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Thermodynamics of Hydrocarbon Oxidations by Superacids

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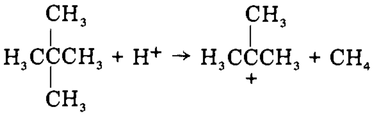
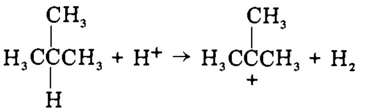
Abstract: The enthalpies of the various reactions which have been proposed to explain the formation of carbenium ions from alkanes in SbF_5-FSO_3H are calculated. Only those reactions which involve both H^+ and SbF_5 (or FSO_3H) as oxidizing agents have favorable enthalpies. For hydride abstraction from isobutane by H^+ in magic acid, the free energy is estimated to be slightly negative. Oxidations of alkanes by SbF_5 without concomitant reduction of H^+ are not possible. The formation of the *tert*-butyl cation from isobutane in magic acid probably occurs by a varying mixture of two reactions, oxidation by H^+ and oxidation by both H^+ and SbF_5.

In 1964 Brouwer and Mackor first reported the formation of stable cations from alkanes.[1] In 1967 Olah and Lukas published the first of a long series of papers dealing with the formation of stable cations from alkanes by methide or hydride abstraction.[2] While neopentane clearly reacts by protonation to give methane (eq 1), the claim that isobutane reacted by



$$\mathrm{H_3C\overset{CH_3}{\underset{CH_3}{C}}CH_3 + H^+ \rightarrow H_3C\overset{CH_3}{\underset{+}{C}}CH_3 + CH_4} \qquad (1)$$



$$\mathrm{H_3C\overset{CH_3}{\underset{H}{C}}CH_3 + H^+ \rightarrow H_3C\overset{CH_3}{\underset{+}{C}}CH_3 + H_2} \qquad (2)$$

protonation followed by loss of hydrogen (eq 2) was clouded by the observation that the necessary quantity of H_2 was not observed.[3] To explain this, it was suggested that the H_2 reduced one of the components of the acid solution, either FSO_3H or SbF_5.[3] Since that time, four different research groups have contacted H_2 and solutions of SbF_5 in HF or FSO_3H and none have observed any reaction.[4-7] However, the reaction between neat SbF_5 and H_2 (50 atm at room temperature) goes completely to HF and SbF_3.[7] Olah suggests that the reaction is slowed by coordination of SbF_5 in the various solvents.[7] He also suggested that the reduction occurs in systems containing alkanes because "nascent" hydrogen, i.e., the hydrogen emerging from the pronated alkane, is particularly active and capable of reducing SbF_5.[7]

In some systems it has been demonstrated that cations can be formed by oxidation of hydrocarbons by FSO_3H or SO_3 formed from FSO_3H.[6,8] In one of these cases,[6] only easily oxidizable hydrocarbons giving very stable carbenium ions were studied, and their observations may not be relevant to alkanes. However, Bobilliart and co-workers[8] have claimed oxidation of *n*-alkanes by SO_3 in fluorosulfonic acid. Much earlier it was established that hydrogen exchange between alkanes and sulfuric acid occurred by an ionic chain mechanism, the first step of which was oxidation of hydrocarbon to give a carbenium ion and SO_2.[9] Lukas has reported the formation of cations from hydrocarbons in SbF_5 in the absence of FSO_3H (eq 3):[10]

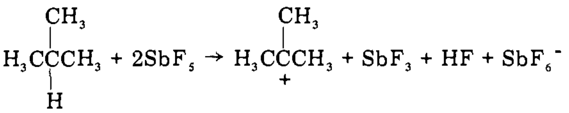
$$2RH + 3SbF_5 \rightarrow 2R^+ + H_2 + SbF_3 + 2SbF_6^- \qquad (3)$$

Olah has criticized Lukas' work pointing out that his observations might be due to hydride abstraction by protons present if the system were not kept completely anhydrous.[7]

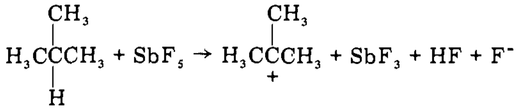
We felt the application of classical thermodynamics to these reactions would yield insight, in the form of establishing which reactions were thermodynamically possible and to identify the driving force for these reactions. Accordingly, we have calculated as best we could the enthalpies of all of the reactions described above. To do this we have had to make a number of approximations and assumptions, some of which are open to just criticism. These calculations are approximate. Our claim is only that *strongly* endothermic reactions will not take place, and strongly exothermic reactions may take place, if the kinetics permit. Fortunately, the results are such that some reactions are obviously impossible, and no conceivable error in our assumptions could make them plausible. It also proved possible to check the most questionable of our assumptions using reliable data.

Oxidation by Antimony Pentafluoride

Equation 4 is best handled as the sum of two reactions, 5 and 6.



$$\mathrm{H_3C\overset{CH_3}{\underset{H}{C}}CH_3 + 2SbF_5 \rightarrow H_3C\overset{CH_3}{\underset{+}{C}}CH_3 + SbF_3 + HF + SbF_6^-} \qquad (4)$$



$$\mathrm{H_3C\overset{CH_3}{\underset{H}{C}}CH_3 + SbF_5 \rightarrow H_3C\overset{CH_3}{\underset{+}{C}}CH_3 + SbF_3 + HF + F^-} \qquad (5)$$

−37 −330 +124 −219 −72 −80

For this reaction, liquid SbF_5 is the solvent. The number under each molecule or ion is its heat of formation in kilocalories/mole. The heat of formation of liquid isobutane from Stull, Westrum, and Sinke[11] is used, assuming that the heat of solution of isobutane in antimony pentafluoride is 0, an assumption which will not be in error by more than 1 or 2 kcal/mol. The heat of formation of liquid SbF_5 is that reported by

Richards and Woolf.[12] The values for liquid HF and crystalline SbF_3 were taken from NBS Technical Note 270-3.[13] Unless noted otherwise, all heats of formation for inorganic compounds were taken from this reference. Heats of solution of HF and SbF_3 in antimony pentafluoride are not available. The heat of solution of SbF_3 in water is 1 kcal/mol, and is not expected to be large in liquid SbF_5. Assuming heats of solution of 0 for HF and SbF_3 in liquid SbF_5 is certainly incorrect, but any error introduced will be only a few kilocalories/mole.

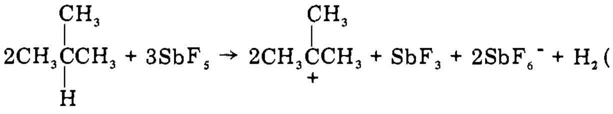
The heat of formation of F^- is another matter. The value for aqueous F^- was used.[13] This will certainly be erroneous since F^- will be very strongly solvated in water. Note that complex formation with SbF_5 has not yet occurred; we are comparing uncomplexed F^- in liquid SbF_5 with solvated F^- in water. The error introduced by ignoring this heat of transfer will be in an exothermic direction, i.e. our assumption is such that the calculated enthalpy for the reaction will be too exothermic by an amount equal to the heat of transfer of F^- from water to SbF_5.

The heat of formation for the trimethyl carbenium ion (gas phase) was taken from the tabulation of Franklin et al.[14] The problem is to estimate its heat of solvation by SbF_5. This can be done using the Born equation or estimates of its solvation by water can be used. The assumptions made are discussed in detail in the section on hydride abstraction by H^+. Suffice it to say that a reliable value for the heat of hydration of the *tert*-butyl cation was used and its heat of transfer from water to liquid SbF_5 was assumed to be 0. This will again introduce an error in the exothermic direction. These data give the heat of reaction for eq 5 as +120 kcal/mol. It is inconceivable that the assumptions made could be in sufficient error to make this reaction exothermic.

$$KF + SbF_5 \rightarrow KSbF_6 \qquad \Delta H = -26 \text{ kcal/mol} \quad (6)$$

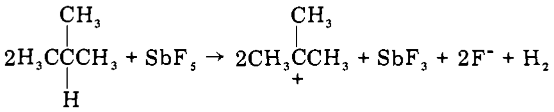
The heats of reaction between NaF and KF and SbF_5 in the solvent BrF_3 to give Na^+ or $K^+SbF_6^-$ have been measured.[12] Summing eq 5 and 6 gives for eq 4 a heat of reaction of 94 kcal/mol. Obviously, this reaction cannot occur.

Equation 7 has been proposed by Lukas for this oxidation:[10]



$$2CH_3\overset{CH_3}{\underset{H}{C}}CH_3 + 3SbF_5 \rightarrow 2CH_3\overset{CH_3}{\underset{+}{C}}CH_3 + SbF_3 + 2SbF_6^- + H_2 \quad (7)$$

The reaction is treated, as before, by summing eq 6 and 8:



$$\begin{array}{cccccccc} 2H_3C\overset{CH_3}{\underset{H}{C}}CH_3 & + SbF_5 & \rightarrow & 2CH_3\overset{CH_3}{\underset{+}{C}}CH_3 & + SbF_3 & + 2F^- & + H_2 & (8) \\ -37 & -330 & & +124 & -219 & -80 & 0 & \end{array}$$

For eq 8, all values were as before. For reaction 7, ΔH_{RX} = +221 kcal/mol is estimated. The reaction is strongly endothermic and will not occur.

Reduction of SbF_5 and FSO_3H by H_2

$$\begin{array}{cccc} SbF_5(l) + & H_2 \rightarrow & SbF_3 + & 2HF(l) \\ -300 & 0 & -219 & -72 \end{array} \; \Delta H_R = -33 \text{ kcal/mol} \quad (9)$$

Using both SbF_5 and HF as liquids and ignoring the heat of solution of HF in liquid SbF_5, the reaction is nicely exothermic and may occur, consistent with its observation by Olah.[7]

$$2HSO_3F(l) + H_2 \rightarrow SO_2(l) + H_3O^+ + HF(l) + SO_3F^- \quad (10)$$

Reaction 10 can best be treated as the sum of reactions 11 and 12. The heat of reaction 11 was measured by solution calorimetry. It is the heat of solution of liquid water in liquid HSO_3F. The reduction of fluorosulfonic acid by hydrogen (eq 10) is exothermic by 49 kcal/mol. Here FSO_3H is taken as the solvent, and we assume the heat of solution of SO_2 in it is 0 kcal/mol. The heat of solution of HF in FSO_3H is +1.3 kcal/mol.[15]

$$H_2O(l) + HSO_3F(l) \rightarrow H_3O^+ + SO_3F^- \qquad \Delta H_R = -19 \text{ kcal/mol} \quad (11)$$

$$\begin{array}{ccccc} HSO_3F(l) + & H_2 \rightarrow & SO_2(l) + & H_2O(l) + & HF \\ -186 & 0 & -77 & -68 & -71 \end{array} \quad (12)$$

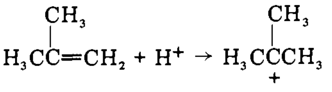
It is important that these processes are exothermic. With one exception they have not been observed by the four groups who have tried the reaction. This must be due to kinetic factors, and if catalyzed the reaction would take place.

Hydride Abstraction by H^+

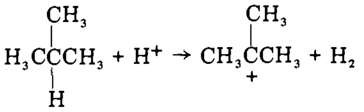
We now turn our attention to the formation of the *tert*-butyl cation by hydride abstraction from isobutane by H^+ in magic acid. The enthalpy of this reaction has been calculated by two independent techniques which show reasonable agreement with each other. The first of these is the more reliable since it requires only modest assumptions. The second technique requires assumptions about the enthalpy of the proton in magic acid and estimates of heats of transfer of carbenium ions. It is fortunate that there are several ways of checking the second set of calculations, all of which indicate their approximate validity.

The first calculation is independent of all acidity function assumptions and solvation assumptions which must be used in the second calculations. It does require the assumption that the heats of protonation of methylcyclopentene and isobutene to give the respective tertiary cations in magic acid are identical. The heat of protonation of methylcyclopentene in 11.5 mol % SbF_5/FSO_3H at −60.5 °C is −18.5 ± 0.5 kcal/mol.[16] The difference between eq 13 and 14 is the difference between the heats of formation of isobutane and isobutene and the heat of solution of H_2 in magic acid. We assume the latter is 0 and that the heats of solution of isobutane and isobutene in magic acid are identical. The difference between the heats of formation of isobutane and isobutene is 28 kcal/mol. Using this value, ΔH for reaction 14 is +10 kcal/mol. It is quite clear that this reaction is not exothermic.[17]

However, it should not be concluded from this that the reaction is unfavorable. In fact, ΔG for this reaction can be estimated and it is slightly favorable. The equilibrium constant for eq 13 has been estimated to be $10^{15.8}$ in HF–SbF_5 by Hogeveen and Bickel.[18a] Assuming an identical K in HSO_3F/SbF_5 gives for reaction 13 ΔS = +13 eu. This assumption may be poor, but we know too little about the relative behavior of cations in HF and FSO_3H to do otherwise. The relative entropies of reactions 13 and 14 are readily available since all of the difficult species, i.e., H^+ and the *tert*-butyl cation, cancel. Taking H_2 in a standard state of 1 atm pressure at 300 K, reaction 14 has an entropy 31 eu more favorable than reaction 13. This value of 44 eu compares favorably with $\Delta S^{\ddagger}$ for proton exchange between isobutane and strong acids. Values of −35 and −43 eu were obtained for HSO_3F and CF_3SO_3H, respectively.[18b] Combining this with the calculated ΔH leads to a free energy for reaction 14 of −3.2 kcal/mol at 300 K. The



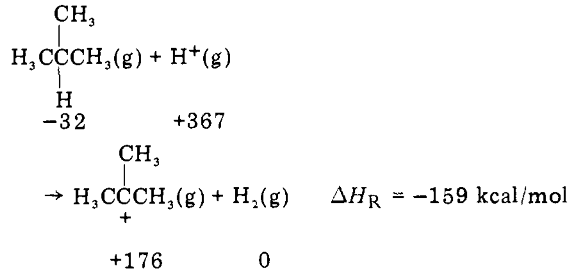
$$H_3C\overset{CH_3}{C}{=}CH_2 + H^+ \rightarrow H_3C\overset{CH_3}{\underset{+}{C}}CH_3 \qquad \Delta H = -18 \text{ kcal/mol} \quad (13)$$



$$H_3C\overset{CH_3}{\underset{H}{C}}CH_3 + H^+ \rightarrow CH_3\overset{CH_3}{\underset{+}{C}}CH_3 + H_2 \quad (14)$$

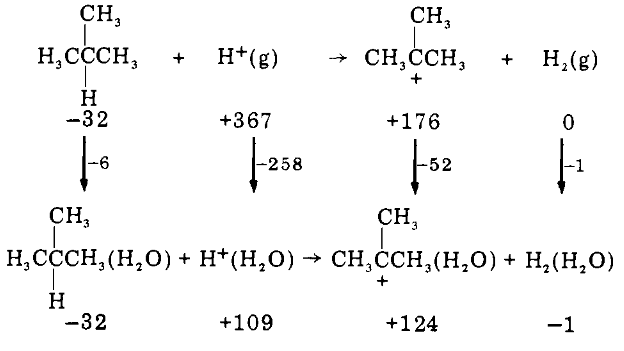
reaction should occur and should become more favorable at higher temperatures. There is obviously some uncertainty in the value of this calculated ΔG, uncertainty rising from the assumption of a solvent-independent ΔG for reaction 13; all other data are quite reliable. Perhaps the fairest statement is that the reaction is probably favorable at 300 K and certainly has a ΔG which will permit study at temperatures not too far from 300 K. This reaction in HF has been studied in detail by the Dutch group.[19]

The second calculation of the enthalpy of hydride abstraction from isobutane by H^+ requires knowledge of the enthalpy of the proton (however it may be solvated) in magic acid. This is not measurable directly and must be estimated. We have done this by considering the hydride abstraction from isobutane in the gas phase, for which there is good data, then in water, which can be done reliably, then transferring it from water to acids using acidity functions to estimate the heat of transfer of the proton. Fortunately our assumptions can be checked. Note that some of the assumptions made are used elsewhere in this paper and that this calculation provides an estimate of the single ion heat of formation of the *tert*-butyl cation in magic acid.



$$\underset{-32}{H_3C\overset{CH_3}{\underset{H}{C}}CH_3(g)} + \underset{+367}{H^+(g)} \rightarrow \underset{+176}{H_3C\overset{CH_3}{\underset{+}{C}}CH_3(g)} + \underset{0}{H_2(g)} \qquad \Delta H_R = -159 \text{ kcal/mol} \quad (15)$$

All values used in eq 15 are from Field and Franklin.[14] This reaction can be calculated quite reliably and is exothermic, due to the very large heat of formation of the proton in the gas phase. In eq 16, this reaction is transferred to water:

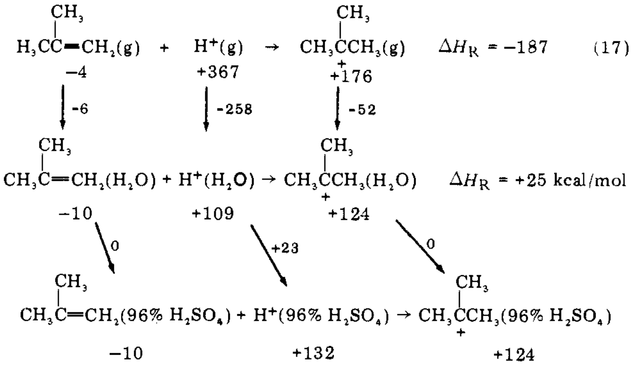


$$\begin{array}{ccccccc} H_3C\overset{CH_3}{\underset{H}{C}}CH_3 & + & H^+(g) & \rightarrow & CH_3\overset{CH_3}{\underset{+}{C}}CH_3 & + & H_2(g) \\ -32 & & +367 & & +176 & & 0 \\ \downarrow -6 & & \downarrow -258 & & \downarrow -52 & & \downarrow -1 \\ H_3C\overset{CH_3}{\underset{H}{C}}CH_3(H_2O) & + & H^+(H_2O) & \rightarrow & CH_3\overset{CH_3}{\underset{+}{C}}CH_3(H_2O) & + & H_2(H_2O) \\ -32 & & +109 & & +124 & & -1 \end{array}$$

$$\Delta H_R = +52 \text{ kcal/mol} \quad (16)$$

All assumptions made here were chosen to give the largest possible exothermic value for the reaction in water. The heat of hydration for isobutane has not been measured; the value for *n*-butane was used and should not be in error.[20] The value for the heat of hydration of the proton has been measured many times; the recent value of Lister et al. was used.[21] The heat of hydration of the *tert*-butyl cation has been estimated by Gold.[22] The most exothermic of a range of values was selected and is quite reasonable. It has been confirmed by Taft,[23] who has also shown that the relative stabilities of a series of charge-delocalized cations are the same in water and in the gas phase.[23] The heat of solution of hydrogen is known and we used the very reliable data of Wauchope and Haque.[20] As expected, the reaction is quite endothermic, due to the large heat of hydration of the proton.

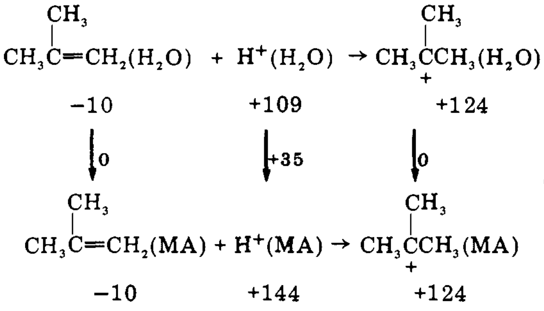
A number of assumptions must be made in transforming this reaction to superacid. To check these assumptions, we first calculate the thermodynamics of a reaction whose behavior is known, the protonation of isobutene.



$$\begin{array}{ccccccl} H_3C\overset{CH_3}{C}{=}CH_2(g) & + & H^+(g) & \rightarrow & CH_3\overset{CH_3}{\underset{+}{C}}CH_3(g) & & \Delta H_R = -187 \quad (17) \\ -4 & & +367 & & +176 & & \\ \downarrow -6 & & \downarrow -258 & & \downarrow -52 & & \\ CH_3\overset{CH_3}{C}{=}CH_2(H_2O) & + & H^+(H_2O) & \rightarrow & CH_3\overset{CH_3}{\underset{+}{C}}CH_3(H_2O) & & \Delta H_R = +25 \text{ kcal/mol} \\ -10 & & +109 & & +124 & & \\ \searrow 0 & & \searrow +23 & & \searrow 0 & & \\ CH_3\overset{CH_3}{C}{=}CH_2(96\%\ H_2SO_4) & + & H^+(96\%\ H_2SO_4) & \rightarrow & CH_3\overset{CH_3}{\underset{+}{C}}CH_3(96\%\ H_2SO_4) & & \\ -10 & & +132 & & +124 & & \end{array}$$

Since Deno has estimated K for the above reaction to be $10^{-3.5}$ in 96% H_2SO_4, we carried out calculations for this solvent.[24] The transfer from gas to water was calculated as before. The estimate of 0 kcal/mol for the heat of transfer of isobutene from water to sulfuric acid is probably correct within 1 kcal or so. The estimate of 0 kcal/mol for transfer of the *tert*-butyl cation is more controversial. With similar dielectric constants, nonspecific Born solvation will be similar in the two solvents. With the higher cohesive energy density of H_2O, the cavity term for the transfer from water to H_2SO_4 will be exothermic. Water, being more basic, should be a better specific solvent for the cation. It seems that the transfer from water to sulfuric acid would probably be endothermic. Arnett has shown that the transfer of a number of bisulfate ammonium salts from water to concentrated sulfuric acid is *slightly* (0-5 kcal/mol) exothermic.[25] Taft's data[23] indicate the relative stability of some cations in water and the gas phase is the same, but extension of his data to the highly charge localized *tert*-butyl cation is questionable. We have assumed it to be 0. We used the following procedure to estimate ΔH_t for the proton. First, we assumed that the H_0 acidity function paralleled a_{H^+} and, for comparative purposes, could be used to estimate a_{H^+}. Yates has published evidence for such a parallel.[26] Arnett's observations on the heat of transfer of cations and H_2SO_4 across the H_2SO_4–H_2O solvent system are also consistent with the notion that the acidity increase is associated *principally* with the behavior of the proton, and the solvation of the cation plays a secondary role. Also, he has demonstrated a linear relationship between heats of protonation and H_0 values.[25,27] Since the H_0 value for 96% H_2SO_4 is -9.98, transfer from water involves a change of -17 units. Using $\Delta G = -RT \ln a_{H^+}$, we calculate $\Delta G_T = -23$ kcal/mol. Now we assume that $\Delta G \simeq \Delta H$; since H^+ is much more highly solvated in H_2O, and the $H_9O_4^+$ unit is highly structured and ties up four molecules of water, the entropy of transfer is expected to be unfavorable (negative). An assumption of 0 will mean the value calculated for the heat of reaction is too endothermic. Obviously, these calculations are not expected to be highly accurate; however, they should be good to 4 or 5 kcal/mol. The agreement with Deno's data is acceptable. He calculates ΔG in 96% H_2SO_4 to be +5 kcal/mol and we estimate ΔH to be +2 kcal/mol.

Having obtained reasonable results for sulfuric acid, the calculations are extended to magic acid. A value for this equilibrium constant (isobutene protonation) in HF–SbF_5 is available, but since no acidity function for this medium has been developed, we cannot estimate it. However, we do have available heats of protonation of olefins in magic acid, so that we can compare our calculated values with reliable experimental data. Using Gillespie's H_0 values for $HFSO_3$–SbF_5, we calculate the heat of reaction for SbF_5 concentrations greater than 8 mol % as follows where MA indicates magic acid



$$\begin{array}{ccccc}
\mathrm{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2(H_2O)} & + & \mathrm{H^+(H_2O)} & \rightarrow & \mathrm{CH_3\underset{+}{\overset{\displaystyle CH_3}{\overset{|}{C}}}CH_3(H_2O)} \\
-10 & & +109 & & +124 \\
\big\downarrow 0 & & \big\downarrow +35 & & \big\downarrow 0 \\
\mathrm{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2(MA)} & + & \mathrm{H^+(MA)} & \rightarrow & \mathrm{CH_3\underset{+}{\overset{\displaystyle CH_3}{\overset{|}{C}}}CH_3(MA)} \\
-10 & & +144 & & +124
\end{array} \qquad (18)$$

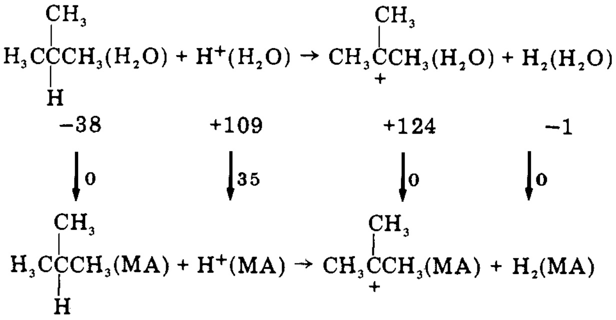
$\Delta H_R = -10$ kcal/mol

(eq 18). This is quite similar to the reaction under consideration and involves the estimation of ΔH for the solvated proton, which is the dominant factor.

The reaction is calculated to be exothermic and does indeed go readily in this solvent. The actual heat of protonation of liquid alkenes to give tertiary cations is -18.5 ± 0.5 kcal/mol[16] for methylcyclopentane in 11 mol % SbF_3 in FSO_3H at -60.5 °C. Its formation from cyclohexene in the same system is $\Delta H = -17.0 \pm 0.8$ kcal/mol.[16] Considering the approximate nature of the calculations, the agreement between these similar processes is satisfactory.

This calculation required many highly questionable assumptions. The calculated results are not too far from experiment and this is encouraging. However we may have made a series of compensating errors. It is worth asking why bother with this tortuous route when the same results have already been produced by a much more reliable method. One reason is that this method does produce an estimate of the single ion heat of formation of the *tert*-butyl cation in a convenient solvent.[28] We do not feel the value we have calculated is sufficiently reliable to use widely. However, a reliable single ion heat or free energy for a carbenium in a convenient solvent would be an extraordinarily useful number, allowing us to systematize a great deal of solution thermodynamics of carbenium ions and to make a variety of valuable calculations. It would seem to be worthwhile to improve on this first crude attempt.

The last step is to calculate ΔH for hydride abstraction from isobutane by a proton in magic acid (eq 18a). Note that the



$$\begin{array}{ccccccc}
\mathrm{H_3C\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}}CH_3(H_2O)} & + & \mathrm{H^+(H_2O)} & \rightarrow & \mathrm{CH_3\underset{+}{\overset{\displaystyle CH_3}{\overset{|}{C}}}CH_3(H_2O)} & + & \mathrm{H_2(H_2O)} \\
-38 & & +109 & & +124 & & -1 \\
\big\downarrow 0 & & \big\downarrow 35 & & \big\downarrow 0 & & \big\downarrow 0 \\
\mathrm{H_3C\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}}CH_3(MA)} & + & \mathrm{H^+(MA)} & \rightarrow & \mathrm{CH_3\underset{+}{\overset{\displaystyle CH_3}{\overset{|}{C}}}CH_3(MA)} & + & \mathrm{H_2(MA)}
\end{array}$$

$\Delta H_R = +17$ kcal/mol (18a)

reaction is changed from the previous one only by the substitution of isobutene for isobutane and the inclusion of H_2. The effect of these changes on the accuracy of the calculations is small. Thus, the reasonable agreement demonstrated for isobutene formation should also be observed here. The reaction is endothermic by 17 kcal/mol, smaller than the values calculated for oxidation by SbF_5 and FSO_3H, but large enough to be outside the error of these calculations.

Hydride abstraction by HSO_3F can be calculated as shown in eq 19 where R = *tert*-butyl. Equation 19 is the sum of eq 20, 21, and 22. For lack of anything better, the value for aqueous F^- was used. All other enthalpies are as before. The reaction is irredeemably endothermic even when all aids such as providing SbF_5 to complex with F^- are provided. The data for reaction 22 were measured by Richards and Woolf.[12]

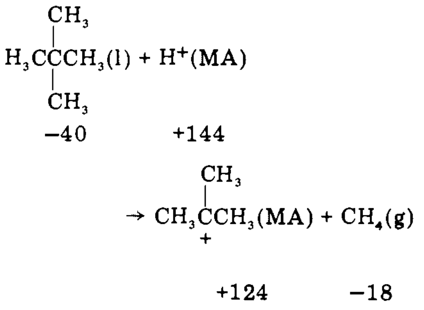
$$\mathrm{RH} + 2\mathrm{HSO_3F} + \mathrm{SbF_5} \rightarrow \mathrm{R^+} + \mathrm{H_3O^+} + \mathrm{SO_2} + \mathrm{SbF_6^-} \qquad \Delta H_R = +79 \text{ kcal/mol} \quad (19)$$

$$\begin{array}{ccccccccccc}
\mathrm{RH} & + & \mathrm{HSO_3F} & \rightarrow & \mathrm{R^+} & + & \mathrm{H_2O} & + & \mathrm{SO_2} & + & \mathrm{F^-} \\
-37 & & -186 & & +126 & & -68 & & -77 & & -80
\end{array}$$

$$\Delta H_R = +124 \text{ kcal/mol} \quad (20)$$

$$\mathrm{H_2O} + \mathrm{HSO_3F} \rightarrow \mathrm{H_3O^+} + \mathrm{SO_3F^-} \qquad \Delta H_R = -19 \text{ kcal/mol} \quad (21)$$

$$\mathrm{F^-} + \mathrm{SbF_5} \rightarrow \mathrm{SbF_6^-} \qquad \Delta H_R = -26 \text{ kcal/mol} \quad (22)$$



$$\begin{array}{ccccccc}
\mathrm{H_3C\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}CH_3(l)} & + & \mathrm{H^+(MA)} & \rightarrow & \mathrm{CH_3\underset{+}{\overset{\displaystyle CH_3}{\overset{|}{C}}}CH_3(MA)} & + & \mathrm{CH_4(g)} \\
-40 & & +144 & & +124 & & -18
\end{array} \qquad \Delta H_R = +2 \quad (23)$$

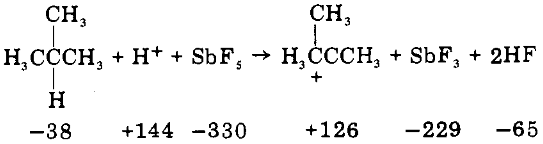
Methide Abstraction from Neopentane

The reaction is calculated to be endothermic by 2 kcal/mol. Certainly the reaction is indicated to be quite possible, particularly considering the approximate nature of these calculations. A calculation based on the second technique (independent of acidity functions) gives a value of -6 kcal/mol. The additional driving force due to the formation of CH_4 rather than H_2 is enough to shift the thermodynamics.

The equilibrium constant for reaction 23 in HF-SbF_5 has been calculated by Hogeveen and Bickel[29] and is about $10.^{10}$ Assuming a similar value in FSO_3H-SbF_5, the calculated entropy change for this reaction is +53 eu. Not surprisingly, this is quite similar to the +44 eu calculated for eq 14, hydride abstraction from isobutane.

Discussion

These thermodynamic data allow a number of insights into the mechanism of carbenium ion formation from alkanes in superacids. First, the formation of H_2 can be explained by the occurrence of reaction 14. But since fairly small amounts of hydrogen are formed, at least one other reaction must be occurring. One candidate for this reaction which has a favorable enthalpy is eq 24.



$$\begin{array}{ccccccccccc}
\mathrm{H_3C\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}}CH_3} & + & \mathrm{H^+} & + & \mathrm{SbF_5} & \rightarrow & \mathrm{H_3\underset{+}{\overset{\displaystyle CH_3}{\overset{|}{C}}}CCH_3} & + & \mathrm{SbF_3} & + & \mathrm{2HF} \\
-38 & & +144 & & -330 & & +126 & & -229 & & -65
\end{array} \qquad (24)$$

Equation 24 is a reaction in which the H_2 which otherwise would be produced is oxidized by SbF_5 to give SbF_3 and HF. The reaction is exothermic by ca. 9 kcal/mol. Unfortunately, the necessary entropy data for SbF_5 and SbF_3 are not available, so ΔG cannot be calculated. It would be surprising if ΔG is not favorable.

The thermodynamic data say nothing about the mechanism of reaction 24. Since H_2 and SbF_5 do not react directly, there are two obvious possibilities:

$$\begin{array}{c}
\mathrm{RH} + \mathrm{H^+} \rightleftarrows \mathrm{RH_2^+} \\
\mathrm{RH_2^+} + \mathrm{SbF_5} \rightarrow \mathrm{R^+} + \mathrm{SbF_3} + \mathrm{2HF}
\end{array} \qquad (25)$$

$$\begin{aligned} RH + SbF_5 &\rightleftarrows RHSbF_5 \\ RHSbF_5 + H^+ &\rightarrow R^+ + SbF_3 + 2HF \end{aligned} \tag{26}$$

The first process is that proposed by Olah. Lukas' data tend to support the second of the two possibilities.[10] We do not wish to enter this controversy except to point out that the reaction is sufficiently complex so that it occurs in several steps; we feel more than two. A thorough kinetic analysis would be quite desirable and probably necessary to pin down the mechanism.

It is obvious that there exists a very rich and complicated chemistry of alkane oxidation in superacids. Thermodynamic calculations such as these represent only the first step in unraveling the reactions involved. A thorough kinetic study is needed. Extension of these calculations to other systems including the interesting TaF_5 system used by Siskin[30] is underway.[31]

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Free-Radical Chemistry of Organophosphorus Compounds. 8.[1] Free-Radical Arbuzov Reaction Stereochemistries and the Question of Available Permutational Modes for Phosphoranyl Radicals

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Abstract: The stereochemistries of the reactions of Ph· and Me_2N· with cis/trans isomeric five- and six-membered ring phosphites have been determined. The reactions are nearly stereospecific with cis phosphite yielding trans phenylphosphonate and phosphoramidate. Reactions with the trans phosphites give the corresponding cis products. Toward Me_2N· the two isomers of the six-membered ring phosphite show a six- to eightfold difference in reactivity, the thermodynamically less stable trans isomer being the more reactive. It is argued that for these phosphoranyl radical intermediates permutational isomerization steps of mode I (Berry or turnstile mechanisms, e.g.) are unable to compete with product-forming β-scission. The reaction stereochemistries would allow but do not require mode 4 or mode 5 isomerizations to occur rapidly.

The oxidation and substitution processes which occur when a free radical attacks a trivalent phosphorus compound have been reasonably well explored.[2] Both ESR[3] and chemical studies[1a,4] support the postulation that many of these reactions proceed via an intermediate species, **1**, termed a phosphoranyl radical. Until very recently, however, only scant attention has been given to the question of possible permutational modes by which these trigonal bipyramidal intermediates[3] might undergo isomerizations in which equatorial and apical substituents are interchanged.[1a,3m,n,4a]

Phosphoranyl radicals are superficially analogous to pentacovalent phosphoranes, PZ_5, if one views the odd electron as a phantom ligand. Stereochemical studies have proved to be very powerful tools in the investigation of the formation and

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