

**7-syn-Deuterionorbornan-2-one.**<sup>8</sup> Norbornene (2 g) was heated with D<sub>2</sub>SO<sub>4</sub> (9 ml) and D<sub>2</sub>O (1 ml) at 80° for 4 hr. Dilution with D<sub>2</sub>O (25 ml) and extraction with pentane (two 20-ml portions) gave a mixture of 7-syn-deuterionorbornan-2-ol and 3-deuterionorbornanol (1.91 g). This material was oxidized with Jones<sup>26</sup> reagent to furnish a mixture of 7-syn-deuterionorbornan-2-one and 3-deuterionorbornanone (1.01 g), mp 89–91°. Repeated washings with 10% potassium hydroxide removed the label from the enolizable position of norbornan-2-one. The resulting 7-syn-deuterio-

norbornan-2-one was sublimed, mp 94–95°, to furnish material containing 70% *d*<sub>1</sub> as determined by mass spectral analysis.

**7-syn-Deuterio-2-phenylnorbornan-2-ol.** 7-syn-Deuterionorbornan-2-one (0.01 mol) was treated with a small excess of phenylmagnesium bromide (0.015 mol) to furnish 7-syn-deuterio-2-phenylnorbornan-2-ol in 91% yield, mp 43–44°.

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(26) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

## Chemistry in Super Acids. III.<sup>1a</sup> Protonation of Alkanes and the Intermediacy of Alkanonium Ions, Pentacoordinated Carbon Cations of the CH<sub>5</sub><sup>+</sup> Type. Hydrogen Exchange, Protolytic Cleavage, Hydrogen Abstraction, and Polycondensation of Methane, Ethane, 2,2-Dimethylpropane (Neopentane), and 2,2,3,3-Tetramethylbutane in FSO<sub>3</sub>H–SbF<sub>5</sub> (“Magic Acid”) Solution<sup>1b</sup>

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**Abstract:** Alkanes undergo hydrogen exchange, protolytic cleavage, and hydrogen abstraction followed by polycondensation in the super acid system, FSO<sub>3</sub>H–SbF<sub>5</sub>. Methane and ethane undergo both hydrogen exchange and polycondensation to produce *t*-butyl cation, *t*-hexyl cations, or higher analogous tertiary alkylcarbonium ions. Neopentane undergoes hydrogen exchange, protolytic fragmentation to trimethylcarbonium ion and methane, and hydrogen abstraction followed by fast rearrangement of the *t*-amyl cation. 2,2,3,3-Tetramethylbutane cleaves to produce the trimethylcarbonium ion. Structures of the intermediate protonated alkane ions (alkanonium ions, of the CH<sub>5</sub><sup>+</sup> type) formed in these reactions were calculated using an all-valence-electron SCF method.

In previous studies we reported that the extremely strong acid FSO<sub>3</sub>H–SbF<sub>5</sub> is capable of forming stable alkylcarbonium ions from alkanes *via* protonation followed by hydrogen abstraction.<sup>3</sup> It was found that even neopentane is sufficiently basic to undergo reaction in “magic acid.” At room temperature neopentane reacted in neat acid solution to yield the trimethylcarbonium ion (*t*-butyl cation) and methane. When treated with FSO<sub>3</sub>H–SbF<sub>5</sub> diluted with SO<sub>2</sub>ClF, the dimethylethylcarbonium ion (*t*-amyl cation) was formed through rapid rearrangement of the intermediate neopentyl cation. Hogeveen and Bickel made similar observations on the protolytic cleavage and hydrogen exchange of neopentane in the related acid system HF–SbF<sub>5</sub>.<sup>4</sup> Although the surprising solubility of methane in sulfuric acid solution was observed 70 years ago,<sup>5</sup>

this observation has since lain dormant. Having observed the solubility of methane in super acid solution, like FSO<sub>3</sub>H–SbF<sub>5</sub>, we started a systematic investigation of methane and related hydrocarbons in strong acid solution. In a preliminary communication we reported that methane undergoes protonation followed by hydrogen abstraction in “magic acid” solution to yield tertiary alkylcarbonium ions. We now wish to report in full our studies relating to the behavior of methane, ethane, neopentane, and 2,2,3,3-tetramethylbutane in the super acid solutions.

### Results

Methane (≥99.5%) when treated either at 150° in an autoclave with tenfold excess of 1:1 FSO<sub>3</sub>H–SbF<sub>5</sub> solution or at 140° under atmospheric pressure, gave primarily the stable trimethylcarbonium ion and insoluble (in SO<sub>2</sub>) polymeric products. In an autoclave at a reaction temperature kept at or below 80°, a mixture of trimethylcarbonium with some *t*-hexyl and *t*-heptyl cations and higher homologous tertiary carbonium ions was formed along with insoluble polymer. Hydrogen gas is liberated in these reactions, but as reported previously,<sup>3</sup> it at least partially reduces the acid. Thus,

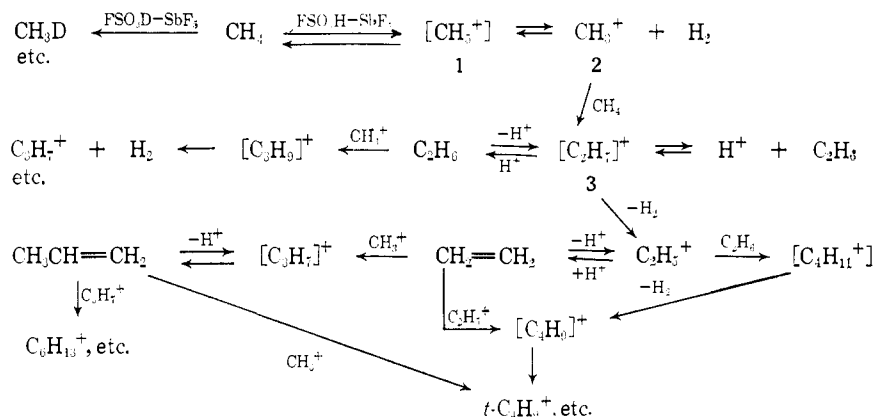
(1) (a) Part II: A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2929 (1969); (b) preliminary communication: G. A. Olah and R. H. Schlosberg, *ibid.*, **90**, 2726 (1968).

(2) Postdoctoral Research Investigator, 1968–1969.

(3) (a) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227 (1967); (b) G. A. Olah and J. Lukas, *ibid.*, **89**, 4743 (1967).

(4) H. Hogeveen and A. F. Bickel, *Chem. Commun.*, 635 (1967).

(5) R. A. Worstall, *J. Amer. Chem. Soc.*, **21**, 245 (1899); A. Christoff, *Z. Physik. Chem.*, **55**, 622 (1906); also L. H. Sommer, W. P. Barie, and J. R. Gould, *J. Amer. Chem. Soc.*, **75**, 3765 (1953).



the reaction cannot be readily monitored by measuring the rate of hydrogen gas formation. At atmospheric pressure in a reaction vessel open to air, the solution was continuously swept out with methane and thus quantitative measurements were not taken. In the autoclave reaction the vessel was flushed with methane prior to the reaction thereby excluding atmospheric oxygen and preventing the occurrence of oxidative processes. Furthermore, no trace of fluorinated hydrocarbon was detected among the products, indicating the absence of free-radical-type fluorinating degradation. The product mixture was solved in  $\text{SO}_2$  at  $-78^\circ$  (approximately one-third of the product mixture was found to be insoluble in  $\text{SO}_2$ ) and the pmr spectrum was taken at  $-30^\circ$ . The spectrum showed as the predominant species the trimethylcarbonium ion (sharp singlet at  $\delta$  3.93). The dimethylisopropylcarbonium ion (doublet,  $J = 4$  Hz, at  $\delta$  3.13) and the dimethyl-*t*-butylcarbonium ion (sharp singlet at  $\delta$  2.95), are also present in the spectrum indicating the formation of *t*-hexyl, *t*-heptyl, and in some experiments also higher homologous tertiary alkylcarbonium ions through polycondensation, isomerization, and fragmentation processes.

Methane- $d_4$  was treated at room temperature and atmospheric pressure in a stainless steel autoclave with a tenfold excess of 1:1  $\text{FSO}_3\text{H-SbF}_5$  solution. After a reaction time of 5 hr, mass spectroscopic analysis of recovered "unreacted" methane indicated about 5% hydrogen-deuterium scrambling. After 96-hr reaction time, the methane was found to have undergone scrambling to the extent of 12%.<sup>6</sup> The mass spectrum of the gaseous reaction mixture (*i.e.*, the vapors above the acid in the autoclave) also indicated the presence of a small but detectable amount of HD ( $m/e$  3).

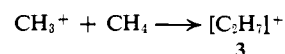
All of these chemical observations can be explained by suggesting that in the super acid solution,  $\text{FSO}_3\text{H-SbF}_5$ , methane indeed behaves as a base. It is protonated in solution to the methanonium ion,  $\text{CH}_5^+$  (1), which can undergo reversible deprotonation leading to hydrogen exchange, or lose hydrogen to form the extremely reactive methyl cation,  $\text{CH}_3^+$  (2). The methyl cation then reacts with excess methane to form the ethanonium ion,  $\text{C}_2\text{H}_7^+$  (3), which loses  $\text{H}_2$  to form the ethyl cation  $\text{C}_2\text{H}_5^+$  which through proton elimination gives ethylene. Ethylene in turn can react with methyl or ethyl cation to give the *t*-butyl, *t*-hexyl, and *t*-octyl

(6) In a communication published simultaneously with our preliminary report, Hogeveen and Gaasbeek reported observation of hydrogen-deuterium exchange with deuterated methane treated with  $\text{HF-SbF}_5$ : H. Hogeveen and C. J. Gaasbeek, *Rev. Trav. Chim. Pays-Bas*, **87**, 219 (1968).

cations or higher molecular weight hydrocarbon ions. Deprotonation of  $\text{C}_2\text{H}_7^+$  to ethane and subsequent alkylation must also be considered. The over-all process is, of course, more complicated as the intermediate ethyl cation, and related carbonium ions can undergo various di-, tri-, and polymerization processes, and the higher molecular weight hydrocarbon ions, in turn, undergo fragmentation.

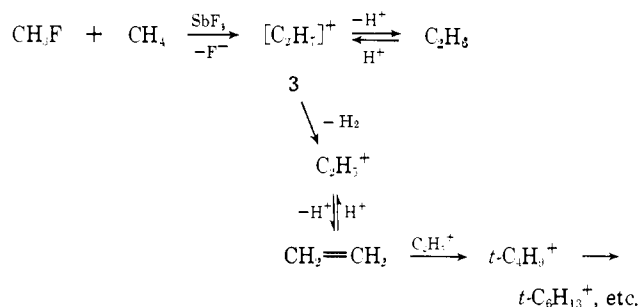
Due to the liberation of hydrogen gas and the subsequent partial reduction of the acid by hydrogen, along with the formation of polymeric hydrocarbon ions, we have been unable to obtain kinetic data for the methane polycondensation reaction. Qualitatively, we found that the hydrogen-exchange reaction is much more rapid than is the growth reaction. Hogeveen and Gaasbeek,<sup>6</sup> have found in  $\text{HF-SbF}_5$  solution that hydrogen exchange occurs at rates of  $k = 10^{-3}$ – $10^{-4}$   $\text{sec}^{-1}$  at temperatures ( $25^\circ$ ) where polycondensation products cannot be detected.

The suggested mechanism for the methane condensation reaction involves the reaction of the methyl cation with excess methane as the key step. Whereas in gas-



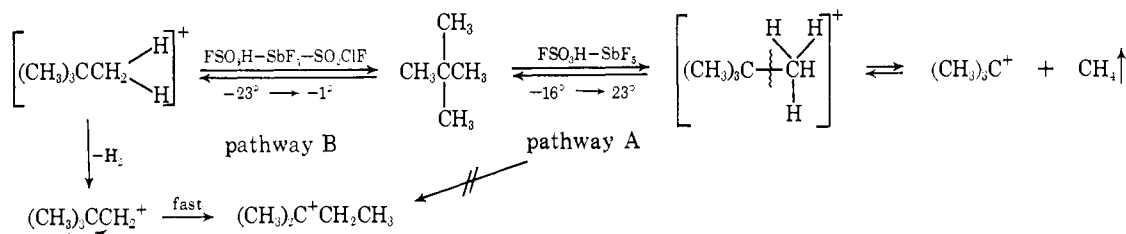
eous molecule-ion reactions there is extensive evidence for the occurrence of this reaction, its novelty as a solution reaction step would indicate a highly speculative mechanistic pathway. We therefore attempted to obtain independent experimental evidence for the suggested mechanism.

When methyl fluoride is treated in the presence of antimony pentafluoride with methane a ready alkylation reaction is observed giving *t*-butyl cation and some *t*-hexyl cations as the major products. Methyl fluoride

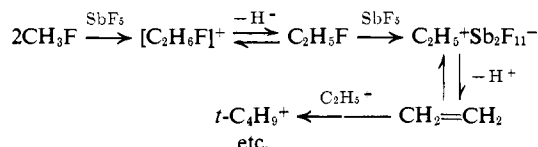


and antimony pentafluoride form a highly polarized donor-acceptor complex (incipient methyl cation) capable of effecting attack on methane.

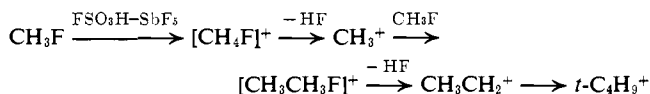
Scheme I



It was also observed that methyl fluoride in neat antimony pentafluoride undergoes a rapid self-condensation reaction yielding *t*-butyl cation, *t*-hexyl cations, and even higher isomeric tertiary alkylcarbonium ions and HF. Again it must be assumed that methyl fluoride and antimony pentafluoride form an incipient methyl cation which then methylates a second molecule of methyl fluoride to form the  $[\text{C}_2\text{H}_5\text{F}]^+$  ion, which by losing  $\text{H}^+$  forms ethyl fluoride which with  $\text{SbF}_5$  gives the  $\text{C}_2\text{H}_5^+$  cation or the related polarized complex. The ethyl cation as shown previously can readily condense to *t*-butyl cation, *t*-hexyl cations, etc. A detailed study of the methyl fluoride-antimony pentafluoride system is reported separately.



Methyl fluoride in  $\text{FSO}_3\text{H-SbF}_5$  solution also undergoes self-condensation indicating a protonation mechanism.



If in the polycondensation reaction of methane the  $\text{CH}_3^+$  ion would abstract  $\text{F}^-$  from the solvent, the methyl fluoride formed would undergo a fast polycondensation. The absence of methyl fluoride among the reaction products thus can not exclude this possibility.

Ethane was treated in an autoclave with 1:1  $\text{FSO}_3\text{H-SbF}_5$  solution at  $55^\circ$  for 4 hr and at room temperature for an additional 20 hr. The product mixture was submitted to analysis by nmr spectroscopy. The nmr spectrum was dominated by a sharp singlet at  $\delta$  4.30 indicative of the trimethylcarbonium ion. A small amount of various other carbonium ions was also present in the spectrum. Quenching the reaction mixture in  $\text{MeOH-NaOH-H}_2\text{O}$  solution led to the formation of *t*-butyl alcohol in 80% yield.

**2,2-Dimethylpropane** (neopentane) was found in our previous work to react in super acid solution at room temperature to produce methane and trimethylcarbonium ion.<sup>9b</sup> The intermediacy of protonated alkane-type ions in this reaction can be substantiated by means of hydrogen-deuterium exchange studies. When neopentane- $d_{12}$  was treated in a stainless steel autoclave at room temperature and atmospheric pressure with excess 1:1  $\text{FSO}_3\text{H-SbF}_5$  solution, the trimethylcarbonium ion and methane formed both indicated that hydrogen-deuterium scrambling had occurred to the extent of 6% after 5 hr (as analyzed by mass spectroscopy). In this case protolytic cleavage (pathway A) occurs more rapidly than does hydrogen exchange. At  $25^\circ$  the

starting hydrocarbon is half consumed in 12 min. A kinetic study was carried out by use of nmr spectroscopy on the protolytic cleavage of neopentane in "magic acid" solution (Table I). From these data the activation parameters were calculated.

Table I. Pseudo-First-Order Rate Constants for Protolytic Cleavage of Neopentane in 1:1  $\text{FSO}_3\text{H-SbF}_5$  Solution

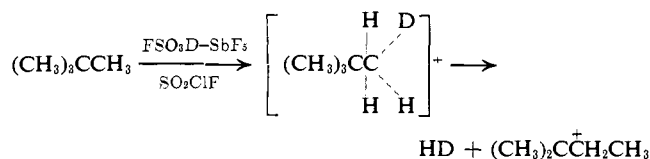
Temp, $^\circ\text{C}$	$k \times 10^5, \text{sec}^{-1}$
-16	2.9
-5	7.8
6	25
23	139
$\Delta H^\ddagger = 14 \text{ kcal/mol}, \Delta S^\ddagger = -19 \text{ eu}$	

When neopentane was added to a 1:1  $\text{FSO}_3\text{H-SbF}_5$  solution diluted with  $\text{SO}_2\text{ClF}$ , a new pathway is followed (pathway B). In this case, the dimethylethylcarbonium ion (*t*-amyl cation) is produced. The starting material liberates hydrogen and the product ion is formed *via* rapid rearrangement of the first formed primary neopentyl cation. A kinetic study was carried out by means of nmr spectroscopy of the hydrogen abstraction reaction (Table II). Differences in the

Table II. Pseudo-First-Order Rate Constants for Hydrogen Abstraction of Neopentane in  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$  Solution

Temp, $^\circ\text{C}$	$k \times 10^4, \text{sec}^{-1}$
-23	3.24
-14.5	14.4
-1.0	33.6
$\Delta H^\ddagger = 13 \text{ kcal/mol}, \Delta S^\ddagger = -22 \text{ eu}$	

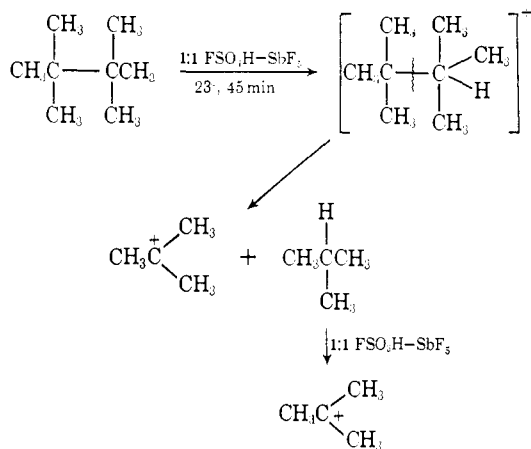
energetics of the two cleavage reactions (pathways A and B) cannot alone cause the widely differing chemical behavior. It is more probable that differences in acidities of the systems and their solvating ability are responsible. The two major reaction pathways are shown in Scheme I. In an attempt to demonstrate that the *t*-amyl cation is produced exclusively through pathway B (involving "front-side" protonation), we treated neopentane with  $\text{FSO}_3\text{D-SbF}_5\text{-SO}_2\text{ClF}$  at  $0^\circ$  for 3 hr. The quenching of the carbonium ion solution with  $\text{CH}_3\text{ONa-CH}_3\text{OH-H}_2\text{O}$  solution led to the formation of *t*-amyl alcohol in 90% yield. If the *t*-amyl cation is formed through pathway B alone (involving "front-side" protonation) there should be no substantial amount of deuterium incorporated into the product. On the other hand, if a trigonal bipyramidal intermediate ion (pathway A) is involved, deuterium scrambling should take place *via* pseudorotation prior to protolytic cleavage. Nmr examination of the



product showed in fact that no H-D exchange had occurred (within the limit of the experimental observation <3%). When neopentane was treated with 2:1 and 4:1 (*M*)  $\text{FSO}_3\text{H}-\text{SbF}_5$  solution only the cleavage reaction occurred as observed by pmr spectroscopy, with the reaction rate decreased in the weaker acid systems. Coupled with the extensive H-D exchange observed (*vide supra*) for the reaction of  $\text{C}_5\text{D}_{12}$  with neat  $\text{FSO}_3\text{H}-\text{SbF}_5$ , we conclude that the experimentally observed reactions indeed take place through pathways A and B.

An extension of this reasoning leads to the conclusion that the  $\text{CH}_5^+$  ion can also be formulated in a similar fashion in the reactions of methane with "magic acid." Experimental evidence in this case, however, is more difficult to obtain.

When 2,2,3,3-tetramethylbutane was added to a 1:1  $\text{FSO}_3\text{H}-\text{SbF}_5$  solution at room temperature, the reaction was complete with stirring after 45 min. The nmr spectrum of the resultant solution indicated the presence of a single species, the trimethylcarbonium ion (sharp singlet at  $\delta$  4.35). Protolytic cleavage and hydride abstraction from isobutane to form the trimethylcarbonium ion is clearly indicated.



In order to explain the chemical reactivity demonstrated by methane, ethane, neopentane, and 2,2,3,3-tetramethylbutane in  $\text{FSO}_3\text{H}-\text{SbF}_5$  ("magic acid") solution, the intermediacy of  $\text{CH}_5^+$  and related hydrocarbon ions must be suggested. These ions were observed previously only in the gas phase. Our observation of the protonation of methane and related hydrocarbons uncovers, for the first time, the solution chemistry of  $\text{CH}_5^+$  and related hydrocarbon ions.

### Quantum Mechanical Calculations

The methanonium ion,  $\text{CH}_5^+$ , is well known in the gas phase from mass spectroscopic studies of methane.<sup>7</sup> Radiation-induced polymerization of methane<sup>8</sup> as well as radiolysis and photolysis of methane in the solid state<sup>9</sup> was suggested to involve similar ion formation.

(7) For example, F. H. Field and M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 3289 (1965), and references therein.

(8) D. R. David and W. F. Libby, *Science*, **144**, 991 (1964).

Recently developed chemical ionization mass spectroscopy also takes advantage of the gaseous ion chemistry of methane.<sup>10</sup>

The gaseous  $\text{CH}_5^+$  ions was suggested by Yamazaki<sup>11</sup> centered method and obtained 7.5 eV; whereas Hartmann and Grein<sup>13</sup> calculated 6.95 eV and Hoyland and Lampe,<sup>14</sup> using single-determinant wave functions for  $\text{CH}_5^+$  and  $\text{CH}_4$  in a one-center approach, obtained a value of 7.26 eV. Rutledge and Saturno<sup>15</sup> using one-center expansion wave functions came to similar conclusions, calculating the proton affinity of methane to be approximately 5 eV.

In our calculations we have used the semiempirical SCF method described by Dewar and Klopman.<sup>16</sup> In this method all valence electrons are included and electron interactions are calculated by means of semiempirical equations. Initially a reasonable guess is made for the electronic distribution and the calculations carried out, until a new charge distribution is obtained. The new set is then used as a starting point and the procedure repeated until self-consistency is attained. Thus, the final charge distribution is independent of the original choice, and the total energy obtained for the self-consistent charge distribution is the energy of the molecule.

This method does not provide the correct bond distance-bond energy relationship and therefore does not guarantee that the chosen structure is the most satisfactory one. However, it has been shown that for bond distances equal to or larger than the equilibrium bond distances, the theoretical method provides heats of formation within  $\pm 4$  kcal of the experimental values. In the following calculations, unless otherwise specified, all C-C bond distances are taken as 1.534 Å and all CH distances as 1.093 Å. Calculated and observed energies are summarized in Table III. In the subsequent discussion the heats of formation used for the alkanes  $\text{C}_n\text{H}_{2n+2}$ , and the carbonium ions  $\text{C}_n\text{H}_{2n+1}^+$ , were the experimentally determined ones; whereas those for the protonated alkanes  $\text{C}_n\text{H}_{2n+3}^+$  were calculated using the method outlined above. The validity of the method for the calculation of heats of formation of carbonium ions has been tested by comparing the results with previously calculated and experimentally determined heats of formation. In agreement with the above-mentioned results, the proton affinity was found to be 5.48 eV if  $\text{CH}_5^+$  was assigned to have the trigonal bipyramidal structure with all C-H bond lengths equal to 1.093 Å. The heat of formation of the  $\text{CH}_3^+$  ion from methane calculated for a  $\text{D}_{3h}$  molecular configuration with all C-H bond lengths 1.06 Å, was found to have  $\text{D}_{3h}$  rather than  $\text{C}_{1v}$  or  $\text{C}_{3v}$  symmetry. He calculated the binding of  $[\text{C}(\text{Is})^2]^4$  with eight electrons and five protons by a multicentered approach. The proton affinity of methane was calculated by Yamazaki to be 5.08 eV. Higuchi<sup>12</sup> studied the  $\text{CH}_5^+$  by a multi-

(9) P. Ansloos, R. E. Rebert, and S. G. Lias, *J. Chem. Phys.*, **42**, 540 (1965).

(10) For a summary see F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).

(11) M. Yamazaki, *J. Phys. Soc. Jap.*, **14**, 498 (1959).

(12) J. Higuchi, *J. Chem. Phys.*, **31**, 563 (1959).

(13) H. Hartmann and F. Grien, *Z. Physik. Chem.*, **22**, 305 (1959).

(14) J. R. Hoyland and F. W. Lampe, *J. Chem. Phys.*, **37**, 1066 (1962).

(15) R. M. Tutledge and Q. F. Saturno, *ibid.*, **43**, 597 (1965).

(16) M. J. S. Dewar and G. Klopman, *J. Amer. Chem. Soc.*, **89**, 3089 (1967).

**Table III.** Heats of Formation of Molecules from Gaseous Carbon and Hydrogen Atoms

Molecule	$\Delta H_f, \text{eV}$	
	Calcd	Exptl <sup>a</sup>
H <sup>+</sup>	13.6	13.6
H <sub>2</sub>	-4.52	4.52
CH <sub>3</sub> <sup>+</sup> (2)	-2.80	-3.04
CH <sub>4</sub>	-17.22	-17.22
CH <sub>5</sub> <sup>+</sup> (4)	-9.10	
CH <sub>3</sub> <sup>+</sup> (5)	-9.46	
CH <sub>3</sub> <sup>+</sup> (6)	-7.86	
C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	[-16.2] <sup>b</sup>	-16.54
C <sub>2</sub> H <sub>6</sub>	-29.37	-29.33
C <sub>2</sub> H <sub>7</sub> <sup>+</sup> (7a)	-21.79	
C <sub>2</sub> H <sub>7</sub> <sup>+</sup> (7b)	-22.03	
C <sub>2</sub> H <sub>7</sub> <sup>+</sup> (8)	-22.23	
C <sub>2</sub> H <sub>7</sub> <sup>+</sup> (9)	-20.60	
C <sub>4</sub> H <sub>9</sub> <sup>+</sup> [(CH <sub>3</sub> ) <sub>3</sub> C <sup>+</sup> ]		-42.8
C <sub>4</sub> H <sub>10</sub> (isobutane)	-53.63	-53.62
C <sub>5</sub> H <sub>11</sub> <sup>+</sup> [(CH <sub>3</sub> ) <sub>2</sub> C <sup>+</sup> CH <sub>2</sub> CH <sub>3</sub> ]		-53.89
C <sub>5</sub> H <sub>12</sub>		-65.86
C <sub>5</sub> H <sub>13</sub> <sup>+</sup> (10a)	-57.46	
C <sub>5</sub> H <sub>13</sub> <sup>+</sup> (10b)	-57.83	
C <sub>5</sub> H <sub>13</sub> <sup>+</sup> (11)	-57.89	
C <sub>5</sub> H <sub>13</sub> <sup>+</sup> (12)	-56.27	

<sup>a</sup> F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957. <sup>b</sup> In calculating the C<sub>2</sub>H<sub>5</sub><sup>+</sup> ion, an additional difficulty arises from the fact that we have to assign a distance to the C-C bond. We calculated therefore an upper and lower limit assuming a C-C single and double bond, respectively. The result was -17.4 and -15.0 eV leaving to a tentative average of -16.2 in fair agreement with the experimental value of 16.54.

be 14.42 eV as compared with the experimental value of 14.39 eV.<sup>17</sup>

### Discussion of Structural and Mechanistic Aspects

**Methane.** If the intermediate CH<sub>5</sub><sup>+</sup> ion exists exclusively as the trigonal bipyramidal species, **4**, indicated by previous theoretical calculations, the hydrogen-exchange reaction is easily accounted for but protolytic dehydrogenation with the formation of CH<sub>3</sub><sup>+</sup> can only be a slow reaction and could hardly compete with deprotonation since each hydrogen atom carries now an appreciable amount of positive charge (Table IV). In order to account for the observed "polycondensation" or "growth reaction" of methane, we can consider attack by the proton-to take place, not only as a back-side attack on the carbon but also as a front-side attack on it (**5**). Finally, a direct attack in the direction of one of the hydrogen atoms may be considered (**6**).

The latter types of attack would offer an easier explanation for subsequent protolytic cleavage. *A priori*, however, there is no clear indication for favoring any of these three possible intermediates as possible forms or the protonated methane and experimental findings, previously discussed offer no solution. In order to determine the possibility of occurrence of these three schemes, we calculated the heat of formation of several possible CH<sub>5</sub><sup>+</sup> intermediates. The trigonal bipyramidal structure, **4**,<sup>18</sup> was found to be 5.48 eV more stable than the isolated CH<sub>4</sub> and H<sup>+</sup> system. In solution, however, this stabilization is largely counterbalanced by the loss

(17) After the completion of this work, a paper by Yonezawa, Naka, Tsuji, and Kato appeared: *J. Amer. Chem. Soc.*, **90**, 1239 (1968). Using a slightly modified semiempirical approach, the authors found the proton affinity of methane to be between 4.68 and 5.92 eV, and the heat of formation of CH<sub>3</sub><sup>+</sup> from methane to be 13.44 eV.

(18) When tetrahedral methane is being deformed into a trigonal pyramid, a loss of stabilization of 0.68 eV is calculated.

of the proton solvation energy due to the partial transfer of charge from the methane molecule to the proton. A rough estimate of the solvation energies involved can be made by using the Born equation and assuming that the solvation energy of the molecule is the sum of the solvation energies of the constituent atoms. In this way, the solvation energy would be

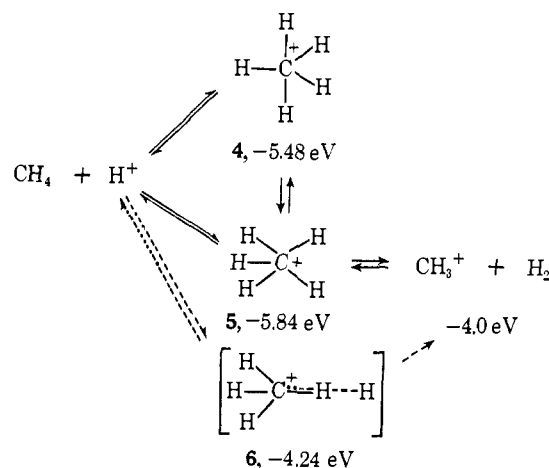
$$E_{\text{solv}} = -\frac{14.388[\sum_A q_A^2]}{2r_A} \left(1 - \frac{1}{\epsilon}\right) \text{eV}$$

where  $\epsilon$  is related to the dielectric constant of the medium and  $r_A$ , the effective proton radius would be about 0.65 Å. The solvation of methane will be approximately zero whereas that of the proton ( $q_A = 1$ ) is  $(-14.388/2r_A)[1 - (1/\epsilon)]eV$  (in water  $\epsilon = 80$ ;  $\Delta E_{\text{solv}} = 10.8 \text{ eV}$ ).

For CH<sub>5</sub><sup>+</sup> we found a charge of 0.1856 on each of the three equatorial hydrogen atoms and 0.3310 on the two axial ones. The central carbon atom carries a charge of -0.2189. Neglecting the difference in radius, we thus obtained  $\sum_A q_A^2$  for CH<sub>5</sub><sup>+</sup> of 0.3704 and a loss of solvation energy of -7.0  $[1 - (1/\epsilon)] \text{ eV}$ . It is clear therefore that under suitable conditions the loss in solvation energy may become comparable to the gain in bonding energy of 5.48 eV, and CH<sub>5</sub><sup>+</sup> therefore could be formed in solution.<sup>19</sup>

Several models of ion **6** were calculated. Whether the attack took place on a hydrogen atom of the undeformed methane or on a trigonal bipyramidal methane, the relative stabilization was 4.2 eV (lower, by 0.2 eV than the CH<sub>3</sub><sup>+</sup> + H<sub>2</sub> system) only when the H-H bond distance became smaller than 0.75 Å. The small stabilization energy thus obtained only when the bond distance become unrealistically short in the intermediate, probably reflects the known overestimation of stabilization energies at short distances. One may therefore conclude that, in all probability, no stable intermediate CH<sub>5</sub><sup>+</sup> ion, **6**, would be formed in this process.

The calculation of models for ion **5** (front-side attack) are less accurate since a good estimate of the exact geometry of this ion is difficult to make. A reasonable model for our calculation was considered the one where all CH bonds remain at 1.093 Å. Three of the hydrogen atoms remain at the same position as they were in methane and the two others would be at an equal dis-

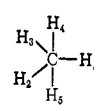
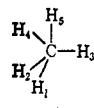
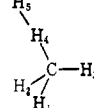


(19) A rough estimate of these relative solvation energies may be given as before by the sum of the square of the charges which is found to be 0.3704 for CH<sub>5</sub><sup>+</sup> and 0.3479 for CH<sub>3</sub><sup>+</sup>.

tance from the remaining  $sp^3$  orbital. The distance between these two hydrogens was chosen arbitrarily to be 0.9 Å as in the analogous trigonal  $H_3^+$  system.<sup>20</sup>

One finds for this type of front-side protonated  $CH_5^+$  ion a relative stabilization of 5.84 eV with respect to the isolated  $CH_4$  and  $H^+$  system. The coordinates and total charge densities for the three models 4, 5, and 6 of protonated methane are summarized in Table IV.

Table IV

		X	Y	Z	Q
	C	0	0	0	-0.2189
	H <sub>1</sub>	1.093	0	0	0.1856
	H <sub>2</sub>	-0.5465	0.9465	0	0.1856
	H <sub>3</sub>	-0.5465	0.9465	0	0.1856
	H <sub>4</sub>	0	0	1.093	0.3310
	C	0	0	0	-0.0469
	H <sub>1</sub>	-0.3642	0.8924	-0.5152	0.1657
	H <sub>2</sub>	-0.3642	-0.8924	-0.5152	0.1657
	H <sub>3</sub>	1.093	0	0	0.2073
	H <sub>4</sub>	-0.7564	0	0.7890	0.2587
	C	0	0	0	0.3316
	H <sub>1</sub>	-0.3642	0.8924	-0.5152	0.1276
	H <sub>2</sub>	-0.3642	-0.8924	-0.5152	0.1226
	H <sub>3</sub>	1.093	0	0	0.1226
	H <sub>4</sub>	-0.3642	0	1.0305	-0.0408
	H <sub>5</sub>	-0.61411	0	1.7376	0.3415

The transition state or intermediate for electrophilic protonation of alkanes in its most primitive form is a three-center, two-electron problem. The  $SN_2$  reaction transition state or intermediate on the other hand is the related four-electron, three-centered bond problem. The  $SE_2$  mechanism is analogous to the  $SN_2$  mechanism in that the new bond is forming as the old one is breaking. In the  $SN_2$  case, however, the incoming group brings with it a pair of electrons and the orbital occupied by the unshared electron pair can overlap with the central carbon atom only to the extent that the leaving group takes away its electrons. Otherwise the carbon atom would have more than eight electrons at once in its other shell. Due to electron repulsion the incoming group attacks at the back side, at a position  $180^\circ$  from the leaving group so that inversion of configuration is found. The situation is different in the case of an  $SE_2$  type of reaction. In this case the incoming group may also approach from the front side, since it brings with it only a vacant orbital. Previous views relating to  $SE_2$  reactions always preferred front-side attack and therefore retention of configuration.<sup>21,22</sup> More recently, however, this view is being questioned as examples of inversion causing  $SE_2$  substitutions become known, indicating the possibility of back-side attack.<sup>23</sup> Considering the geometry and the atomic orbitals involved, front-side attack appears however to be a

(20) H. Conroy, *J. Chem. Phys.*, **40**, 603 (1964).

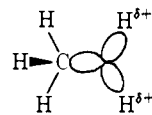
(21) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, **244** (1935), and subsequent publications.

(22) O. A. Reutov, *Rec. Chem. Progr.*, **22**, 1 (1961), and references cited therein.

(23) For an excellent review see F. R. Jensen and B. Rickborn "Electrophilic Substitution of Organomercurials," McGraw-Hill Book Co., Inc., New York, N. Y., 1968.

reasonable expectation for an  $SE_2$  type reaction involving a three-centered, two-electron bond.

Front-side attack with retention of configuration may occur with no change in hybridization on the central carbon atom through attack on the bond rather than the carbon atom itself. Repulsion of the positive charges on the hydrogen atoms could, however, occur thereby causing back-side attack.



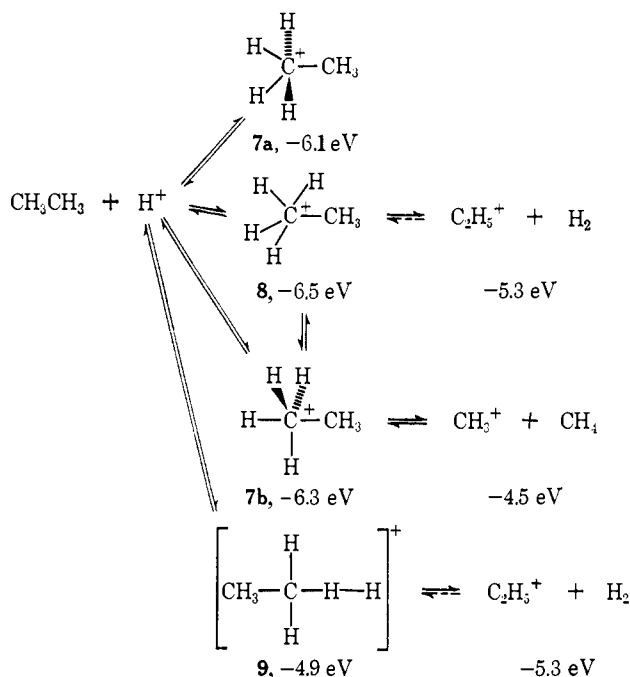
In general in  $SE_2$ -type reactions a metal ion is the leaving group. Invariably these atoms have vacant orbitals available for complex formation (bridging) or expansion of their electron shell. Thus the importance of bridging atoms between the electrophile and the leaving group in front-side attack is clearly established. Protonation, however, could be considered as a case for a pure  $SE_2$  reaction and no prediction as to the nature of the transition state can be made in our view, based on analogy with the metal-organic systems studied.

Our calculations gave the front-side coordinated methanonium ion **5** a 0.36 eV ( $\sim 9$  kcal) advantage over the back-side coordinated ion **4**. Protonation on hydrogen (ion **6**) seems less favored, although obviously in this case bent bond models should be more properly considered. The symmetrical bent bond model is, in fact, **5**. The relatively small differences between ions **5** and **4** can be much affected by solvation in various systems, as is clearly indicated in the related case of neopentanonium ion (see subsequent discussion).

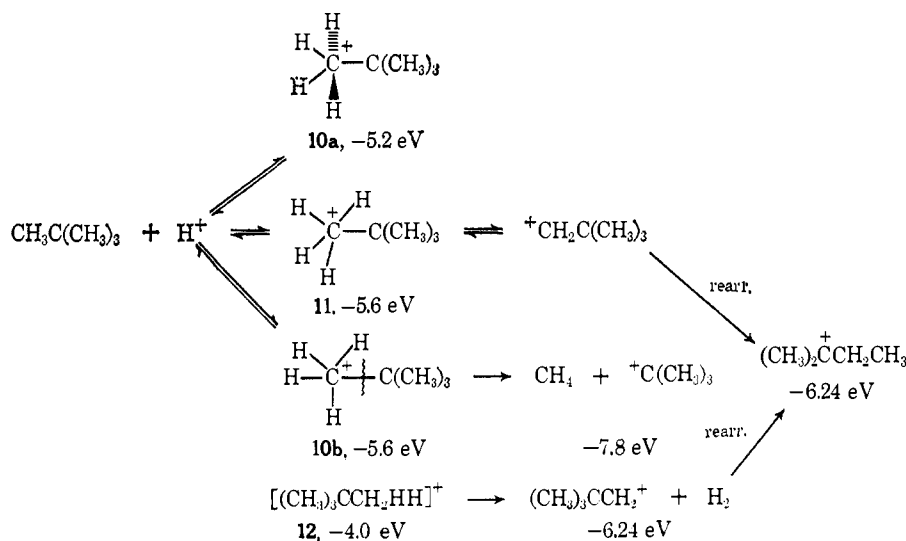
In our work in  $FSO_3H-SbF_5$  solution as well as the work of Hogeveen and Gassbeek<sup>5</sup> in  $HF-SbF_5$  it was found that hydrogen exchange occurs at rates of  $k = 10^{-3}$  to  $10^{-4}$   $sec^{-1}$  at temperatures ( $25^\circ$ ) where polycondensation cannot yet be detected. No polycondensation of methane in  $HF-SbF_5$  solution was achieved. These differences again could indicate differences in the nature of the methanonium ion as a consequence of the reaction medium.

**Ethane.** In the case of ethane, as for related higher alkanes, besides the frontal protonation and that from the direction of hydrogen two possible trigonal bipyramidal structures can be drawn depending on whether the proton attacking along one of the C-H bond axes or on the C-C bond axis. The various possibilities together with the calculated stabilization energies are illustrated in Scheme II. The stabilization of the intermediate **7a** is found slightly lower (6.1 eV) than that of **7b** (6.3 eV). Both of them, however, liberate a larger amount of energy than the reaction producing **9** and are therefore believed to occur faster. In contrast with the reaction of methane, however, the trigonal bipyramidal ion **7b** may also lead to cleavage products and cleavage of ethane is thus predicted to occur at a faster relative rate than hydrogen exchange. Subsequent attack of excess ethane by the newly formed  $CH_5^+$  ion is also possible. The intermediate  $C_2H_7^+$  ion is postulated on the grounds that its stabilization energy is higher than that of the starting reagent by 6.3 eV and also higher than that of the final product by 1.8 eV.

Scheme II



Scheme III



The reaction leading from **9** to  $\text{C}_2\text{H}_5^+$  and  $\text{H}_2$  liberates only 4.9 eV to form the transition state ( $R_{\text{H}-\text{H}} = 0.75 \text{ \AA}$ ) and could therefore be negligible. The pathway leading through frontal-protonated ion **8** is again most probable. All the stabilization energies are larger than those occurring for methane, and the over-all reactivity of ethane is therefore predicted to be larger than that of methane.

**Neopentane.** Consideration of the protolytic cleavage and hydrogen exchange reactions of neopentane in "magic acid" solution leads to the necessity of intermediate ions of similar structure to those for ethane. The protolytic cleavage reaction in neat magic acid leads to the *t*-butyl cation and methane. In acid diluted with  $\text{SO}_2\text{ClF}$ , only the *t*-amyl cation is formed, through rapid rearrangement of the reactive neopentyl cation. When the reaction was carried out in  $\text{FSO}_3\text{D}-\text{SbF}_5-\text{SO}_2\text{ClF}$  no deuterium incorporation into the *t*-amyl cation was observed. Ion **10a** or **10b** would explain the former cleavage, whereas the latter pathway

indicates ion **11** or **12**. The hydrogen-scrambling reaction observed in recovered neopentane in this case would indicate the intermediacy of ion **10a** or **10b** as ion **11** or **12** cleaves to the neopentyl cation, which rearranges very rapidly to the *t*-amyl cation. This rearrangement would not allow reformation of any appreciable amount of exchanged neopentane, which indeed was experimentally verified. As protolytic cleavage was found experimentally to be much faster than hydrogen exchange, **10a** can be only of lesser importance than **10b**. The absence of hydrogen exchange in formation of the *t*-amyl cation from neopentane seems to rule out **10** as a common intermediate ion and strongly supports **11**.

In the case of neopentane and ethane, the different reaction paths with the calculated stabilization energies can be summarized as shown in Scheme III

The stabilization brought about by reaction leading through **10b** is significantly larger than for **10a**. Moreover, additional stability is produced by the decomposition of the  $\text{C}_5\text{H}_{13}^+$  ion **10b** into products.

Depending on the specific nature of the transition state and thus on the solvent, any of these mechanisms could be considered. Reaction going through **12** is less

favoured but the number of sites where reaction can take place is larger than for reactions going through **10a** or **b**. Ion **11** or **12** can be much better solvated than **10**, thus reaction going through **11** or **12** is expected to take place in lower acidity solvents than that going through **10b**. Another possible mechanism involving direct attack by the proton on the central carbon atom could also be envisaged but the calculations there would require a rearrangement of the C-C bonds and the results might not be consistent with those for the other processes.

### Conclusions

The formation of  $\text{CH}_5^+$  and related alkanonium ions in super acid solutions ( $\text{FSO}_3\text{H}-\text{SbF}_5$ ,  $\text{HF}-\text{SbF}_5$ , or related acids) is remarkable.  $\text{CH}_5^+$  is well known in the gas phase from mass spectroscopic and related studies of methane.<sup>10,24</sup> Our observation, however, of the pro-

(24) See Table III, footnotes *a* and *b*.

tonation of methane and related hydrocarbons seems to open up, for the first time, the solution chemistry of  $\text{CH}_5^+$  and related alkanonium ions. As hydrogen exchange, as well as intermolecular acid catalyzed hydrogen and alkyl transfer reactions (transalkylations) can be considered as typical electrophilic substitution reactions on saturated carbon, work presented on the formation of  $\text{CH}_5^+$  type ions in solution, also presents important implications for the mechanism of these reactions.

Based on the results presented in this work, it seems appropriate to recommend that saturated hydrocarbons should be referred to only as alkanes and not as paraffins. The high chemical reactivity demonstrated by methane and other alkanes in strong acid system is no longer compatible with a name referring to "parum affinis."

## Experimental Section

All hydrocarbons used were commercial chemicals of the highest purity. Methane ( $\geq 99.95\%$ ) and ethane ( $\geq 99.9\%$ ) were obtained from the Matheson Company. Neopentane ( $\geq 99.88\%$ ) was obtained from Phillips Petroleum Co. and 2,2,3,3-tetramethylbutane ( $\geq 99\%$ ) from Chemical Samples Co. Methane- $d_4$  ( $\geq 99\%$ ) and neopentane- $d_{12}$  were obtained from Isomet Corp. All pmr spectra were recorded on a Varian Associates Model A56/60A nuclear magnetic resonance spectrometer equipped with a variable-temperature probe. The mass spectra were recorded with a Consolidated Engineering Corp. Model 21-620 mass spectrometer. Fluorosulfuric acid- $d$  was prepared by exchange with sulfuric acid- $d_2$ .

**The Reaction of Methane with 1:1  $\text{FSO}_3\text{H-SbF}_5$  Solution.** In a typical experiment, 6.5 g (0.02 mol) of 1:1  $\text{FSO}_3\text{H-SbF}_5$  solution was placed in a 125-cc Teflon bottle. The unstoppered bottle was placed in a 500-cc stainless steel autoclave, and the autoclave was sealed. The reaction vessel was flushed with nitrogen and then methane gas introduced *via* a needle valve. Methane (475 cc) was introduced into the autoclave at a pressure of 21 psi (0.7 g, 0.05 mol) and the autoclave was sealed. The reaction was carried out at 70–80° for 4 hr and then left standing at room temperature overnight. The autoclave was opened; the acid solution was diluted with  $\text{SO}_2$  and analyzed by nmr spectroscopy. The nmr spectrum of the solution consisted of a major peak at  $\delta$  2.93 (trimethylcarbonium ion) as well as peaks at  $\delta$  3.13 (doublet,  $J = 4$  Hz, dimethylisopropylcarbonium ion) and  $\delta$  2.94 (dimethyl-*t*-butylcarbonium ion). Quenching experiments with  $\text{NaOMe-MeOH-H}_2\text{O}$  solution verified the assignments. In atmospheric pressure reactions, methane gas was passed through a heated solution of the  $\text{FSO}_3\text{-SbF}_5$  solution at various temperatures and for various time periods with exclusion of atmospheric moisture and oxygen.

Ions formed in the acid solution were identified as previously mentioned.

**The Reaction of Methane- $d_4$  with 1:1  $\text{FSO}_3\text{H-SbF}_5$  Solution.** Into a 75-cc stainless steel autoclave was placed 10 g (0.03 mol) of a 1:1 solution of  $\text{FSO}_3\text{H-SbF}_5$ . The bomb was closed and then attached to a high vacuum line by means of a glass tube connected to the bomb with a Kovar seal and to the vacuum line with a ball joint. The bomb was evacuated to a pressure of 1 mm. Methane- $d_4$  (1 l. at STP) was attached to the vacuum line and after the evacuation of the bomb, the breakseal on the methane flask was smashed. The deuterated hydrocarbon was introduced into the autoclave (70 cc at 1 atm; 0.06 g, 0.003 mol). The bomb was sealed, and the 10:1 mixture of acid and hydrocarbon was allowed to react. Gas samples were taken and analyzed by mass spectroscopy.

**The Reaction of Ethane with 1:1  $\text{FSO}_3\text{H-SbF}_5$ .** The procedure used in the reaction of methane with super acid was followed. Nmr examination of the product mixture (after reaction at 55° for 4 hr and room temperature for 20 hr) indicated a predominance of the trimethylcarbonium ion. The reaction mixture was quenched in  $\text{NaOMe-MeOH-H}_2\text{O}$  solution at  $-78^\circ$ , extracted into pentane and analyzed by gas chromatography and nmr, giving 80% *t*-butyl alcohol.

**The Reaction of Neopentane- $d_{12}$  with 1:1  $\text{FSO}_3\text{H-SbF}_5$ .** The procedure was identical with that used for the reaction of methane- $d_4$  with super acid. Samples of the vapors above the 10:1 mixture of acid and hydrocarbon were taken and analyzed by mass spectroscopy for methane. The acid solution was analyzed by nmr spectroscopy for *t*-butyl and *t*-amyl cations, respectively.

**Kinetic Study of the Cleavage of Neopentane with 1:1  $\text{FSO}_3\text{H-SbF}_5$ .** In its nmr spectrum, neopentane appears as a sharp singlet at  $\delta$  1.3 and the trimethylcarbonium ion appears as a sharp singlet at  $\delta$  4.3. By measuring the areas under these peaks *vs.* the area under a standard peak (capillary TMS) with time, the kinetics of the reaction were followed. Using a fivefold excess of 1:1  $\text{FSO}_3\text{H-SbF}_5$ , kinetics of the protolytic cleavage reaction were measured at  $-16$ ,  $-5$ , 6, and  $23^\circ$ . Linear pseudo-first-order rate constants were obtained and an Arrhenius plot gave the activation parameters ( $\Delta H^\ddagger = 14$  kcal/mol;  $\Delta S^\ddagger = 1.9$  eu). Using  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$  as the acid system, the kinetics of the hydrogen abstraction reaction of neopentane (to the *t*-amyl cation) was investigated by nmr spectroscopy. The activation parameters found in this reaction are  $\Delta H^\ddagger = 13.0$  kcal/mol;  $\Delta S^\ddagger = -22$  eu.

**The Reaction of 2,2,3,3-Tetramethylbutane with 1:1  $\text{FSO}_3\text{H-SbF}_5$ .** 2,2,3,3-Tetramethylbutane (100 mg, 0.007 mol) was stirred with 1.5 g (0.005 mol) of a 1:1  $\text{FSO}_3\text{H-SbF}_5$  solution at room temperature for 45 min (until a homogeneous solution was obtained). The nmr spectrum of the resultant solution consisted of a singlet peak at  $\delta$  4.35 (trimethylcarbonium ions) along with peaks attributable to the acid system.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research.