H/D exchange, protolysis and oxidation of C_3–C_5 alkanes in $HF–SbF_5$. σ-Basicity *vs.* reactivity of C–H bonds

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The relative reactivity and basicity of CH bonds in C_3–C_5 alkanes was studied using the strongest deuterated superacid, $DF–SbF_5$, at various concentrations of SbF_5. In all cases, at concentrations up to approximatively 18 mol % SbF_5 in DF(HF), the predominant reaction, beside minor protolytic cleavage, was rapid isotope exchange of all C–H bonds *via* reversible protonation. The relative rate of exchange follows the Olah σ-basicity concept: tertiary > secondary > primary C–H bonds independently of the further reactivity of these bonds. At higher concentrations of SbF_5 the exchange process gives way to increasing ionization of the alkane, first *via* protolysis and later *via* an oxidative process with concomitant reduction of SbF_5.

Acid-catalyzed transformation of hydrocarbons, such as cracking, isomerization and alkylation, are large-scale industrial processes using solid or strong liquid acids, such as H-zeolites, chlorinated aluminas, sulfuric acid, and hydrogen fluoride.[1,2] The high acidity and/or high temperature compensate the well-known inertness of the starting material. In fact, since the late 1960s, when Hogeveen[3] and Olah[4] published their pioneering work, it is known that saturated hydrocarbons do react, even at room temperature and below, with various liquid superacids.[5] Now, it is widely accepted that the key step in these reactions is the formation of reactive carbocations. The initial step is often ascribed[6] to proton attack on a C–H or C–C bond, following the σ-basicity concept developed by Olah.[7] However, protonated alkanes, characterized by a three-center-two-electron bonded structure with pentacoordinated carbon atoms,[8] generally have a lifetime too short to allow direct observation in superacidic media by NMR. Nevertheless, initial product distribution and H/D exchange studies suggest the existence of these cations as reaction intermediates or transition states.[8] The theoretical approach of alkane protonation by Mota and colleagues using *ab initio* and DFT methods[9] seems to indicate that protonated alkanes are not minimas on the potential energy surface. This was also confirmed by experimental and theoretical studies of reversible methane protonation by Ahlberg *et al.*[10]

For alkane activation studies, isobutane has often been used as a convenient probe molecule as the higher reactivity of its tertiary C–H bond leads to very simple product distribution even under superacidic conditions.[11–13] The groups of both Hogeveen[14] and Olah[15] have observed protium-deuterium exchange of the methine hydrogen during isobutane ionization in a $HF–SbF_5$–freon system and in "magic acid" at −78 °C, respectively, and both authors concluded that a substantial exchange of this type of hydrogen had occurred compared to ionization. No exchange was observed in the methyl group. More recently, however, we showed that in $DF–SbF_5$ the protonation site on isobutane is independent of the further reactivity of the pentacoordinated carbonium ion. It takes place on both types of C–H bonds in correlation with the basicity:[12] tertiary C–H > primary C–H. Beside rapid hydron exchange, partial C–C and C–H bond cleavage also occur, leading to ionization.

In contrast, H/D exchange in weaker acids such as D_2SO_4[16–18] or D_2O-exchanged solid acids[19] takes place only in the methyl positions *via* successive deprotonation of the *t*-butyl cation and reprotonation of isobutene. In triflic acid, a weak superacid with $H_0 = -14.1$ the same regiospecificity in H/D exchange was observed.[20]

Direct hydron exchange *via* formation of carbonium ions occurs only in the very strong superacid system $DF–SbF_5$ at low temperature.

To compare directly the relative basicity *vs.* reactivity of each kind of C–H bond, we found it of interest to compare the H/D exchange and ionization of a series of small alkanes varying from propane to isopentane in $DF–SbF_5$, isopentane being the simplest alkane containing primary, secondary as well as tertiary C–H bonds. We present here our results based on ^1H, ^2H NMR and GC analysis including earlier results obtained in the case of isobutane and *n*-butane. In order to prevent hydride transfers or skeletal rearrangement in carbenium ion intermediates, all reactions were conducted in the presence of excess carbon monoxide, which converts these ions into oxocarbenium ions, stable in this superacid under our experimental conditions.[21]

Result and discussion

Reactivity of propane in $DF–SbF_5$ superacids

Propane has only primary and secondary C–H bonds and reacts in $HF–SbF_5$ in the presence of CO to give, besides hydrogen, methane and ethane, isopropyloxocarbenium and ethyloxocarbenium ions.[21] Reacting propane with $DF–SbF_5$ (Scheme 1) leads to protonation of the C–H and C–C bonds with formation of carbonium ions **1** to **3**. C–C bond protolysis in species **3** leads to the formation of deuterated methane and ethyl cation, which can undergo hydride transfer with a propane molecule. Regioselective deuteration in the primary and secondary positions is respectively obtained with carbonium ions **1** and **2**. In $DF–SbF_5$ mixtures acidity is directly correlated with the SbF_5 concentration.[22] The product distribution, especially the ratio isotope exchange/conversion of propane

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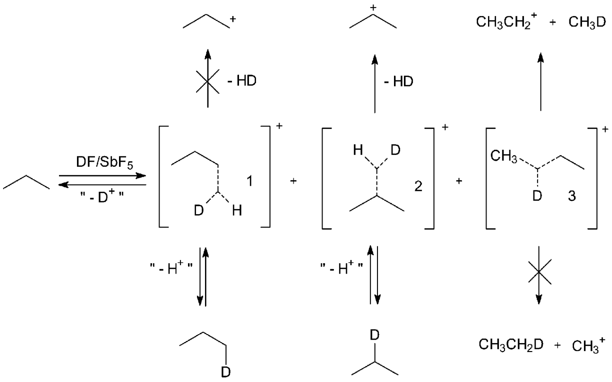


Scheme 1 H/D exchange and ionization of propane in DF–SbF_5.

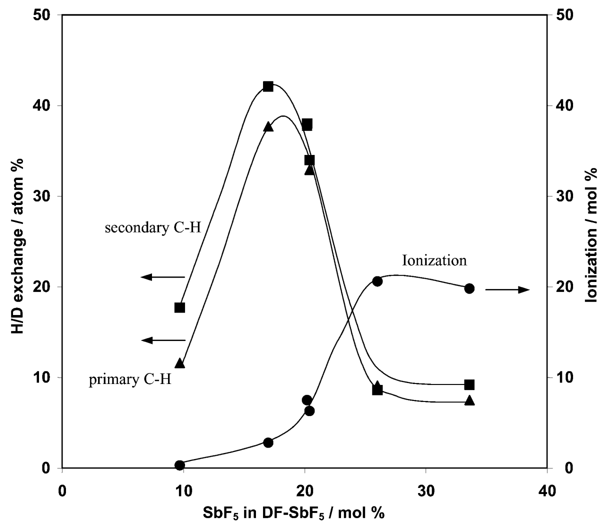


Fig. 1 H/D exchange and conversion of propane reacted with DF–SbF_5 at various SbF_5 concentrations.

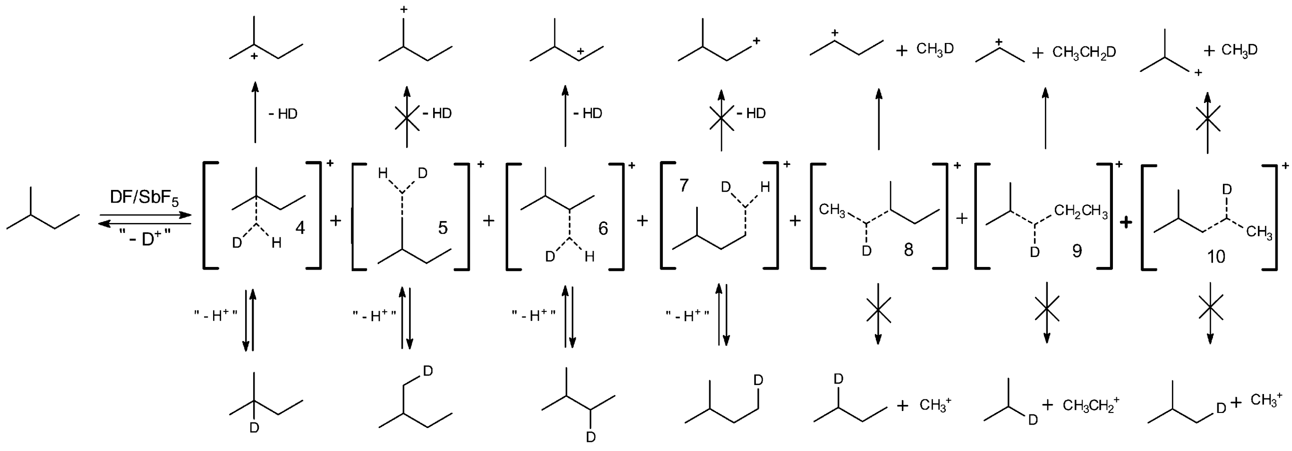
via protolysis, depends very much on the acidity of the media as shown in Fig. 1. This exchange is similar to the one observed with isobutane and described earlier.[12] SbF_5 is not only governing the acidity but also the stabilization of the resulting cations. When the concentration of SbF_5 in DF is increased from 10 to 18 mol %, the exchange rate increases substantially but then decreases dramatically at higher SbF_5 concentrations due to predominant ionization with simultaneous reduction of SbF_5. Ionization was measured by quenching the oxocarbenium ions with excess ethanol and neutralizing.

Reactivity of isopentane in DF–SbF_5 superacids

The exchange and protolysis pathways for isopentane in DF–SbF_5 are described in Scheme 2. C–H and C–C bonds are protonated to form the very reactive carbonium ions **4** to **10**. C–H bond protonation leads to species **4** to **7**, which yield either pentylium ions by loss of HD or H/D exchanged isopentane. Deuteration in the primary positions is obtained *via* carbonium ions **5** and **7**. Secondary and tertiary hydrons are exchanged *via* carbonium ions **6** and **4**, respectively. Deuterolysis of a C–C bond in species **8** to **10** leads to the formation of deuterated methane and 2-butylium ion with carbonium ion **8** whereas deuterated ethane and 2-propylium ion are generated *via* carbonium ion **9**. Alternative pathways leading to very energetic primary carbocations are much slower and generally negligible when other pathways are available.

As it was observed with propane, the product distribution depends on the acidity of the media. Fig. 2 shows the conversion of isopentane as a function of the concentration of SbF_5. A strong increase in conversion was noted when the concentration of the Lewis acid increased. At the same time hydrogen formation was measured (Fig. 2) and it appears that for up to 20 mol % SbF_5 in DF–SbF_5, ionization and hydrogen production are parallel in accord with a protolytic ionization pathway. For higher SbF_5 concentrations, however, a change in the product distribution was noticed: conversion was still increasing whereas hydrogen production decreased drastically. The same phenomenon was observed for isobutane[12] and can be rationalized by the presence of uncomplexed SbF_5 in HF at concentrations higher than 18 mol % SbF_5 in HF as demonstrated by ^{19}F NMR studies.[23] This free SbF_5 can be reduced during isopentane conversion, producing SbF_3 and HF as suggested earlier by Olah,[5,7] forming directly carbenium ions by an oxidative process.

Fig. 3 shows the deuteration expressed as atom % of primary, secondary and tertiary C–H bonds in isopentane reacted with DF–SbF_5 as a function of acidity. The shape of the curves is similar to the one described above for propane or reported earlier for isobutane in the same acid,[12] but gives more information. At SbF_5 concentrations up to 15 mol %, H/D exchange in all positions is increasing with acidity, depending only on the σ-basicity of each C–H bond. Nevertheless, protolysis of the tertiary CH bond (monitored by HD production) occurs at almost the same rate as H/D exchange. Above 15 and up to 18 mol % SbF_5 however, protolysis increases in comparison with H/D exchange, leading to tertiary pentyl ion from



Scheme 2 H/D exchange and ionization of isopentane in DF–SbF_5.

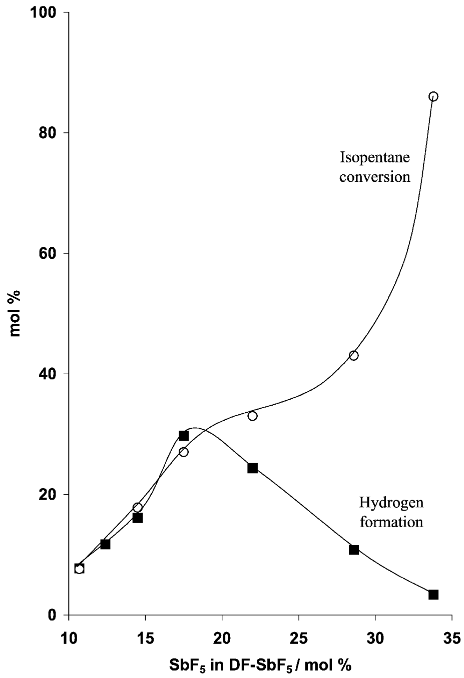


Fig. 2 Isopentane conversion compared to hydrogen production.

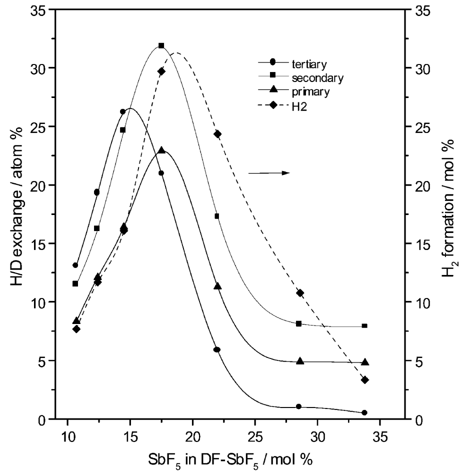


Fig. 3 Isopentane in DF–SbF_5: H/D exchange and HD formation as a function of the acidity.

carbonium ion **4**. Above 18 mol % SbF_5, protolysis as well as H/D decrease again, in contrast with the still increasing conversion of isopentane and simultaneous reduction of SbF_5.

The total isotope exchange, at various acidities, representing the number of mol of hydrons exchanged per mol of isopentane collected during the initial 20 min, was calculated by summing up the measured H/D exchange on each position expressed in atom %, taking into account that isopentane has 9 methyl, 2 methylene and 1 methine hydrogens. For example at 10.7 mol % SbF_5: $0.083\times9+0.115\times2+13.1\times1=0.747+0.230+0.131=1.108$ mol of protons exchanged per mol isopentane as illustrated in Table 1. This total exchange shows also a maximum around 17.5 mol % SbF_5. The deuterium distribution between primary, secondary and tertiary positions is, however, changing with acidity. Whereas the secondary/primary ratio increases from 1.38 at 10.7 mol % SbF_5 to 1.65 at 33.8 mol % SbF_5, the tertiary/primary ratio, first stable at 1.6 upto 14.5 mol % SbF_5, decreases drastically to reach a minimum at 0.1 for 33.8 mol % SbF_5. This can be rationalized by the fact that, at higher SbF_5 concentrations, protolysis and oxidative cleavage of the tertiary CH bond become the preferred pathways. On the other hand, with higher acidity, cracking products also increase at higher SbF_5 concentrations as can be seen on Fig. 4 showing the alkane distribution in the recovered gas phase after reaction (isopentane is omitted for clarity). Below 15 mol % SbF_5 the amount of cracking products is very low but increases rapidly with increasing SbF_5 concentrations over 15 mol %. Up to 19–20 mol % SbF_5, propane and *n*-butane represent an important part of these cracking products due to the protolytic C–C bond cleavage from carbonium ions **8** and **9**. At higher SbF_5 concentrations methane and ethane, the least reactive alkanes, are the predominant products in the gas phase.

H/D exchange of primary, secondary and tertiary C–H bonds in small alkanes: σ-basicity vs. σ-reactivity

The σ-basicity scale as proposed by Olah in the early seventies was essentially based on the reactivity of the various C–H and C–C bonds:

tertiary C–H > C–C bond > secondary C–H > primary C–H

Theoretical *ab initio* studies by Mota and colleagues[9] provide a clear insight in the exchange mechanism, which is suggested to occur not *via* a *bona fide* carbonium ion (protonated alkane) intermediate but rather *via* a transition state complex (Fig. 5) in which the amount of positive charge developed on the alkane depends on the basicity of the counterions, SbF_6^-, $Sb_2F_{11}^-$ and higher. The reversible protonation of the C–C bond unfortunately cannot be measured with our experimental procedure. Nevertheless, protolysis can be avoided when weak nonoxidizing superacid media are used, such as DF containing less than 13 mol % SbF_5. However, under our experimental conditions, below 9 mol % isotope exchange is too slow to be accurately measured. The results are collected in

Table 1 H/D exchange in isopentane at various concentration of SbF_5 in DF

	SbF_5/mol % in DF[a]	Primary C–H	Secondary C–H	Tertiary C–H	Total exchange/mol D[b]
Exchange/atom %[c] (normalized to primary position)	10.7	8.3 (1)	11.5 (1.38)	13.1 (1.57)	1.108
	12.4	12.1 (1)	16.2 (1.34)	19.3 (1.60)	1.606
	14.5	16.4 (1)	24.6 (1.50)	26.2 (1.60)	2.230
	17.5	22.9 (1)	31.8 (1.39)	21.0 (0.92)	2.907
	22	11.3 (1)	17.3 (1.53)	5.8 (0.52)	1.421
	28.6	4.9 (1)	8.1 (1.66)	1 (0.20)	0.614
	33.8	4.8 (1)	7.9 (1.65)	0.5 (0.1)	0.595

[a] Mol % determined by weight, ±1% of the indicated value. [b] The total exchange represents the number of mol protons exchanged per mol isopentane. The maximum value is 12. [c] Determined by ^1H, ^2H NMR, ±3% of the indicated value.

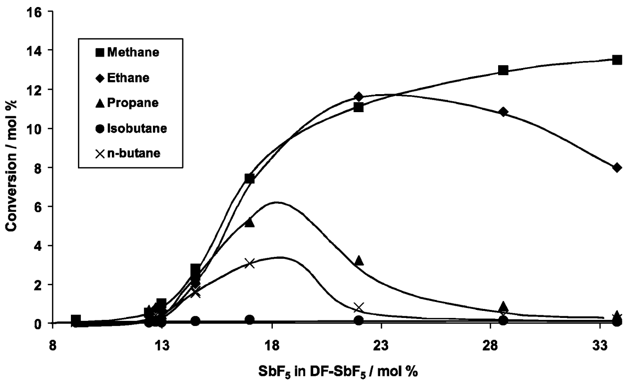


Fig. 4 Alkane distribution in the recovered gas phase after reaction of isopentane in DF–SbF$_5$ at various SbF$_5$ concentrations (isopentane is omitted for clarity).

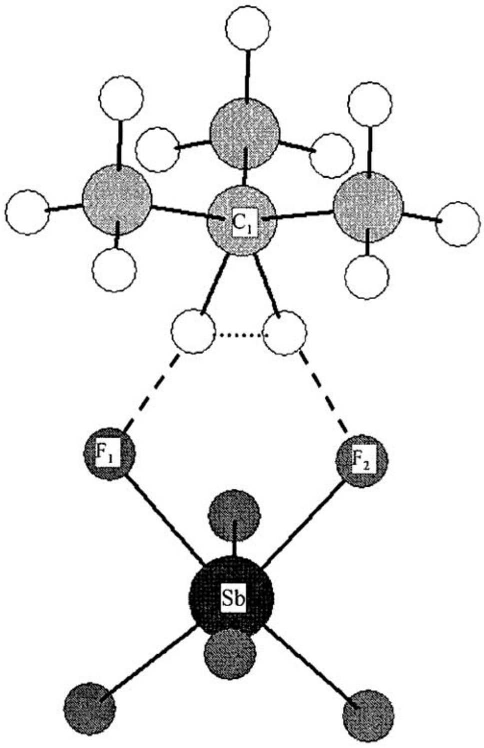


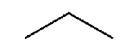
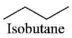
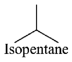
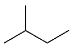
Fig. 5 Geometry of the transition state for protonation in the tertiary C–H bond of isobutane (H/H exchange) suggested by Mota et al. in ref. 9a.

Table 2 for SbF$_5$ concentrations of about 12 mol %. Data for isobutane and *n*-butane reported in this table were previously published.[12,24]

The secondary/primary ratio is the same for propane, *n*-butane and isopentane. The tertiary/primary ratio, however, is quite different between isobutane and isopentane (2.27 and 1.6, respectively), which may be related to the relative reactivity of the tertiary C–H bond as discussed above.

We suggest that in the absence of side reactions such as protolysis and cracking, the rate of exchange following the sequence: tertiary C–H > secondary C–H > primary C–H is in accordance with the relative σ-basicity or proton acceptor ability of these bonds. The relative enthalpies calculated for 1-H-isobutonium and 2-H-isobutonium show a much larger difference (17 kcal mol^{-1}) than expected for the H/D exchange reactions.[a] This can be rationalized both by the fact that our results are obtained in the condensed phase and that the exchange occurs *via* a concerted mechanism in the alkane-acid complex. This is also in line with the H/D exchange experiments and calculations performed on the methane/acidic zeolite system, albeit at much higher temperatures.[25,26] It is interesting to note that the relative rates, going from 1 for primary hydrons to 1.60 for tertiary hydrons, show only a very small difference in comparison with the large difference in reactivity when the bonds undergo protolytic cleavage to generate primary, secondary or tertiary carbenium ions.

Table 2 H/D exchange observed in small alkanes reacted with DF–SbF$_5$[a]

	SbF$_5$/mol % in DF[b]	Exchange on/atom %[c] Primary C–H	 Secondary C–H	 Tertiary C–H
Propane 	12	12.0	16.5	
		1	*1.38*	
n-butane [d] 	12.7	28.1	38.9	
		1	*1.38*	
Isobutane [e] 	12.7	7.7		17.5
		1		*2.27*
Isopentane 	12.4	12.1	16.2	19.3
		1	*1.34*	*1.60*

[a] All the numbers in italics are normalized to the exchange in the primary position. [b] Mol % determined by weight, ±1% of the indicated value. [c] Determined by ^1H, ^2H NMR, ±3% of the indicated value. [d] See ref. 24 for complete study. [e] See ref. 12 for complete study.

Conclusion

The behavior of small alkanes in nonoxidizing liquid superacids is typical of an acid-base reaction. The H/D exchange in DF–SbF$_5$ takes place in the protonated alkane-acid complex. At SbF$_5$ concentrations in DF–SbF$_5$ below 15 mol %, in the presence of carbon monoxide, rapid reversible hydron exchange occurs on all C–H bonds with negligible competition of side reactions. It is noteworthy to underline that the relative rates of the reversible protonation are in the same order of magnitude of the basicity of the σ-bonds, following the concept developed by Olah, and do not follow the large order of magnitude of the usual relative reactivity of these bonds associated with the activation energy needed to generate primary, secondary and tertiary carbenium ions.

Experimental

Experimental procedures

Isopentane. CO was bubbled in isopentane at −10 °C in order to obtain an alkane partial pressure of approximately 175 Torr and a 1 : 3 molar ratio of alkane–carbon monoxide. This mixture was bubbled for 20 min at a rate of 4 mL min^{-1} at atmospheric pressure through 1 mL of DF–SbF$_5$ superacid in a KelF reactor at −10 °C.

Propane. The alkane and carbon monoxide (1 : 3 molar ratio) mixture was bubbled for 30 min at a rate of 4 mL min^{-1} at atmospheric pressure through 1 mL of DF–SbF$_5$ superacid in a KelF reactor at −10 °C.

In both cases the gaseous products were analysed by GC and further condensed at −119 °C for ^1H and ^2H NMR analysis to determine the deuterium content. The superacid reaction mixture containing the oxocarbenium 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 after addition of a given amount of cyclohexanone as internal standard.

Expression of the H/D exchange

To express the amount of hydrons that have been exchanged at the different carbon atoms of the alkane we generally use the unit atom % referring to the amount of H exchanged by D to the initial amount of H times 100.

To calculate the total amount of protons exchanged by D in the alkane we sum up all the exchange values obtained for each position in atom % multiplied by the number of hydrons in this position. Example for propane in DF–SbF_5, 12 mol % SbF_5 : exchange in the methyl groups : 12 atom % (of each primary hydron) and in the methylene group : 16.5 atom % (of each secondary position). Total exchange in mol % per mol propane: $6 \times 12\% + 2 \times 16.5\% = 105$ mol % H exchanged for D in propane.

NMR measurements

^1H and ^2H NMR spectra were recorded on a Bruker AM 400 (400 MHz) spectrometer. Quantitative and qualitative deuterium content was calculated by comparison of the ^1H and ^2H NMR spectra recorded after addition of an adequate amount of freon-113 ($CF_2ClCClF_2$) solution of a CD_3Cl–$CHCl_3$ mixture used as internal standard.

Gas chromatography

The analysis of hydrocarbons were performed on a Girdel 300 with FID detector using a packed Hayesed R column ($Ø = 1/8''$, $l = 2$ m). Helium was used as carrier gas. The concentration of H_2 (HD in our case) was determined on an Intersmat IGC 112M equipped with a 5 Å molecular sieve. Argon was employed as carrier gas. The results were computed on a Delsi Instrument ENICA recorder integrator.

Acknowledgements

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