We wish to emphasize that an enzymatic reaction is not meaningfully defined until it can be related to known nonenzymatic reactions and this cannot yet be done for reactions involving cobalamins. For these reactions it may well be that the relevant nonenzymatic chemistry has not as yet been discovered.

Acknowledgment. The authors wish to thank Mrs. Lynda B. Ellis for writing the computer program which was used to obtain the curves shown in Figure 3. This work was supported by grants from the National Institutes of Health (Research Grant No. 12633 and Training Grant No. GM-212).

Communications to the Editor

Electrophilic Reactions at Single Bonds. III.[1] Hydrogen–Deuterium Exchange and Protolysis (Deuterolysis) of Alkanes with Superacids. The Mechanism of Acid-Catalyzed Hydrocarbon Transformation Reactions Involving the σ Electron Pair Donor Ability of Single Bonds (Shared Electron Pairs) *via* Three-Center Bond Formation[2]

Sir:

The reactivity of olefins, acetylenes, and aromatic hydrocarbons toward electrophiles is based on the π-electron donor ability of the unsaturated $C{=}C$ or $C{\equiv}C$ bonds and π-aromatic systems. Unshared electron pair donor (n donor) heteroatom compounds represent the other major type of substrates in electrophilic reactions.[3] Contrary to frequent textbook references to electrophilic aliphatic substitution, authenticated examples are restricted to reactions involving organometallic compounds like organomercurials. No "pure" electrophilic substitutions of alkanes have been reported[4] with the exception of the recently observed hydrogen–deuterium exchange and protolytic cleavage reactions in FSO_3H-SbF_5, $HF-SbF_5$, and related[1,5,6] superacid media.

We now present evidence, detailed also in the accompanying two communications, for the *general electrophilic reactivity of covalent C–H and C–C single bonds of alkanes* (*cycloalkanes*). *This reactivity is due to what we consider the third major type of electron donor ability, i.e., the σ-donor ability* (*σ basicity*) *of shared electron pairs* (*single bonds*) *via two-electron, three-center bond formation.* It is our observation that C–C and C–H single bonds of all types (*i.e.*, tertiary, secondary, and primary) show substantial general reactivity in electrophilic reactions such as protolytic processes (isomerization, hydrogen–deuterium exchange, protolysis), alkylation, nitration, and halogenation. These observations promise to open up a new area of chemistry wherein alkanes and cycloalkanes are used as substrates in a wide variety of electrophilic reactions. Saturated single bonds, in general, can undergo electrophilic reactions.

The acid-catalyzed transformation reactions of saturated hydrocarbons (fragmentation, alkylation, isomerization) are generally considered to be carbocation reactions involving trivalent carbenium ions.[7] Whitmore[8] and subsequently Bartlett, Condon, and Schneider[9a] as well Schmerling[9b] 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.

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

It should be pointed out that the possibility of a triangular transition state was first suggested in a review article by Lewis and Symons[10] in 1958. It received relatively little interest until 1967–1968 when, based on chemical evidence and semiempirical self-consistent field calculations,[1,11,12] we concluded that protonation

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[1] Parts I and II, respectively, are considered: G. A. Olah and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **90**, 2126 (1968), and G. A. Olah, G. Klopman, and R. H. Schlosberg, *ibid.*, **91**, 3261 (1969).

[2] Presented in part at the Thirteenth Conference on Reaction Mechanisms, Division of Organic Chemistry of the American Chemical Society, University of California, Santa Cruz, Calif., June 1970, and at the Symposium on The Transition State of the French Physico Chemical Society, Paris, Sept 1970.

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

[4] F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968.

[5] G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227, 4739 (1967); **90**, 933 (1968).

[6] H. Hogeveen and A. F. Bickel, *Chem. Commun.*, 635 (1967); H. Hogeveen, C. J. Gaasbeek, and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, **88**, 703 (1969); H. Hogeveen and C. J. Gaasbeek, *ibid.*, **87**, 319 (1968).

[7] For a suggestion to name all cations of carbon compounds as carbocations and to differentiate trivalent carbenium ions as distinct from penta- or tetracoordinated carbonium ions, see G. A. Olah, *ibid.*, in press.

[8] F. C. Whitmore, *ibid.*, **54**, 3274 (1932); F. C. Whitmore and E. E. Stahly, *ibid.*, **55**, 4153 (1933).

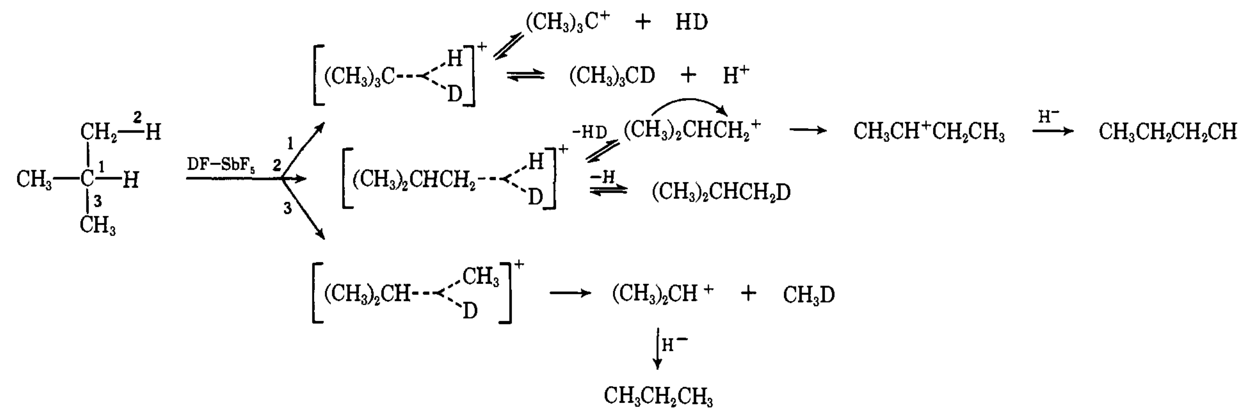
[9] (a) P. D. Bartlett, F. E. Condon, and A. Schneider, *ibid.*, **66**, 1531 (1944); (b) L. Schmerling, *ibid.*, **66**, 1422 (1944); **67**, 1778 (1945); **68**, 153 (1946).

[10] E. S. Lewis and M. C. R. Symons, *Quart. Rev., Chem. Soc.*, **12**, 230 (1958).

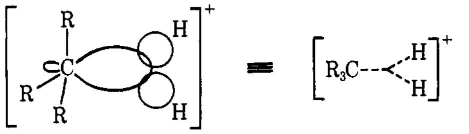
[11] G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227, 4739 (1967).

[12] A. F. Bickel, C. J. Gaasbeek, H. Hogeveen, J. M. Oelderik, and J. C. Platteeuw, *Chem. Commun.*, 634 (1967).

Scheme I



of methane and related alkanes can be achieved in superacids like FSO_3H–SbF_5 (magic acid) and occurs through "frontside" attack on the C–H or C–C bond forming a pentacoordinated carbonium ion type transition state



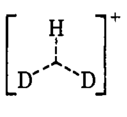
For simplicity we will depict the triangular three-center bonds with dotted lines.

Hogeveen, Gaasbeek, and Bickel[13] 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 suggested a linear transition state

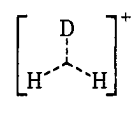
$$\overset{+}{\overbrace{R\text{---}H\text{---}H}}$$

for the reactions. Their arguments were based on the expected steric strain in a triangular transition state in the hydride transfer reactions between tertiary carbenium ions and the corresponding alkanes, as already pointed out by Stewart[14a] and Deno.[14b]

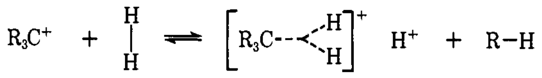
Hogeveen also stated that he found no evidence for hydrogen–deuterium exchange when molecular D_2 was treated with HF–SbF_5 and used this observation to strengthen the argument for a linear transition state. Since we recently were able to demonstrate[15] exchange of hydrogen (and deuterium) in a number of superacid solutions, like HF(DF)–SbF_5, $FSO_3H(FSO_3D)$–SbF_5, and $H_2SO_4(D_2SO_4)$–SbF_5, it was our suggestion that these reactions go through a trigonal H_3^+ type transition state, in accordance with Conroy's calculations.[16]



and



Consequently, the reverse reaction of carbenium ions with molecular hydrogen[13,17] can be best considered as an alkylation of H_2 by the carbenium ion on the H–H bond through what is a pentacoordinated carbonium ion type transition state (or intermediate) identical with that of the hydride abstraction reaction.



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

We consider "hydride abstraction," even when tertiary C–H bonds are involved, as protonation (or alkylation) of the C–H bond involving what amounts to frontside attack and formation of a three-centered bound transition state (or intermediate). The hybridization of the pentacoordinated carbon is tetrahedral, with one sp^3 orbital overlapping in the three-center bond with two other bonding orbitals. Furthermore, protolysis also involves C–C bonds through similar sharing of the bonding electron pair in three-center bond formation.

Strong indication for the mode of protolytic attack is obtained when isobutane is treated with deuterated superacids like DSO_3F–SbF_5 or DF–SbF_5[18] at atmospheric pressure and low temperature (−78°). The *tert*-butyl cation is formed under these conditions as a stable entity, with no isobutylene formation. Recovered isobutane shows substantial exchange of the methine proton (as determined by combining results of mass spectrometry and ${}^2H$ and ${}^1H$ nmr spectroscopy) but negligible exchange in the methyl group (in an obviously very slow reaction). There is also some isomerization to *n*-butane and methane cleavage (as CH_3D). See Scheme I.

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 present in solu-

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

(14) (a) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, New York, N. Y., 1966, p 22; (b) N. C. Deno, G. Saines, and M. Spangler, *J. Amer. Chem. Soc.*, **84**, 3295 (1962).

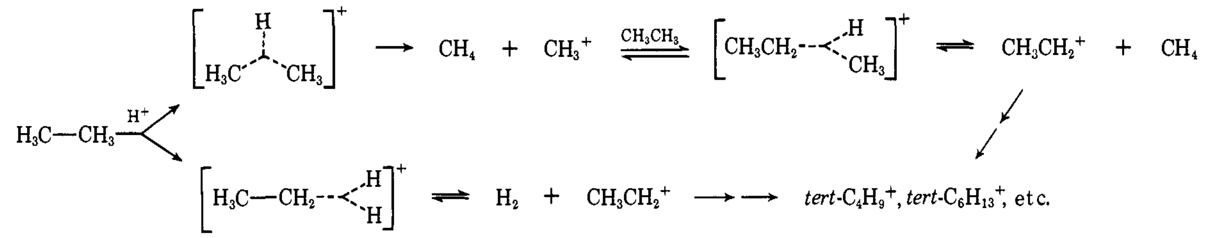
(15) G. A. Olah, J. Shen, and R. H. Schlosberg, *ibid.*, **92**, 3831 (1970).

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

(17) H. Pines and N. E. Hoffman in "Freidel-Crafts and Related Reactions," G. A. Olah, Ed., Vol. II, Wiley-Interscience, New York, N. Y., 1964, pp 1216–1217, and references given therein.

(18) 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.

Scheme II



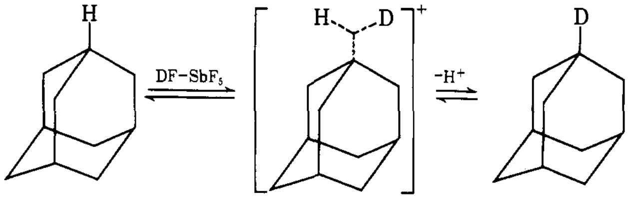
tion is very low and deuteration of carbenium ions is generally negligible.

It is noteworthy that in the reaction of isobutane in D_2SO_4, Eotvos found exchange of the nine methyl hydrogens, but not the methine hydrogen.[19] He,

$$(CH_3)_3CH \xrightarrow{D_2SO_4} (CD_3)_3CH$$

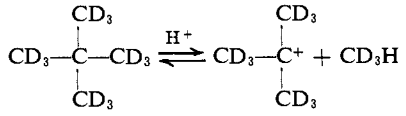
therefore, rightly argued that reaction under these conditions involves isobutylene formation and its reversible protonation (deuteration) whereas the tertiary hydrogen is only involved in intermolecular hydride transfer from isobutane. Under superacid conditions where no olefin formation takes place, no reversible isobutylene protonation can be involved in the exchange reaction.

Further, substantiation for the triangular transition state in protolytic reactions was found by studying adamantane, a rigid-cage hydrocarbon, in $DF-SbF_5$ solution. Besides stable ion formation, 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. In this case, backside attack is obviously impossible, as is deprotonation to an olefin. In addition, a linear transition state producing HD cannot explain the high yields of deuterated product. It is evident, therefore, that the only explanation for the observed deuteration results is the involvement of a three-center bond in the reaction pathway. Similarly 1,3,5,7-tetradeuterioadamantane in $HF-SbF_5$ and FSO_3H-SbF_5 solution was studied and showed similar exchange.

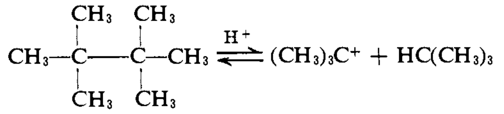


As mentioned, the reaction of isobutane with superacids is not limited to the C-H bonds. Up to 10-12% of the reaction is observed (when the reaction is run in a bomb at 25°) at the C-C bond (*i.e.*, protolysis) with formation of methane and isopropyl cation. The isopropyl cation subsequently reacts further either by intermolecular hydride transfer or alkylation. When the reaction is carried out with $DF-SbF_5$ or FSO_3D-SbF_5, CH_3D is formed even when the reaction is carried out at $-60°$, where the exchange reaction of methane itself plays no role.

Protolysis (deuterolysis) of C-C bonds was also observed in our previous work[1,2,5] and that of Hogeveen[6,12,13] in the superacid reactions of neopentane and 2,2,3,3-tetramethylbutane.



$$CD_3-C(CD_3)_2-CD_3 \overset{H^+}{\rightleftharpoons} CD_3-C^+(CD_3)_2 + CD_3H$$



$$CH_3-C(CH_3)_2-C(CH_3)_2-CH_3 \overset{H^+}{\rightleftharpoons} (CH_3)_3C^+ + HC(CH_3)_3$$

It is now our finding, based on the stable carbenium ions observed (nmr) and the gaseous cleavage products detected (mass spectrometry) in the reaction of 21 alkanes in FSO_3H-SbF_5 and $HF-SbF_5$ solution summarized in Scheme I, that protolysis of C-C bonds is indeed a general predominant reaction.

Ethane was found to undergo C-C bond protolysis in preference to C-H bond cleavage, as indicated by CH_4-H_2 (8:1) (in $HF-SbF_5$ as found by mass spectrometry) in the gaseous products of the reaction. Thus protonation on the C-C bond and subsequent cleavage takes preference, with the CH_3^+ ion immediately reacting with excess ethane (the bulkier carbenium ion now preferring the more accessible C-H bond). See Scheme II. When ethane is treated with $DF-SbF_5$, hydrogen-deuterium exchange in recovered ethane (as CH_3CH_2D) and cleavage of CH_3D is observed.

Similar observations were made with propane, *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane. Scheme III summarizes data showing observed products. Thus, we feel that the observation of preferential C-C bond protolysis in *n*-alkanes can readily explain why there is relatively little hydrogen formed in many acid-catalyzed hydrocarbon transformation reactions, suggested to be of carbenium ion nature, and the formation of lower molecular weight alkanes. Many of these reactions were previously suggested to first form a trivalent carbenium ion *via* hydride abstraction (with only qualitative reference to H_2 formation) which then undergoes Whitmore β cleavage.

Recent *ab initio* calculations by Pople[20] gave substantial preference in the protonation of ethane for the C-C bond over the C-H bond, in good agreement with our experimental findings.

Our experimental data indicate an empirical reactivity order of single bonds in alkanes tertiary CH > C-C > secondary CH ≫ primary CH, although it should be emphasized that the nature of each system (for example, steric hindrance) can influence relative reactivities. Any more precise, even semiquantitative reactivity order must await results of more extensive

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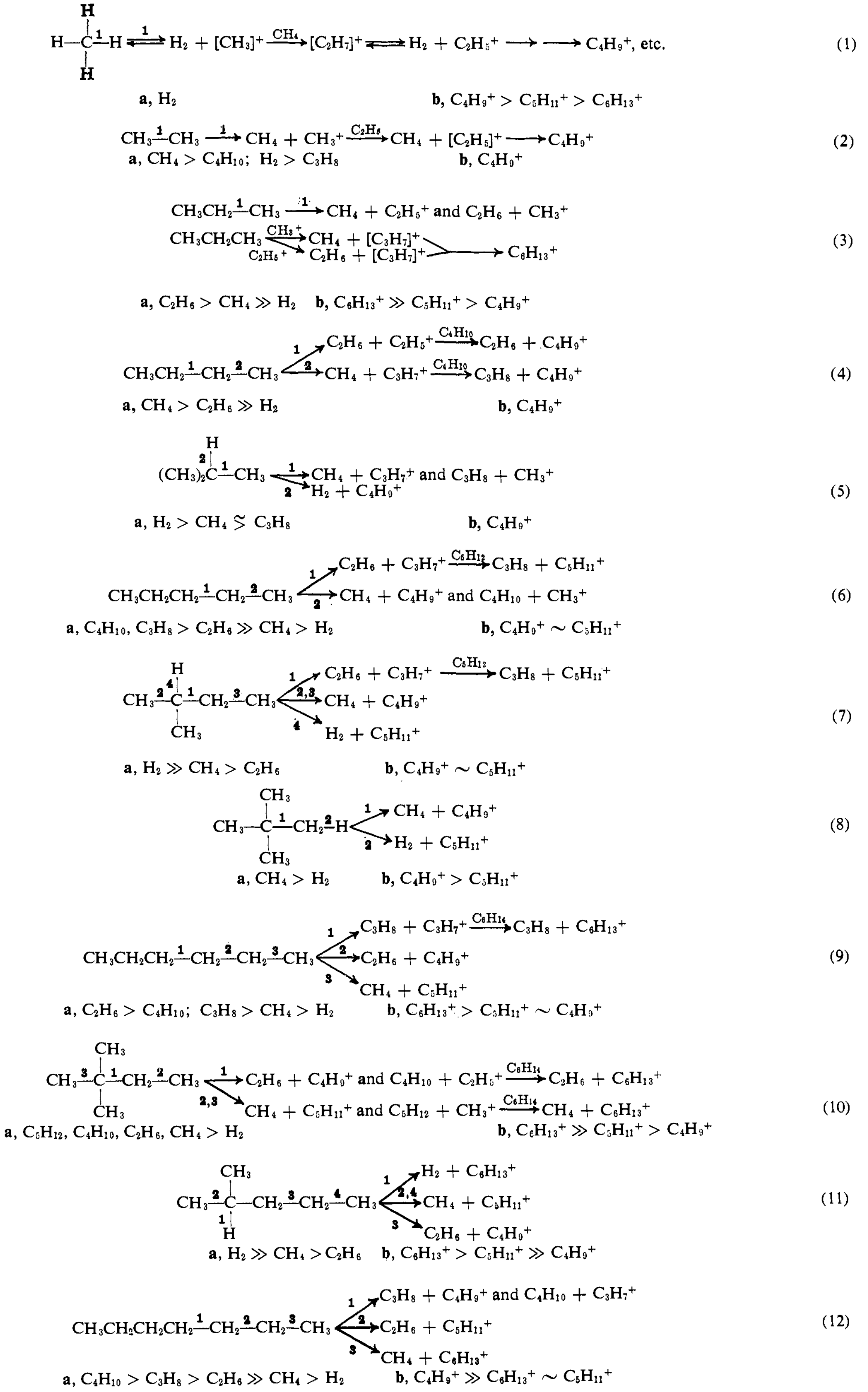
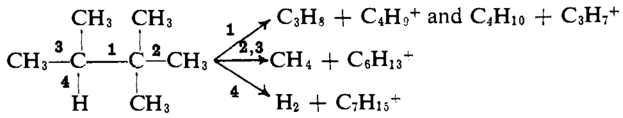
(19) J. W. Eotvos, D. P. Stevenson, C. D. Wagner, and O. Beek, *J. Amer. Chem. Soc.*, 73, 5471 (1951); D. P. Stevenson, C. D. Wagner, and J. W. Eotvos, *ibid.*, 74, 3769 (1952).

(20) Professor J. A. Pople, personal communication; W. A. Lathan, W. J. Hehre, and J. A. Pople, *Tetrahedron Lett.*, 2699 (1970).

Scheme III. Protolytic Behavior of Alkanes in FSO_3H-SbF_5 Solution at 25° [a]

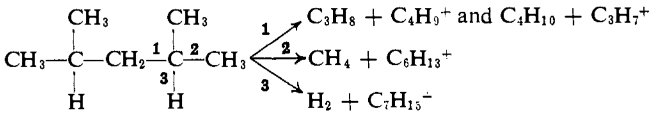




a, C_4H_{10}, $C_3H_8 \gg$
CH_4, $H_2 > C_2H_6$ (trace)

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

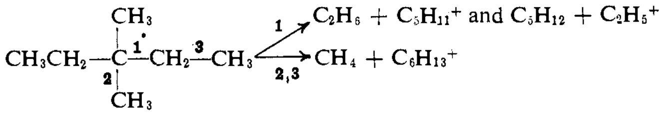
(13)



a, C_4H_{10}, $C_3H_8 \gg$
CH_4, $H_2 > C_2H_6$ (trace)

b,[b] $C_4H_9^+ > C_6H_{13}^+ > C_5H_{11}^+$

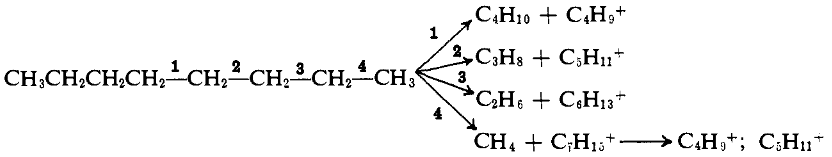
(14)



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

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

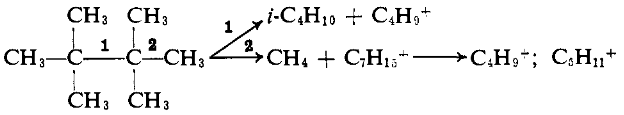
(15)



a, $C_4H_{10} > C_3H_8 > C_2H_6 \gg CH_4 > H_2$

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

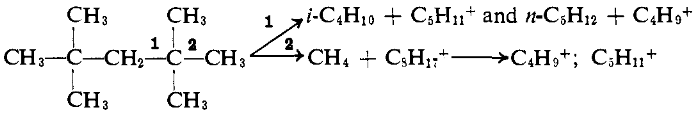
(16)



a,. $C_3H_8 > C_2H_6 >$
$CH_4 > H_2$

b, $C_4H_9^+$

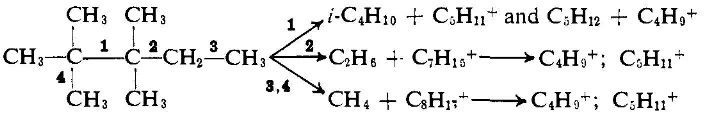
(17)



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

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

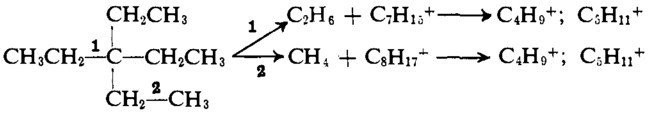
(18)



a, $C_4H_{10} > C_2H_6 >$
$CH_4 > H_2$

b, $C_4H_9^+ \backsim C_5H_{11}^+$

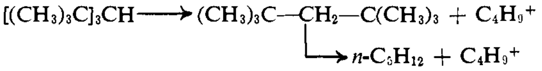
(19)



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

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

(20)



a, C_4H_{10}, $C_3H_8 > CH_4 \gg C_2H_6$, H_2

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

(21)

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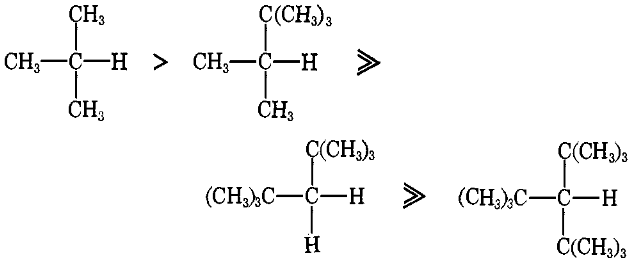
[a] **a**, volatile products, determined by mass spectrometry; **b**, carbocations in acid solution, determined by nmr spectroscopy. [b] −60°; *tert*-$C_7H_{15}^+$ is the only product.

kinetic studies (in progress) and must always be related to specific systems studied. Isoalkanes containing a tertiary C–H bond show preference of reactivity of this bond. (This can also include hydride transfer to alkylcarbenium ions formed in C–C bond protolysis.) Increased branching and steric crowding can cause a shift of reactivity in favor of C–C bond protolysis. Comparison of isobutane, triptane, di-*tert*-butylmethane, and tri-*tert*-butylmethane[21] demonstrates well this point. The decreasing order of tertiary C–H bond reactivity is



$$(CH_3)_3CH > CH_3C(CH_3)(C(CH_3)_3)H \gg ((CH_3)_3C)_2CH_2 \gg ((CH_3)_3C)_3CH$$

In isobutane, C–H over C–C reactivity at −78° is 50:1 and at 25° it is about 9:1. In triptane under similar conditions the reactivity ratio is 20:1 and 3:1, respectively. In di-*tert*-butylmethane, C–C bond reactivity is nearly exclusive and in tri-*tert*-butylmethane[21] there is absolutely no observable reactivity on the highly shielded C–H bond. Similar to the well-studied steric factors of n- or π-donor bases,[22] steric strain thus effects σ bond basicities of alkanes.

The concept of triangular three-center bond formation in pentacoordinated carbonium ion type transition states (or even probable intermediates in some favorable cases) satisfactorily explains the mechanism of acid-catalyzed saturated hydrocarbon transformation reactions. These include isomerizations (involving hydrogen and alkyl shifts), fragmentations, and alkylations (see subsequent communication). This concept supplements Whitmore's and Bartlett's mechanisms where trivalent carbenium ion processes (frequently associated with subsequent deprotonation leading to olefin formation) are involved . At the same time our work substantially extends the scope and understanding of electrophilic reactions, based on the realization of the general electron pair donor ability of single bonds (shared electron pairs) which eventually may equal the importance of lone electron pairs (unshared electron pairs, Lewis bases).

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

(22) H. C. Brown and R. D. Johanessen, *J. Amer. Chem. Soc.*, **75**, 16 (1953), and earlier papers referred to therein.

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Received September 12, 1970

Electrophilic Reactions at Single Bonds. IV.[1a] Hydrogen Transfer from, Alkylation of, and Alkylolysis of Alkanes by Alkylcarbenium Fluoroantimonates[1b]

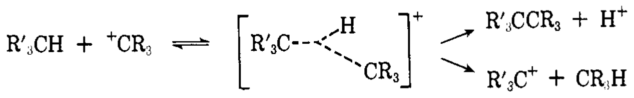
Sir:

Despite frequent literature references to electrophilic alkylation of alkanes by olefins, from a mechanistic point of view these reactions must be considered as alkylations of the olefin by the carbenium ion derived from the isoalkane by intermolecular hydride transfer.[2] The suggested reaction pathway is reflected by the

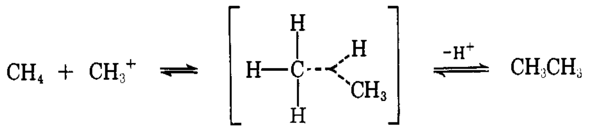
$$R'_2C{=}CH_2 \xrightarrow{H^+} R'_2\overset{+}{C}CH_3 + R_3CH \longrightarrow R'_2CHCH_3 + R_3C^+$$

$$R_3C^+ + R'_2C{=}CH_2 \longrightarrow R'_2C^+{-}CH_2CR_3 \xrightarrow{H^-} R'_2CHCH_2CR_3$$

products formed in the reaction of propylene and isobutylene with isobutane. Products do not contain 2,2,3-trimethylbutane or 2,2,3,3-tetramethylbutane, which would be expected primary alkylation products in direct alkylation of isobutane with propylene and isobutylene, respectively. In the Bartlett–Nenitzescu intermolecular hydride abstraction from a tertiary isoalkane by a carbenium ion, the transition state either could be considered linear or triangular (from frontside attack on the C–H bond). The latter would not be symmetrical due to a steric effect between the carbenium ion and the tertiary isoalkane. With an even strongly distorted triangular transition state (*i.e.* the reaction taking place on the C–H bond and not at the hydrogen atom), it becomes obvious that cleavage can result not only in intermolecular hydride transfer, but also, *via* proton elimination, in direct alkylation



For simplicity we are depicting the triangular three-center bonds with dotted lines. To study the reaction of alkanes with alkylcarbenium ions with the hope of carrying out "direct" alkane alkylations, it was necessary to find carbocation reaction conditions unfavorable for olefin formation in order to eliminate the previously discussed reaction pathway for olefin–isoalkane alkylation. To our knowledge the only alkane alkylation reported so far in the literature fulfilling these conditions was our recently discovered methane and methyl fluoride condensation reaction.[3] The methyl cation (CH_3^+) formed in the course of the reactions methylates excess methane (or methyl fluoride) in the key step.



We report now the first systematic study of the direct alkylation of alkanes (both isoalkanes and *n*-alkanes)

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(1) (a) Part III: G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Amer. Chem. Soc.*, **93**, 1251 (1971). (b) For a general definition of carbocations and differentiation of trivalent carbenium ions from penta- or tetracoordinated carbonium ions see G. A. Olah, *ibid.*, in press.

(2) For a summary, see L. Schmerling in "Friedel-Crafts and Related Reactions," G. A. Olah, Ed., Vol. II, Wiley-Interscience, New York, N. Y., 1964, pp 1075–1131, and references given therein.

(3) G. A. Olah and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **90**, 2726 (1968); **91**, 3261 (1969).