

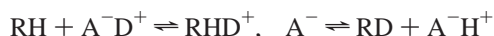
Protonation of Small Alkanes in Liquid Superacids: Absence of Intramolecular ^{13}C and ^2H Scrambling in Propane and Isobutane

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Acid-catalyzed hydrocarbon conversion processes such as isomerization, alkylation, and cracking are industrial transformations of high economic importance.¹ The common key step in these reactions is the formation of the reactive carbocations. Whereas a consensus has been reached on the nature of these reaction intermediates, the mode of their formation remains controversial. The initial step is often ascribed² to proton attack on a C–H or C–C bond, following the concept of σ -basicity developed by Olah in the framework of extensive investigation of electrophilic reactions on single bonds in superacidic media.³ We have reported earlier that isobutane, after short contact times with DF/SbF₅ at low temperatures, exchanged all its hydrons for deuterons.⁴ This isotope exchange, several orders of magnitude faster than protolytic activation, was rationalized by reversible protonation of the alkane by the superacid leading to carbonium ion intermediates (or transition states).⁵



Primary as well as the tertiary hydrons were exchanged in relation with their relative basicity and independently of the chemical reactivity of the C–H bond. We were interested in knowing if the isotope exchange between the acid and the alkane was accompanied by intramolecular hydron scrambling or skeletal rearrangement of the carbonium ion, a well-established process in carbonium ion chemistry. To investigate this possibility, we used regioselectively labeled alkanes and monitored the label in the recovered alkane, after reaction. Skeletal rearrangement, as demonstrated by ^{13}C labeling, does occur in *n*-butane when contacted with HF/SbF₅.⁶ Both ^{13}C and ^2H scrambling in the propyl cation were studied by Saunders.⁷ As hydride shifts or skeletal rearrangements are well known to occur in carbonium

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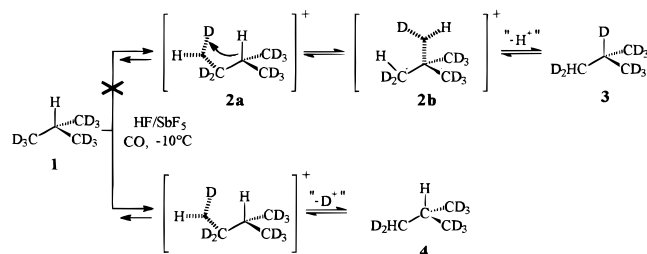
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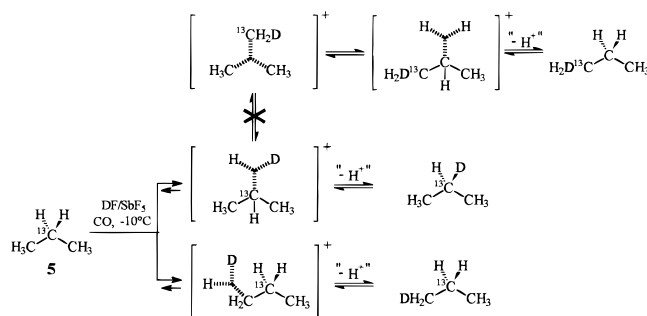
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Scheme 1



Scheme 2



ion intermediates, we have conducted all reactions in the presence of excess carbon monoxide, which converts the reactive carbonium ions into much more stable oxocarbenium ions,⁸ preventing hydride transfers between alkanes and carbonium ions in solution. We present here our results obtained using ^{13}C - or ^2H -labeled propane and ^2H -labeled isobutane in the presence of HF or DF/SbF₅.

A mixture of 2-(methyl-*d*₃)-propane-1,1,1,3,3,3-*d*₆ (nonadeuterated isobutane) (**1**) and carbon monoxide (1:3 molar ratio) was bubbled during 30 min at a rate of 4 mL·min⁻¹ at atmospheric pressure through 1.5 mL of HF/SbF₅ (12% mol SbF₅) in a Kel-F reactor at -10 °C. The gaseous products were analyzed by GC and further condensed at -119 °C for ^1H and ^2H NMR analysis, after addition of an adequate amount of a CDCl₃/CHCl₃ mixture, used as internal standard, for the H/D distribution measurement. The NMR spectra of the recovered alkane show that 4 atom % of the primary deuterons was exchanged for protium. However, no deuterium was detected in the tertiary position (Scheme 1). To confirm these results, nonadeuterated isobutane was recirculated through a HF/SbF₅ (12% mol SbF₅) mixture for 2 h under CO. As expected, in accordance with the previous one-pass experiment, no deuterium exchange was observed in the tertiary position, even after 15 atom % deuterons had been exchanged in the primary position. Even if we take into account the probability of partial dedeuteration of the tertiary position of 2-(methyl-*d*₂)-propane-1,1,1,2,3,3,3-*d*₇ (**3**), this result indicates that there is no intramolecular rearrangement of the 1-H-isobutonium cation (**2a**) to the 2-H-isobutonium cation (**2b**). Indeed, recent theoretical calculations⁹ of the potential energy surface of the *i*-C₄H₁₁⁺ species pointed out that the 1-H-isobutonium cation undergoes a facile rearrangement to the C-isobutonium cation, rather than to the 2-H-isobutonium, in agreement with the experimental results.

When propane-2- ^{13}C (**5**) was used, under the same conditions of temperature and flow rate, but with DF/SbF₅ and 52 min of reaction time, the ^1H and ^2H NMR spectra show that 14 atom % of the primary and 17.5 atom % of the secondary hydrons were

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Table 1. H/D Exchange in Propane-1,1,1,3,3,3- d_6 and Propane-2,2- d_2 in Superacidic Media HF/SbF₅

entry	species	SbF ₅ in HF/SbF ₅ (mol %) ^a	H/D exchange (atom %) ^b		exchange/ protolysis ^c
			primary	secondary	
1	CD ₃ CH ₂ CD ₃	12.3	8.3	—	— ^d
2	CD ₃ CH ₂ CD ₃	12.3	5.9	—	— ^d
3	CD ₃ CH ₂ CD ₃	15.1	14.6	—	60
4	CD ₃ CH ₂ CD ₃	16.0	15.8	—	63
5	CD ₃ CH ₂ CD ₃	17.4	15.2	—	58
6	CH ₃ CD ₂ CH ₃	11.9	—	6.2	— ^d
7	CH ₃ CD ₂ CH ₃	13.1	—	13.1	17
8	CH ₃ CD ₂ CH ₃	15.0	—	12.6	16
9	CH ₃ CD ₂ CH ₃	17.8	—	18.1	18

^a Mol % determined by weight, $\pm 1\%$ of the indicated value.

^b Determined by ¹H, ²H NMR, $\pm 3\%$ of the indicated value. ^c Protolysis calculated by determination of ethyl isobutyrate formed after addition of ethanol to the superacidic solution. Precision: $\pm 10\%$ of the indicated value. ^d Not determined.

exchanged for deuterons. However, no ¹³C scrambling was detected (Scheme 2). GC analysis of the gas-phase products showed the presence of methane and ethane, due to protolytic C—C bond cleavage, indicating an apparent conversion of ca. 2%. As in the case of isobutane, when **5** was recirculated through a DF/SbF₅ (12% mol SbF₅) mixture for 2.5 h, in the presence of CO, no ¹³C scrambling was observed. However, recovered propane showed that 49 atom % of the primary hydrons and 59 atom % of the secondary hydrons were exchanged for deuterium atoms. The absence of ¹³C scrambling demonstrates the efficiency of carbon monoxide in trapping isopropyl cations and preventing intermolecular hydride transfer. ²H and ¹³C scrambling in isopropyl cations is known to be very fast, even at $-50\text{ }^\circ\text{C}$, in liquid superacids.

We investigated the reaction of regiospecifically deuterated propanes. When propane-1,1,1,3,3,3- d_6 was used, under the same conditions as the one-pass experiment but with a HF/SbF₅ (16% mol SbF₅) mixture, 16% of hydron exchange in the primary position was observed, without introduction of deuterium in the secondary position. The experiment was repeated using propane-2,2- d_2 . In the recovered propane, 18% deuteration of the secondary position was observed, without introduction of deuterium in the primary position. Increasing the acidity, by increasing the SbF₅ concentration, increases the rate of exchange in accordance with

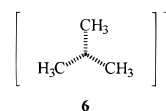
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a typical acid–base reaction. Nevertheless, deuterium was not detected in the primary positions, as shown in Table 1.

The results with propane are consistent with the calculated¹⁰ potential energy surface of C₃H₉⁺ ions, the protonated propane. As in the case of protonated isobutane, the 1-H-proponium cation rearranges to the C-proponium cation, rather than to the 2-H-proponium cation, with almost no activation energy. The 2-H-proponium cation decomposes to isopropyl carbenium ion plus hydrogen with an activation energy of only 0.04 kcal/mol, at the MP4(SDTQ)/6-311++G**//MP2(full)/6-31G** level. Therefore, an intramolecular rearrangement between the H-proponium cations is not a favored process. In addition, calculations, at the MP2-(full)/6-31G** level of the C-ethanemethonium cation (**6**), proposed as intermediate in the ¹³C scrambling in protonated propane (Scheme 2), indicated that this species has one imaginary frequency (314i cm⁻¹), and, consequently, it cannot be considered as an intermediate, but only as a transition state. The C-ethanemethonium cation was calculated to lie 46.3 kcal/mol above of the C-proponium cation, the calculated¹⁰ most stable C₃H₉⁺ species at the MP4(SDTQ)/6-311++G**//MP2(full)/6-31G** level. This result reinforces the experimental findings of no ¹³C scrambling in propane under superacidic conditions.



In summary, no ¹³C or ²H scrambling was detected in propane and isobutane after reaction in the HF(DF)/SbF₅ superacidic conditions, even after long contact times and extensive H/D exchange. Consequently, we have shown that, in contrast with well-documented carbenium rearrangements, intramolecular hydron scrambling between H-carbonium ions or skeletal rearrangement does not occur in protonated alkanes. These results also exclude the possibility of the formation of a C-ethanemethonium **6** type intermediate to rationalize the ¹³C scrambling in propane¹¹ over HZSM-5, but they do not rule out their formation as transition states in alkane alkylation.¹²

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Supporting Information Available: Experimental details, including materials, preparation of DF, 2-(methyl- d_3)-propane-1,1,1,3,3,3- d_6 , propane-1,1,1,3,3,3- d_6 , propane-2,2- d_2 , and gas chromatography, and main geometrical parameters and frequency calculation of the C-ethanemethonium cation (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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