Electrophilic Reactions at Single Bonds. X.[1] Hydrogen Transfer, Alkylation, and Alkylolysis of Alkanes with Methyl and Ethyl Fluoroantimonate

George A. Olah,* John R. DeMember, and Jacob Shen

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received April 15, 1972*

Abstract: Methyl and ethyl fluoroantimonates (*i.e.*, the exchanging $CH_3F–SbF_5$ and $C_2H_5F–SbF_5$ complexes) in SO_2ClF solution were found to be hydrogen abstracting reagents, as well as alkylating agents toward a series of alkanes: CH_4, C_2H_6, C_3H_8, *i*-C_4H_{10}, *n*-C_4H_{10}, and *neo*-C_5H_{12}. Reaction pathways, product distributions, and relative reactivities of alkylated C–C and C–H bonds are discussed in the light of the involved three-center bound carbonium ion type transition states, steric factors, and solvation effects. Energetic considerations similar to those of gas-phase ion–molecule reactions are found important in determining the relative importance of the several possible cleavage paths of the carbonium ion transition states.

Alkylation processes are of fundamental importance. Despite the massive body of existing literature, the direct alkylation of alkanes (by alkylcarbenium ion complexes in low nucleophilicity media) was only recently achieved.[2] Previous claims for alkylation of alkanes were indeed alkylations of olefins by carbenium ions derived from isoalkanes by intermolecular hydride transfer.[2]

Previously reported alkylations of alkanes by alkylcarbenium ions[1] (such as the isopropyl cation, as well as isomeric butyl cations) were carried out in sulfuryl chloride fluoride solution by reacting alkanes (such as propane, isomeric butanes, and neopentane) with stable alkylcarbenium hexafluoroantimonates[3] (such as isopropyl, *sec*-butyl, and *tert*-butyl hexafluoroantimonate).

The methyl and ethyl fluoride–antimony pentafluoride complexes were found in our work as extremely reactive alkylating agents.[4,5] The structures of these complexes were studied,[4,6] showing fast intramolecular exchange processes (fluorine, as well, in the case of the ethyl system, as hydrogen and carbon scrambling). The ethyl fluoride–antimony pentafluoride complex clearly equilibrates through the ethyl cation. The intramolecular fluorine exchange observed in the methyl fluoride–antimony pentafluoride complex is also difficult to explain, with a frontside S_N2 type mechanism (due to repulsion in a triangular four electron three-center system) considered unlikely. It must be therefore considered that these complexes indeed behave like methyl and ethyl fluoroantimonates.

The powerful alkylating ability of methyl and ethyl fluoroantimonates toward π- and n-donor systems was demonstrated in our preceding work,[4,5] and they were recognized as the most powerful methylating and ethylating agents known. We now report their ability to alkylate (or hydrogen abstract from) alkanes, *i.e.*, σ-donor systems, in reactions closely related to those of the higher homolog alkylcarbenium fluoroantimonates.[1]

Results and Discussion

Methylation and ethylation of a series of alkanes (methane, ethane, propane, butane, 2-methylpropane (isobutane), and 2,2-dimethylpropane (neopentane)) were studied using the methyl and ethyl fluoride–antimony pentafluoride complexes in low nucleophilicity sulfuryl chloride fluoride solution at 0° (as described in the Experimental Section). Whereas product compositions (expressed for convenience generally in mole ratios) were determined with high accuracy by gas chromatography, mass spectrometry, and nmr spectroscopy in individual runs, it must be emphasized that due to the complexity of the systems these data should only be considered representative and may vary even upon small changes in conditions. From the point of view of our studies, however, the emphasis clearly is on the relative composition of product mixtures and not so much on absolute, quantitative yields of individual components, which are always extremely difficult to define in Friedel–Crafts type alkylation systems.

Methylation with Methyl Fluoroantimonate. Methane was found always as the major gaseous reaction product in all the studied methylations of alkanes by methyl fluoride–antimony pentafluoride complex. Since methane could only be formed *via* intermolecular hydrogen transfer involving alkonium ions formed *via* C–H bond attack, the observation that methane is the major product indicates the preference of C–H bond over C–C bond attack. This is the reverse of the empirical order of single bond reactivities observed previously in the protolysis of alkanes in superacids, where the relative order of reactivity of single bonds was tertiary CH > C–C > secondary CH ≫ primary CH.[5] Our present results of methylation seem to suggest that even secondary or primary C–H bonds are more reactive than C–C bond toward the $CH_3F–SbF_5$ complex. This is not surprising if we take into account the nature of each system under study, particularly

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[1] Part IX: G. A. Olah, Y. K. Mo, and J. A. Olah, *J. Amer. Chem. Soc.*, **95**, 4939 (1973).

[2] For the difference between electrophilic alkylation of alkanes and alkylation of olefins by carbenium ions, see G. A. Olah and J. A. Olah, *ibid.*, **93**, 1256 (1971).

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

[4] G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **91**, 2112 (1969).

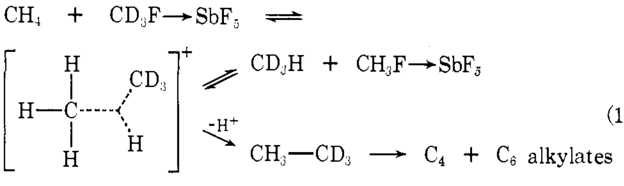
[5] G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, *ibid.*, **94**, 156 (1972).

[6] J. Bacon and R. J. Gillespie, *ibid.*, **93**, 6914 (1971).

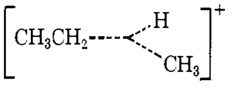
steric factors. In the course of our studies of protolysis, it has been our observation that increased branching and steric crowding of substrates can shift the order of single bond reactivity such that even tertiary C–H bonds would become less favorable than C–C bonds. For example, the protolytic reactivity of 3° C–H over C–C bond is 9:1 at 25° for isobutane, 3:1 for triptane, and 0 for tri-*tert*-butylmethane.[5] If, instead of increasing the branching or steric crowding of the substrates, one alternatively increases the size of the electrophile, one would expect a similar kind of steric hinderance to exist. For the methyl fluoride–antimony pentafluoride complex, Raman spectroscopic evidence has shown that the overall weakening of the C–F bond is not sufficient to alter significantly the overall tetrahedral geometry of methyl fluoride.[4] This indicates that the actual attacking electrophile under present methylating conditions is the tightly bound donor–acceptor complex $CH_3F–SbF_5$ or the ion pair $CH_3^+SbF_6^-$, rather than the "free" methyl cation (carbenium ion). Furthermore, when SO_2ClF is used as solvent in preparing the $CH_3F–SbF_5$ complex, there is also the possibility of 1:2 and 1:3 complexes in addition to the 1:1 complex formation,[5,6] *i.e.*, dimeric and trimeric, or even bulkier, antimony pentafluoride complexes can be involved. This is due to the ease with which SbF_5 forms fluorine-bridged polymers. Therefore, as the size of the hydrocarbon substrate increases, methylation on less sterically hindered primary and secondary C–H bonds becomes easier than on the relatively hindered C–C bonds.

Intermolecular hydrogen transfer is, however, not the only reaction in the system, and alkylation, indeed, occurs as shown by the formation of higher molecular weight hydrocarbon alkylates than the parent starting alkane.

Methylation of Methane. At 60° the reaction of methane with the $CH_3F–SbF_5$ complex is extremely slow. However, when $CD_3F–SbF_5$ is used (or CD_4 with $CH_3F–SbF_5$) in the reaction, hydrogen transfer is observed forming CD_3H (CH_3D) as the major product. Alkylation products are observed only in the 30–50° temperature range, but even then the amount of alkylate is low (<3%). Products are mostly C_4, C_6, and some C_8, with some ethane (in the case of $CD_3F–SbF_5$, CD_3CH_3) also observed. Self-condensation of metal fluoroantimonate also can take place, complicating the system.


(1)

Methylation of Ethane. When ethane was treated with the $CH_3F–SbF_5$ complex, alkonium ion transition states IV and V can be formed through the insertion of the methyl group into the C–H and C–C bonds, respectively. Alkonium ion IV would yield methane through cleavage which is equivalent to what is formally a hydride transfer reaction, or give propane through proton elimination (the direct alkylation path). The ethyl cation (methylcarbenium ion) formed *via* C–H bond cleavage can undergo further reaction with excess ethane to form alkonium ions VI and VII, which in turn could yield C_3 and C_4 hydrocarbons through deprotonation or C–C bond cleavage. It should also be pointed out that, due to the ease with which intramolecular "bond to bond" rearangements can take place in carbonium ions,[7] the question of a singularly directed attack by the electrophile (methylating agent) on a specific bond is a rather mute one. Whatever the nature of the initial interaction, the attacking electrophile will eventually insert into either the C–C or C–H bond.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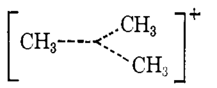
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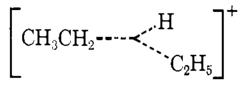
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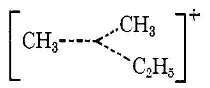
VII

The experimental results show that the amount of methane formed in methylation of ethane is at least 30 times that of propane and isomeric butanes (which are obtained in a ratio 1:7.) Since only alkonium ion IV can cleave to give methane, it thus shows that formation of alkonium ion IV *via* C–H bond attack is much easier than the formation of ion V *via* C–C bond attack, and than secondary formation of ions VI and VII. Steric hindrance due to the relatively bulky alkylating agent, as was discussed previously, could cause the preference for the C–H bond attack. However, the same observations also tell that for ion IV methane cleavage (*i.e.*, the hydrogen transfer reaction) goes far more easily than deprotonation (*i.e.*, alkylation). In other words, the driving force for hydrogen transfer is much greater than that for alkylation. Since there is no difference between the two pathways as far as the reactants are concerned, the difference could very well lie in the different stability of the products obtained from both cleavages.

Recent studies of isomeric $(H, D)_3^+$ ions[8] and protolysis of alkanes in superacids[9] have shown the close parallelism between gas-phase ion–molecule reactions and chemistry in superacids. The major element that differentiates gas-phase ion–molecule reaction from solution ionic chemistry is the solvent effect. However, this effect is minimized when solvents of extremely low nucleophilicity are used, such as superacids. That long-lived alkylcarbenium ions can be observed in superacids when SO_2ClF is used as solvent is attributed to the low nucleophilicity of the system.[6] If we consider the gaseous counterparts of the cleavage pathways of alkonium ion IV, which are shown in eq 2 and 3,

$$\underset{\text{IV}}{C_3H_9^+} \begin{cases} \rightarrow C_2H_5^+ + CH_4 & \Delta H = 16 \pm 7\,\text{kcal/mol} & (2) \\ \rightarrow C_3H_8 + H^+ & \Delta H = 156 \pm 7\,\text{kcal/mol} & (3) \end{cases}$$

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(7) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

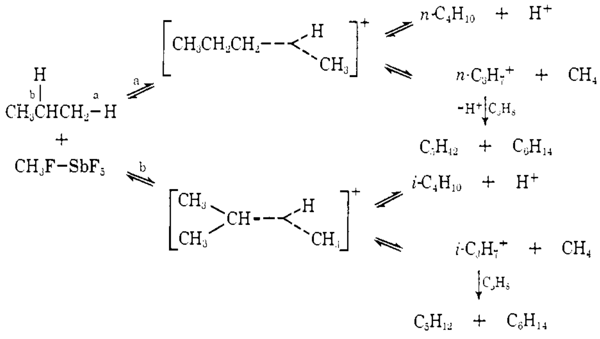
(8) G. A. Olah, J. Shen, and R. H. Schlosberg, *ibid.*, **92**, 3831 (1970).

(9) (a) G. A. Olah and R. H. Schlosberg, *ibid.*, **90**, 2126 (1968); (b) G. A. Olah, G. Klopman, and R. H. Schlosberg, *ibid.*, **91**, 3261 (1969); (c) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *ibid.*, **93**, 1251 (1971); (d) G. A. Olah and H. C. H. Lin, *ibid.*, **93**, 1259 (1971); (e) G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, *ibid.*, **94**, 156 (1972).

we can see that the energetic consideration in determining the preference of the two possible cleavages is important. Recently we have actually observed the two processes of the $C_3H_9^+$ ion in pure ethane by employing icr spectroscopy at near threshold energy.[10] These give an estimation of the heat of formation of $C_3H_9^+$ as 185 ± 7 kcal/mol.[11] By using other best estimated values of heat of formation,[12–14] the heat of reaction of reaction 2 is endothermic by 16 ± 7 kcal/mol, and that of reaction 3 is endothermic by 156 ± 7 kcal/mol. Since in the gas phase there are no solvent molecules around the gaseous ions to supply solvation energy, and since the proton is far more unstable than all other gaseous alkyl cations,[15] the reaction (3) that yields a proton is less favorable. In fact, reaction 3 is hardly possible in the gas phase because the $C_3H_9^+$ ion could hardly be excited to such an extent. Indeed, Field and Beggs have recently observed reaction 2 to be a reversible process in the range between room and liquid nitrogen temperatures. Reaction 2 was found to be favored at higher temperature, while its reverse is favored at lower temperature. At temperatures below −150°, $C_3H_9^+$ became dominant. This then agrees with a slightly endothermic nature of reaction 2 discussed previously. Reaction 3 has not been observed in the gas phase in any case, apparently due to its large endothermicity. In view of the extremely low nucleophility of the solution alkylation system, as well as the low temperature experimental conditions used, it seems reasonable to suggest that energetic considerations similar to those of gas-phase ion–molecule reaction can be important in determining the most preferred cleavage pathway among the possible channels that are available to the three-center bonded carbonium ions, such as alkonium ion IV.

It has been our experience that gas-phase ion–molecule reactions can often give indications in understanding the newly developed superacid chemistry. The discussed experimental observation that, in the reaction of ethane with $CH_3F–SbF_5$ involving alkonium ion IV, intermolecular hydrogen transfer is much preferred over alkylation (that would mean elimination of a proton which would not be easily stabilized under the used low nucleophilicity and low temperature conditions) is at least qualitatively in agreement with the above mentioned energetic considerations.

Methylation of propane with $CH_3F–SbF_5$ complex in SO_2ClF at low temperature again gives CH_4 as the hydrogen transfer product, along with the alkylation products *n*-butane, isobutane (the major product), and some C_5, C_6 hydrocarbons. Three types of carbonium ion transition states that could be formed through the interaction of the methyl fluoride–antimony pentafluoride complex with either C–H bonds or C–C bonds, together with the cleavage pathways, are shown in eq 4, 5, and 6. Equation 6 represents electrophilic attack on a C–C bond, and is of minor importance under present condition. The isopropyl cation, either formed directly *via* eq 5 or from the isomerization of $n\text{-}C_3H_7^+$ *via* eq 4, can undergo further reaction with excess propane to yield *tert*-amyl and *tert*-hexyl cations, as was observed by nmr spectroscopy, as well as giving C_5 and C_6 alkylation products (analyzed by glc), in agreement with our previous results of alkylation of propane with propyl cation.[2]



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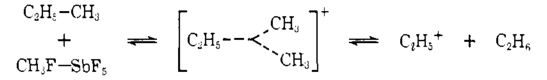
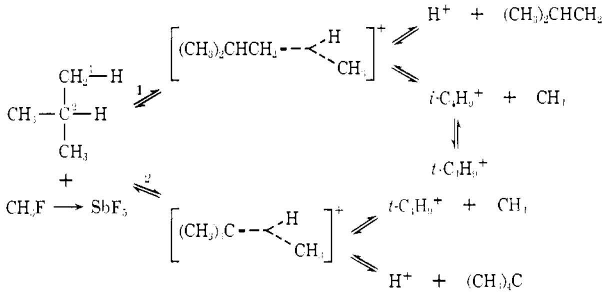


(6)

Methylation of Butanes. When either *n*-butane or isobutane is reacted with $CH_3F–SbF_5$, similar results are obtained for both systems. In addition to the substantial amount of methane formed (hydrogen transfer product), isopentane is the major alkylation product. When isobutane is methylated, neopentane should be formed in preference to isopentane if the tertiary C–H bond were more reactive than the primary one. Since tertiary C–H bonds indeed have much higher reactivity than primary ones in the protolysis of alkanes in superacids, the preferential formation of isopentane over neopentane (in a ratio 20:1) is again indicative of steric hindrance. Due to the bulkiness of the $CH_3F–SbF_5$ complex, as compared to protic acids or alkylcarbenium



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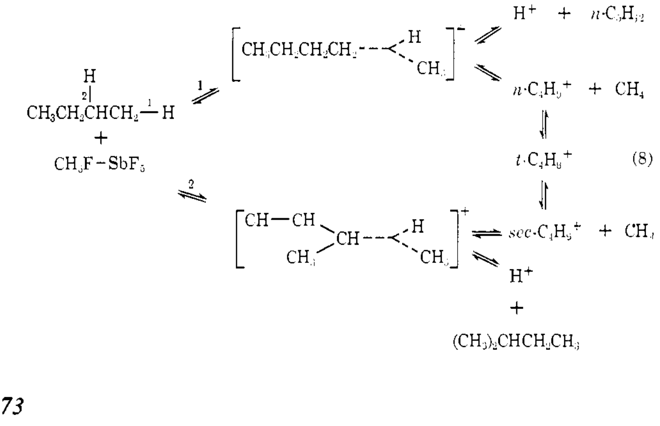

(8)

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[10] R. C. Dunbar, J. Shen, and G. A. Olah, *J. Chem. Phys.*, **56**, 3794 (1972).

[11] $\Delta H(C_3H_9^+)$ has also been calculated recently by Field and Beggs[12] as 199 kcal/mol. However, since the reaction $C_2H_6^+ + C_2H_6 \rightarrow C_3H_9^+ + CH_3$ has also been indicated by photoionization mass spectroscopy,[12] we feel that 192 kcal/mol should truly represent the upper limit of $\Delta H(C_3H_9^+)$. Consequently, we tend to use the only other available value, 186 ± 7 kcal/mol.

[12] F. H. Field and D. P. Beggs, *J. Amer. Chem. Soc.*, **93**, 1585 (1971).

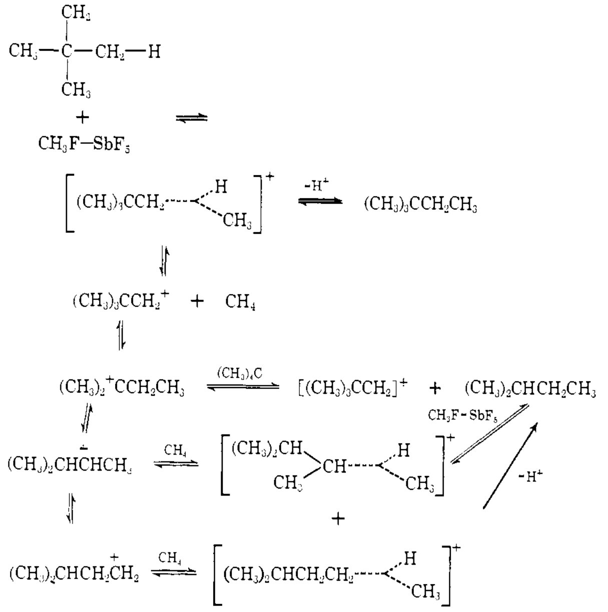
[13] S. K. Searles, L. W. Sieck, and P. Ausloos, *J. Chem. Phys.*, **53**, 849 (1970).

[14] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser.*, *Nat. Bur. Stand.*, **No. 26** (1969).

[15] For example, H^+ is 166 kcal/mol less stable than CH_3^+ which is 41 kcal/mol less stable than $C_2H_5^+$.

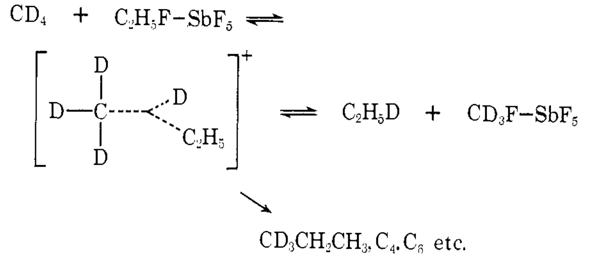
ions, the tertiary C–H bond in isobutane becomes relatively more hindered than the primary C–H bonds. However, in the case of methylation of *n*-butane, the preferential formation of isopentane over *n*-pentane, as shown in eq 8, indicates that in this case the secondary C–H bond is preferred over the primary C–H bond. Obviously, the secondary C–H bond is less hindered than the tertiary one. That *n*-butane is observed as product in the methylation of isobutane is clearly the result of hydrogen transfer between the secondary butyl cation (formed in intermolecular hydrogen transfer) and excess isobutane.

Neopentane. The reaction of neopentane with CH_3F-SbF_5 complex gives as the major products methane and isopentane (in comparable amounts) and <5% hexanes. The formation of these products is again best understood by considering that the reactivity of alkanes toward strong electrophiles is mainly on the single bonds. Major reaction paths and the resulting products are shown in eq 9. Since neopentane has only two types of single bonds, the quite hindered C–C bond and the less hindered primary C–H bond, most reaction products are resulting from C–H bond attack.


(9)

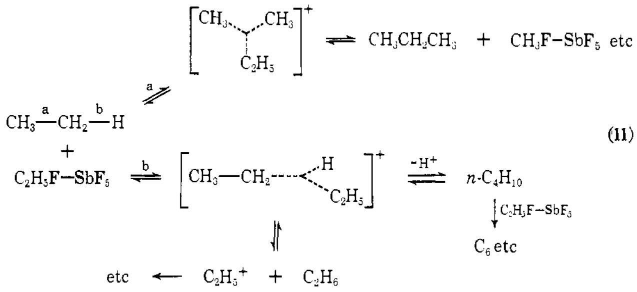
Ethylation with Ethyl Fluoroantimonate. Results of ethylation of alkanes with the ethyl fluoride–antimony pentafluoride complex are basically similar to those of methylation with the methyl fluoride–antimony pentafluoride complex.

Ethylation of Methane. Ethylation of methane with $C_2H_5F-SbF_5$ is very slow at 0°. Using deuterated ethyl fluoride (or deuterated ethane), however, intermolecular hydrogen transfer was shown to take place readily.


(10)

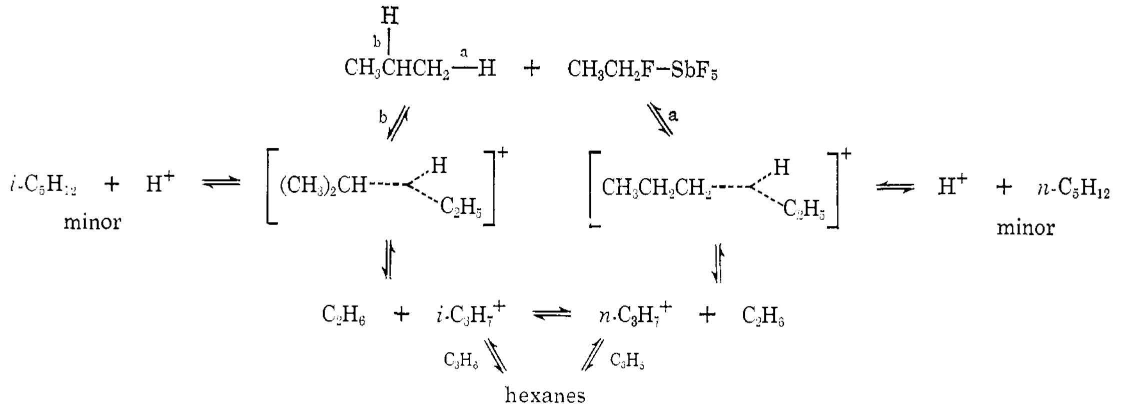
Ethylation leading to propane (7.5%), as well formation of isobutane (11%) and some higher alkanes, is observed only above 20°, but at this temperature self-condensation of the $C_2H_5F-SbF_5$ complex also can take place, complicating the system.

Ethylation of Ethane. When ethane is ethylated by $C_2H_5F-SbF_5$ at low temperature, a significant amount (15–20%) of *n*-butane is formed indicating the reaction path b of eq 11. When SO_2 is used instead of SO_2ClF as solvent, there is a further increase in the formation of *n*-butane. The ease of C–H bond alkylation in SO_2 is also reflected by an increase in yield of hexanes which apparently are the products of the secondary process between the newly formed *n*-butane and excess $C_2H_5F-SbF_5$. As analyzed by capillary gas–liquid chromatography, *n*-butane and C_6 hydrocarbons contribute more than 80% of the total alkylated hydrocarbon yield. That C–C bond attack is relatively minor is indicated by the fact that the amount of odd carbon number hydrocarbons (particularly propane) present in the system is relatively low (<5%). All the odd numbered hydrocarbons present in the system must be formed through C–C bond attack (or secondary protolytic cleavages). The differing solvation and association of the alkylating agent in SO_2 and SO_2ClF may explain the observed differences. There is no evidence, as shown in control experiments, that SO_2 would cause deprotonation of ethyl fluoroantimonate to ethane under the used experimental conditions (see also ref 5).


(11)

Ethylation of propane with $C_2H_5F-SbF_5$ complex yields ethane and hexanes as the dominant products. After the gas sample, which contains mostly ethane, was taken from the bomb at −78°, ether extraction of the remaining solution showed (by glc) it to contain more than 90% of hexanes in the alkylated hydrocarbons. The formation pathway is shown in eq 12.

Butanes. The reactions of *n*-butane and isobutane with $C_2H_5F-SbF_5$ show the same preference to primary or secondary C–H bond attack followed by cleavage leading to hydrogen transfer. Thus ethane and isomeric hexanes such as 2-methylpentane, 3-methylpentane, and *n*-hexane dominate over other hydrocarbon products. In addition, apparent *n*-buane ⇌ isobutane isomerization occurs in both systems. This is a result of the rapid intermolecular hydrogen transfer reaction among the isomeric butyl cations and either excess isobutane or butane present in the system. That very minor amounts of octanes result from the reaction mixture, even when SO_2 is used as the solvent, reflects the increasing endothermicity of alkylation (*i.e.*, deprotonation of carbonium ion transition states) going from the parent alkanes to higher homo-



(12)

logs. A simple plot[16] of the proton affinities of a series of gaseous $C_nH_{2n+3}^+$ ions against the number of carbon atoms they contain allows the prediction that the heat of formation of alkonium ions would decrease as the number of carbon atoms increases. As a consequence, unless the eliminated proton is otherwise stabilized (*i.e.*, solvated), reaction 13 will become increasingly unfavorable as *n* increases.

$$C_nH_{2n+3}^+ \rightleftharpoons H^+ + C_nH_{2n+2} \qquad (13)$$

Neopentane. When neopentane is reacted with the C_2H_5F–SbF_5 complex, ethane and propane (in a ratio of about 3:2), with some (~5%) isobutane, are the major products. The interaction between the hindered C–C bonds and the ethylating agent is obviously strained. The alkonium ion formed *via* C–H bond attack will predominate, and consequently in the system alkylation will be much less favorable than hydrogen transfer, which yields ethane and the *tert*-amyl cation (*via* rearrangement of the reactive primary neopentyl cation). Hydrogen transfer then gives isopentane, which seems to cleave further under the reaction conditions. Propane (and isobutane) formation also indicates C–C bond alkylation (alkylolysis).

Conclusions

All observed reactions of alkanes with the methyl and ethyl fluoride–antimony pentafluoride complexes can be best explained involving two electron three center bound carbonium ion formation, the involved single bonds acting as σ-electron donors.

The substantial reactivity shown by the methyl and ethyl fluoride–antimony pentafluoride complexes toward C–H and C–C single bonds is quite comparable, or even surpasses that found in previously studied related reactions with alkylcarbenium fluoroantimonates. In our studies relating to the structure of the ethyl fluoride–antimony pentafluoride complex[4,5] we concluded, based on ^1H, ^{13}C, and ^{19}F nmr studies, that it is an intramolecularly equilibrating complex with the ethyl cation involved in the equilibration process, in all probability as a tight ion pair. The methyl fluoride–antimony pentafluoride complex showed similar nmr and Raman spectroscopic characteristics to the ethyl complex, but for obvious reasons only fluorine equilibration could be proven in the single carbon species. Thus the involvement of the methyl cation in the equilibration process could not be proven. Present data on hydrogen transfer and alkylating ability of both complexes seem to strongly indicate that the corresponding methyl and ethyl fluoroantimonates, either in the form of ion pairs or highly polarized complexes, are involved in the reactions.

Experimental Section

Materials. Antimony pentafluoride was obtained from the Allied Chemical Co. and was twice distilled before use. Methyl and ethyl fluoride were commercially available and donated by Cationics, Inc.

The methyl and ethyl fluoride–antimony pentafluoride complexes in SO_2ClF solution were prepared as previously reported.[4,5]

Alkylation of Alkanes. Methylation and ethylation of ethane, propane, *n*-butane, isobutane, and neopentane were carried out under identical conditions. Five milliliters of a 20 mol % solution of CH_3F–SbF_5 (or C_2H_5F–SbF_5) in SO_2ClF (prepared at −78°) was added into a 75-ml stainless steel, Teflon-lined bomb cooled to −78°. The alkane (in 5 mol excess) to be reacted was introduced and the bomb was sealed. The reaction mixture was then shaken at 0° for 0.5 to 1 hr, respectively. Gaseous samples were taken at −78° at the end of each run and analyzed by mass spectrometry. After opening the bomb at low temperature (−78°), samples of the solutions were neutralized ($NaHCO_3$), extracted with ether, and analyzed by capillary gas–liquid chromatography for hydrocarbon products. Cations present in aliquot samples of the SO_2ClF solution were studied by nmr spectroscopy.

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

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(16) R. C. Dunbar, J. Shen, and G. A. Olah, unpublished results.