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Activation, isomerization and H/D exchange of small alkanes in triflic acid

Alain Goeppert, Benoît Louis and Jean Sommer [*]

Laboratoire de Physico-Chimie des Hydrocarbures, Faculté de Chimie, Université Louis Pasteur, 67008 Strasbourg UMR 7513, France

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In contrast with the HF/SbF$_5$ superacid system and despite its strong acidity ($H_0 = -14.1$), CF$_3$SO$_3$H is not able to protonate reversibly small alkanes. At room temperature propane and n-butane do not exchange their hydrons for deuteriums with deuterated triflic acid. The H/D exchange occurring between isobutane and the CF$_3$SO$_3$D acid is regiospecific as observed in weaker acids such as D$_2$SO$_4$ or solid acids such as sulfated zirconia or zeolites. In the same way, the formation of C$_5$ alkanes during C$_4$ isomerization is indicative of a classical bimolecular process. In the presence of carbon monoxide, isomerization as well as H/D exchange are suppressed due to chemical trapping of the carbenium intermediates.

Keywords: isomerization, alkane activation, butane, isobutane, H/D exchange, superacids, carbon monoxide

1. Introduction

Acid-catalyzed transformation of hydrocarbons, such as cracking, isomerization and alkylation, are of importance in the petrochemical industry [1]. For the understanding of these reactions, there is, however, a strong contrast between the general agreement on the role of carbocations as reaction intermediates and the lack of information over their mode of formation. The initial step is often ascribed [2] to proton attack on a C–C or a C–H bond, following the concept of σ-basicity developed by Olah in the framework of extensive investigations of electrophilic reactions of a single bond in superacid media [3].

Protonated alkanes (or carbonium ions) characterized by a three-center, two-electron bonded structure with pentacoordinated carbon atoms [4] have generally a lifetime too short to allow direct observation in superacidic media by NMR. However, initial product distribution, H/D exchange measurements and theoretical calculations support the existence of these cations as reaction intermediates or transition states.

Trifluoromethanesulfonic acid (CF$_3$SO$_3$H, triflic acid) is known to be one of the strongest simple protic acids similar to HSO$_3$F or HClO$_4$. The acidity of the neat acid mesured with Hammett indicators shows indeed a H_0 value of -14.1 [5]. As it lacks the sulfonating properties of oleums and HSO$_3$F, it has gained a wide range of application as a catalyst in Friedel–Crafts alkylation, polymerization and organometallic chemistry [6]. Recently, an industrial process of isobutane alkylation was developped by Topsøe based on a triflic-acid-supported catalyst [7].

Earlier reports in the litterature on triflic-acid-catalyzed n-butane isomerization [8] have assumed that the alkane activation was of protolytic nature. Based on our experience in small alkane activation both in liquid superacids and on strong solid acids we have reinvestigated the behaviour of propane, butane and isobutane in triflic acid. We report in this paper our results based on H/D exchange measurements, product distribution during isomerization and effect of carbon monoxide on these reactions.

2. Experimental

CF$_3$SO$_3$D was prepared by hydrolysis of trifluoromethanesulfonic anhydride with D$_2$O at 50 °C for 12 h and then distilled twice through a short Vigreux column under vacuum, $\text{bp}_{15\ \text{mm Hg}} = 85\,^\circ\text{C}$, yield = 85%, 97% isotopic purity.

Trifluoromethanesulfonic anhydride was synthesized by dehydration of CF$_3$SO$_3$H with an excess of P$_2$O$_5$ [9].

CF$_3$SO$_3$H 99% weight purity from ACROS Chemicals was used without further purification. Isobutane N35, n-butane N35, propane N35 and carbon monoxide N20 were commercially available from Alphagaz.

2.1. Isomerization reactions

10 ml (0.45 mmol) of alkane and 25 ml (1.1 mmol) CO or N$_2$ were introduced in a preevacuated round bottom flask containing 1.3 g (8.6 mmol) CF$_3$SO$_3$H. The mixture was stirred at room temperature and the amount of reaction products versus reaction time was monitored by GC.

2.2. H/D exchange procedures

For H/D exchange studies three procedures were employed.

One-pass experiments. The alkane/CO or alkane/N$_2$ (1 : 3 molar ratio) mixture was bubbled through 1.3 g

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[*] To whom correspondence should be addressed.

(8.6 mmol) CF_3SO_3D superacid at a rate of 4 ml min^{-1}. The experiments were stopped after 15 min. At the outlet of the Kel-F reactor, the alkane was condensed continuously during the experiment directly in a NMR tube kept at $-117\,^{\circ}$C.

Recirculation experiment. The catalytic reaction was run in an all glass, grease-free set-up with a recirculation pump. An isobutane 30 ml (1.3 mmol)/N_2 (1 : 6 molar ratio) mixture was bubbled at a rate of 4 ml min^{-1} through 1.4 g (9.2 mmol) CF_3SO_3D (97% D), and recirculated at room temperature during 4 h. Under these conditions it was not possible to condense isobutane in a cold trap for NMR analysis. Deuterium distribution in isobutane was thus obtained by GC-MS.

Static experiment. Isobutane 36 ml (1.6 mmol) was introduced in a preevacuated round bottom flask containing 4.9 g (32.6 mmol) CF_3SO_3D. The mixture was stirred at room temperature during 4 h. At the end, isobutane was condensed in a cold trap at $-117\,^{\circ}$C. Qualitative and quantitative analysis of deuterium content and distribution in isobutane was obtained by GC-MS and by comparison of the ^{1}H and ^{2}H NMR spectra.

2.3. NMR measurements

NMR analyses of the hydrocarbons were carried out on a Bruker AM 400 (400 MHz) spectrometer. Quantitative and qualitative deuterium content was calculated by comparison of the ^{1}H and ^{2}H NMR spectra recorded after addition of an adequate amount of a freon-113 (CF_2ClCCl_2F) solution of a $CDCl_3/CHCl_3$mixture used as internal standard.

2.4. Mass spectroscopy

MS analysis was performed on a Carlo–Erba QMD-1000 spectrometer with a JSW Scientific DB 624 column ($\varnothing = 0.25$ mm; film 1.4 μm, $l = 30$ m).

2.5. Gas chromatography

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

3. Results and discussion

3.1. H/D exchange occurring between isobutane and CF_3SO_3D

Isobutane is a convenient model for alkane activation studies as, even under superacidic conditions, it leads to very simple product distribution based on the higher reactivity of its tertiary C–H bond [10,11]. In agreement with the formation of carbonium ion intermediates, the reversible protonation of the alkane in DF/SbF_5 occurs on all C–H bonds and contrasts markedly with the H/D exchange observed in D_2SO_4 [12] or D_2O-exchanged solid acids in which case the methine proton is not exchanged. In the weaker acids, H/D exchange takes place via successive deprotonation of the t-butyl cation and reprotonation of isobutene. As the last step is a hydride transfer, the methine proton cannot be exchanged. The generality of this reaction scheme was verified for all branched small alkanes and a large variety of D_2O-exchanged solid acids including SZ, H-ZSM5, HBEA, HUSY, H-EMT, H-MAZZ, and heteropoly acids [13–15].

The observed regiospecificity is based on the rule (adapted from Markovnikov's[1] observations) which states that protonation of an alkene should always lead to the most stable trivalent carbenium ion.

In the absence of SbF_5, triflic acid is known to be a relatively weak superacid with an H_0 value of -14.1 [5,16]. If we follow the pattern of reactivity observed for isobutane in liquid superacids like DF/SbF_5, we would expect the H/D exchange in all C–H positions. On the other hand, if the reactivity observed for this molecule in CF_3SO_3D follows the same pattern as observed in D_2SO_4, H/D exchange should occur only in positions adjacent to the tertiary C–H bond (methine), after an initial oxidoreduction activation step.

An isobutane/carbon monoxide or isobutane/N_2 mixture (molar ratio 1 : 3) was bubbled during 15 min at a rate of 4 ml min^{-1} through 1.3 g of CF_3SO_3D in a Kel-F reactor maintained at $0\,^{\circ}$C. The gaseous products were analysed by GC-MS and further condensed at $-117\,^{\circ}$C for ^{1}H and ^{2}H NMR analysis.

When the reaction was run under N_2, 9.0 at% of the primary hydrons were exchanged for deuterium. No deuterium was found in the tertiary position. At $20\,^{\circ}$C we noticed an increasing deuteration in the primary position (43.3 at%) but no deuterium in the tertiary. The exchange was regioselective.

When the reaction was run at $0\,^{\circ}$C under the same conditions but replacing N_2 by CO on the basis of GC-MS analysis, no H/D exchange could be noticed (figure 1(b)). At $20\,^{\circ}$C only a very small amount of D could be detected (figure 1(d)). Carbon monoxide inhibited the H/D exchange between isobutane and CF_3SO_3D.

These observations lead us to the following remarks:

(1) As no hydron exchange was observed in the tertiary position, the direct electrophilic substitution between C–H bonds and triflic acid as it occurs in stronger superacids did not take place. This was confirmed by experiments involving linear alkanes showing that no H/D exchange occurred between propane or n-butane and deuterated triflic acid at $20\,^{\circ}$C in the same conditions as the reaction with isobutane.

(2) The regiospecific exchange pattern in isoalkanes as observed in D_2SO_4 is typical of deprotonation of the carbe-

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[1] V. Markovnikov (1838–1904); born in Russia, Moscow University.

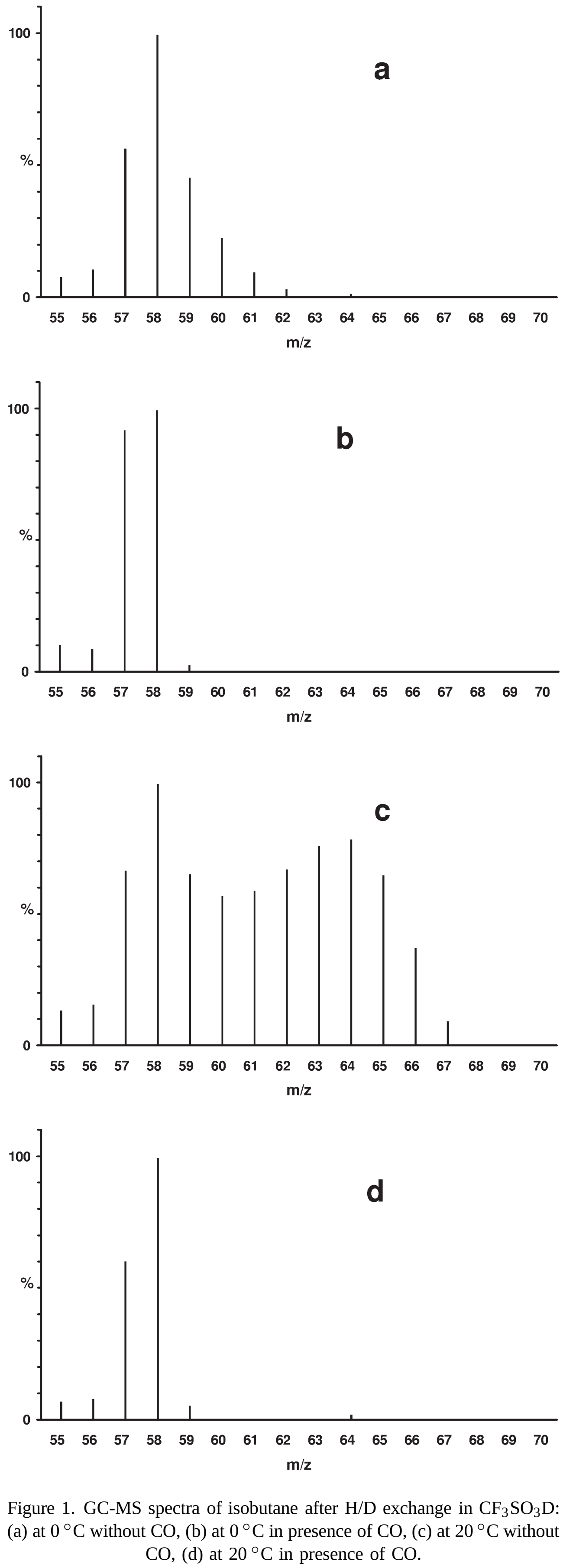
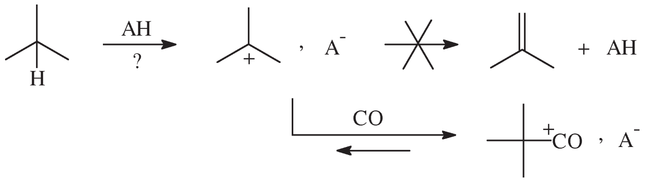


Figure 1. GC-MS spectra of isobutane after H/D exchange in CF_3SO_3D: (a) at 0 °C without CO, (b) at 0 °C in presence of CO, (c) at 20 °C without CO, (d) at 20 °C in presence of CO.



Scheme 1. Trapping of the reactive carbenium ion by carbon monoxide.

nium ion intermediate and redeuteration of the corresponding alkene. In the presence of CO [17], the carbenium ion is trapped and the formation of the oxocarbenium ion blocks the exchange process (scheme 1).

(3) In principle, as no hydrogen was detected by GC, the hypothesis of a protolytic pathway should be ruled out. However, in the MS spectrum, a m/z 64 peak was unambiguously assigned to SO_2. As triflic acid is generally considered as a non-oxidizing reagent, the origin of sulfur dioxide could come from traces of SO_3 still free in the acid despite distillation. In this case the initial step would be as in H_2SO_4, oxidation of the alkane. As the exchange reaction is catalytic in t-butyl ion, only traces of this reaction intermediate are necessary (scheme 2).

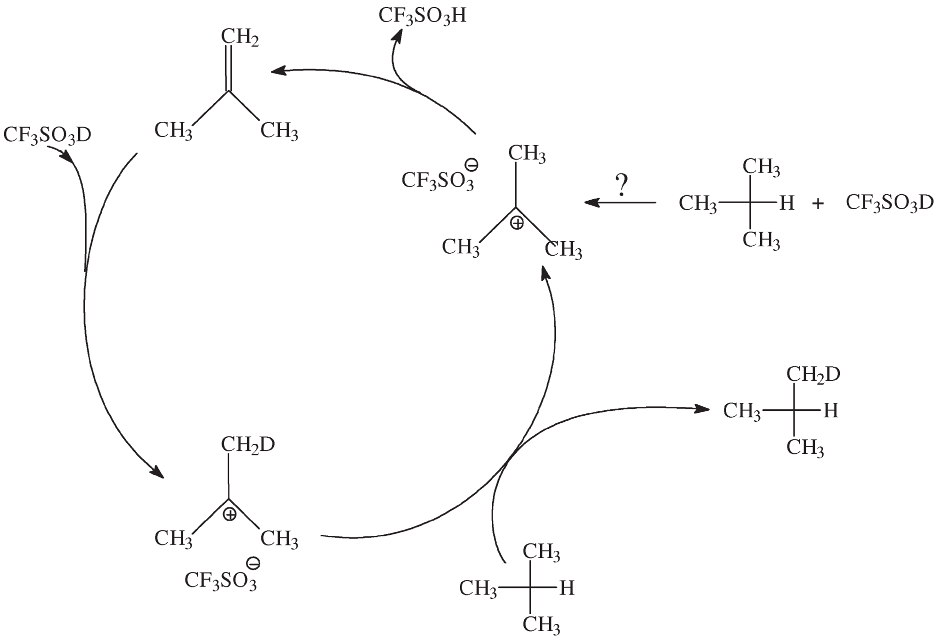
3.1.1. Isotopolog distribution

The number of deuteriums which have been introduced in isobutane before recovery depends on the number of catalytic cycles followed by the alkyl cation before hydride transfer. The isotopolog distribution as determined by MS gives thus a good indication of the rate of hydride transfer between isobutane and the deuterated t-butyl ions.

It is interesting to notice that the MS spectra of the recovered isobutane contrasted markedly with the one observed when D_2SO_4 was used. In triflic acid the isotopolog distribution appears as a Gaussian type curve in which all isotopologs are present. In D_2SO_4, however, only d_0–d_1 peaks are observed next to d_8–d_9 isotopologs [15]. We assign the origin of this difference to the difference in rate of hydrid tranfer [15]: in D_2SO_4 the very low solubility of isobutane limits the hydride transfer to the gas–liquid interface. Thus the cation solvated in the acid has a long residence time during which it undergoes repeated deprotonation and reprotonation steps leading to high H/D exchange before hydride transfer. We assume that in triflic acid the solubility of isobutane is much higher in which case the hydride transfer can take place also in the liquid phase. This results in a more statistic distribution of the isotopologs in recovered isobutane. In a separate experiment we used a batch reactor and monitored the time dependence of deuteration of isobutane during the reaction. In good accordance with our assumption, a Gaussian curve (figure 2) could be observed which shifted progressively from the small d_1–d_3 m/z values to the larger d_7–d_9 values as the D content increased.

3.1.2. H/D exchange in the methine position

In the same way as in D_2SO_4 [15] we noticed that after long contact times deuterium does also appear in the tertiary



Scheme 2. Catalytic cycle of H/D exchange in CF_3SO_3D.

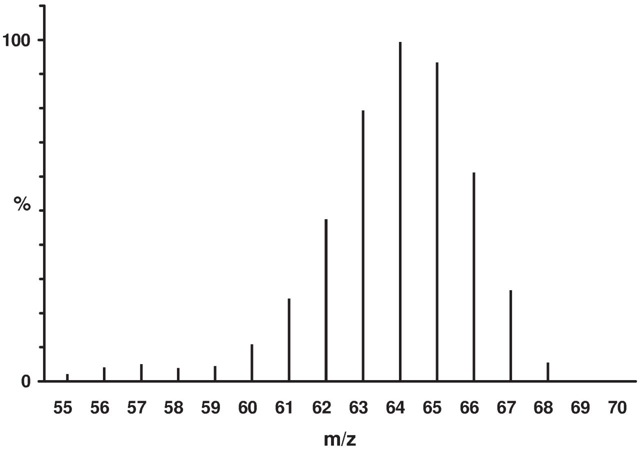


Figure 2. GC-MS spectra of isobutane after 4 h static H/D exchange reaction in CF_3SO_3D at 20 °C.

position in isobutane. When 75 ml (3.3 mmol) isobutane was introduced in a preevacuated round bottom flask containing 2.7 g (18 mmol) CF_3SO_3D and stirred during 4 h at 20 °C, the recovered isobutane showed that both the primary and the tertiary hydrogens were exchanged (40.3 at% of the hydrogens in the methyl groups and 5.5 at% of the methine hydrons). In the other experiment (4.9 g (33 mmol) CF_3SO_3D and 36 ml (1.63 mmol) isobutane) with a stirring time of 10 h at 20 °C, the recovered isobutane showed 70.1 at% D of the methyl hydrons and 70.5 at% D on the methine. Clearly, the regioselectivity was lost.

This was rationalized as before [15] by the oligomerization reaction of isobutene leading to the formation of polyenic material able to transfer an α-deuteride to the t-butyl cations. The formation of dienyl cations could be confirmed by a strong band at 290 nm [18] appearing in the UV spectrum of the CF_3SO_3H solution after 3 h of reaction time.

Oligomerization, cyclization and aromatization processes are here similar to those at the origine of coke formation on solid acids [15,19].

3.2. Isomerization reaction of n-butane and isobutane

In acid-catalyzed isomerization of alkanes, isomerization of n-butane represents a case different from that of higher alkanes (pentanes, hexanes, heptanes, etc.) because monomolecular isomerization must proceed through the isobutyl cation, a relatively high energy primary carbocation (although of partially delocalized protonated cyclopropane nature) [20] which raises the activation energy of the process. For this reason, generally, a bimolecular pathway is suggested in which a C_8 ion rearranges before β-scission [20,21].

HF/SbF_5 superacid is not efficient to isomerize butane to isobutane, but causes extensive hydrocracking besides carbon and hydrogen scrambling, as shown by Brouwer [22]. Similarly, treatment of butane with 1 : 1 FSO_3H/SbF_5 [23] results also in extensive hydrocracking and only limited isomerization. In HF/HSO_3F (5% HF) Olah has shown [24] that n-butane was efficiently isomerized at room temperature.

In weaker superacids as neat CF_3SO_3H, linear or cyclic non-branched alkanes are isomerized only very slowly, probably due to the high energy needed for the initiation step.

A mixture of 40 ml n-butane (1.8 mmol) and 1.27 g (8.5 mmol) triflic acid (CF_3SO_3H) was introduced at room temperature in a preevacuated round bottom flask. The mixture was stirred and the amount of isobutane produced versus reaction time was monitored by GC (figure 3). Our results are in accordance with those of Choukroun et al. [8]: under these conditions, isomerization of n-butane is

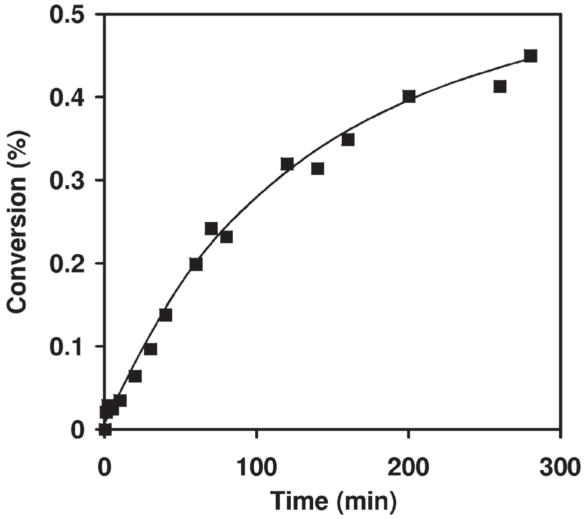


Figure 3. n-butane isomerization in CF_3SO_3D at 20 °C.

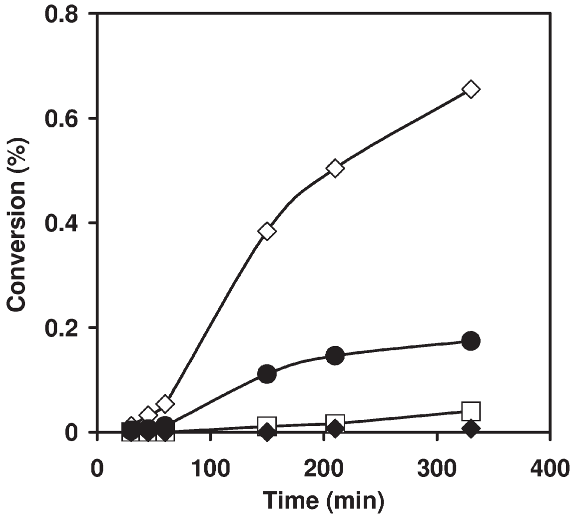


Figure 4. Reaction of isobutane in CF_3SO_3D at 20 °C. (□) Propane, (◇) n-butane, (●) isopentane, (◆) n-pentane.

very slow and no secondary reactions such as cracking or oligomerization were observed. However, in contrast with the protolytic activation step suggested earlier, no hydrogen could be detected among the reaction products.

On the other hand, when excess carbon monoxide was used as coreactant, the isomerization reaction was totally inhibited, and even after 13 h no isobutane was detected. The reactive carbocations are converted into stable oxocarbenium ions.

In order to better understand the mechanism of the reaction of n-butane with triflic acid, we investigated the reverse reaction – isomerization of isobutane into n-butane. The same experimental procedure as described above was applied in the reaction with 45 ml (1.9 mmol) isobutane and 1.3 g (8.6 mmol) CF_3SO_3H. The results are shown in figure 4. In this case, isomerization of isobutane was as slow as the isomerization of n-butane into isobutane. The significant difference appears in the amount of by-products: isopentane, n-pentane and propane. This observation is in accordance with the bimolecular mechanism in which a C_8 intermediate is formed, isomerizes and generates C_3, C_4 and C_5 fragments via β-cleavage.

When an excess of CO was used as coreactant, the isomerization reaction of isobutane to n-butane was also completely inhibited, and even after 13 h no n-butane, C_5 or C_3 was formed, as shown by GC analysis. Furthermore, as no hydrogen was detected, the activation step seems to follow, as in the case of n-butane, another way that does not involve the formation of carbonium ions. The situation is consequently similar to the reaction of n-butane on SZ and we suggest that the isomerization reaction is essentially bimolecular.

These results can be compared with those obtained by Pinna et al. [25] on sulfated zirconia at 150 °C. When helium was replaced by CO as carrier gas, the conversion of n-butane into isobutane was reversibly suppressed. This effect was then attributed to the complexation of Lewis sites vital for the occurrence of catalytic activity. But in CF_3SO_3H, a pure Brønsted acid, the negative effect of CO cannot be ascribed to Lewis acid sites, but is rather due to the trapping of the carbenium ion intermediates as in the Koch reaction. Thus, on solid acids, the blocking of Lewis sites is perhaps not, or not the only way to explain the loss of catalytic activity of SZ in the presence of CO, as on the other hand, the catalytic activity seems to be rather correlated with the presence of Brønsted acid sites as proposed by Komarov and Sinilo [26] and by a quantum mechanical study of Babou et al. [27].

4. Conclusion

The regiospecific H/D exchange taking place between isobutane and deuterated triflic acid shows that this acid behaves like D_2SO_4 or solid D_2O-exchanged strong acids such as zeolites or sulfated zirconias. In contrast with the direct exchange observed with DF/SbF_5, it involves the deprotonation of the t-butyl ion intermediate and reprotonation of isobutene. In accordance with this scheme, carbon monoxide blocks the isotope exchange by reaction with the carbenium ion intermediate. The formation of C_5 alkanes indicates that the isomerization of n- to isobutane occurs very slowly via a bimolecular process. The formation of SO_2 in the initial stage is in accordance with an oxidative pathway of activation of the alkane. Despite the H_0 value of -14.1, triflic acid does not behave towards alkanes as the strong HF/SbF_5 system but rather as H_2SO_4 or the strongest solid acids.

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