

Reversible Protonation of Isobutane in Liquid Superacids in Competition with Protolytic Ionization

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Abstract: The deuterium distribution observed in isobutane recovered after short contact times with the DF–SbF₅ superacid at 0 °C shows that a very fast reversible protonation of all C–H bonds occurs before ionization of the alkane, in accord with the Olah σ -basicity concept. Comparison of the amounts of hydrogen with the amount of *tert*-butyl ions generated during ionization shows that the reaction is purely protolytic in HF containing up to 20 mol % SbF₅, but becomes oxidative at higher concentrations.

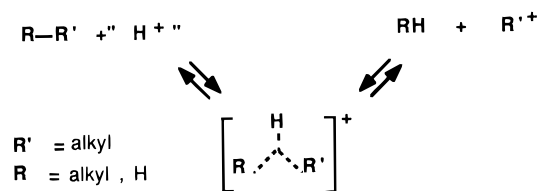
Introduction

Acid-catalyzed hydrocarbon transformations, such as catalytic cracking, isomerization, and alkylation, are large-scale industrial processes using solid or liquid strong acids, such as H-zeolites, chlorinated aluminas, sulfuric acid, and hydrogen fluoride.¹ The high acidity of the catalysts and high temperature compensate for the well-known inertness of the starting material. It is widely accepted that the reactions proceed via a classical carbenium ion mechanism.² The initial step is, however, often ascribed³ to proton attack on a C–C or a C–H bond, following the concept of σ -basicity developed by Olah and his group in the framework of extensive investigations of electrophilic reactions of single bonds in superacid media⁴ (Scheme 1).

Protonated alkanes or carbonium ions are characterized by a three-center, two-electron bonded structure having pentacoordinated carbon atoms.⁵ While these species have a lifetime too short to allow direct observation in superacid media by NMR, hydrogen exchange, and cleavage reactions have been described.⁶ Small alkonium ions, such as CH₅⁺ and C₂H₇⁺, have been detected first in high-pressure mass spectrometry experiments⁷ and later studied on a quantitative basis.⁸ In 1989, Lee and co-workers reported the IR spectrum of C₂H₇⁺, indicating the presence of two isomeric ions (C–H or C–C protonated form).⁹

The structures of CH₅⁺ and C₂H₇⁺ have been investigated by increasingly refined ab initio computational methods,¹⁰ and even di- and triprotonated methanes (CH₆²⁺ and CH₇³⁺) have been described as minima on their potential energy surface.^{10b,c} Following the proposition made by Haag^{3c} a decade ago that

Scheme 1. The Concept of σ -Basicity of Alkanes



cracking of hexanes on zeolites at high temperature occurs via carbonium ion intermediates, semiempirical and ab initio computations on protonated alkanes in small zeolite clusters have developed.¹¹ In the frame of our interest in selective electrophilic alkane activation,¹² we now report our results on the reversible protonation reaction that occurs in competition with ionization of isobutane in liquid superacid media.

Experimental Section

Experimental Procedure. The alkane/CO (1:3 molar ratio) mixture was bubbled through 1 mL of HF(DF)–SbF₅ superacid at 0 °C at a rate of 4 mL/min. The experiments were generally stopped after 30 min. by freezing the reaction mixture at –78 °C. At the outlet of the Kel-F reactor, the alkane was condensed continuously during the first 30 min directly in an NMR tube at –78 °C.

The superacid reaction mixture containing the acyl ions was neutralized by mixing with excess ethanol bicarbonate mixture at –78 °C. The ethanol solution of the resulting esters was used for GC analysis.

NMR Measurements. ¹H and ²H NMR spectra were recorded on a Bruker AM 400 (400 MHz) spectrometer. To the condensed alkane, a standard mixture of CDCl₃/CHCl₃ (1:4 molar ratio) was added. The sample volume was then adjusted by addition of freon-11 (CFCl₃ trichlorofluoromethane). NMR spectra of H(D)F–SbF₅ solutions were taken in quartz tubes at temperatures below ~–10 °C after addition of a standard mixture of acetone/acetone-d₆.

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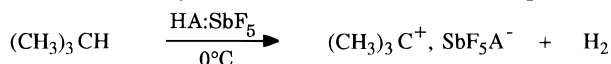
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Table 1. Product Distribution Obtained from Isobutane^a

expt	acids (mmol)		gas mixture (mmol) before reaction		products after reaction (mmol)						
	HF	SbF ₅	iC ₄ H ₁₀	CO	H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	Epiv	EiB	iC ₄ H ₁₀ *
1	28.5	7.7	2.63	7.27	0.77	0.05	0.001	0.03	0.78	tr.	1.64
2	28.8	7.8	2.84	7.23	0.86	0.05	0.001	0.03	0.62	tr.	1.96
3	30.9	8.4	2.65	6.80	0.80	0.05	0.002	0.03	0.85	tr.	1.76
4	29.5	8.0	2.83	7.29	0.87	0.05	0.002	0.03	0.74	tr.	1.74
5	37.4	9.3	2.71	8.13	0.91	0.05	0.002	0.04	0.82	0.008	1.83
6	37.4	9.3	2.63	7.89	0.86	0.05	0.003	0.02	0.76	0.014	1.68

^a After 60 min on stream. ^b Apparently unreacted.

Scheme 2. Protolytic Ionization of Isobutane in Superacids

A: FSO₃; F

Scheme 3. Simultaneous-Occurring Reactions

1. $\text{R H} + \text{"D}^+ \text{"} \rightleftharpoons \text{R D} + \text{"H}^+ \text{"}$
2. $\text{R H} + \text{"H}^+ \text{"} \rightleftharpoons \text{R}^+ + \text{H}_2$
3. $\text{R}-\text{R}' + \text{"H}^+ \text{"} \rightleftharpoons \text{R}^+ + \text{R}'\text{H}$
4. $\text{R H} + \text{R}'^+ \rightleftharpoons \text{R}^+ + \text{R}'\text{H}$
5. $\text{R H} + \text{SbF}_5 \rightleftharpoons \text{R}^+ + \text{"H}^+ \text{"} + 2 \text{F}^- + \text{SbF}_3$

Results and Discussion

I. Ionization of Isobutane in HF–SbF₅ in the Presence of Carbon Monoxide. The high reactivity of isobutane in superacidic media was first reported independently by Olah and Lukas¹³ and by Hogeveen and co-workers¹⁴ (Scheme 2).

The *tert*-butyl ion is remarkably stable and the NMR spectrum of the solution is unchanged even after 1 week at room temperature. Its formation was ascribed to protolytic cleavage of the methine C–H bond via a carbonium ion intermediate. The fact that the yield of hydrogen was not stoichiometric with that of the *tert*-butyl ion was the subject of a two decade long controversy on the ability of SbF₅ to participate in the ionization process by directly oxidizing the alkane. We demonstrated this possibility in 1990, using a proton trap (acetone) as coreactant in the superacid.¹⁵ Taking into account the reactivity of C–C and C–H bonds, the competitive reactions of an alkane in the superacid can be summarized with the following reaction scheme (Scheme 3).

The simultaneously occurring reactions involve the following steps: (1) fast reversible protonation (deuteronation unobserved in the absence of isotopic labeling), (2) protolytic cleavage of a C–H bond yielding a carbenium ion and hydrogen, (3) protolytic cleavage of a C–C bond yielding a reactive carbenium ion and a smaller alkane, (4) hydride transfer reaction between the various carbenium ions and the various alkanes, and (5) oxidation of the alkane by SbF₅.

As each alkane obtained by protolytic cleavage or by hydride transfer can, in turn, undergo protolytic cleavage, etc., it is understandable that all reports in the past described qualitative rather than quantitative studies. Olah and his group in the early 1970s classified the relative reactivity of the σ -bonds in alkanes

as follows:¹⁶ tertiary C–H > C–C > secondary C–H \gg primary C–H.

During our studies on superacid-catalyzed alkane carbonylation related with an alternative synthesis for metacrylic ester from propane,¹⁷ we noticed that the reaction system could be simplified very much by using carbon monoxide as coreactant in the superacid medium. Since the early attempt of Hogeveen¹⁸ to carbonylate methane, reports on direct carbonylation of alkanes in superacid media include reactions of cycloalkanes,¹⁹ C₅–C₈ alkanes,²⁰ and adamantane.²¹ Whereas in the classical Koch–Haaf synthesis²² the intermediate carbocation is obtained by protonation of an alkene, in the superacid it is generated directly from the alkane. Moreover, under these conditions, the unstable carbenium ions generated in the acid are transformed into stable oxocarbenium ions, thereby limiting hydride transfer reactions.²³ These oxocarbenium ions can also be trapped by quenching the superacid in excess ethanol, and since the resulting esters can be analyzed by GC, a quantitative study becomes possible.¹² We show here that a satisfactory balance between the reactant and the products in gas and liquid phase can be obtained, which is helpful to establish the relative importance of the initial competitive reaction pathways.

An isobutane/carbon monoxide mixture (molar ratio 1:3) was bubbled during 1 h at a rate of 220 mL/h through 1.0 mL of HF–SbF₅ solution (molar ratio 4:1) in a Kel-F reactor at –10 °C. The gaseous products as well as the ethyl esters obtained by quenching the oxocarbenium ions in the liquid phase were collected and analyzed by GC. The reactants and product distribution measured in a series of experiments are collected in Table 1, and the various pathways for product formation are presented in Scheme 4.

The product distribution shows that the main pathway for ionization involves protolytic cleavage (path 1) of the tertiary C–H bond, producing the *tert*-butyl ion, which is titrated as ethyl pivalate, and a stoichiometric amount of hydrogen. Some ethyl pivalate is also formed as a byproduct (path 2b) when the carbon–carbon bond is cleaved with formation of methane and propyl cation. The secondary cation, even in the presence of carbon monoxide will, in part, ionize isobutane by hydride transfer as shown by the small amount of propane detected in

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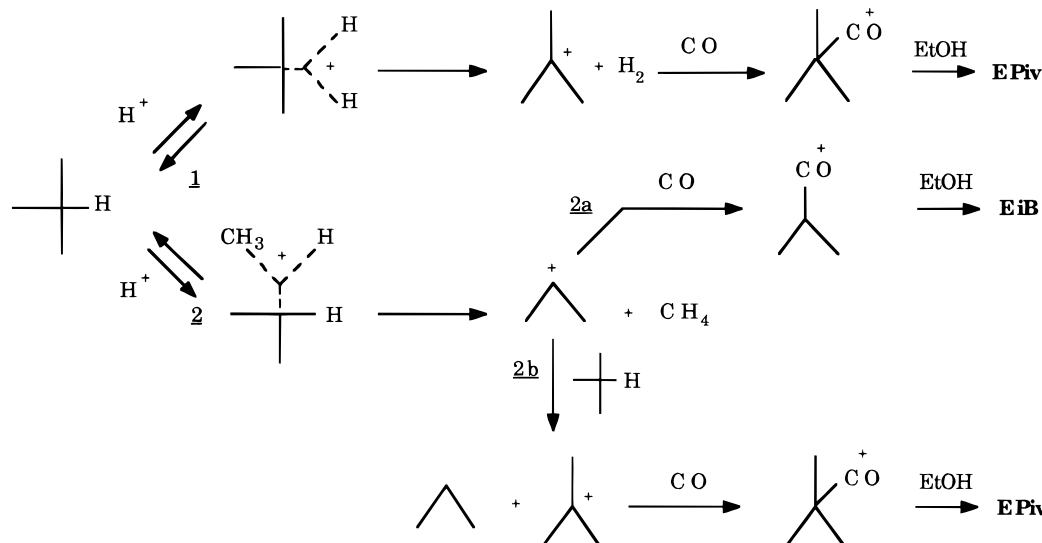
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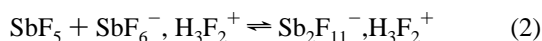
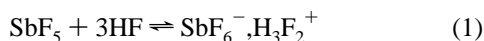
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Scheme 4. Ionization and Carbonylation of Isobutane in Superacids

the gas phase. In accord with a purely protolytic activation of isobutane in this superacid medium, no precipitate of SbF_3 was noticed. As ethyl pivalate (Epiv) can be formed via both pathways 1 and 2b we should find more Epiv than hydrogen. As this is not the case, we assume that this discrepancy arises during the neutralization step of the superacid solution, during which the pivalyl ion loses, in part, CO. The *tert*-butyl ion which is thus formed under non-superacidic conditions eliminates a proton producing small quantities of isobutene which are not recovered under our experimental conditions. On the basis of product distribution, we assign the relative rates of pathways 1 and 2 as being on the order of 18:1. This order confirms all earlier reports on the high reactivity of the tertiary C–H bond. The relative rates of pathways 2a and 2b which are here roughly on the order of 1:5 are very much dependent on the CO/hydrocarbon ratio which controls the competitive hydride transfer or carbonylation of the propyl cation.

II. Change in Activity of the Superacid Depending on the SbF_5 Concentration. For reasons described above, conversion of isobutane in HF will be dependent on the concentration of SbF_5 which not only governs the acidity of the medium but also allows for the stabilization of the resultant cations.

In the concentration range of 10–22 mol % SbF_5 in HF, the anions are essentially SbF_6^- and $\text{Sb}_2\text{F}_{11}^-$ in slow equilibrium.²⁴



During the reaction of isobutane, the superacidic and positively charged species H_3F_2^+ is progressively replaced by the carbenium (or oxocarbenium ion), (HF is generated) and the acidity decreases accordingly (eq 3).



When the average conversion of isobutane (based on the formation of ethyl pivalate during the 1 h experiment), is plotted as a function of the concentration of SbF_5 in HF, a steady and strong increase of conversion is noted when the concentration of the Lewis acid increases (Figure 1, curve a).

When the amount of hydrogen is measured (Figure 1, curve b) it appears that, up to 20–25 mol % SbF_5 in HF, conversion

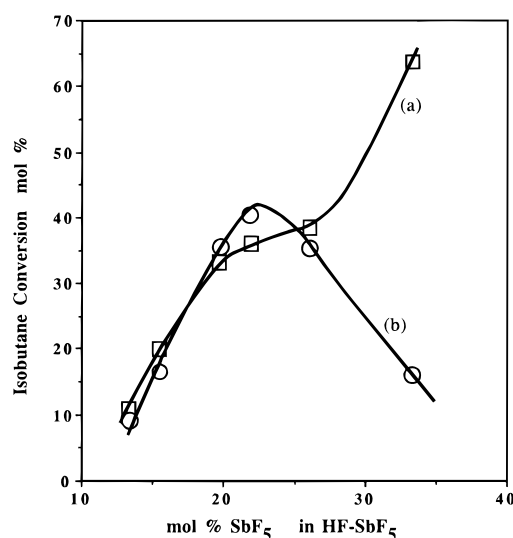
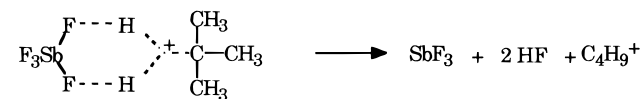


Figure 1. Isobutane conversion based on ethyl pivalate production (a) compared with hydrogen production (b) (60 min time on stream).

Scheme 5. Reduction of SbF_5 by Isobutane

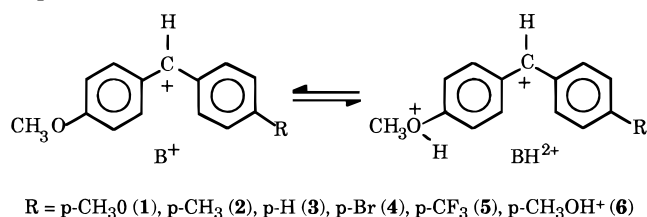
and hydrogen production are roughly parallel, in agreement with the protolytic ionization. For concentrations higher than 25 mol % SbF_5 , however, a change in product distribution is noticed: notably the production of ethyl pivalate increases whereas the hydrogen production decreases drastically. The production of SbF_3 , observable as a white precipitate indicates that SbF_5 is reduced during isobutane conversion with production of HF as earlier suggested by Olah⁴ (Scheme 5).

In order to understand why the change of reactivity of the acid occurred around the concentration of 20–25 mol % SbF_5 , we reconsidered the results on the anionic composition of the HF– SbF_5 system we obtained some years ago by ^{19}F NMR.²⁶ We noticed that, in addition to the SbF_6^- , $\text{Sb}_2\text{F}_{11}^-$, and $\text{Sb}_3\text{F}_{16}^-$ anions, a small but increasing amount of uncomplexed SbF_5 was present for concentrations higher than 18 mol % SbF_5 in

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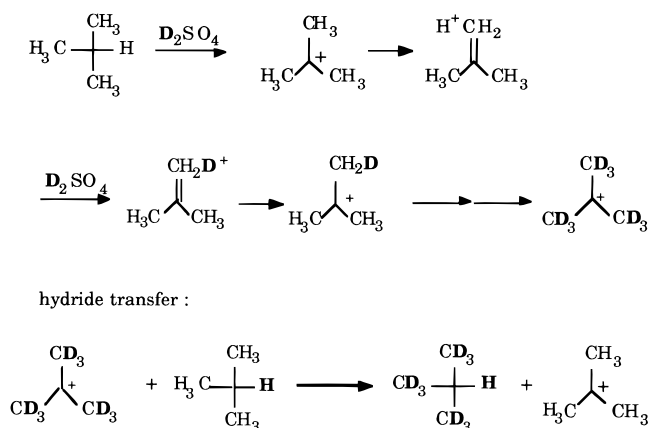
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Scheme 6. Hammett-Type Indicators Used in Strong Superacids

HF. We assume that the change in product distribution is related to the change in composition of the superacid. At the higher SbF₅ concentrations in HF, SbF₅ becomes more available for participation in the activation process. This observation should be considered in relation with the limits of superacidity which we published earlier.²⁷ By measuring the chemical shift variation of a family of very weak bases, such as 4-methoxybenzhydryl ions (1–5) (Scheme 6), we found that the weakest bases 5 and 6 (estimated pK values –22.5 and –23.0, respectively) could not be protonated even in HF–SbF₅ (1:1) whereas indicator 4 (pK = –22) was protonated in HF containing 12% SbF₅. This indicated that the acidity of HF–SbF₅ is close to its limit in the 15–20 mol % SbF₅ range and that increasing the concentration of SbF₅ beyond 20% does not increase the acidity and thus should not result in an increase of the rate of protolysis.

III. Protium/Deuterium Exchange between DF–SbF₅ and Isobutane. Direct hydron exchange, occurring between alkanes and superacids, constitutes the simplest example of electrophilic substitution and was described by Olah in the late 1960s¹³ and also by the group at Shell.¹⁴ Due to the occurrence of side reactions (as described on Scheme 3), only a few quantitative studies have been reported. The rates of dedeuteration of monodeuteromethane and monodeuteroethane (5 and 6.0 L mol^{–1} s^{–1}, respectively) in HF–SbF₅ (11:1 molar ratio) were measured by Hogeveen.²⁸ The relatively small difference in rate between the two compounds was assigned to a small difference in basicity of the primary C–H bonds. The time dependence of dedeuteration of 2-deutero-2-methylpropane at 0 °C in HF containing 4 mol % SbF₅ has been also described by Hogeveen,²⁹ who noticed that the rate of exchange of the tertiary hydrogen of isobutane was less than 10 times faster than that of the primary hydrogens of ethane and also that the exchange was faster than hydride abstraction. Other reports of H/D exchange between alkanes and superacids are of qualitative nature. Olah found that in FSO₃D/SbF₅ or DF/SbF₅ at –78 °C only the methine proton of isobutane was substantially exchanged and, for adamantane, the bridgehead hydrogens exchanged preferentially.¹⁶

These reports, in excellent agreement with formation of carbonium ion intermediates in superacid media contrast markedly with the H/D exchange observed earlier by Stevenson and Otvos,³⁰ who found that, in D₂SO₄, isobutane readily exchanged all nine primary protons for deuterons but not the methine proton. In this case, the exchange could be rationalized by a carbenium ion mechanism, including successive deprotonation and reprotonation followed by a hydride transfer step (Scheme 7).

Scheme 7. H/D Exchange between Branched Alkanes and D₂SO₄

The same regioselectivity in H/D exchange on the positions vicinal to the branching has recently been reported³¹ by us for isoalkanes contacted with D₂O-exchanged solid acids, such as zeolites or sulfated zirconia.

In comparison with other small alkanes, the behavior of isobutane in HF–SbF₅ is rather simple, especially at low SbF₅ concentrations. For this reason, we reinvestigated the H/D exchange process occurring between isobutane and DF–SbF₅ in the presence of carbon monoxide.

When a mixture of isobutane and carbon monoxide (molar ratio RH/CO 1:3) is bubbled through 1 mL of DF–SbF₅ (molar ratio 4:1) during 30 min at a rate of 4 mL/min, the ¹H and ²H NMR spectra of the recovered isobutane show that both the primary and the tertiary hydrogens have been exchanged (7.4 atom % of the hydrogens in the methyl groups and 17.4 atom % of the methine hydrogens were exchanged for deuterons). In another experiment with a slightly smaller space velocity, the recovered isobutane showed 9.1 atom % D of the methyl hydrogens and 24.3 atom % D on the methine. These values, which are average values for 30 min experiments, are in line with the relative σ -basicity of the tertiary and primary C–H bonds.^{3b} It is interesting to note that the difference in exchange rates is rather small, in comparison with the relative energies needed to ionize these two bonds.

Analysis of the DF–SbF₅ solution by ¹H and ²H NMR at –30 °C at the end of the experiment but before neutralization shows the presence of the pivalyl cation in equilibrium with the *tert*-butyl ion formed by slow loss of carbon monoxide. It is interesting to note that both ions show an important H/D exchange at the CH₃ groups (approximately 8 atom %). (The quantitative measurement was made by addition of a standard mixture of acetone-*d*₆ and acetone used as an internal reference in the superacid.)

In order to check whether the deuteriums were incorporated in these ions before ionization, we generated the ions, in a separate experiment, by dissolving their precursors, *tert*-butyl chloride and pivalyl chloride, in DF–SbF₅. Even after 6 h at –10 °C, the observable H/D exchange in both cations was on the order of 1 atom %. This is in good accord with the results published recently by Olah and his group on studies of the protosolvation of alkyl cations showing that H/D exchange can be observed between long-lived ions, such as 2-propyl and *tert*-butyl cation and DF–SbF₅ (1:1),³² but the exchange rate is extremely slow. As deprotonation can be excluded under these conditions, isotopic exchange was explained by protosolvation

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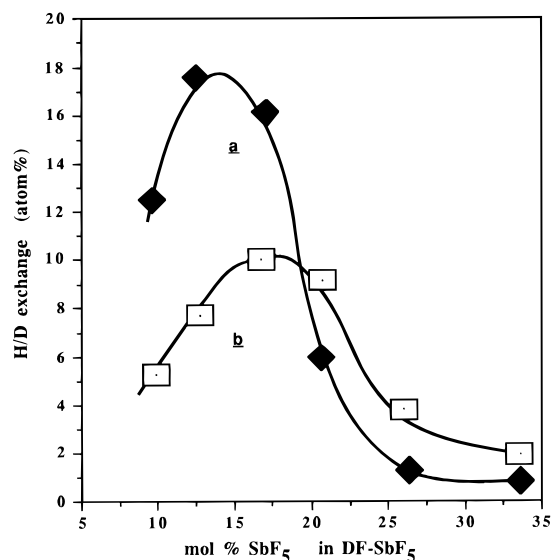
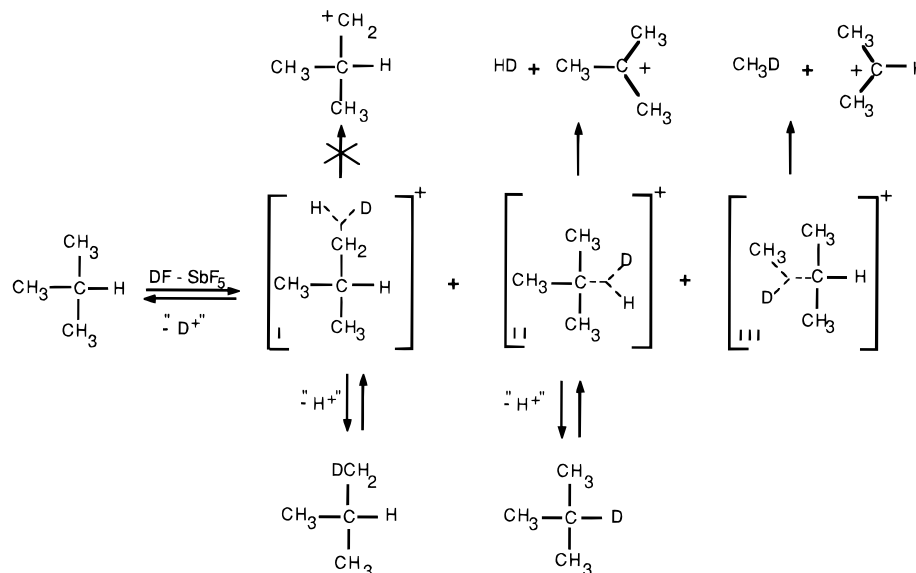
Scheme 8. Ionization versus Exchange

Figure 2. H/D exchange observed on tertiary (a) and primary (b) protons of isobutane versus SbF_5 concentration in HF (30 min on stream).

of the cation (distic cations). Thus, our results demonstrate that, in superacid medium, reversible protonation of the alkane is much faster than the corresponding ionization reaction. Since we know that the ionization rate is steadily increasing with SbF_5 concentration, it was interesting to monitor the influence of acidity on the H/D exchange rates. In a series of experiments in DF containing increasing amounts of SbF_5 , we collected isobutane after 30 min on stream for ^1H and ^2H NMR analysis. Figure 2 illustrates the results of this variation and Table 2 compares the ionization of isobutane with H/D exchange for increasing concentration of SbF_5 in HF.

The competitive protonation and ionization of isobutane in DF-SbF_5 can be described by Scheme 8.

Isobutane is reversibly protonated on the various σ -bonds forming the three isomeric carbonium ions in equilibrium. The relative concentration of these pentavalent reaction intermediates

Table 2. Ionization and H/D Exchange Observed in Isobutane at Various Concentrations of SbF_5 in $\text{HF}^{\text{a,b}}$

expt	SbF_5 (mol % in HF)	exchange on			ionization ^d (mol %)	E/E ^e
		tertiary C-H	primary C-H	total exchange ^c		
1	9.7	12.5 (0.13)	4.8 (0.43)	(0.56)	2.3 (0.02)	28.0
2	12.7	17.5 (0.18)	7.7 (0.69)	(0.87)	3.9 (0.04)	21.7
3	17.0	16.0 (0.16)	10.0 (0.90)	(1.06)	14.7 (0.15)	7.1
4	20.0	9.9 (0.10)	6.5 (0.58)	(0.68)	20.7 (0.21)	3.2
5	26.0	0.8 (0.01)	8.3 (0.75)	(0.76)	29 (0.29)	2.6
6	33.6	0.8 (0.01)	1.8 (0.16)	(0.17)	64 (0.64)	0.3

^a After 30 min of time on stream. ^b All values between brackets are normalized to 1 mol of isobutane. ^c The maximum exchangeable is 10 mol of protons per mole of isobutane. ^d Based on product analysis. ^e Ratio of total H/D exchange versus ionization.

depends only on the relative σ -basicity of the proton-accepting bond and does not reflect the ability of that bond to undergo protolytic cleavage. The fate of the carbonium ions depends on the relative energies required for the available reaction pathways: namely, deprotonation or cleavage to form a trivalent carbenium ion and a neutral species (in this case HD or deuteromethane). For this reason, ion I will only exchange protium for deuterium and ion II will give the stable *tert*-butyl ion in competition with H/D exchange. Unfortunately, reversible protonation of C-C bonds (ion III) cannot be detected by this technique, but in accord with the higher energy needed for the formation of the 2-propylium ion in comparison with the tertiary ion, protolytic cleavage of the C-C bond is a pathway of minor importance as shown by the product distribution.

The relative importance of H/D exchange compared with ionization depends very much on the acid composition.

In Table 2 we have compared the total amount of protons exchanged for deuteriums per mole of isobutane with the amount of isobutane ionized during the same time interval (0–30 min). If we compare the exchange rate of the tertiary C/H with the ionization rate of isobutane, we notice that at the concentration of 9.7 mol % SbF_5 in HF, H/D exchange on this tertiary bond alone is 6 times faster than ionization (0.13 versus 0.02). If, however, we take into account the total amount of protons

(32) (a) Olah, G. A.; Hartz, N.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1993**, *115*, 6985. (b) Olah, G. A.; Hartz, N.; Rasul, G.; Prakash, G. K. S.; Burkhardt, M.; Lammertsma, K. *J. Am. Chem. Soc.* **1994**, *116*, 3187.

(33) Sommer, J.; Bukala, J.; Rouba, S.; Graff, R.; Ahlberg, P. *J. Am. Chem. Soc.* **1992**, *114*, 5884.

exchanged for deuterium per mole of isobutane, we have to take into account the nine primary protons which multiplies by nine the value expressed in atom %. This gives a ratio of 28 for E/I (0.56 versus 0.02) in isobutane at this concentration in SbF_5 .

We would like to stress here that the reversible protonation of the alkane is much faster than apparent from isotope exchange, as the intermediate carbonium ion can also give back a deuteron. The importance of dedeuteration of the carbonium ion in comparison with deprotonation depends on the isotope effect but cannot unfortunately be estimated in these experiments.

The exchange over ionization ratio (E/I) diminishes gradually with increasing concentration of SbF_5 in HF and three areas can roughly be distinguished.

(1) Below 20 mol % SbF_5 , the reversible protonation of the alkane not only on the methine bond but also on the primary C–H bonds is faster than ionization.

(2) From 20 to 25 mol % SbF_5 , based on H_2 production, we notice that protolysis becomes more important than H/D exchange. The amount of deuterium incorporated in isobutane especially on the reactive tertiary C–H bond decreases drastically with increasing concentration of SbF_5 .

(3) At concentrations higher than 25% H/D exchange becomes negligible in comparison with ionization which occurs predominantly with simultaneous reduction of SbF_5 .

Conclusion

The superacid catalyzed H/D exchange of isobutane in DF-SbF_5 takes place via a fast reversible protonation (deuteronation) of the primary and tertiary C–H bonds by the superacid following the σ -basicity concept developed by Olah. At concentrations up to 20 mol % SbF_5 in HF, H/D exchange is much faster than ionization of the isoalkane which occurs essentially via protolytic cleavage of the tertiary C–H bond. The superacidity limit is reached. At higher concentration, the increasing ionization of isobutane is accompanied by simultaneous reduction of SbF_5 at the expense of hydrogen production.

Supporting Information Available: Experimental details including materials, preparation of DF, and gas chromatography (2 pages). See any current masthead page for ordering and Internet access instructions.

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