tion is general in carbocation chemistry. Similar structures are also found in boron hydride chemistry. For example, the structure of BH_5 is similar to that of CH_5^+.[30] The orbital description of the $B_5H_{10}^+$ ion also involves a framework of $B_5H_9^+$ and H^+ is added at B_1 to form a three-center bond constructed from two s orbitals on H atoms and a p orbital extented along the symmetry axis.[31]

The formation of H_3^+ ion in solution chemistry may have implications concerning the effect of hydrogen in catalytic reactions, isomerization and alkylation. For example, the ability of aluminum chloride to activate molecular hydrogen was observed previously.[32] Our work may clarify the nature of this activation as aluminum chloride always contains enough moisture to act as a strong Brønsted acid ($H^+AlCl_3OH^-$ or the like). Hydroisomerizations observed on noble metal hydrogenation catalysts may also involve formation of H_3^+. The well-recognized effect of hydrogen pressure to decrease protolytic cracking processes can be considered as quenching of carbenium ion centers by H_2, *i.e.*, alkylation of the H–H bond resulting in alkane formation.

Acknowledgment. Support of our work by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged.

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(30) G. A. Olah, P. Westerman, Y. K. Mo, and G. Klopman, *J. Amer. Chem. Soc.*, **94**, 7859 (1972).

(31) J. J. Solomon and R. F. Porter, *ibid.*, **94**, 1443 (1972).

(32) L. W. Wright, S. W. Weller, and G. A. Mills, *Ind. Eng. Chem.*, **49**, 1054 (1957).

Electrophilic Reactions at Single Bonds. XII.[1a] Hydrogen–Deuterium Exchange, Protolysis (Deuterolysis), and Oligocondensation of Alkanes with Superacids[1b]

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Abstract: Twenty-one alkanes, including methane, ethane, propane, butane, 2-methylpropane, 2-methylbutane, and 2,2-dimethylpropane, were studied in $FSO_3H–SbF_5$ and $HF–SbF_5$ (SO_2ClF) as well as in the corresponding deuterated superacid systems. Hydrogen–deuterium exchange and protolysis, followed frequently by oligocondensation, were observed, indicating the general reactivity of C–H and C–C single bonds toward superacid systems. All data indicate frontside electrophilic attack on the involved bonds involving pentacoordinated carbonium ions.

Two types of electron donor ability have been recognized: π- as well as n-donor (unshared electron pair donor) ability.[2] The reactivity of olefins, acetylenes, and aromatic hydrocarbons toward electrophiles lies in the π-electron-donor abilities of the unsaturated C=C and C≡C bonds and π-aromatic systems. Compounds with unshared pairs of electrons on heteroatoms, as well as carbanions or singlet carbenes, represent the major types of n-donor substrates most frequently encountered. Both types are characterized in that an electron-releasing substituent group will facilitate the electron-donor ability while an electron-withdrawing group will decrease it.

The acid-catalyzed transformation reactions of saturated hydrocarbons (fragmentation, alkylation, isomerization) are generally considered to be carbocation reactions involving trivalent carbenium ions. Whitmore[3] and subsequently Bartlett, Condon, and Schneider[4a] as well as Schmerling[4b] in landmark publications developed the mechanistic concepts of acid-catalyzed alkane alkylations, isomerizations, and fragmentations. The major steps in the mechanism are the intermolecular transfer of hydride ion from a tertiary position in an isoparaffin to a carbenium ion and the ease of shift of a hydrogen atom or alkyl group from one carbon atom to another.

Contrary to frequent textbook references to electrophilic aliphatic substitution of saturated compounds, authenticated examples are limited to reactions involving organometallic compounds, such as organomercurials.[5] Protolytic reactions, such as hydrogen exchange,[6] migration of double bonds,[7] and keto–enol tautomerization,[8] involve either π- or n-donor inter-

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(1) (a) Part XI: G. A. Olah, J. Shen, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **95**, 4957 (1973); (b) a preliminary communication was published: G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *ibid.*, **93**, 1251 (1971).

(2) G. N. Lewis, *ibid.*, 38, 762 (1916); G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Corp., New York, N. Y., 1923.

(3) (a) F. C. Whitmore, *ibid.*, **54**, 3274 (1932); (b) F. C. Whitmore and E. E. Stahly, *ibid.*, **55**, 4153 (1933).

(4) (a) P. D. Bartlett, F. E. Condon, and A. Schneider, *ibid.*, **66**, 1531 (1944); (b) L. Schmerling, *ibid.*, **66**, 1422 (1944); **67**, 1778 (1945); **68**, 153 (1946).

(5) F. R. Jensen and B. Rickborn, "Electrophilic Substitutium of Organomercurials," McGraw-Hill, New York, N. Y., 1968.

(6) J. March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968, Chapter 12, p 452.

(7) For a review, see W. Mackenzie in S. Patai "The Chemistry of Alkanes," Interscience, New York, N. Y., 1964, pp 416–436.

(8) (s) For discussion of the mechanism, see C. R. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 530–575; (b) for a recent example, see M. Senn, W. J. Richter, and A. L. Burlingame, *J. Amer. Chem. Soc.*, 87, 680 (1965).

actions. For example, 2-methylpropane exchanges in D_2SO_4 all nine methyl hydrogens, but not the methine hydrogen. The reaction thus proceeds through isobutylene as a reactive π-donor species and not through a σ donor (*vide infra*). No "pure" electrophilic substitutions of alkanes have been reported[9] with the exception of the recently observed hydrogen–deuterium exchange and protolytic cleavage reactions in FSO_3H-SbF_5, and related superacid media.[9–11]

Previous studies have established the intermediacy of CH_5^+ type alkonium ions in the reactions of alkanes in superacids.[9–11] Theoretical calculations[12] also indicate that in the formation of CH_5^+ (methonium ion) the preferential site of protonation is the main lobe of the C–H bond. The most stable configuration of the CH_5^+ ion is the one resulting from frontside attack on the C–H bond rather than on the carbon atom itself, with retention of configuration and with no change in hydridization of the central carbon atom. Experimental results showed hydrogen–deuterium scrambling in recovered methane in the $CD_4 + FSO_3H-SbF_5$ system,[10,11c] or loss of hydrogen forming the extremely reactive methyl cation (CH_3^+) which in turn initiates oligocondensation by reacting with excess CH_4. Methylation of alkanes by the carbenium ion (CH_3^+) was also independently evidenced by reacting alkanes with powerful methylating agents such as the CH_3F-SbF_5 complex.[13]

The general electrophilic reactivity of covalent C–H and C–C single bonds of alkanes is due to what we consider the third major type of electron-donor ability beside π- and n-donor, *i.e.*, the σ-donor ability (σ basicity) of shared electron pairs (single bonds) activity.[12] To study the general behavior of single bond reactivity in alkanes, we undertook a study of the protolytic behavior of alkanes in "magic acid" (1:1 FSO_3H-SbF_5)[14] and anhydrous fluoroantimonic acid (1:1 $HF-SbF_5$). For comparison we also carried out studies in acids of varying molar ratios and in "neat" antimony pentafluoride (which due to the extreme difficulty of complete purification always contains some protic acid impurities).[15] All solutions were diluted with sulfuryl chloride fluoride, an extremely low nucleophilicity solvent well suited for studies with superacids.[10]

Results and Discussion

A. Protolytic Cleavage and Oligocondensation Reactions. The protolytic (deuterolytic) behavior of 21 alkanes was studied in $FSO_3H-SbF_5(SO_2ClF)$ and $HF-SbF_5(SO_2ClF)$ solution. Stable carbenium ions formed were observed by nmr spectroscopy, whereas neutral cleavage products (hydrogen and hydrocarbons) were analyzed by gas–liquid chromatography and mass spectrometry.

We have reported in some detail in our preceding work the protolytic behavior of methane.[9] In FSO_3H-SbF_5 (magic acid) solution at around 60° it undergoes protolytic condensation as evidenced by formation of higher molecular weight alkylcarbenium ions, mainly *tert*-butyl cation and formation of molecular hydrogen. The amount of the latter, however, was always found to be considerably less than the expected stoichiometric amount (based on initial formation of CH_5^+ and its cleavage to CH_3^+ and H_2). It was suggested that reduction of the acid system, particularly of antimony pentafluoride, is using up the formed hydrogen. Similar polycondensation was found when using 1:1 $HF-SbF_5$ or "neat" antimony pentafluoride, but not, as reported by Hogeveen, in more dilute (such as 10:1) $HF-SbF_5$ solutions.[18]

Hogeveen and Lukas who studied the carbonylation of methane in "neat" antimony pentafluoride solution[19] suggested that the reaction takes place *via* direct oxidation of methane to CH_3^+, without prior protolytic formation of CH_5^+.

$$\begin{tikzcd} CH_4 + SbF_5 \arrow[r] & CH_3^+SbF_5H^- \arrow[d, "CO"] \\ & CH_3CO^+ \end{tikzcd}$$

They claimed: "The fact that oligocondensation of methane proceeds in pure SbF_5 (without FSO_3H as a Brønsted acid) is in itself a very strong argument against the initial formation of CH_5^+."[20]

Concerning the action of "neat" antimony pentafluoride it was known in our laboratory for some time[16,17] that antimony pentafluoride itself, preferentially in SO_2ClF solution, is a very efficient ionizing medium for forming alkylcarbenium ions from alkanes (a similar observation by Lukas was quoted by Brouwer and Hogeveen[20]). We have, however, pointed out that caution must be exercised to assign this reaction to "hydride abstraction" by the Lewis acid fluoride, as implied by Lukas.[21] As it is practically impossible, under usual reaction conditions used, to remove protic acid impurities from "neat" antimony pentafluoride, it is always possible that protic acid impurities in the system are responsible for the observed hydrogen abstraction reactions. Indeed in our hands hydrogen abstraction reactions with "neat" antimony pentafluoride were always found to produce some molecular hydrogen as the by-product of the reactions (see subsequent discussion). If SbF_5 itself as a Lewis acid would abstract H^-, the formed gegenion would be SbF_5H^- (or $Sb_2F_{10}H^-$). Due to the extreme weakness of the Sb–H bond (antimony hydrides are known to be most unstable compounds), this anion would be expected to lose HF with ease, thus producing in the

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[9] (a) G. A. Olah and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **90**, 2726 (1968); (b) G. A. Olah, G. Klopman, and R. H. Schlosberg, *ibid.*, **91**, 3261 (1969).

[10] G. A. Olah and J. Lukas, *ibid.*, **89**, 2227, 4739 (1967); **90**, 933 (1968).

[11] (a) H. Hogeveen and A. F. Bickel, *Chem. Commun.*, 635 (1967); (b) H. Hogeveen, C. J. Gaasbeek, and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, 87, 319 (1968); (c) A. F. Bickel, C. J. Gaasbeck, H. Hogeveen, J. M. Deldrick, and J. P. Phateew, *Chem. Commun.*, 634 (1967).

[12] For a general discussion of the carbocation ion concept, see G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972), and references given therein.

[13] G. A. Olah, J. R. DeMember, and J. Shen, *ibid.*, **95**, 4952 (1973).

[14] Registered trade mark of Cationics, Inc., Cleveland, Ohio 44143.

[15] "Neat" $SbF_5(SO_2ClF)$ was also found in our work for some time (see ref 16, 17) as an effective ionizing medium for alkanes. We are, however, not necessarily considering it different in its activity from $HF-SbF_6$ acid systems with a high molar ratio of antimony pentafluoride (see subsequent discussion).

[16] G. A. Olah, P. R. Clifford, Y. Halpern, and R. G. Johanson, *J. Amer. Chem. Soc.*, **93**, 4219 (1971).

[17] G. A. Olah and J. A. Olah in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 761.

[18] H. Hogeveen, C. J. Gaasbeek, and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, **88**, 703 (1969).

[19] H. Hogeveen, J. Lukas, and C. F. Roobeck, *Chem. Commun.*, 920 (1969).

[20] D. M. Brouwer and H. Hogeveen, *Progr. Phys. Org. Chem.*, **9**, 179 (1972), and references quoted therein.

[21] As quoted in ref 19 and 20.

system the Brønsted superacid HF–SbF_5, which is well known and discussed extensively also in this paper. It is capable of hydrogen abstraction in a protolytic fashion, forming carbenium ions and hydrogen or lower molecular weight alkanes in the corresponding C–H or C–C bond cleavage reactions. It thus seems to us a rather mute point to overemphasize the use of "neat" antimony pentafluoride as a distinct and differing hydrogen abstracting agent. Even if such reaction initially would be possible (which is not proven at the present time and seems somewhat improbable based on the extensive literature of related studies with other "neat" Lewis acid halides in Friedel–Crafts chemistry[22]) the system will produce HF according to

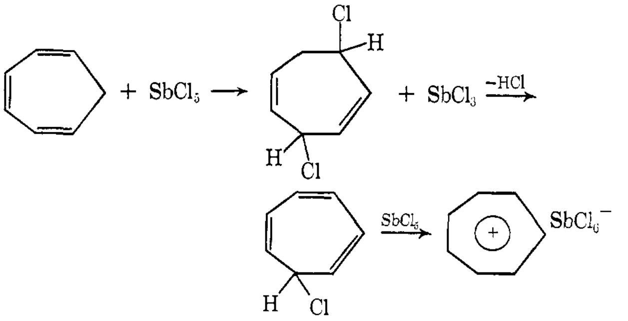
$$RH + SbF_5 \longrightarrow R^+SbF_5H^- \longrightarrow RF + SbF_3 + HF$$

and in the presence of excess SbF_5 the reaction

$$RH \xrightarrow{HSbF_6} R^+SbF_6^- + H_2$$

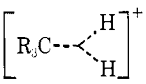
will proceed as typical protolysis. As antimony pentafluoride itself is highly polymeric, interaction with the monomeric Lewis acid is even more improbable.

Quoted[20] analogy with hydride abstraction from cycloheptatriene by antimony pentachloride yielding tropylium ion[23] is not considered by us relevant, as this reaction was found[24] to proceed by chlorination of the triene (probably *via* 1,4 addition), followed by dehydrochlorination and ionization of the resulting chlorotropylidene, and not by direct hydride abstraction with the Lewis acid halide.



Concerning the reactivity of antimony pentafluoride with hydrocarbons, π systems react with ease. Aromatic hydrocarbons, such as benzene and substituted benzenes, undergo both oxidative Scholl-type condensations and Friedel–Crafts metalation giving arylfluorostibines.[25] Similar one-electron oxidations or electrophilic metalations are also very readily possible with alkenes and alkynes.[26] The much higher oxidation potential of alkanes over unsaturated hydrocarbons, however, makes similar processes considerably less likely.[26a]

A further question which must be considered is the fate of abstracted hydrogen in the acid-induced reactions of methane and higher homolog alkanes (to be discussed). Antimony pentafluoride is known to undergo reduction with ease. We have found in control experiments that when shaking neat antimony pentafluoride under hydrogen pressure (~50 atm) at room temperature for 24 hr, nearly quantitative reduction to SbF_3 and HF could be achieved. By raising the temperature the reduction can be much accelerated. In solvent systems (which in most instances are coordinating with the strong Lewis acid, such as SO_2, and to a much lesser degree even SO_2ClF) and particularly at low temperatures, the reduction is, however, very slow, if it takes place at all. It must be, however, also considered that reductions with molecular hydrogen gas may be not identical in their activity with reductions with nascent hydrogen, generated in the course of the hydrogen abstraction reactions of alkanes. In the protolysis of a C–H bond a two-electron, three-center bonded carbonium ion



is formed. When this three-center bond cleaves the bonding interaction between H and H is not yet complete and interaction with an active substrate (*i.e.*, antimony pentafluoride) can start before molecular hydrogen would be completely formed. Thus we consider this form of "nascent" hydrogen responsible for effective reduction of SbF_5 containing solvent systems and the fact that molecular hydrogen found in the system involving hydrogen abstraction reactions is never stoichiometric. Antimony pentafluoride thus also acts as an easily reducible ("sacrificial") halide, contributing to the driving force of the reactions. Schmerling in a different context found $AlCl_3$–$CuCl_2$ systems suitable to effect alkylation of aromatics by alkanes.[27] We have suggested[28] a similar role to $CuCl_2$ as to SbF_5, which we have found also effective to cause alkylation reactions of aromatics, such as benzene, with alkanes, including methane.[28]

The next higher alkane homolog, ethane, contains not only C–H bonds as methane, but also a C–C bond. Thus it is the simplest alkane that permits simultaneously the occurrence of C–H as well as C–C bond protolysis in superacids. This in fact gives an opportunity for a direct comparison between the reactivity of C–H *vs.* C–C bond cleavage in the protolytic reactions of ethane.

Ethane was found to undergo C–C bond protolysis in preference to C–H bond cleavage. The ratio of CH_4 and H_2 formed as the gaseous cleavage products of the reaction with HF–SbF_5 (1:1) SO_2ClF is about 15:1 (depending on the reaction conditions). However, the ratio may be affected by the possibility of concurrent reduction of SbF_5. This could reduce the amount of H_2 observed and could be responsible for observation of lower ratios which, however, never were

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(22) G. A. Olah "Friedel-Crafts and Related Reactions," Wiley-Interscience, New York, N. Y., 1963–1965, and references given therein.

(23) J. Holmes and R. Pettit, *J. Org. Chem.*, 28, 1695 (1963).

(24) (a) G. A. Olah and J. J. Svoboda, presented at the meeting of the Chemical Society, Manchester, April 1972; (b) publication in preparation.

(25) G. A. Olah, P. Schilling, and I. Gross, *J. Amer. Chem. Soc.*, submitted for publication.

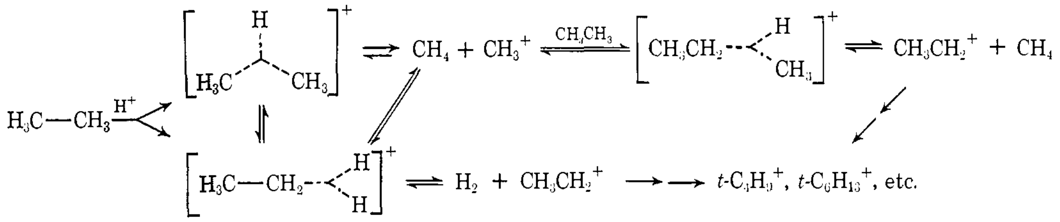
(26) G. A. Olah, *et al.*, unpublished results.

(26a) NOTE ADDED IN PROOF. Even the electrochemical oxidation of alkanes in fluorosulfuric acid, as just shown, involves rapid protonation to alkonium ions (of the CH_5^+ type) prior to the electron transfer steps: J. Bertram, J. P. Coleman, M. Fleischmann, and D. Pletcher, *J. Chem. Soc., Perkin Trans. 2*, 374 (1973). The unprotonated alkane is stable at the potentials where oxidation occurs, *i.e.*, the alkonium ion is much more readily oxidized than the present alkane.

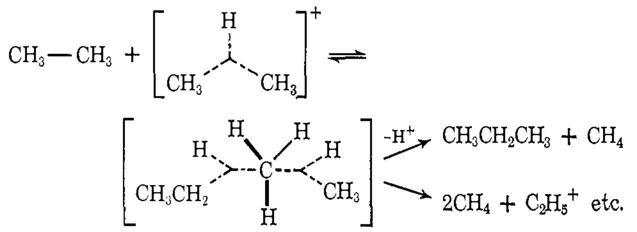
(27) L. Schmerling and J. A. Vesely, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, 16, B12 (1971).

(28) G. A. Olah, P. Schilling, J. S. Staral, and Y. Halpern, *J. Amer. Chem. Soc.*, submitted for publication.

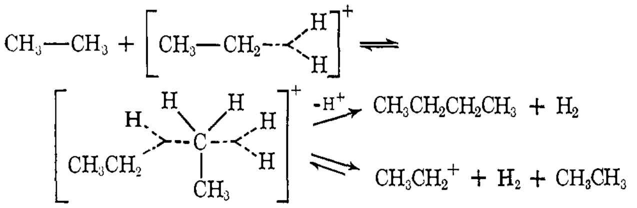
found to be less than 8:1. It is interesting to note that "neat" antimony pentafluoride gave results quite similar to those observed with fluoroantimonic acid, with a $CH_4:H_2$ ratio of about 10:1 (at −50°, where reduction of SbF_5 should be slow). This result very strongly indicates the protolytic nature of the ionization reaction



Protonation of the C–C bond is followed by cleavage of the carbonium ion, with the resulting CH_3^+ ion being bulkier than the protonating agent. Thus subsequent reaction with excess ethane takes place on the more accessible C–H bond, forming in the second reaction again a mole of methane and ethyl cation. Only a small part of the latter is formed by direct C–H bond protolysis. It further is not necessary to visualize complete cleavage to a free and, therefore, energetically unfavorable CH_3^+ ion to take place, before interaction with excess ethane starts. The reaction is visualized more as a displacement reaction, the σ base (in this case the C–H bond of ethane) displacing the developing methyl cation.



or



That indeed the protolysis of ethane involves carbonium ion intermediates is also shown when ethane is treated with $DF-SbF_5$ or DSO_3F-SbF_5. Extensive hydrogen–deuterium exchange is observed in recovered ethane (as CH_3CH_2D, etc.) and CH_3D is formed in the cleavage reaction (see subsequent discussion). These data indicate that the involved pentacoordinated carbonium ion states must have finite lifetime and consequently must be considered as bona fide intermediates, although generally too reactive to be directly observed before their further reaction or cleavage to trivalent carbenium and hydrogen (alkane). Triangular pentacoordinated carbonium ion intermediates are also indicated by the alkylative formation of higher molecular weight condensation products (as well as lower molecular weight cleavage products) not only under stable ion conditions (*i.e.*, using excess superacid solution, when the main product ion observed is *tert*-butyl cation, with smaller amounts of $t\text{-}C_5^+$ and $t\text{-}C_6^+$ ions also formed) but also when excess ethane is treated with superacids. In this case oligocondensation, similar to that observed in the case of methane, takes place. Ethane undergoes oligocondensation more readily than methane, even at room temperature. The oligocondensation process can be considered as alkylative condensation, the transition states of which are similar to those of previously discussed alkylation of alkanes.[29]

The study of the products of protolysis of ethane, *i.e.*, the ratio of CH_4 to H_2, indicates the ratio of C–C to C–H bond cleavage. This ratio does, however, not necessarily indicate the initial, preferential site of protonation. C–C or C–H bond protonation both lead to a pentacoordinated ethonium ion, differing in the nature of the three-center bonds, *i.e.*

Recent *ab initio* calculations by Pople[30] gave definite preference in the protonation of ethane for the C–C over C–H bonds (although it may not be surprising to see this difference diminished, or even reversed, in future calculations). In any case, ethonium ions can readily undergo intramolecular bond-to-bond rearrangement processes, irrelevant of the exact initial site of attack. This point was previously raised[12] in the context of the general concept of carbocation behavior, and we would like to reemphasize now its importance in explaining the protolytic behavior of alkanes.

FSO_3H-SbF_5 (1:1) (magic acid) reacts with ethane in SO_2ClF solution to give a much lower $CH_4:H_2$ ratio (about 1:1) in the protolytic cleavage reaction. The difference between this ratio and those observed with 1:1 $HF-SbF_5$ and "neat" SbF_5 is particularly interesting. It raises the question of the nature of the protolytic agent.

The differing behavior of $HF-SbF_5$ and FSO_3H-SbF_5 in the protolysis of ethane (as well of subsequently discussed alkanes, particularly 2,2-dimethylpropane and 2,2,3,3-tetramethylbutane) could indicate differences in the nature of the protonating agent, *i.e.*, in the nature of the specifically solvated proton.

The "naked" proton H^+ never exists as such in solution, but only as its solvated form, such as H_3O^+, $H_5O_2^+$, $H_2O^+SO_2F$, H_2F^+ etc., although as a matter of convenience we usually write H^+ for the hydrogen ion and assume to be well understood that it is solvated.

In water the lifetime of an individual H_3O^+ ion is

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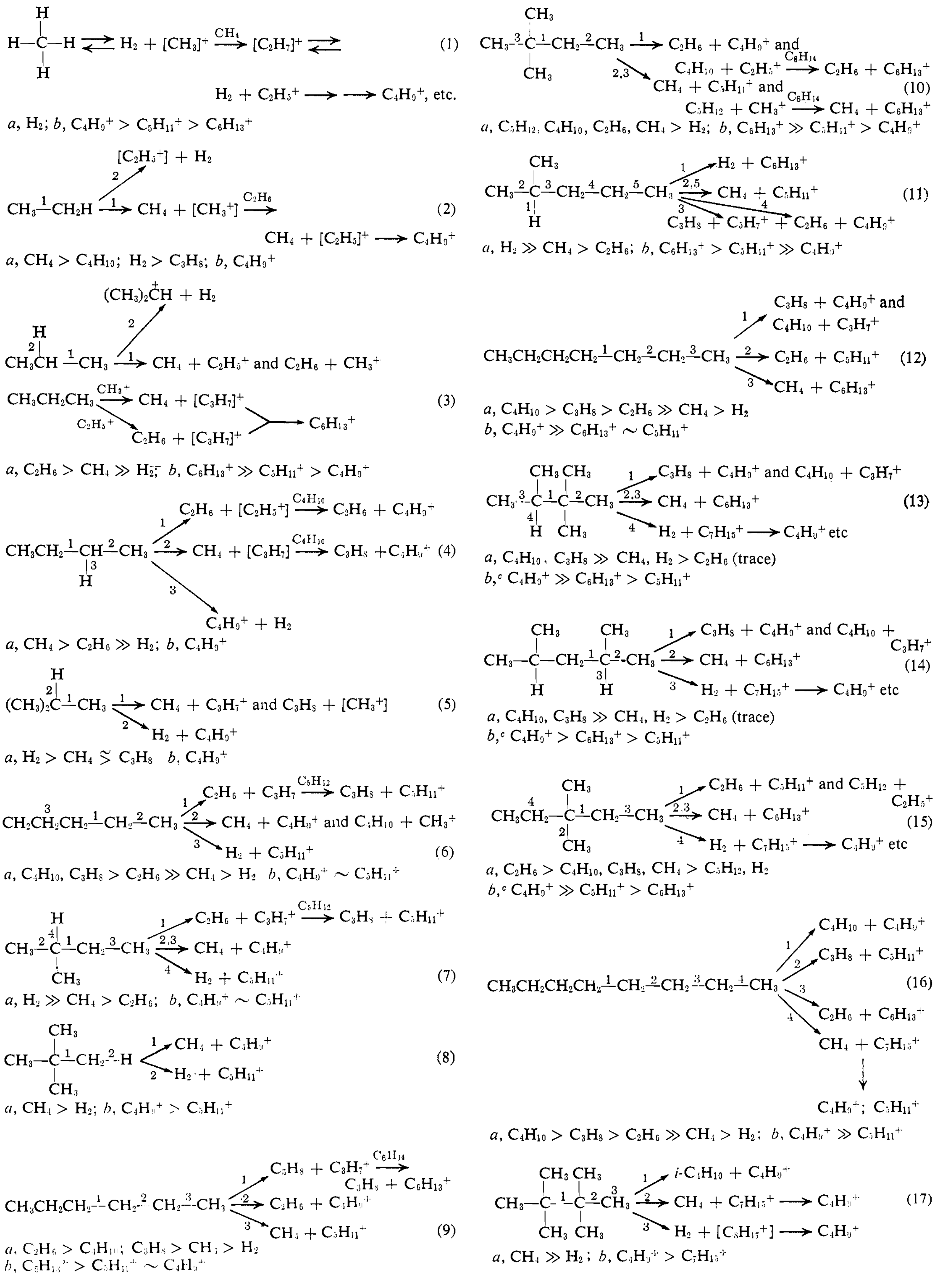
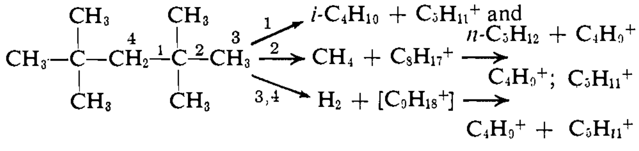
(29) G. A. Olah, Y. K. Mo, and J. A. Olah, *J. Amer. Chem. Soc.*, **95**, 4939 (1973).

(30) W. A. Lathan, W. J. Hehre, and J. A. Pople, *Tetrahedron Lett.*, 2699 (1970); *J. Amer. Chem. Soc.*, **93**, 808 (1971); W. A. Lathan, W. J. Hehre, L. A. Curtin, and J. A. Pople, *ibid.*, **93**, 6377 (1971).

Scheme I. Protolytic Cleavage Paths of Alkanes in Superacids[a]

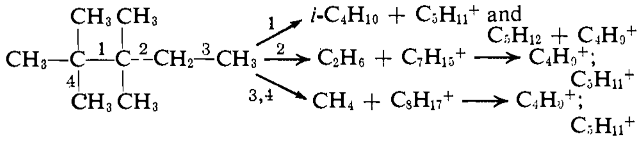


Scheme I (*Continued*)



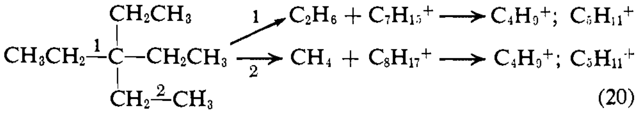
(18)

a, $CH_4 \gg H_2 > C_5H_{12}, C_4H_{10}, C_2H_6$; b, $C_4H_9^+ \gg C_5H_{11}^+$



(19)

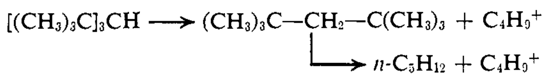
a, $C_4H_{10} > C_2H_6 > CH_4 > H_2$; b, $C_4H_9^+ \backsim C_5H_{11}^+$



(20)

a, $C_4H_{10}, C_2H_6 > C_5H_{12}, C_3H_8 > CH_4, H_2$

b, $C_4H_9^+ > C_5H_{11}^+ \gg C_6H_{13}^+$



(21)

a, $C_4H_{10}, C_3H_8 > CH_4 \gg C_2H_6, H_2$; b, $C_4H_9^+ \gg C_5H_{11}^+$

[a] Volatile products, determined by glc and mass spectrometry. [b] Carbocations in acid solution, determined by nmr spectroscopy. [c] $-60°$; t-$C_7H_{15}^+$ is the only product.

exceedingly short, ~10^{-13} sec, since all protons undergo rapid migration from one O to another. The solvated proton is becoming, however, relatively long-lived in superacids. We suggest that, indeed, there is substantial difference in the nature of the solvated proton between systems such as HF–SbF_5 and FSO_3H–SbF_5. The 1:1 acid systems based on ^1H and ^{19}F nmr studies can be considered as

$$2HF + (SbF_5)_2 \rightleftharpoons \overset{+}{H}\text{—}\overset{-}{F}\text{--}\overset{+}{H} \longleftrightarrow \overset{+}{H}\text{--}\overset{-}{F}\text{—}\overset{+}{H}\ Sb_2F_{11}^-$$

$$2HSO_3F + (SbF_5)_2 \rightleftharpoons H_2\overset{+}{O}\text{—}SO_2F\ Sb_2F_{10}FSO_3^-$$

Higher degrees of association are also possible and it must be seen whether reasonable equilibrium constants can be obtained for the systems (to be reported separately). It explains why HF–SbF_5 is a stronger acid than FSO_3H–SbF_5. At the same time $H_2SO_3F^+$ is more space demanding than H_2F^+ and will, therefore, react preferentially with the more open C–H than the more crowded C–C bond.

A further significant factor which can affect the association and nature of the protolytic agent is the solvent medium. The most frequently used solvents in connection with superacidic systems are SO_2, SO_2ClF, and SO_2F_2. The experimentally observed decreasing order of nucleophilicity is $SO_2 > SO_2ClF > SO_2F_2$. The more nucleophilic SO_2 will solvate ions as will free SbF_5 present in the superacidic systems, more so than SO_2ClF or SO_2F_2. Consequently, significant differences depending on the solvent medium can be expected (see subsequent discussion particularly of the protolysis of 2,2-dimethylpropane).

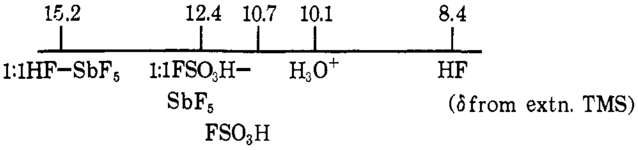
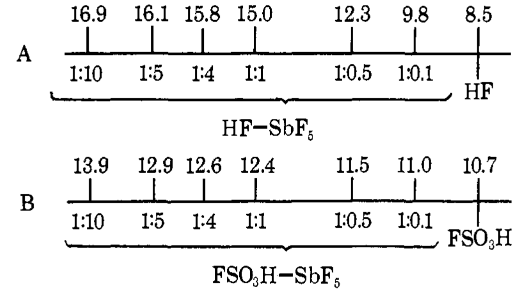


Figure 1. Pmr shifts of HF and HSO_3F and their 1:1 acids with SbF_5.

Figure 2. Pmr shifts of varying molar ratios of HF–SbF_5 and HSO_3F–SbF_5.



The differing nature of the protolytic agent (solvated proton) can at least in a qualitative way also be demonstrated by pmr spectroscopic studies of different acid systems.

Pmr spectroscopic study of HF, FSO_3H, HF–SbF_5, and HSO_3F–SbF_5 systems indicate the widely differing nature of the solvated (associated) proton. Figure 1 shows, in a schematic way, the pmr shifts of the acids, as well as the hydronium ion (in HF–SbF_5 solution) as 1:1 v/v solutions in SO_2ClF. These shifts are of course concentration and to a lesser degree temperature dependent, and therefore, clearly at this point are not suggested to give any quantitative indication of either acid strength or association, although they seem to indicate the relative trends. In HF–SbF_5 and FSO_3H–SbF_5 the molar ratio of the Brønsted and Lewis acid do substantially affect the acidity of the systems and pmr shifts (Figure 2a and b, again for 1:1 v/v acid–SO_2ClF solution). The data indicate that observed shifts are averages of the rapidly exchanging solvated proton with excess acid, the concentration of the latter decreasing with increasing SbF_5 ratios. The trends of proton shifts are interesting and would seem to indicate decreasing exchange of the solvated proton with the solvent medium with increasing Lewis acid concentration.

Whereas previous studies of superacidic systems (by Gillespie,[31a] and Commeyras and Olah[31b]) emphasized primarily the association of the counterions ($Sb_2F_{11}^-$, $Sb_2F_{10}FSO_3^-$, etc.), clearly the association of the solvated proton (H_2F^+, $H_2SO_3F^+$, etc.) is also indicated.

A further strong indication of the differing nature of the protonating agent in different superacids also comes from consideration of the measured activation parameters of reactions with alkanes.[20]

Hogeveen and Bickel[32] measured the kinetics and activation parameters for the reaction

$$(CH_3)CH + H^+ \longrightarrow (CH_3)_3C^+ + H_2$$

in 45:1 mol/mol HF–SbF_5 solution in the presence of excess isobutane. They found $\Delta H^{\ddagger} = 18$ kcal/mol,

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(31) (a) R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and B. A. Rothenbury, *Inorg. Chem.*, 4, 1641 (1965); R. J. Gillespie and K. C. Moss, *J. Chem. Soc. A*, 1170 (1966). (b) A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, 91, 2929 (1969).

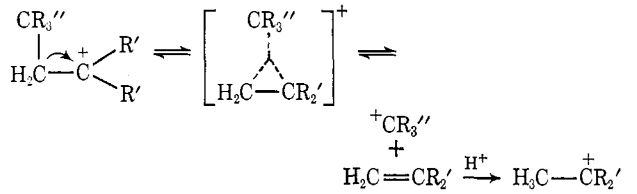
(32) H. Hogeveen and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, 86, 1313 (1967).

$\Delta S^{\ddagger} = 9 \pm 3$ eu (cal/(mol deg) for [mol/l.] as unit of concentration). The seemingly small value of activation entropy for a bimolecular reaction was accounted for by suggesting that the proton actually occurs as the HF_2^+ ion, and a molecule of HF is liberated during the reaction. That this, indeed, is the case can be more clearly seen when comparing measured activation parameters for the C–C bond protolysis

$$(CH_3)_4C + H^+ \longrightarrow (CH_3)_3^+ + CH_4$$

in $HF-SbF_5$ (21:1 mol/mol) by Hogeveen and Bickel,[11a] $\Delta H^{\ddagger} = 21.3$ kcal/mol, $\Delta S^{\ddagger} = -6 \pm 3$ eu, and in FSO_3H-SbF_5 (1:1 mol/mol) by Olah, Klopman, and Schlosberg,[9] $\Delta H^{\ddagger} = 14$ kcal/mol and $\Delta S^{\ddagger} = -19$ eu. The large difference in activation entropy is indicative that in the protolytic reactions, HF and FSO_3H, respectively, are also liberated from the very different protolytic agents. The seemingly small value of $\Delta S^{\ddagger}$ in the reaction with $HF-SbF_5$ indicates the easier liberation of HF from the more loosely bound HF_2^+ as compared to $H_2SO_3F^+$ in the FSO_3H-SbF_5 system.

The protolytic behavior of propane, butanes, pentanes, hexanes, heptanes, and octanes were also studied in superacids. Protolytic cleavage paths observed are shown in Scheme I. Relatively little hydrogen is formed in any of the straight chain systems, again suggesting the preference of C–C to C–H bond protolysis in *n*-alkanes. We feel the observation of the preferential C–C bond over primary and secondary C–H bond protolysis can readily explain why there is not much hydrogen formed in acid catalyzed hydrocarbon transformation reactions. The cleavage reactions of alkylcarbenium ions generally take place in a position β to the carbenium center and are called Whitmore β-cleavages[33] (who first called attention to their importance in acid catalyzed hydrocarbon reactions). We are depicting β-cleavage as the opposite of the alkylation reaction, involving delocalization of the C–C bond in the β position through a three center bonded carbonium ion



Cleavage of R″ will be preferential with tertiary systems. Deprotonation of alkylcarbenium ions can be considered as an identical reaction, which, however, can be suppressed in superacid media. As alkylative condensations and cleavage reactions are taking place with ease in superacid systems, it is not surprising to find that most alkanes investigated eventually, particularly at higher temperatures, form *tert*-butyl cation as the most stable end product. Cleavage reactions of carbenium ions in excess superacids take place without formation of olefins. C–H bond cleavage in the β position and protonation of the developing olefin could take place in a more or less concerted fashion. This should lead, however, in case of deuterated acids, to rapid hydrogen–deuterium exchange, for example, of the methyl groups of the *tert*-butyl cation. This was not found experimentally.

When an excess of alkanes are treated with superacids, they undergo oligocondensation with increasing ease, going from methane to ethane to propane to butane, etc. The oligocondensation of lower alkanes giving higher molecular weight branched alkanes is an interesting new reaction of substantial practical interest (natural gas can be converted by this reaction to gasoline range branched liquid hydrocarbons). Details of this reaction will be reported separately.

Our studies indicate that with the exception of tertiary C–H bond protolysis alkanes preferentially undergo first C–C bond protolysis forming fragment carbenium ions and alkanes. The former ions then can abstract hydrogen from starting alkanes, due to their relative bulkiness preferring the less hindered C–H bonds.

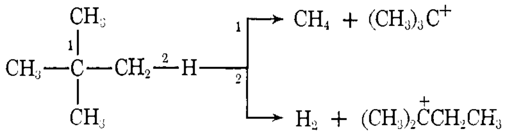
$$R_3C—CR_2H \overset{H^+}{\rightleftharpoons} R_2CH_2 + \overset{+}{C}R_3$$

$$R_3\overset{+}{C} + R_3CCR_2H \rightleftharpoons R_3CH + R_3\overset{+}{C}CR_2 \text{ etc.} \quad R = \text{H or alkyl}$$

In sharp contrast to *n*-alkanes, both isobutane and isopentane (as well as other isoalkanes) gave tertiary alkyl cations and H_2 in superacids, as the most predominant products. This seems to suggest that preferential protonation occurs at tertiary C–H bonds instead of C–C bonds, or primary and secondary C–H bonds. Therefore, the experimental data indicate the empirical reactivity order of single bonds in alkanes: $R_3C\cdots H > C–C > R_2HC\cdots H > RH_2C–H$

However, it should be emphasized that the nature of each system (for example, steric hindrance) can influence the relative reactivities. Any relative order of reactivities must be therefore limited to specific systems studied. For example, as discussed, isoalkanes containing a tertiary C–H bond show preferential reactivity of this bond (both in protolysis and also in hydrogen transfer to alkylcarbenium ions formed in C–C bond protolysis). Increased branching can cause a shift of reactivity in favor of C–C (or 1° C–H) bond protolysis. Comparison of isobutane, triptane, di-*tert*-butylmethane, and tri-*tert*-butylmethane demonstrates well this point. For example, in isobutane, C–H over C–C reactivity at −78° is 50:1, whereas in 2,2,3-trimethylbutane (triptane) under similar conditions the reactivity ratio is 20:1. In case of the even further crowded di-*tert*-butylmethane, C–C bond reactivity is nearly exclusive and in tri-*tert*-butylmethane there is no observable reactivity at all on the highly shielded C–H bond. Similarly to the well-studied steric factors of n- or π-donor bases,[34] steric hindrance thus also affects σ-donor alkanes.

The protolytic behavior of 2,2-dimethylpropane (neopentane) is of particular interest. C–C bond protolysis gives *tert*-butyl cation and methane, whereas C–H bond protolysis gives *via* rapid intramolecular 1,2-methyl shift of a participating β-methyl group the *tert*-amyl cation.



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[33] F. C. Whitmore, *Chem. Eng. News*, **26**, 668 (1948), and references given therein.

[34] For example, H. C. Brown and R. D. Johanessen, *J. Amer. Chem. Soc.*, **75**, 16 (1953), and earlier papers referred therein.

There is again no reason to assume that a primary neopentyl cation ($[CH_3]_3CCH_2^+$) of separate existence is first formed during path 2. As protolysis of the C–H bond proceeds, the developing p orbital will start to delocalize the H_3C–C bond; thus the process can be best visualized as an internal displacement process.

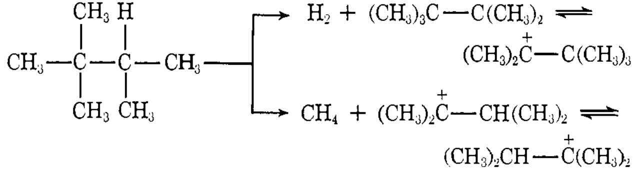
2,2-Dimethylpropane, as observed in our preceding work in FSO_3H–SbF_5 solution[9,10] and by Hogeveen[11a] in HF–SbF_5, undergoes readily protolytic C–C bond cleavage to give methane and *tert*-butyl cation. However, we also found that when SO_2ClF was used as solvent with FSO_3H–SbF_5 between −30 and 0° C–H bond protolysis took place giving *tert*-amyl cation.[9,10]

The differing protolytic behavior of neopentane was now further studied in our investigations. Neopentane in HF–SbF_5–SO_2ClF solution at −80 to −50° gives about 98% *tert*-butyl cation and 2% *tert*-amyl cation. In 5:1 HF–SbF_5 (in SO_2ClF) at −80°, 95% *tert*-butyl cation and 5% *tert*-amyl cation is formed. In 1:1 FSO_3H–SbF_5 (SO_2ClF) solution the protolysis of neopentane can be studied only from −40 to 0° (below this temperature the reaction is too slow to be studied and above this temperature due to the low boiling point of SO_2ClF studies at atmospheric pressure are not feasible). However, under pressure at 25° cleavage to *tert*-butyl cation and methane is observed.

The behavior of neopentane was also studied in "neat" antimony pentafluoride, a system claimed by Hogeveen and Lukas[17] to oxidize alkanes directly, and by a mechanism different from protolysis by superacids. However, in our studies "neat" SbF_5 (in SO_2ClF solution), which always contains sufficient protic acid impurity to act as a strong superacid, showed typical protolytic behavior. Its reaction with neopentane gave the following ratios of *tert*-butyl and *tert*-amyl cations: −80°, 28% $t\text{-}C_4H_9^+$ and 72% $t\text{-}C_5H_{11}^+$, −50°, 45% $t\text{-}C_4H_9^+$ and 55% $t\text{-}C_5H_{11}^+$, −40°, 38% $t\text{-}C_4H_9^+$, 62% $t\text{-}C_5H_{11}^+$, 0°, 43% $t\text{-}C_4H_9^+$ and 57% $t\text{-}C_5H_{11}^+$, at 25°, 74% $t\text{-}C_4H_9^+$ and at 26% $t\text{-}C_5H_{11}^+$.

The differing reactivity of neopentane in HF–SbF_5–SO_2ClF (or "SbF_5") and FSO_3H–SbF_5–SO_2ClF solution seems again to reflect the differing nature of the protolytic agent. FSO_3H–SbF_5 in SO_2ClF solution seems to be a more space demanding protonating agent (*i.e.*, $H_2SO_3F^+$) preferring C–H bond protonation, whereas HF–SbF_5 (due to the lesser space demand of H_2F^+) shows greater preference for C–C bond protolysis. "Neat" antimony pentafluoride shows intermediate behavior, as it can be considered more associated (the gegenion being $Sb_2F_{11}^-$ or $Sb_3F_{16}^-$) than HF–SbF_5 solution containing higher proportions of HF.

2,2,3-Trimethylbutane (triptane) undergoes in HF–SbF_5 (SO_2ClF), between −80 and −50° C–H *vs.* C–C protolysis giving $C_7^+:C_6^+$ in a ratio of 19:1.



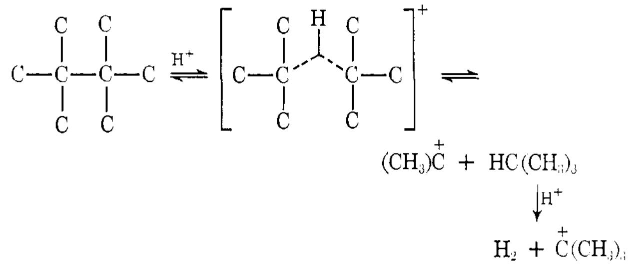
At 0° cleavage to *tert*-butyl cation is becoming apparent ($C_7^+:C_6^+:C_4^+$ = 18:1:0.5) and at room temperature after 15 min becoming predominant ($C_4^+:C_6^+$ = 20:1). In "neat" SbF_5 up to 0° *tert*-heptyl cation formation is only observed; when the solution is warmed to room temperature for 15 min again cleavage to *tert*-butyl cation takes place. The protolytic behavior of triptane in FSO_3H–SbF_5 (SO_2ClF) is very similar to that in fluoroantimonic acid.

The protolytic behavior of triptane in superacids thus closely resembles that of isobutane. Tertiary C–H bond protonation predominates and the steric effect of a single *tert*-butyl group replacing a methyl group is not sufficient to change the behavior. Fluoroantimonic acid and "magic acid" do not seem to differ much in their reactions with a not much hindered tertiary C–H bond. Competing C–C bond protonation, although observed, is less than 5%.

When a second *tert*-butyl group is introduced into isobutane, *i.e.*, in 2,2,3,4,4-pentamethylpentane, it results in such steric crowding that practically no C–H bond protolysis can be observed, only C–C bond protolysis giving through subsequent cleavage reactions *tert*-butyl and *tert*-amyl cations as the only observable product ions.

Introduction of the third *tert*-butyl group even further increases steric crowding. Thus in tri-*tert*-butylmethane[35] only CH_3–C protolysis is observed giving methane as the gaseous product, and *tert*-butyl cation as sole observable ion.

A further example of the steric effect on bond shielding against protonation became obvious in the study of 2,2,3,3-tetramethylbutane. This hydrocarbon was observed both in our previous studies,[9] as well as in those of Hogeveen's,[20,36] to cleave quantitatively to *tert*-butyl cation. Consequently, it was suggested that protolysis of the C_2–C_3 bond took place giving *tert*-butyl cation and isobutane, which subsequently (*via* C–H protolysis) gave another mole of *tert*-butyl cation.



Indeed, in our related studies[23] of the reaction of the *tert*-butyl cation and isobutane, besides fast intermolecular exchange, some alkylation giving 2,2,3,3-tetramethylbutane was observed, thus proving the feasibility of the reverse cleavage reaction.

Studying in more detail the protolysis of 2,2,3,3-tetramethylbutane we observed, however, that in the gaseous product of the reaction methane predominates to the extent that not only in HF–SbF_5 or FSO_3H–SbF_5 solution, but also in "neat" SbF_5–SO_2Cl, the $CH_4:H_2$ ratio exceeds 200:1! Further, when studying protolysis with fluoroantimonic acid–SO_2ClF at −80° (where reaction is slow, but detectable) the only carbocation observed is the pentamethyl-

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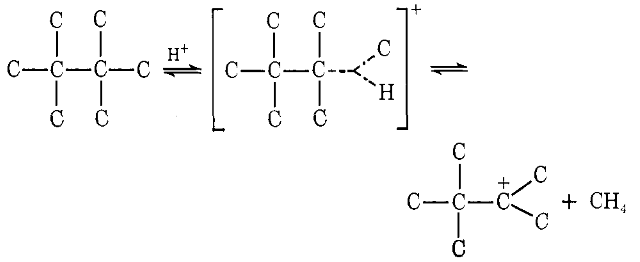
(35) Professor M. Stiles is thanked for a sample of tri-*tert*-butylmethane and information related to the synthesis of the compound prior to publication.

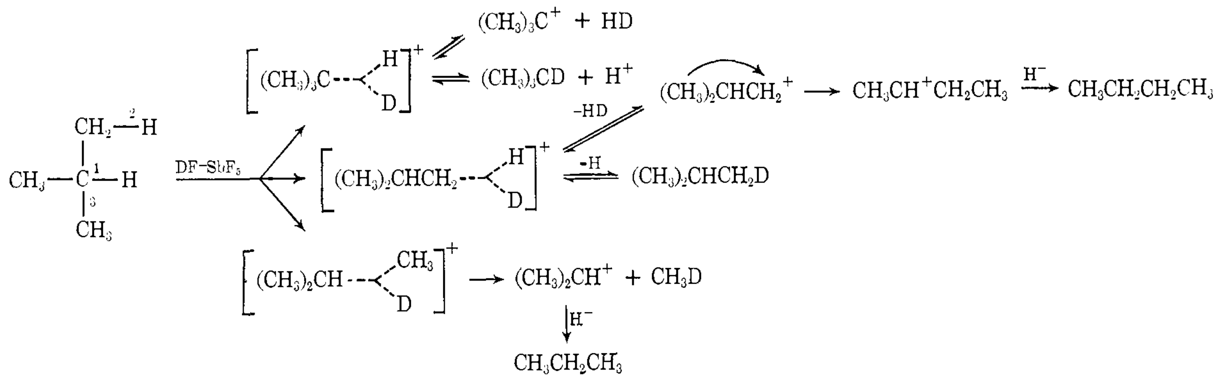
(36) H. Hogeveen and A. F. Bickel, *Recl. Trav. Chim., Pays-Bas*, 88, 371 (1969).

ethyl cation. By raising the temperature to −50°, 75% pentamethylethyl cation and 25% *tert*-butyl cation are observed. The ratio changes at 0° to 36:69 $C_4^+:C_7^+$ and at room temperature only the *tert*-butyl cation is observed. The protolytic behavior in "SbF_5"–SO_2ClF is quite similar. The relative amounts of $C_4^+:C_7^+$ are at −80°, 42:58%; −50°, 48:52%; 0°, 67:33%, and at room temperature 90:10%. In magic acid–SO_2ClF no comparable low-temperature study is possible as the reaction is very slow (probably also because of very limited solubility of the hydrocarbon in the solvent system). At 0° where slow ionization is observed already about 99% *tert*-butyl cation and only 1% pentamethylethyl cation is observed. Cleavage of the pentamethyl cation in this system thus is very fast.

We feel these data conclusively show that protonation of 2,2,3,3-tetramethylbutane takes place not at the C_2–C_3, but at the terminal C–C bonds. The primary protolytic process thus is similar to the C–C bond protolysis in neopentane.



Inspection of molecular models further shows that the C_2–C_3 bond is extremely shielded by the surrounding methyl groups. The protolytic agent, which as discussed previously is a strongly solvated proton with a quite definite steric requirement, cannot attack this bond, in sharp contrast to gaseous molecule–ion reaction conditions, and will attack the more accessible terminal C–C bonds. In FSO_3H–SbF_5–SO_2ClF solution there is also indicated some degree of C–H protonation (about 1–2% H_2 compared to CH_4 is found in the gaseous products, despite possible reduction of the solvent system), but clearly immediate rearrangement of the developing neooctyl cation (by *tert*-butyl or methyl shift) is followed by fast β-cleavage; thus only *tert*-butyl cation is observed.



B. Hydrogen–deuterium exchange is always found to accompany protolytic cleavage reactions. Whereas there is no reason to suggest that the reactions proceed through identical transition states (hydrogen–deuterium exchange takes place on C–H or C–D bonds, respectively, whereas protolysis also involves C–C bonds), the involved transition states, however, should be of closely related nature.

Hydrogen–deuterium exchange of methane with DSO_3F–SbF_5 or DF–SbF_5 (or CD_4 with FSO_3H–SbF_5 or HF–SbF_5) was reported in our previous studies as well in the independent work of Hogeveen.[9–11]

Ethane under similar conditions undergoes both C–C and C–H bond deuterolysis, forming CH_3D and C_2H_5D. As in C–C bond deuterolysis, CH_2D^+ is also formed; hydrogen abstraction from excess ethane then yields CH_3D. Other *n*-alkanes show similar behavior.

When isobutane is treated with deuterated superacids, like DSO_3F–SbF_5 or DF–SbF_5,[37] at atmospheric pressure and low temperature (−78°), the *tert*-butyl cation free of deuterium and HD are formed. Recovered isobutane shows substantial exchange of the methine proton (as determined by combined results of mass spectrometry and ^1H and ^2H nmr spectroscopy) but negligible exchange of the methyl groups. There is also some isomerization to *n*-butane and limited (<5%) cleavage to methane and dimethylcarbenium ion, which reacts further (either by intermolecular hydrogen abstraction or alkylation). At the low temperature methane itself is slow to undergo exchange. All these results, obtained under reaction conditions where no isobutylene is formed in the system, can be best accounted for by the alternate reaction path involving C–H and C–C bond protolysis, respectively. Again it should be kept in mind that facile intramolecular bond-to-bond rearrangement processes are always possible regardless of the initial site of deuteration.

The alternate explanation, *i.e.*, that HD is formed in what amounts to a linear transition state and then reacts in the reversible reaction with the *tert*-butyl cation, is considered improbable, as the reaction of carbenium ions with hydrogen generally necessitates high concentration and thus pressure of H_2. The proton exchange reaction was observed at atmospheric pressure where the HD concentration in solution is very low and deuteration of carbenium ion is generally negligible.

It is interesting to notice that in the reaction of isobutane in D_2SO_4, Eotvos found[38,39] exchange of the nine

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[37] A similar observation of exchange was made by Hogeveen, who observed hydrogen–deuterium exchange when $(CH_3)_3CD$ was treated with HF–SbF_5. He suggested that the reaction could be due to ionization followed by reaction with HD: $(CH_3)_3CD + H^+SbF_6^- \rightleftharpoons (CH_3)_3C^+SbF_6^- + HD$ and then $(CH_3)_3C^+SbF_6^- + HD \rightleftharpoons (CH_3)_3CH + D^+SbF_6^-$) or direct H–D substitution, without expressing preference or providing evidence for the *de facto* reaction.

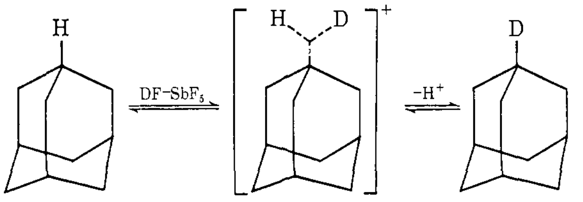
methyl hydrogens, but not of the methine hydrogen. He has rightly argued that reaction under these conditions involves isobutylene formation and its reversible protonation (deuteration), whereas the tertiary hydrogen is only involved in intermolecular hydride transfer from isobutane. Under low temperature (−78°) superacid conditions where no olefin formation takes place, no reversible isobutylene protonation can be involved in the exchange reaction. Consequently, only exchange of the methine proton has been found.

2,2-Dimethylpropane and 2,2,3,3-tetramethylbutane show predominant C–C bond protolysis; recovered hydrocarbons from deuterated superacids also show hydrogen–deuterium exchange of the methyl groups, indicative of C–H bond deuteration.

Further substantiation for the triangular nature of the transition states in protolytic reactions was found by studying adamantane, a rigid-cage hydrocarbon, in DF–SbF_5 solution.[40]

Besides formation of the 1-adamantyl cation, ready hydrogen–deuterium exchange is observed on recovered adamantane (by direct ^2H nmr spectroscopy, peak area decrease in the ^1H nmr spectra and mass spectrometry) with great preference for the bridgehead positions. Similarly, 1,3,5,7-tetradeuterioadamantane in HF–SbF_5 and FSO_3H–SbF_5 solution was studied and showed similar exchange.

The ready hydrogen–deuterium exchange at the bridgehead positions cannot be explained by backside attack or deprotonation, which would lead to a bridgehead olefin. In addition, a linear transition state producing HD cannot explain the high yields of deuterated product. It is thus evident that the only explanation for the observed deuteration is the involvement of a three-center bonded carbonium ion in the reaction pathway.



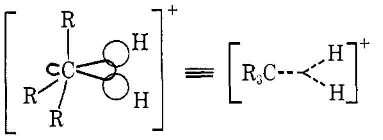
Whereas no detailed kinetic study of the hydrogen–deuterium exchange reaction was yet carried out, in preliminary experiments we have compared the reactivity of adamantane and 1,3,5,7-tetradeuterioadamantane in HF–SbF_5 solution by measuring in identical parallel experiments the amount of the stable ion formed by pmr spectroscopy. These experiments indicate that light adamantane reacts four times as fast as the heavy compound; thus $k_H/k_D = \sim 4$. The sizeable kinetic hydrogen isotope effect is noteworthy and will be further studied.

Frontside deuterolytic attack on C–H bonds should result in retention of optical activity, if the exchange reactions were carried out on optically active hydrocarbons. Indeed, preliminary results of our studies on optically active 3-methylhexane indicate that substantial retention of optical activity occurs, but much further experimental work is needed before these findings can be fully substantiated. Results will be reported separately.

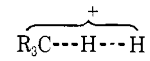
Conclusions

The key, we suggest, to the understanding of the hydrogen–deuterium exchange and protolytic cleavage reactions of alkanes, as well their oligocondensation, is the realization (based on products obtained and theoretical calculations) that *the protolytic attack takes place on the main lobes of the C–H or C–C bonds where the major part of the electron density in covalent single bonds resides and not on the back lobes, i.e., the hydrogen or carbon atoms themselves.* The transition states of the reactions are of three-center bonded pentacoordinated carbonium ion nature.

The possibility of a triangular transition state was first suggested by Lewis, Hawthorne, and Symons[41] in 1958. It received little attention until 1967–1968 when, based on chemical evidence and quantum mechanical calculation,[9–11] it was concluded that protonation of methane and related alkanes can be achieved in superacid media such as FSO_3H–SbF_5 and HF–SbF_5 and occurs through "frontside" attack on the C–H or C–C bonds forming a pentacoordinated carbonium ion (for simplicity we depict throughout the triangular three-center bonds with dotted lines, as suggested in ref 12).



Hogeveen, Gaasbeek, and Bickel,[11] on the other hand, studying independently the protolytic formation of carbenium ions, deuterium–hydrogen exchange in HF–SbF_5 solution and the reversible hydrogenation of carbenium ions, initially suggested a linear transition state for the reactions.



$$\overset{+}{\overbrace{R_3C\text{---}H\text{---}H}}$$

Their arguments were based on the expected steric strain in a triangular transition state in the hydride transfer reaction between tertiary carbenium ions and the corresponding alkanes, as already pointed out by Stewart[42] and Deno.[43] (Subsequently, however, Brouwer and Hogeveen[18] also gave preference to triangular carbonium ions.)

Hogeveen also stated that he found no evidence for hydrogen–deuterium exchange when molecular D_2 was treated with excess HF–SbF_5 and used this observation to strengthen the argument for a linear transition state. That exchange of hydrogen (and deuterium) in a number of 1:1 (mol/mol) superacid solutions like HF(DF)–SbF_5, $FSO_3H(FSO_3D)$–SbF_5, and H_2SO_4-

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(38) J. W. Eotvos, D. P. Stevenson, C. D. Wagner, and O. Beek, *J. Amer. Chem. Soc.*, 73, 5471 (1951).

(39) D. P. Stevenson, C. D. Wagner, and J. W. Eotvos, *ibid.*, 74, 3769 (1952).

(40) G. A. Olah and G. D. Mateescu, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, No. PETR-0 39.

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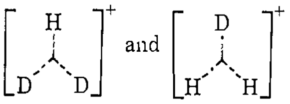
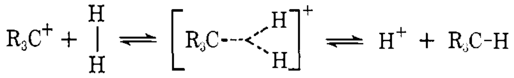
(D_2SO_4)–SbF_5 did occur has been shown in our studies.[44] In accordance with Christoffersen and Shull,[45] Conroy,[46] as well as Schwartz and Schaad's[47] calculations, we suggested that these reactions go through a trigonal $(H,D)_3{}^+$ type transition state.



Consequently, the reaction of trivalent carbenium ions with molecular H_2 can be best considered as alkylation of H_2[10,48] by the carbenium ion on the H–H bond through a pentacoordinated carbonium ion transition state (or intermediate) the reverse of that of the hydride abstraction reaction. Based on the principle of microscopic reversibility, the protolytic nature of the hydrogen abstraction reaction is thus further proven.



$$R_3C^+ + \overset{H}{\underset{H}{|}} \rightleftharpoons \left[R_3C\cdots\langle{}^{H}_{H}\right]^+ \rightleftharpoons H^+ + R_3C\text{–}H$$

We consider the commonly called "hyride abstraction," even when tertiary C–H bonds are involved, as protolysis (alkylolysis) of the C–H bond from the front-side *via* formation of a pentacoordinated, three-center bonded carbonium ion. Whereas the process formally indeed results in the transfer of the hydrogen atom with its bonding electron pair, the overall process is better described as just "hydrogen transfer" (in a clearly electrophilic process on a single bond, where no hydride ion is ever involved). Transfer of alkyl groups involving C–C bond protolysis takes place in a similar fashion.

In conclusion it is our observation that C–C and C–H single bonds of all types (*i.e.*, tertiary, secondary, or primary) show substantial general reactivity in electrophilic reactions such as protolytic processes. These observations promise to open up a new area of hydrocarbon chemistry wherein alkanes can be used as substrates in a wide variety of electrophilic reactions.

The concept of pentacoordinated carbonium ion formation, with subsequent cleavage to trivalent carbenium ions, satisfactorily explains the mechanism of acid-catalyzed saturated hydrocarbon transformation reactions. These include isomerizations (involving hydrogen and alkyl shifts), fragmentations, and alkylations. This concept supplements Whitemore's[3] and Bartlett's[4] mechanisms where trivalent carbenium ion processes (frequently associated with subsequent deprotonation leading to olefin formation) were exclusively involved. At the same time our work substantially extends the scope and understanding of electrophilic reactions based on the realization that the general electron-donor ability of single bonds (shared electron pairs) eventually may equal the importance of lone-electron pairs (unshared electron pairs, Lewis bases).

Experimental Section

Materials. All alkanes used were of commercially available highest purity. 1,3,5,7-Tetradeuterated adamantane was a gift from Professor P. v. R. Schleyer.

Protolysis of Alkanes. In a typical experiment, 0.1 mol of alkane and 0.3 mol of superacid (1:1 FSO_3H-SbF_5 or HF-SbF_5) in SO_2-ClF were mixed in a Teflon-lined stainless steel bomb, at −78°. The bomb was then sealed and shaken vigorously for 1 hr at room temperature or at the temperatures given. It was subsequently cooled to −78° for opening.

In studies of oligocondensation of alkanes the ratio of alkane to superacid was generally 10:1. Experiments were carried out in pressure bombs as before, generally with reaction times at room temperature for 24 hr.

Nmr studies were carried out using a Varian A56/60A nmr spectrometer equipped with a variable-temperature probe. Sample preparations and techniques were as described in our preceding papers.

Products Analysis. The gaseous products were analyzed by capillary gas–liquid chromatography using a Perkin-Elmer Model 226 chromatograph and by mass spectrometry (on a Consolidated Engineering Corp. Model 21-620 mass spectrometer). Carbocations in aliquot samples of the SO_2ClF solutions were analyzed by ^1H nmr spectrometry using a Varian Associates Model A-56-60A nmr spectrometer equipped with a variable-temperature probe. External capillary TMS was used as reference.

Liquid hydrocarbons were analyzed by capillary gas chromatography, with experimental conditions described in our preceding paper.[29]

Deuterated alkanes were analyzed by ^2H nmr (on a Varian Associates Model HA60 spectrometer) and by high resolution mass spectrometry, through courtesy of the Department of Chemistry, University of Alberta, Canada, using an AEI Model 902 mass spectrometer.

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