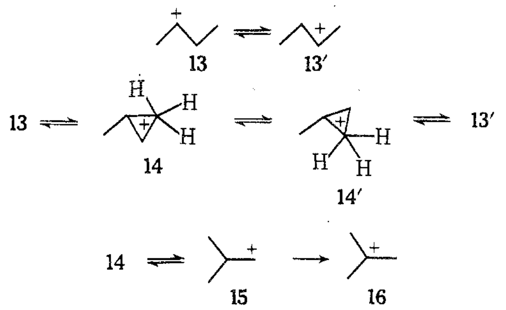

Figure 7.

If a combination of mechanisms I and II is assumed, the rate constant for I is found to be 1.5 ± 0.5 times that for II. A combination of mechanisms I and III fits equally well and yields similar ratios. Thus proton interchange (direct return to 3 from 4) is slightly, but distinctly, faster than carbon interchange (5 or 6 as transition state or intermediate); however the two processes are *remarkably* similar in energy.

Mechanism III allows the protonated cyclopropane, required by the observed carbon interchange, to undergo a further scrambling process *via* a corner-to-corner proton migration. If the barrier for this process were comparable to, or lower than, the barrier toward return to the isopropyl cation, more or less *complete* mixing of all the hydrogen and carbon atoms would occur at a rate comparable to carbon scrambling. Although observation of neither simple proton nor carbon interchange could detect such a process, *multiple* deuterium labeling, which enables the fate of more than one atom at a time to be followed, makes this possible.

Structure 7 would be converted into 8 by a single step of mechanism I or II (Figure 6). In order to go from 7 to 9 or 10, either *repeated* successive steps according to mechanism I or II or one step of a process involving the corner-to-corner migration of a proton such as mechanism III (indicated by the multiheaded arrow in Figure 6) is required. To observe what occurred, we quenched the ion by reducing it to propane using methylcyclopentane as a hydride donor.[23] Analysis *via* nmr spectroscopy has been difficult, but very preliminary results are consistent with mechanisms I and II alone.

If edge-protonated cyclopropane 6 were an intermediate rather than a transition state in mechanism III, its symmetry would require at least a 50% probability of net corner-to-corner migration every time it was formed. The edge-protonated ion would decompose with equal probability to a different corner-protonated cyclopropane than the one which led to it. We suggest that this property be an operational definition for the term "edge-protonated cyclopropane." Our preliminary results thus suggest that the edge-protonated structure is at least a few kcal/mol less stable than corner-protonated cyclopropane which is an intermediate in these reactions. Our results do not at the present seem capable of answering the question of whether the methyl group in the corner-protonated species is freely rotating or the related question of whether the hydrogens are or rapidly become equivalent. We hope to obtain and report more precise and complete experimental results in the near future, since this case is of particular importance due to its simplicity. Baird and Aboderin[2] concluded on the basis of their results that an edge-protonated species which can be opened through displacement by a nucleophile to give *n*-propyl derivatives is the most likely intermediate in the reaction of cyclopropane with deuteriosulfuric acid. It is not clear, on the basis of what is known so far, what is the best way of rationalizing these two sets of data.

Recently, Pople, *et al.*,[24] have performed *ab initio* molecular orbital calculations with geometry optimization on the $C_3H_7^+$ ion. Only two potential minima in the energy surface were found. They correspond to the expected isopropyl cation 3 and to a distorted form of corner-protonated cyclopropane 5, related to *n*-propyl cation 4. The popularly invoked edge-protonated cyclopropane 6 was calculated to be about 10 kcal/mol higher in energy than the corner-protonated structure. Face-protonated cyclopropane (the proton on the threefold axis) was predicted to be very unstable. These calculations thus lead to conclusions which agree with those which can be derived from our experimental results on the isopropyl cation.

sec-Butyl Cation: Protonated Methylcyclopropane

Although earlier attempts to prepare *sec*-butyl cation yielded only *tert*-butyl ion, it was found[16] that slow addition of *sec*-butyl chloride to SbF_5/SO_2ClF solution at −110° gave the cation. Study of the nmr spectrum and its temperature dependence led to the conclusion that the secondary ion 13 undergoes a very rapid degenerate 2,3-hydride shift with an upper limit for the barrier of 6 kcal/mol (Figure 7). The spectrum at −100° consists of two peaks at frequencies predicted by averaging the shifts expected (on the basis of analogous shifts in *tert*-amyl and isopropyl cations) for the two methyl groups and of the methine and the methylene groups.

A second process which scrambles all the protons in 13 was detected from observation of line broadening and coalescence at temperatures from −100 to −40°. Its activation energy of 7.5 ±0.1 kcal/mol with log $A = 12.3 \pm 0.1$ was obtained from line-shape analysis of the nmr spectrum. This low barrier requires a *different* process to be proposed from that which interchanges hydrogens in isopropyl cation. Reversible rearrangement to the primary ion would be expected to require about 9 additional kcal/mol.

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[23] G. M. Kramer, *J. Amer. Chem. Soc.*, **91**, 4819 (1969).

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

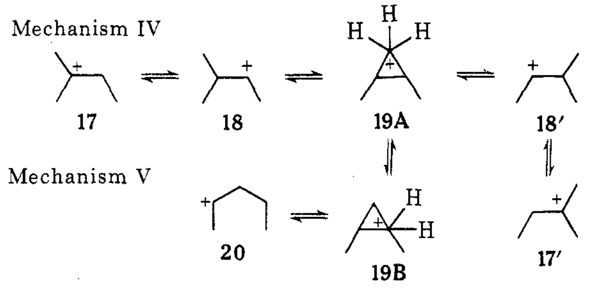

Figure 8.

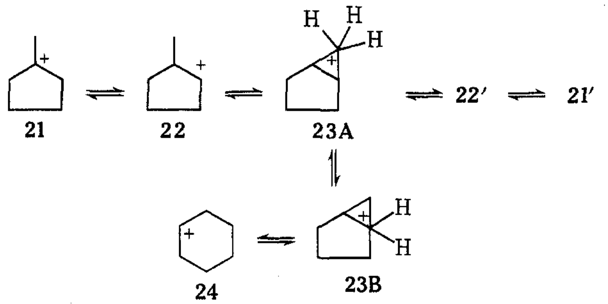

Figure 9.

The most probable mechanism involves closure to a corner-protonated methylcyclopropane intermediate, 14, followed by degenerate corner-to-corner proton rearrangement and reopening. The protonated cyclopropane and the transition state for corner-to-corner hydrogen migration are required to be far lower in energy than the primary ion in order to be acceptable in this mechanism, and it is *necessary* for protonated cyclopropane to be an intermediate.

At higher temperatures the ion rearranges to *tert*-butyl cation **16** with an activation energy of approximately 18 kcal/mol and a normal log A. The similarity of this barrier to that found for the proton interchange in isopropyl cation is consistent with the view that both processes proceed through similar transition states, namely, structures close to primary ions. Opening of **14** another way leads to isobutyl cation **15** which requires only a single hydride shift to go on to *tert*-butyl cation **16**. Since the nmr spectrum of *sec*-butyl cation at low temperature exhibits no peaks that could be attributed to other species in equilibrium with it, we can conclude that the protonated methylcyclopropane (or other) intermediate is at least 2 (and certainly less than 7.5) kcal/mol higher in energy than *sec*-butyl cation.

tert-Amyl Cation: Protonated Dimethylcyclopropane

The nmr spectrum of the *tert*-amyl cation **17** exhibited temperature dependence indicating that the two types of methyl groups interchange intramolecularly. Mechanism IV (Figure 8) is the simplest one consistent with the observed line shapes. Fitting the nmr spectra yielded an activation energy of 15.3 ± 0.2 kcal/mol with log $A = 13.2 \pm 0.2$.[12,13] Since the hydride shift leading to return to the tertiary ion probably requires a relatively small activation energy, the major part of the measured energy barrier is probably due to the formation of the secondary alkyl ion **18** (10–13 kcal/mol). In mechanism IV, the corner-protonated cyclopropane **19A** could be a transition state or an intermediate.

At temperatures above 80°, a slower process which mixes the two methylene protons with the nine methyl protons was detected. It finally results in a single nmr peak for all 11 hydrogens at very high temperature. An activation energy of 18.8 ± 1.0 kcal/mol, with log $A = 13.2 \pm 0.5$, was found using mechanism V.[25]

Interchange of all protons in **17** might be considered to occur *via* reversible hydride shifts to primary ions. But, this is highly unlikely since their energies would be so much above that of the starting tertiary cation. An analogous process would have interchanged deuterium and hydrogen in $(CD_3)_2(CH_3)C^+$, and the barrier for this process has been shown to be *more than* 28 kcal/mol.[21] If **19A** were an *intermediate*, corner-to-corner proton shifts, as in mechanism V, could account for the observed hydrogen scrambling.

Methylcyclopentyl Cation: Protonated Bicyclo[3.1.0]hexane

Methylcyclopentyl cation behaves similarly to *tert*-amyl cation.[12b,25] An activation energy of 15.4 ± 0.5 kcal/mol with log $A = 13.0 \pm 0.3$ was measured for a process that interchanges the α and β hydrogens in **21** (analogous to methyl interchange in **17**). Above 110° coalescence to a single peak was observed in the nmr spectrum of **21**. An activation energy of 18.2 ± 0.1 kcal/mol with log $A = 13.6 \pm 0.1$ was found for the interchange of ring and methyl hydrogens. The protonated cyclopropane required here might undergo an additional reversible ring opening to cyclohexyl cation **24** (to 2-pentyl cation **20** in case of **15**). To investigate this possibility, deuterium and carbon scrambling rates were simultaneously measured using a mixture containing ^{13}C- and deuterium-labeled methyl groups in methylcyclopentyl cations.[25] The two observed rates were related in exactly the manner predicted if the protonated bicyclo[3.1.0]hexane **23B** (analogous to **19B**) opens to **24** more rapidly than it returns to **23A** *via* a corner-to-corner hydrogen shift.

Tertiary Hexyl and Heptyl Cations

The isomeric tertiary hexyl and heptyl cations can be prepared from the corresponding chlorides and can be shown to undergo all of the processes described above with similar kinetic parameters.[26-31] Degenerate and nondegenerate 1,2-hydride and -methide shifts occur leading to proton scrambling and isomerization reactions which do not change the degree of chain branching. Changes in chain branching can be accounted for through corner-to-corner hydrogen migration in intermediate protonated cyclopropanes *via* mechanisms entirely analogous to

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(25) M. Saunders and J. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 7756 (1969).

(26) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 4739 (1967); G. A. Olah, J. R. DeMember, A. Commeyras, and J. L. Bribes, *J. Amer. Chem. Soc.*, **93**, 459 (1971).

(27) M. Saunders and P. Vogel, *J. Amer. Chem. Soc.*, **93**, 2561 (1971).

(28) D. M. Brouwer and J. M. Oeldrick, *Recl. Trav. Chim. Pay-Bas*, **87**, 721 (1968); D. M. Brouwer and J. A. van Doorn, *ibid.*, **88**, 573 (1969).

(29) H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, **88**, 1305 (1969).

(30) M. Saunders, M. H. Jaffe, and P. Vogel, *J. Amer. Chem. Soc.*, **93**, 2558 (1971).

(31) M. Saunders and P. Vogel, *J. Amer. Chem. Soc.*, **93**, 2560 (1971).

those previously presented. The activation energies for these processes are about 2-3 kcal/mol higher than those for the reactions which do not change the number of chain branches.

It is worth noting that the equilibrium constants between the three isomeric tertiary hexyl ions and also those between the seven isomeric tertiary heptyl cations have all been found to be very close to unity and affected little by temperature changes.[12] Thus, within each family, the enthalpy and entropy differences among isomeric tertiary cations are small. It is tempting to conclude that *all* acyclic tertiary carbonium ions have the same energy relative to each corresponding chloride and to make similar statements about secondary and primary systems. Pople[32] has suggested that the larger ions should be relatively more stable in the gas phase, but that the polarizability of solvent molecules which can approach smaller ions more closely might equalize energies in solution.

Even though substitution of methyl for hydrogen has remarkably little effect on carbonium ion equilibria among these ions, the substitution of deuterium produces effects which not only can be detected but can be accurately measured.[27,30,31] This has been done by choosing cases where rapid hydride or methide shifts interchange chemically identical ions. Nuclear magnetic resonance lines, which represented chemically different groups which were averaged by the rapid reactions, appear split when the degeneracy is broken by deuteration. The splittings can be used to determine accurate values for isotope effects and their temperature dependences.

Energies of Protonated Cyclopropanes

In no case which has been studied has a detectable quantity of a protonated cyclopropane been seen in equilibrium with a simple aliphatic cation. We can thus set a *lower* limit of about 2 kcal/mol above the corresponding tertiary or secondary ions for the energy of these protonated cyclopropanes.[33] On the other hand, measurement of activation barriers to processes proceeding through these species sets *upper* bounds on their energies.

In tertiary heptyl cation (Figure 1), the degenerate 1,2-methide shift is unobservably rapid allowing us to set an upper limit for the energy of protonated tetramethylcylopropane, **1A**, of 6 kcal/mol above the tertiary ion with 2 kcal/mol as the lower limit. In a similar way upper and lower limits for the energy of protonated methylcyclopropane, **14**, can be set as 7.5 and 2 kcal/mol, respectively, above *sec*-butyl cation. This conclusion is based on the rearrangements observed in this cation. Since secondary cations have been shown to be 11-15 kcal/mol above tertiary ions, protonated methylcyclopropane must be 14 ± 7 kcal above protonated tetramethylcyclopropane (**1A**). Each methyl substituent on the protonated cyclopropane thus contributes approximate)y 5 kcal/mol of stabilization, which is one-half or one-third of the stabilization produced by substituents directly attached to the charged atom in simple carbonium ions.

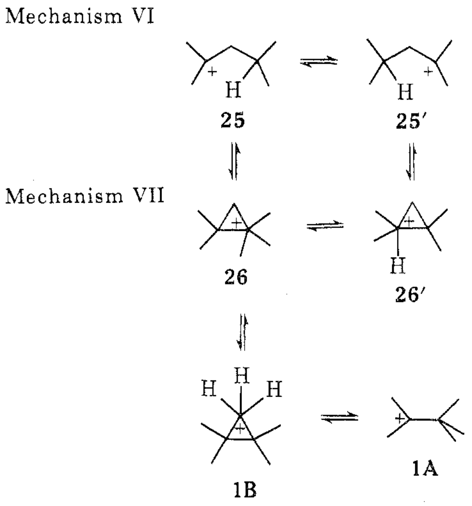

Figure 10.

1,3-Hydride Shifts

The nmr spectrum of isobutyldimethylcarbonium ion **25** changes in the temperature range from −110 to −70°, indicating rapid interchange of the nonequivalent methyl groups. Since the peak due to the methylene group is unaffected, two successive 1,2 shifts can be ruled out as a mechanism, and a direct 1,3 shift of a hydrogen (mechanism VI) is the most obvious possible explanation. Simulation of the line shape yields a barrier of 8.5 ± 0.1 kcal/mol.[36] This reaction might proceed *via* initial closure to a protonated cyclopropane and corner-to-corner migration followed by opening (mechanism VII). If so, it might be expected that migration of the proton in **26** toward the methylene should occur about as readily as migration toward the carbon bearing the other two methyl groups. This would lead to **1A**, the intermediate in the very rapid methyl migration seen in *tert*-butyldimethylcarbonium ion (Figure 1). This protonated cyclopropane is less than 6 kcal/mol above the tertiary cation. Interconversion of these isomeric ions would then be expected to be a process about as facile as the degenerate 1,3-hydride shift. Yet the reaction is much slower, as it occurs at a noticeable rate only at −50° and has an activation barrier of about 18 kcal/mol.

We conclude that a direct 1,3 shift occurs (mechanism VI) with a transition state *distinct* from the transition state for a corner-to-corner hydrogen shift in the protonated cyclopropane (mechanism VII) and that there is a large barrier separating these transition states. The most likely geometry for them is, of course, different in that one has a cyclopropane ring and the other does not. The substantial barrier between noninterconverting isomeric pairs **27** and **28** (Figure 11) is a possible precedent for this situation. Similar degenerate 1,4- and 1,5-hydride shifts have been shown to occur in ions which are higher homo-

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(32) J. A. Pople, private communication.

(33) The norbornyl[34] and the bicyclo[2.1.1]hexyl[35] cations show every indication of being *stable* protonated cyclopropanes.

(34) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970).

(35) K. B. Wiberg, G. Seybold, M. Saunders, and P. Vogel, *J. Amer. Chem. Soc.*, in press.

(36) M. Saunders and J. J. Stofko, Jr., *J. Amer. Chem. Soc.*, **95**, 252 (1973); see also D. M. Brouwer and J. A. van Doorn, *Recl. Trav. Chim. Pays-Bas*, **88**, 573 (1969).

27 28

Figure 11.

logs of **25**. The 1,4 shift occurs more slowly and the 1,5 shift more rapidly than the 1,3 shift.[36] There is, of course, no possibility of protonated cyclopropane intermediates in these cases.

Conclusion

We conclude from the preceding evidence that protonated cyclopropanes are intermediates in many rearrangements of secondary and tertiary alkyl cations. For each rearrangement studied, a consistent explanation could be provided through proposing that *corner-protonated* cyclopropanes are intermediates in 1,2-alkyl shifts and that they can undergo corner-to-corner hydrogen migration with an additional barrier.

Appendix: Edge or Corner?

The question of whether edge- or corner-protonated cyclopropanes are transition states or intermediates requires consideration of an interesting special consequence of one of the choices. If one selects the view (and it has been a popular one) that the edge-protonated cyclopropane is an intermediate in the reactions we have discussed and the corner-protonated species is a transition state, one must carefully consider the detailed energy surface in the neighborhood of the proposed transition state.

A corner-protonated cyclopropane transition state, **2**, can decompose in *four* distinct ways (Figure 12). It can give rise to two different edge-protonated intermediates, but it can (and must) *also* open to two simple acyclic cations. If one considers it a single entity, one can then assign four distinct probabilities for its decomposition (barring symmetry).

No precedent for this situation comes readily to mind. One might conclude that different rotational conformations of the formally pentavalent carbon would be limited to two or three modes of decomposition each. However, while this kind of assumption removes the unprecedented four-way branch point, it does not simplify the model but makes it more complicated. Another way of looking at the situation is to consider that any of the four intermediates related to the transition state or states could pass through it or them and proceed to any of the three other intermediates, a total of twelve paths in all, or *six* reaction channels plus their reversals.

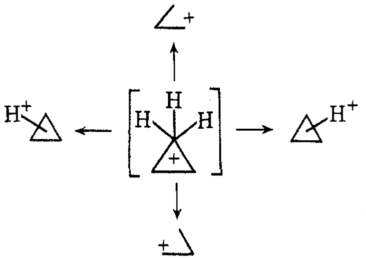

Figure 12.

Thermodynamics prescribes only the relation between each path and its reverse, but imposes no further limitation. Therefore we could choose six independent rates in attempting to fit any set of experimental results to a corner-protonated cyclopropane transition state. This very great flexibility would certainly enable us to achieve agreement in almost all cases, but makes such a mechanistic scheme an unattractive choice. It is a requirement of a useful scientific hypothesis that it should be possible to rule it out experimentally. This would be almost impossible in the case of a corner-protonated cyclopropane transition state.

Another way of expressing the same idea is to examine appropriate definitions for the terms intermediate and transition state. It is not unreasonable to propose that a species which can branch in three or more directions should be *defined* to be an intermediate regardless of energy. The corner-protonated cyclopropane would thus always be an intermediate by definition independent of its energy. If the edge-protonated species were a transition state, the situation of a possible four-way branching transition state would not arise; hence from this consideration alone, this possibility would be preferred. Fortunately it also seems to provide a consistent and harmonious way of fitting a substantial body of well established facts.

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