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Reactivity of isobutane in fluorosulfonic based superacids[†]

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ABSTRACT: The behavior of isobutane in DSO_3F containing various amounts of SbF_5 has been studied in relation to the acid strength of the superacid system. In contrast to the DF–SbF_5 system, H/D exchange occurs only in the weakest superacid via deprotonation of the *t*-butyl ion intermediate formed by an oxidative process. Kinetic isotope effect determination shows that the slow step is hydride transfer. At higher acidity, the increasing stability of this intermediate impedes isotopic exchange. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: superacids; isobutane; alkane activation; H/D exchange; oxidation

INTRODUCTION

The transformation of saturated hydrocarbons by cracking, isomerization and alkylation is a matter of great importance for the petrochemical industry. In order to overcome the poor reactivity of the starting material, high temperatures and/or strong acidic catalysts have to be used.[1,2] The key step of these acid-catalyzed reactions is the formation of carbocations as reaction intermediates. In the strongest superacids, the initial step is often ascribed to proton attack on a C—C or C—H bond to form a carbonium ion, following the σ-basicity concept developed by Olah and coworkers.[3,4] These protonated alkanes, characterized by a three-center two-electron bond, with a pentacoordinated carbon atom, have a lifetime too short to allow direct observation in superacidic media by spectroscopic methods, such as NMR. However, initial product distribution, H/D exchange measurements and theoretical calculations support the existence of these cations as reaction intermediates or transition states.[5–8]

The protonation site on isobutane in DF–SbF_5 is independent of the further reactivity of the pentacoordinated carbonium ion.[9,10] It takes place on both types of C—H bonds in relation to the basicity, i.e. tertiary C—H >primary C—H. Besides rapid hydron exchange, partial C—C and C—H bond cleavage are also occurring, leading to ionization.

In contrast, H/D exchange in weaker acids, such as D_2SO_4[11–13] or D_2O-exchanged solid acids,[14–18] takes place only in the methyl positions, via successive steps of deprotonation of the *t*-butyl cation and reprotonation (deuteration) of the isobutene. In triflic acid (HSO_3CF_3) a superacid with $H_0 = -14.1$, the same regiospecificity in H/D exchange was observed.[19]

The acidity of fluorosulfonic acid (HSO_3F), based on Hammett indicator measurements, is $H_0 = -15.1$.[20] This makes it the strongest simple protic acid, slightly more acidic than HSO_3CF_3 ($H_0 = -14.1$).[21] It is employed as a catalyst and chemical in various processes, including alkylation, acylation, polymerization, sulfonation, isomerization and production of organic fluorosulfonates. As in the case of HF, the acidity of HSO_3F can be significantly enhanced by addition of a fluorinated Lewis acid, like SbF_5. This procedure may increase the H_0 values up to -23.[22] The ability of these mixtures (a 1:1 HSO_3F/SbF_5 mixture is called Magic Acid) to ionize alkanes was demonstrated by Olah and coworkers[23–26] in the late 1960s. The mechanism of formation of stable tertiary carbenium ions from alkanes via protolysis or oxidation has been a long-standing controversy.[27–30]

Recently, the mode of activation of alkanes on solid acids, sometimes called solid superacids, such as sulfated zirconia and related materials, has been the subject of similar discussions.[31–33]

Based on our recent results on liquid and solid acids alkane activation, using labeling techniques, we considered it of interest to reinvestigate the alkane activation in HSO_3F-based superacids. We report here our results

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for isobutene, based on kinetic isotope effects (KIEs) for ionization and H/D exchange measurements, in relation to the acidity of the superacids.

EXPERIMENTAL

DSO_3F was prepared by reaction of sulfur trioxide with DF at −30 °C and then distilled twice, through a short Vigreux column under vacuum, $Bp_{15\ mmHg} = 85\,°C$, yield = 85%, 97% isotopic purity.

DF was synthesized by a method described elsewhere[34] by reacting benzoylfluoride with D_2O. HSO_3F (99% weight purity) was acquired from Aldrich Chemicals and used without further purification. Isobutane N35 and carbon monoxide N20 were commercially available from Alphagaz.

Experimental procedures for the H/D exchange reactions

One-pass experiments. The alkane/CO or alkane/N_2 (1:3 molar ratio) mixture was bubbled through 2 ml DSO_3F or DSO_3F–SbF_5 superacid at a rate of 4 ml min^{-1}. The experiments were stopped after 30 min. At the outlet of the Kel-F reactor, the alkane was collected and analyzed by gas chromatography–mass spectrometry (GC–MS). It was also condensed in an NMR tube, kept at −117 °C, for determination of the deuterium content by comparing the ^1H and ^2H NMR spectra.

KIE determination. The same experimental procedure previously described was used. The deuterium content of the discharged isobutane was determined by GC–MS as a function of time to allow a kinetic measurement. The correction of mass spectra from the natural abundance (^{13}C contribution) and fragmentation pattern of isobutane was made with a program, based on the work of Price and Iglesia.[35] Owing to the excess of acid, the H/D exchange rate (min^{-1}) was calculated assuming first-order kinetics on the hydrocarbon.

Analysis

NMR measurements. NMR analysis of the hydrocarbons was carried out on a Bruker AM 400 (400 MHz) spectrometer. Quantitative and qualitative deuterium contents were obtained by comparison of the ^1H and ^2H NMR spectra, recorded after addition of an adequate amount of a $CDCl_3$–$CHCl_3$ mixture in freon-113 (CF_2ClCCl_2F), used as internal standard.

Mass spectrometry. GC–MS analysis was performed on a Carlo-Erba QMD-1000 spectrometer operated 70 eV ionization voltage and equipped with a JSW Scientific DB 624 column (∅ = 0.25 mm; film, 1.4 μm, *l* = 30 m). The oven temperature was kept constant at 35 °C.

Gas chromatography. The analyses of the hydrocarbons were performed on a Girdel 300 instrument with flame ionization detector, using packed column HAYESED R (∅ = 1/8″, l = 2 m). Helium was used as a carrier gas. The concentration of hydrogen was determined on an Intersmat IGC 112M provided with a 5 Å molecular sieve columm. Argon was employed as a carrier gas. The results of our analyses were computed on a Delsi Instruments ENICA 21 recorder integrator.

RESULTS AND DISCUSSION

H/D exchange between isobutane and DSO_3F

Isobutane is often selected as a model for activation studies, in preference to other small alkanes, because of the high reactivity of its tertiary C—H bond, which leads to simple product distribution.

In DF–SbF_5 superacid, under non-oxidizing conditions (less than 20 mol% SbF_5), isobutane exchanges all its hydrons at a rate exceeding, by far, protolysis of the tertiary bond.[10] This is in contrast with the H/D exchange observed, when isobutane is contacted with D_2SO_4[11,12] or various solid acids, in which case isotope exchange occurs via deprotonation of the *t*-butyl cation and reprotonation of isobutene. This leads to selective exchange of the primary hydrons; this has been verified on a large variety of solids,[13–17] but also in HSO_3CF_3,[19] which is classified as superacid,[4] based on its H_0 value of −14.1.

Fluorosulfonic acid, $H_0 = -15.1$, is slightly more acidic than triflic acid. As a consequence, the H/D exchange mechanism should not be very different in both systems.

When an isobutane–N_2 mixture was bubbled into DSO_3F, at 5 °C, an extensive deuterium incorporation (Fig. 1) was observed in the primary position (53 at.%), together with a minor extent in the tertiary position (5.8 at.%). The same reaction conducted under CO, at 5 °C, showed a much lower deuteration (Fig. 1) selectivity in the primary position (6.2 at.%). No deuterium was found in the tertiary position. Even at 25 °C, under CO, despite an extensive H/D exchange in the primary position (50.8 at.%, Fig. 2), no exchange was observed in the tertiary position. These observations lead us to the following remarks.

In contrast with DF–SbF_5,[10] no H/D exchange was observed on the methine hydron in the presence of CO. Thus, direct electrophilic substitution, via reversible protonation, can be excluded in HSO_3F. The small amount of deuterion observed in the tertiary position in the absence of CO can be assigned to polyenylic species,

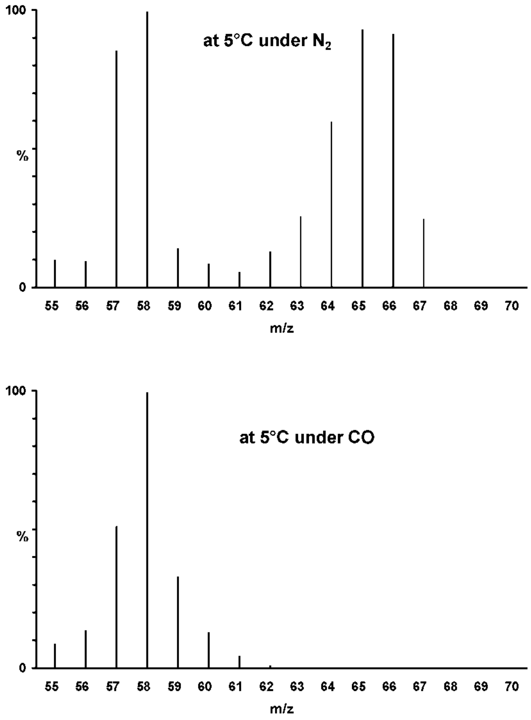


Figure 1. GC–MS spectra of isobutane after H/D exchange in DSO_3F at 5 °C in to presence and absence of CO

able to transfer deuteride to the *t*-butyl ion intermediates.[13,19]

Thus, hydron exchange occurs via the classical Otvos scheme of ionization to *t*-butyl cations, deprotonation, reprotonation and hydride transfer. The ionization step here is most probably oxidative, as no hydrogen was detected under our experimental conditions, as would be expected in the case of protolysis of the tertiary C—H bond.

The fact that, in contrast with D_2SO_4, H/D exchange is observed even in the presence of CO is in agreement with the reversibility of the Koch reaction and with higher concentration of *t*-butyl ions in HSO_3F in comparison with D_2SO_4. The competition between carbonylation and deprotonation is observed as an induction period, in the initial stage of the reaction, when a low concentration of carbenium ions is present in solution (see Fig. 4).

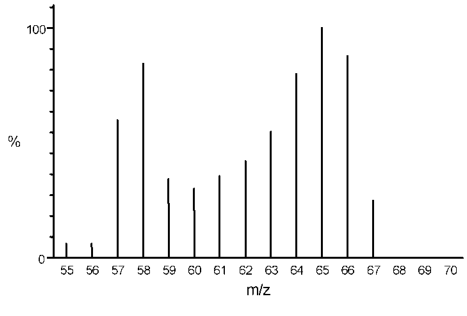


Figure 2. GC–MS spectra of isobutane after H/D exchange in DSO_3F at 25 °C under CO

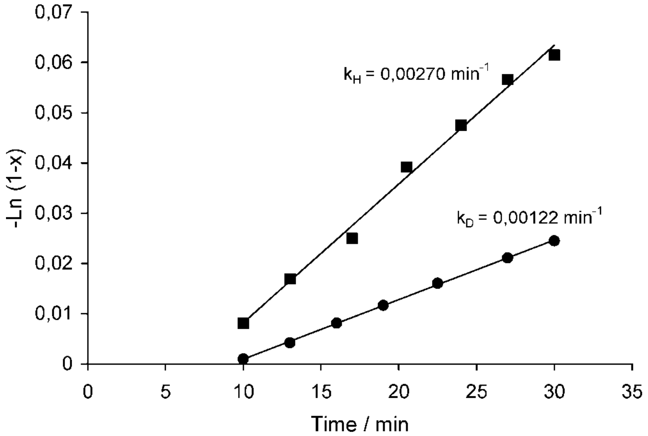
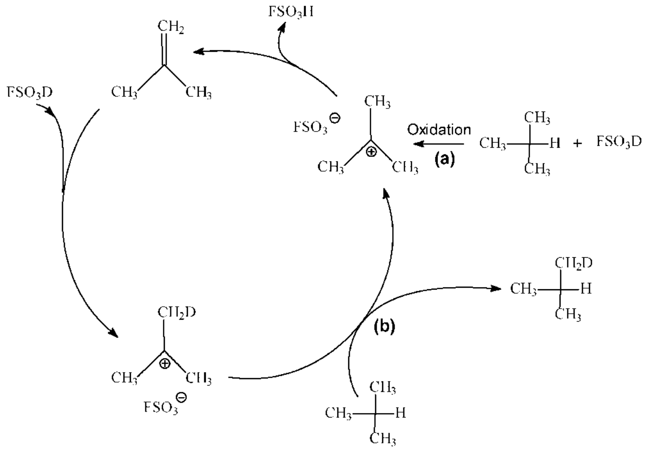


Figure 3. H/D exchange of isobutane (■) and isobutane-2-*d* (●) in DSO_3F at 5 °C in the presence of CO

Kinetic isotope effect

In order to shed some light on the reaction mechanism, especially on the rate-limited step, we used KIE measurements. This procedure has been widely employed[36–40] since the first paper concerning isotope effects by Bigeleisen *et al.*[41] The isotope effects on the rate of chemical reactions arise from the difference in zero-point energy.[42,43]

As seen in Fig 3, the replacement of isobutane by isobutane-2-*d*[44] shows a $k_H/k_D = 2.13 \pm 0.2$ at 5 °C under CO. The proposed mechanism for H/D exchange is shown in Scheme 1. The primary KIE found can either be related to the activation (step a) of the alkane to give the *t*-butyl cation, or the hydride transfer from an incoming alkane to an exchanged cation (step b). Thus, the question



Scheme 1. Catalytic cycle of H/D exchange in FSO_3D

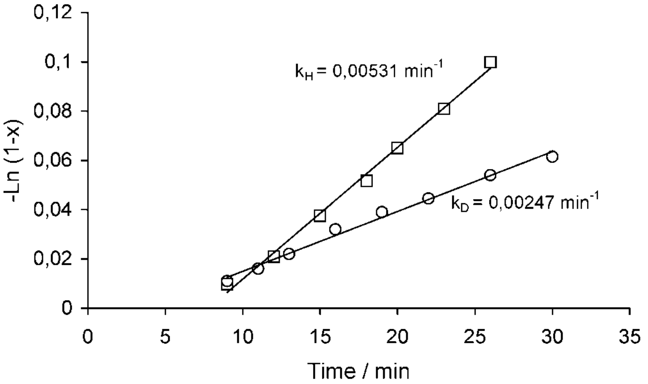


Figure 4. H/D exchange of 2% isobutene–98% isobutane (□) and 2% isobutene–98% isobutane-2-*d* (○), in DSO_3F at 5 °C in the presence of CO

which now remains unanswered is: which step is responsible for the KIE measured? Alkane activation or hydride transfer? Both steps involve breaking of C—H(D) bonds in the transition state.

In order to bypass the activation step, we added 2% of isobutene to the isobutane and isobutane-2-*d*. Protonation of olefin is usually much faster than alkane activation; therefore, step a, from Scheme 1, will be virtually bypassed with the addition of the olefin. If the KIE previously measured was related to the activation (step a), then addition of the olefin should give a KIE of unity (no isotopic effect). On the other hand, if the KIE was related to hydride transfer (step b), addition of the olefin should not lead to significant modification in the k_H/k_D results.

The $k_H/k_D = 2.06 \pm 0.2$ measured for the H/D exchange in the presence of 2% isobutene is consistent with the second hypothesis (Fig. 4). Hence, the KIE measured in the absence of olefin was related to the hydride transfer, from the alkane to the deuterated cation.

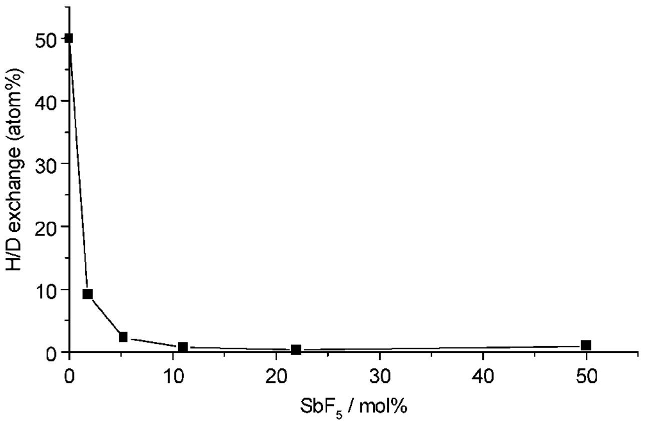


Figure 5. Isobutane H/D exchange in $DSO_3F–SbF_5$ at 25 °C as a function of the SbF_5 concentration

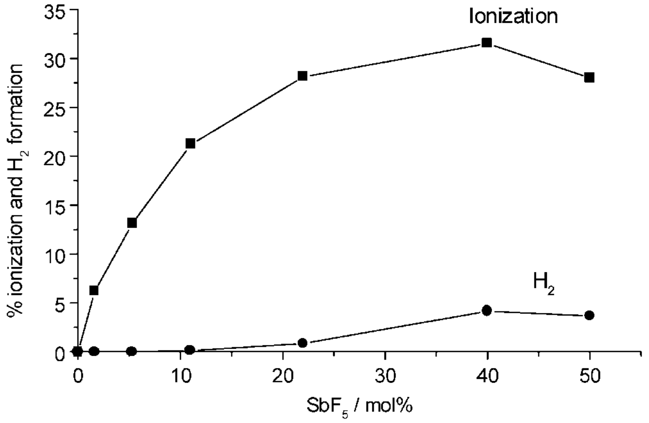


Figure 6. Conversion and H_2 production with isobutane in $DSO_3F–SbF_5$ under CO at 25 °C as a function of the SbF_5 concentration

H/D exchange and ionization of isobutane in $DSO_3F–SbF_5$ at various concentrations of SbF_5

As the acidity of HSO_3F is rapidly increasing with SbF_5 concentration, we were expecting a corresponding increase in deuteration via direct reversible protonation of the alkane, and thus a modification of the regioselectivity of the exchange process, going from exclusive exchange of the primary hydrons to a more pronounced exchange in the tertiary position (carbonium ion mechanism). To avoid deuteration in the tertiary position, due to hydride transfer from polyenic species, all the experiments were conducted under CO, at 25 °C.

As can be seen in Fig. 5, the opposite was observed: deuteration was exponentially decreasing with increasing SbF_5 concentration, going from 50.8 at.% in neat DSO_3F to 9.1 at.% at 1.6% SbF_5 and 2.2 at.% at 5.3% SbF_5. Moreover, with the exception of traces of deuterium in the tertiary position, at SbF_5 concentrations above 20% the deuterium incorporation occurred only in the primary position. These observations are not in accord with reversible alkane protonation, even in the strongest Magic Acid with a 1:1 concentration of $HSO_3F–SbF_5$. An experiment recirculating an isobutane/CO mixture (1:2) for 4 h, at a rate of 4 ml min^{-1}, in $DSO_3F–SbF_5$ (21% SbF_5), at 20 °C, showed that all isobutane disappeared from the gas phase and ionized to carbenium ions, which were quenched by CO as oxocarbenium ions.

In single-pass experiments, when increasing SbF_5 concentration from 0 to 50%, ionization became the major reaction (Fig 6). In fact, unlike the HF–SbF_5 system, in which ionization of isobutane by oxidation occurs only above 20% SbF_5 due to the presence of uncomplexed SbF_5,[10] HSO_3F is known to be, itself, a strong oxidizing agent. In pure HSO_3F, at low SbF_5 concentrations, the *t*-butyl cations undergo rapid H/D exchange via deprotonation and reprotonation of isobutene. As the amount of SbF_5 increases, especially above 10 mol% SbF_5, the concentration of the counter ions of $SbF_6SO_3^-$ type are sufficient to inhibit deprotonation, thus blocking the H/D exchange. The acidity level, however, even in the 1:1 HSO_3F/SbF_5 system, is not high enough to achieve reversible protonation of the alkane, at least at the temperatures employed in this study. The small amount of hydrogen, produced at high acidity levels, seems to indicate that, besides oxidation, protolysis is competing as a secondary pathway.

CONCLUSIONS

In DSO_3F and DSO_3F–SbF_5 systems, despite their ranking as superacids by acidity measurement with Hammett indicators, the H/D exchange with isobutane is not following a carbonium ion mechanism as observed in HF–SbF_5 solutions. The mechanism follows a carbenium ion route, with successive steps of deprotonation/protonation, as observed in weaker acids like sulfuric and triflic acid. Owing to the high reactivity of the tertiary C—H bond and its sensitivity to oxidation, the behavior of isobutane seems to depend more on the oxidant character than on the acidity of the acidic medium.

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