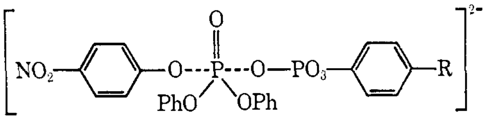
(Table VI), because these results show that phosphate is several times more reactive than the phenyl phosphate dianion, and therefore we are seeing a situation in which nucleophilicity in the micellar-catalyzed reaction is influenced strongly by nonbonding interactions. We could suppose that the greater efficiency of *p-t*-butylphenyl over phenyl phosphate as a nucleophile and inhibitor is caused by its more effective incorporation into the micellar phase. This explanation is completely satisfactory so far as the inhibition is concerned, but in considering nucleophilicity we must consider not only the concentrations of reactants in the micellar as compared with the aqueous phase but also their activity coefficients and that of the transition state (III) which is a bulky anion of low charge density. The results show that the aryl phosphate dianions and the substrate must be able to orient themselves so that they form the activated complex in the micellar phase without losing the hydrophobic and electrostatic bonding between the reagents and the cationic micelle. The enhancement of nucleophilicity caused by 0.003 *M* CTA is shown by the following second-order rate constants (l. mol^{-1} sec^{-1}) for the micellar catalyzed reactions: OH$^-$, 34.3 (0.73); HPO_4^{2-}, 2 × 10^{-2} (5 × 10^{-4}); $C_6H_5OPO_3^{2-}$, 10^{-1} (1 × 10^{-4}); *p-t*-$BuC_6H_4OPO_3^{2}$, 5 × 10^{-1}. The rate constants for the phosphates come from the results shown in Figure 1 for inorganic phosphate and from the initial slopes of the plots in Figures 2 and 3 for reactions at pH 7.5. The values in parentheses are for reaction in the absence of detergent.



III

The detergent enhances the nucleophilicity of hydroxide ion *ca.* 45-fold, of inorganic phosphate dianion *ca.* 40-fold, and of phenyl phosphate dianion *ca.* 1000-fold.

Experiments using spin-labled nitroxides have shown that the solute is not rigidly held to an anionic micelle of sodium lauryl sulfate, and can move freely from the hydrocarbon-like interior of the micelle to the water rich exterior.[23] If this behavior is general for solubilization in ionic micelles it would be easy for attack of an aryl phosphate dianion upon a triaryl phosphate in the micellar phase to be influenced strongly by hydrophobic interactions.

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(23) O. H. Griffith and A. S. Waggoner, *Accounts Chem. Res.*, **2**, 17 (1969).

Trapping Carbonium Ions in SbF_5–HSO_3F

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Contribution from the Central Basic Research Laboratories, Esso Research and Engineering Company, Linden, New Jersey 07036. *Received November 26, 1968*

Abstract: Butyl, amyl, and hexyl cations have been generated by the solvolysis of alkyl halides in 2 *M* SbF_5–HSO_3F solutions and trapped by hydride transfer from methylcyclopentane both before and after reaching an equilibrium distribution of cations. Tertiary cations predominate at equilibrium in these systems. Under kinetic control tertiary ions may be trapped after little rearrangement but secondary and primary cations show increasing tendencies to isomerize. The data suggest that simple methyl group migrations occur *via* protonated cyclopropane intermediates rather than by direct methide shifts in the interconversion of methylpentyl and methylbutyl cations.

Many solutions containing antimony pentafluoride have been reported to be capable of stabilizing high concentrations of alkyl cations. The ions have generally been detected by spectral means, particularly nmr. This investigation has been concerned with studying the nature of the cations in 2 *M* SbF_5–HSO_3F solutions through the use of hydride transfer trapping experiments. This medium has previously been used both to generate stable alkyl ions[1] and to investigate calorimetrically the energetics of their rearrangement.[2] It has long been known that carbonium ion intermediates in strongly acidic systems can be trapped by reaction with a strong donor such as methylcyclopentane, but this powerful means of probing the nature of the intermediates in solutions containing SbF_5 has been relatively neglected.

The present investigation gives information about the equilibrium distributions of C_4, C_5, and C_6 ions and the ability of methylcyclopentane to trap ionic intermediates before equilibrium is attained. The *t*-butyl and *t*-amyl cations appear to be the stable C_4 and C_5 ions. The C_6 system yields a mixture of 2-methylpentyl, 3-methylpentyl, and 2,3-dimethylbutyl cations at low temperatures. The distribution shifts slightly with temperature but conditions leading to only the stable 2,3-dimethyl-2-butyl cation have not been found.

Rearrangements of ions originating from primary, secondary, or tertiary halides to the equilibrium mixtures are usually complete in less than 3 min at −50°. These rearrangements can be severely restricted by generating the ions in the presence of excess methylcyclopentane. In this case the initial ions or intermediates on the way to the equilibrium may be trapped and much information about mechanistic paths can be obtained. For example, *n*-butane is a major product of the reaction of 1-chlorobutane or 2-chlorobutane indi-

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(1) (a) G. A. Olah and J. Lukas, *J. Am. Chem. Soc.*, **89**, 2227 (1967); (b) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *ibid.*, 87, 2997 (1965).

(2) (a) E. M. Arnett and J. W. Larsen, *ibid.*, **90**, 791 (1968); (b) E. M. Arnett and J. W. Larsen, *ibid.*, **90**, 792 (1968).

cating that secondary cations are real intermediates in the rearrangement to the *t*-butyl cation.

Trapping through hydride transfer is also sufficiently rapid to catch the *t*-2-methylpentyl ion before isomerization to a 3-methylpentyl ion, to snare methylpentyl ions before isomerizing to dimethylbutyl ions, and to trap dimethylbutyl ions before isomerizing to the methylpentyl system. Primary or secondary cations tend to undergo considerable rearrangement however before being intercepted. Thus neopentane is not obtained from neopentyl chloride and *n*-amyl and *n*-hexyl halides lead to substantially rearranged products. Much of the data is consistent with the idea that rearrangements leading to a change in branching occur through protonated cyclopropane intermediates, a proposal recently advanced to explain the fact that, although *n*-butane doesn't isomerize to isobutane in SbF_5–HF, scrambling of the carbon atoms along the chain occurs readily.[3]

The mechanistic and equilibrium information derived in this study is relatively independent of the rates of hydride transfer to secondary and tertiary ions. As indicated hydride transfer was sufficiently fast to trap tertiary ions before they underwent simple rearrangements and secondary ions with varying efficiency depending on the specific species. The rapid transfer essentially freezes the tertiary cation distribution and permits its evaluation. Use is made of this result in interpreting rearrangements originating with primary and secondary ions under otherwise identical reaction conditions because mechanisms involving a tertiary intermediate are necessarily eliminated.

Procedures

Solutions (2 *M*) of redistilled antimony pentafluoride in commercially available fluorosulfonic acid were used in most of the work. Samples for either spectral analysis or trapping experiments were prepared by adding alkyl halides, 0.4 *M*, to acid solutions cooled to −78.5°. The pmr spectra of solutions of butyl, amyl, and hexyl chlorides or bromides agreed with those reported by others. At −50°, all butyl chlorides appeared to show the *t*-butyl cation, all amyl chlorides appeared to isomerize to the *t*-amyl cation, while all hexyl chlorides appeared to isomerize to a mixture of tertiary cations.

The integrated areas of the butyl ions formed from *n*-butyl chloride or *t*-butyl chloride accounted quantitatively for the concentration of added alkyl halide. This was determined using protonated mesitylene as an internal standard.

Two trapping procedures were employed. In the first, A, the alkyl halide was mixed with the acid at −78.5°, then brought to reaction temperature and allowed to stand for 3 min. Excess methylcyclopentane was then added and the system was vigorously shaken for about 10 sec. The hydrocarbon phase was allowed to separate and products were recovered by vacuum distillation, still at reaction temperature. This procedure is believed to lead to the recovery of an equilibrated system of ions.

The second recovery method, B, varied from the first in that the alkyl halide was placed over the acid and dispersed in methylcyclopentane at −78.5° before being brought to reaction temperature. The system was then shaken vigorously for 10 sec and products recovered as before. It is believed that little reaction occurred before contacting. Primary and secondary halides were partially, and tertiary halides quantitatively, converted during the reaction period. This procedure appears to give kinetically controlled prodcuts and qualitative information about the relative rates of isomerization and hydride transfer.

Butyl Halides

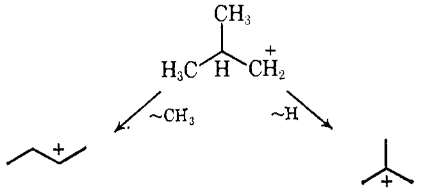
All the butyl halides readily ionize and rearrange to the *t*-butyl cation within 3 min in 2 *M* SbF_5–HSO_3F. Upon reaction with methylcyclopentane, MCP/t-$C_4H_9^+$ = 11/1, at −78.5° a typical solution prepared with *n*-butyl chloride gave >97% isobutane, <3% *n*-butane, and trace quantities of other higher paraffins.

By contrast, when reacted *via* method B, the alkyl halides may be trapped with a minimum of structural rearrangement (Table I). At −50° 1-chlorobutane and 2-chlorobutane yield mainly *n*-butane while *t*-butylchloride gives isobutane. The behavior of the normal chlorides is consistent with the existence of a large baririer in the rearrangement of *sec*-butyl cations to *t*-butyl cations.[4]

Table I. Trapping Butyl Ions with Methylcyclopentane, −50°

Butyl chloride	Kinetically controlled products, % *n*-Butane	 Isobutane
1-Chlorobutane	>99.5	<0.5
2-Chlorobutane	99.4	0.6
Isobutyl chloride	18.6	81.4
t-Butyl chloride	0	100

Of considerable interest is the finding that isobutyl chloride yields both isobutane and *n*-butane in approximately their equilibrium concentrations. One interpretation of the product ratio would be that the relative rates of hydride and methide shifts in the cation are no greater than 4.4/1. This corresponds to a maximum difference in activation energy of 0.67 kcal/mol, and is based on the assumption that all the isobutane formed



after isomerization of the isobutyl to the *t*-butyl cation. Direct hydride transfer to the isobutyl cation is, of course, possible and to the extent that it occurs will further lower these differences. The postulate of a methide shift, however, is at odds with the behavior of related C_5 and C_6 halides and an alternative explanation should be considered.

Thus, it is possible that the formation of *n*-butane comes about through the intervention of a protonated cyclopropyl intermediate which subsequently isomerizes to a secondary butyl cation. If this is the case, the difference in activation energy observed should be mainly

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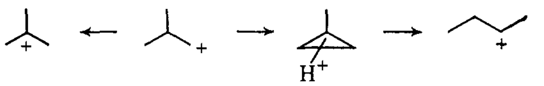
[3] D. M. Brouwer and J. M. Oelderik, *Preprints Div. Pet. Chem.*, 13, 184 (1968).

[4] M. Saunders, E. L. Hagen, and J. Rosenfeld, *J. Am. Chem. Soc.*, **90**, 6882 (1968).

associated with the relative ability of the isobutyl cation to either undergo a hydride shift or form the protonated cyclopropane. This hypothesis is consistent with the behavior of primary 2-methylbutyl and 2-methylpentyl halides and is believed to closely describe the reaction of the isobutyl ion.



The *n*-butyl chlorides primarily lead to the formation of *n*-butane under the kinetically controlled conditions but isomerization to the *t*-butyl cation still occurs. In this respect, the SbF_5–HSO_3F system appears to differ from SbF_5–HF in which *n*-butane does not isomerize to isobutane but undergoes a facile rearrangement interconverting the methyl and methylene carbon atoms.[3] That reaction has been proposed to occur through the same protonated methylcyclopropane intermediate discussed above. The activation energy for its rearrangement to the *t*-butyl structure in SbF_5–HSO_3F is therefore considerably lower than in SbF_5–HF.

Nevertheless, the fact that excess *n*-butane is obtained in SbF_5–HSO_3F indicates that there is a sizeable barrier to the rearrangement of a secondary butyl cation and a small barrier to the intermolecular hydride transfer reaction with methylcyclopentane. The relative rates of these reactions should be independent of the ion concentration, but they are difficult to assess quantitatively, because hydride transfer may occur at the hydrocarbon–acid interface or in either phase which complicates kinetic analyses. In any case, however, the kinetically controlled products in Table I and the prior equilibrium results indicate that secondary butyl ions are bonafide intermediates in SbF_5–HSO_3F with lifetimes of the order of minutes or less at −50°.

Amyl Halides

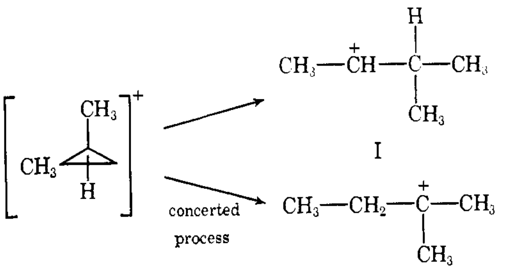
The behavior of amyl halides is analogous to that of the butyl halides. For example, after 3 min in the acid at −78.5 or −50°, 1-chloropentane has ionized and rearranged to the *t*-amyl cation so that more than 99% isopentane is recovered by reaction with methylcyclopentane. However, predispersal of the alkyl halides in methylcyclopentane again leads to competitive isomerization and trapping processes. Normal amyl chlorides may be trapped before rearrangement but not quite as well as with the butyl compounds and isopentane is the major product (Table II). Side reactions leading to disproportionation account for less than 1% of the products for all the halides except *t*-amyl chloride where 8% isobutane + hexanes formed.

Table II. Trapping Amyl Ions with Methylcyclopentane, −50°

Amyl halide	—Kinetically controlled— product, % *n*-Pentane	Isopentane
1-Chloropentane	16.7	83.3
2- and 3-Chloropentane	14.8	85.2
1-Chloro-2,2-dimethylpropane	0	100
2-Chloro-2-methylbutane	0	100
1-Bromo-2-methylbutane	0	100

Neopentane was not detected in the reaction of 1-chloro-2,2-dimethylpropane indicating that hydride transfer to the primary ion if it is a true intermediate is not competitive with the strongly exothermic rearrangement to the *t*-amyl cation. The tendency of secondary amyl ions to isomerize more readily than secondary butyl ions may be rationalized by arguments analogous to Brouwer's concerning ion behavior in HF–SbF_5.[3] Thus if protonated cyclopropanes are intermediates in both sets of rearrangements, isomerization of the methylcyclopropyl system would be expected to be slower than that of the 1,2-dimethylcyclopropyl system because cleavage in the first involves passage through a transition state partially resembling a primary cation while in the latter a relatively stable secondary ion may be reached. From the product ratios obtained with the secondary alkyl halides, the preceding argument leads to an estimated difference in activation energy for the rearrangement secondary butyl and amyl cations of 3.0 kcal/mol.

The fact that 1-bromo-2-methylbutane under kinetically controlled conditions yields isopentane with essentially no *n*-pentane suggests that the primary ion initially formed suffers a 1,2-hydride shift to the tertiary cation and perhaps the formation of a protonated 1,2-dimethylcyclopropane intermediate. The latter intermediate could open either to the secondary ion, I, or the *t*-amyl cation by a concerted ring opening and hydride shift. Failure to observe *n*-pentane indicates that the methyl shift is really not competitive with either the 1,2-hydride shift or cyclopropane formation. The behavior of 1-bromo-2-methylbutane is exactly analogous to that of 1-bromo-2-methylpentane to be discussed below in which a stronger case can be made for a cyclopropyl intermediate.



Hexyl Halides

Hexyl chlorides ionize and isomerize primarily to a mixture of 2-methylpentyl, 3-methylpentyl, and 2,3-dimethylbutyl cations in 2 *M* SbF_5–HSO_3F solutions. The relative concentrations of the cations change very little between −50 and +65° even though side reactions are excessive at the upper temperature (Table III).

In Table IV the kinetically controlled products obtained from seven hexyl halides are shown. 1-Chlorohexane yields a mixture of *n*-hexane, 2-methylpentane, and 3-methylpentane with essentially no dimethylbutanes. The yield of *n*-hexane is a little less than that of *n*-pentane obtained from 1-chloropentane indicating a similarity in mechanism, but the striking results are the lack of formation of a dimethylbutane and the recovery of a 2:1 ratio of 2-methylpentane:3-methylpentane. When coupled with the fact that the tertiary ion precursors 2-chloro-2-methylpentane and 2-chloro-2,3-dimethylbutane under the same conditions are trapped by

Table III. Effect of Temperature on Equilibrated Ion Distribution

Temp, °C	n-Hexyl chloride n-C_6	 3-MC_5	 2-MC_5	 2,3-DMC_4	 2,2-DMC_4
−80	0	31.5	68.5	Trace	0
−50	0	22.9	46.9	30.3	0
−30	0	22.3	48.3	29.2	0.2
+30	0.6	21.6	45.1	22.0	10.8
+65[a]	1.0	17.3	51.8	24.7	5.3

[a] Cracking is severe. The product contains only 39% hexane. Above −30°, 2,2-dimethylbutane is observed indicating some isomerization of the 2,3-dimethylbutyl cation to the secondary 3,3-dimethyl-2-butyl cation.

hydride transfer before isomerization, even between the methylpentyl ions, we are led to some interesting conclusions about the origin of these products.

Table IV. Trapping Hexyl Ions with Methylcyclopentane, −50°

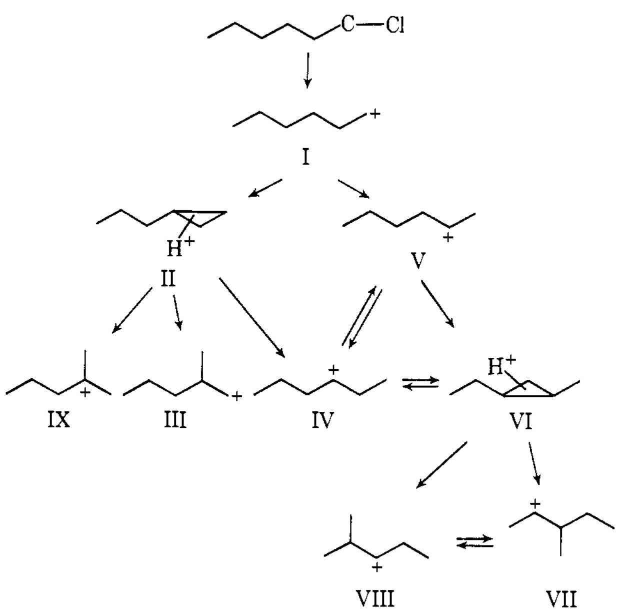
Compound	Kinetically controlled products, % n-C_6	 2-MC_5	 3-MC_5	 2,3-DMC_4	 2,2-DMC_4
1-Chlorohexane	3.4	66.3	30.3	Trace	0
2-Chloro-2-methylpentane	0	97.6	2.4	0	0
2-Chloro-2,3-dimethylbutane	0	0	0	100	0
3-Bromo-3-methylpentane	0	15.3	84.7	0	0
2-Chloro-4-methylpentane	0	88.1	10.5	1.4	0
1-Bromo-4-methylpentane	0	86.7	13.3	0	0
1-Bromo-2-methylpentane	0	80.7	19.3	0	0

Before extending this discussion it is informative to note the effect of temperature upon the kinetically controlled products obtained from n-hexyl chloride. In Table V it is seen that there is very little effect of temperature between −80 and +30°. The products generally contain about 10% n-hexane, 60% 2-methylpentane, and a 2-MC_5/3-MC_5 ratio of (2–3)/1. The relative consistency of these values indicates that methylcyclopentane traps a pseudo-equilibrium distribution of n-hexyl and methylpentyl ions.

Table V. Effect of Temperature on Kinetically Controlled Product Distributions

Temp, °C	Products from n-hexyl chloride, % n-C_6	 3-MC_5	 2-MC_5	 2,3-DMC_4	 2,2-DMC_4
−80	9.5	27.4	63.2	Trace	0
−50	3.4	30.3	66.3	Trace	0
−30	10.9	25.5	61.0	2.6	0
+10	10.6	20.3	61.8	7.3	0
+30	11.0	26.6	57.6	3.1	1.7

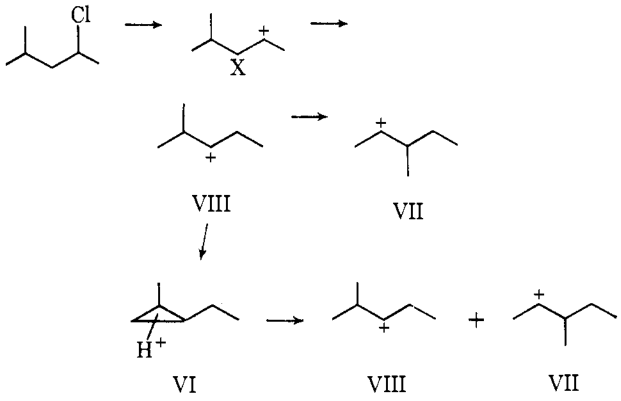
Scheme I



In Scheme I, a sequence of reactions is shown which may be used to consider the behavior of 1-chlorohexane. The halide is assumed to ionize to I which rapidly isomerizes to II and V. Ion II is a protonated cyclopropane which can either form a primary methylpentyl ion III in a relatively slow step, undergo a concerted ring opening and proton shift to tertiary ion IX, or rapidly convert to IV and V. Ions IV and V can cyclize to VI which may or may not form the secondary 2- and 3-methylpentyl ions at an equal rate. Since it was shown that the tertiary 2-methylpentyl ion does not readily isomerize to the 3-methylpentyl ion the finding of a (2–3)/1 ratio of methylpentanes when starting with 1-chlorohexane means that the corresponding distribution of ions was formed by the simultaneous conversion of II to IX and VI to VII and VIII or the corresponding tertiary cation. The relative uniformity of the distribution in Table V indicates little difference in activation energy for these paths.

The reaction of 2-chloro-4-methylpentane indicates that a secondary ion of the 2-methylpentyl skeleton is more prone to rearrange than the tertiary cation. Two paths resulting in the formation of a 3-methylpentyl ion may be considered (Scheme II). Thus after ionizing and undergoing a rapid 1,2-hydride shift ion VIII is reached. It may convert to VII directly through a methide shift or alternatively rearrange through the cyclopropyl intermediate VI.

Scheme II

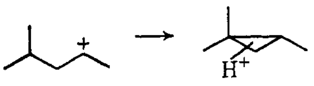


The reaction coordinate for the interconversion of VII and VIII may therefore look like A corresponding to the direct methyl shift or B in Figure 1. If isomerization occurs *via* A the reaction passes through a transition state characterized by a methyl group bridging 2 partially electron-deficient carbon atoms.

If isomerization occurs *via* path B VI is a discrete intermediate, whose geometry cannot be closely defined on the basis of these data, but whose existence might perhaps be detected by proton-exchange studies. This intermediate could either be classified as a point or edge protonated cyclopropane. Besides the fact that the intermediate by definition may be conceivably isolated it should differ from the methyl-bridged transition state by virtue of its containing a particularly loosely bound and labile proton.

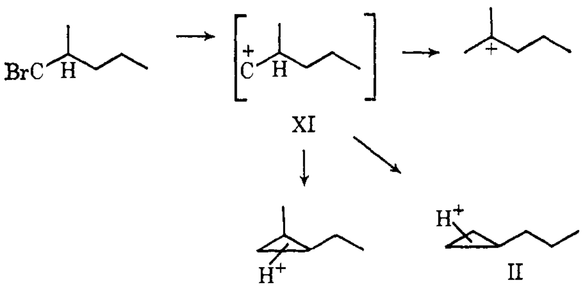
The fact that *n*-paraffins were not obtained from 1-bromo-2-methylbutane (Table II) and 1-bromo-2-methylpentane (Table IV) where primary and therefore "hotter" cations are initially formed indicates that path A rearrangement is less likely than formation of the discrete intermediate.

The isomerization of X to VIII has been proposed rather than direct cyclization of X to XI for several reasons. The formation of this cyclopropane is likely to be subject to severe steric restrictions because the charged carbon atom must approach the tertiary carbon in a narrow corridor between two protective methyl groups. In addition, a tertiary proton is being displaced, and since these are less acidic than secondary or primary hydrogen atoms, this ring closure is considerably less likely on electronic grounds than the others discussed in this paper. On the other hand, if XI had formed, its cleavage to the 2,3-dimethylbutyl cation would be expected, but relatively little of this ion appears to have been made.



X XI

The products obtained from 1-bromo-2-methylpentane can best be rationalized by assuming that both 1,2-hydride transfer and cyclization to II and VI are competitive in ion XI. Ions VI and II can open to methylpentyl cations in the ratio observed with 1-chlorohexane but the 1,2-hydride shift leads to the formation of additional 2-methylpentane. From the product distributions one can estimate that 62% of the initial ions converted through the cyclopropyl intermediates while 38% underwent the 1,2-hydride shift.



XI VI II

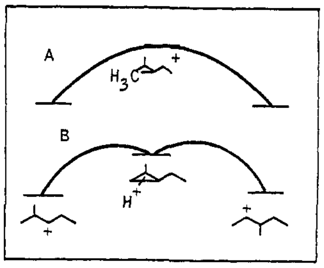


Figure 1. Possible reaction coordinates for the interconversion of secondary 2- and 3-methylpentyl cations.

The equilibrated hexyl cation distribution in 2 *M* SbF_5–HSO_3F between −50 and +65° according to these results contains about 25 to 30% of the 2,3-dimethyl-2-butyl cation and mainly a mixture of 2- and 3-methylpentyl ions. These distributions are essentially the same as those reported by Brouwer and Oelderik in HF–SbF_5.

In summary the isomerization of butyl, amyl, and hexyl cations in 2 *M* SbF_5–HSO_3F at −50° leads to mixtures of tertiary cations which may be recovered from the acid by hydride transfer from methylcyclopentane.

Intermediates present during the isomerization may also be trapped. From the fact that isobutyl chloride yields significantly large quantities of *n*-butane while 1-bromo-2-methylbutane and 1-bromo-2-methylpentane do not yield *n*-paraffins it is proposed that a direct methyl shift in the primary cation does not occur, but rather that reaction proceeds through the formation of an intermediate, protonated methylcyclopropane. Support for this hypothesis comes from the reaction of 1-bromo-2-methylpentane which yields both 2- and 3-methylpentanes under conditions where isomerization of the tertiary 2-methylpentyl cation is slow. Formation of 3-methylpentane is however consistent with partial cyclization of the initial primary ion to protonated 1-methyl-2-ethylcyclopropane.

The postulate of protonated cyclopropanes as true intermediates in alkyl cation isomerizations provides a consistent explanation of the behavior of butyl, amyl, and hexyl cations in this acid.

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