Chem. Rev. 1982, 82, 591-614

Thermodynamic Behavior of Alkanes in Superacid Media

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Received May 21, 1982

Contents

I. Introduction

The study of the behavior of saturated hydrocarbons in highly acidic media led to the discovery of their isomerization, observed for the first time in 1902 in the transformation with aluminum chloride of cyclohexane into methylcyclopentane.[1,2] A catalytic cracking with $AlCl_3$ was described later;[3] subsequently, alkylation reactions have been carried out with $AlCl_3$[4] and in sulfuric acid.[5] These acid-catalyzed transformations of saturated hydrocarbons (fragmentation, alkylation, isomerization) were generally considered to be carbocation reactions involving trivalent carbenium ions.[6–10]

Direct evidence for the existence and structures of alkylcarbenium ions became possible largely through the application of NMR spectroscopy and the use of superacid media.[11,12] The observation of long-lived carbocations has opened a wide field of investigation, first concerning the physicochemical properties of these species and then relative to reactions that can proceed from them.[13–16] In this respect, the catalytic isomerization or alkylation of alkanes, of special interest for the upgrading of motor fuels, may be regarded as one of the most promising applications of superacid media.

TABLE I. Conversion Ratios in the Isomerization of *n*-Hexane with Different Catalysts

catalyst	working temp, °C	2,2DMBH[a] mole ratio, %
Pt/zeolite	~250	20
Pt/chlorinated alumina	~150	29
$AlCl_3$-$SbCl_3$	~85	36
SbF_5-HF	~25	53

[a] 2,2-Dimethylbutane.

The isomerization of alkanes being slightly exothermic, the reaction is enhanced by a decrease of temperature. Table I shows that the superacid catalyst (HF + SbF_5) leads to higher ratios of conversion than the conventional processes. In superacid media, the isomerization process is represented as follows:

$$n\text{-RH} + H^+ \rightleftarrows n\text{-RH}_2^+ \rightleftarrows n\text{-R}^+ + H_2 \qquad (1)$$

$$n\text{-R}^+ \rightleftarrows i\text{-R}^+ \qquad (2)$$

$$i\text{-R}^+ + H_2(n\text{-RH}) \rightleftarrows i\text{-RH} + H^+(n\text{-R}^+) \qquad (3)$$

The initial step (reaction 1) is an oxidation process by H^+ ion into the carbenium ion n-R^+ through a pentacoordinated carbonium n-RH_2^+ resulting from the basic nature of n-RH. The existence of such species has not been proved by spectroscopic methods, but the participation in the process of a three-center bound pentacoordinated carbonium ion raised a controversy[17–21] that we shall not enter. The carbenium ion n-R^+ is rearranged into the more stable ion i-R^+ (branched cation), which is reduced by hydrogen or the excess of alkane n-RH. After an induction period, corresponding to the saturation of the acid phase by carbenium ions, the process is catalytic.

In practice, the overall reaction is not so simple; side reactions, such as condensation, cracking, or alkylation, are observed. From the amount of data published on the chemistry of alkanes in superacid media, the acidity level of the solvent appears to be a major parameter in the orientation of the different reactions. As the acidity levels of the various superacid media present differences that can affect the reactions, it is of prime importance to establish a quantitative scale of these levels;[22] this is the subject of section II.

Recent studies have shown the influence of the acidity level on the reactivity of two hydrocarbons in anhydrous hydrogen fluoride–isopentane[23] and –methylcyclopentane.[24] Furthermore, thermochemical data of the redox reactions in which these two compounds are involved have been determined and represented under the form of a potential–acidity diagram that traduces the reactivity of an alkane as a function of the acidity level. Thus, taking into account these results

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and thermochemical data from literature, it is possible to calculate the thermochemical properties of any alkane and to describe, from the thermodynamic point of view, its reactivity as a function of the acidity level of the solvent.[25] This is realized for alkanes from methane to hexanes; then the comparison between experimental results and thermochemical previsions is widely discussed and conditions (choice of a medium) for alkylation or isomerization reactions are deduced.

II. ***Superacid Media***

The most acidic media known are made up by dissolving strong Lewis acids, such as BF_3, TaF_5, or SbF_5, in solvents that are strong Brønsted acids, such as hydrogen fluoride, sulfuric acid, fluorosulfuric acid, or perfluoroalkanesulfonic acid; these solutions are currently referred to as "superacid media", according to a designation introduced by Gillespie, who has assigned it to any solution in which the activity of H^+ ion is greater than it is in pure sulfuric acid.[26]

A. Acidity Scale of the Solvent

The superacid media being made up with a protonic acid HS as a solvent, the acido-basic properties are related to the autoprotolysis equilibrium of HS. We present the acidity scale in anhydrous hydrogen fluoride; the results are easily transferred to other solvents. In HF, the autoprotolysis equilibrium is represented as

$$HF \rightleftarrows H^+ + F^- \qquad (4)$$

where H^+ and F^- represent the solvated species.

The acidity of the medium (H^+ activity, a_{H^+}) is defined by the thermodynamical standard unit.

$$pH = -\log a_{H^+}$$

The acidity parameter is reduced to

$$pH = -\log [H^+]$$

in the same way as aqueous solutions in diluted ones,[27-29] and related to the autoprotolysis constant K_i of equilibrium 4 as follows:

$$K_i = [H^+][F^-]$$

or

$$pH + pF = pK_i$$

The value of pK_i ($=-\log K_i$) determines the length of the acidity scale of diluted solutions; pH = 0 corresponds to a 1 M solution of a strong acid ($[H^+] = 1$ M), and pH = pK_i corresponds to a 1 M solution of a strong base ($[F^-] = 1$ M).

The autoprotolysis constants of the different solvents HS have been determined by various methods: conductimetric measurements,[30-35] acidity function determinations,[36-39] or potentiometric titrations.[40-42] The more reliable values are reported in Table II; among the different solvents, hydrogen fluoride presents the widest acidity scale (nearly 14 units), which represents a large variation of the H^+ ion activity by a factor of about 10^{14} from basic media ($[F] = 1$ M) up to acid media ($[H^+] = 1$ M).

It stands to reason that the H^+ ion activity variations are not restricted to the acidity scale. There is a continuous increase of H^+ ion activity from aqueous solutions up to superacid mixtures ($HS + MF_n$) through the

TABLE II. Acidity Properties of Various Solvents for Superacid Media[a]

superacid media	pK_i	H	$R_0(H)$
HF, $[H^+] = 1$ M, pH 0		−20.5	−27.9
neat	13.7	−11.0	−21.1
$[KF] = 1$ M, pH = pK_i		−8.4	−14.2
HSO_3F, $[H^+] = 1$ M, pH 0		−19.4	
neat	7.4	−15.0	
$[SO_3F^-] = 1$ M, pH = pK_i		−11.5	
H_2SO_4, $[H^+] = 1$ M, pH = 0		−14.0	
neat	3.6	−12.1	
$[HSO_4^-] = 1$ M, pH = pK_i		−10.4	
CF_3SO_3H (neat)	?	−14.1	
$C_2F_5SO_3H$ (neat)	?	−14.0	
$C_2F_5SO_3H$-SbF_5 (10% mol)		−18.4	

[a] pK_i (= −log K_i) autoprotolysis constant.

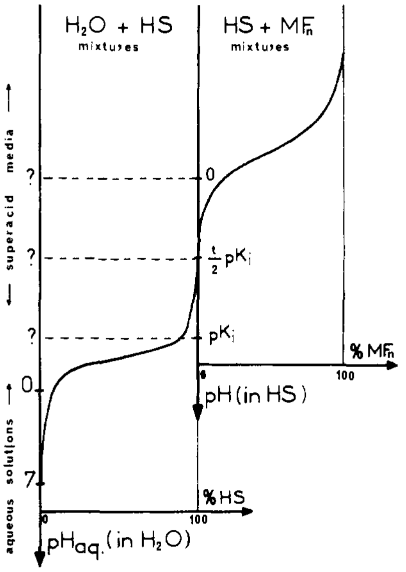


Figure 1. Schematic diagram of the acidity increase from aqueous solutions up to superacid mixtures.

H_2O + HS mixtures and then HS solvent (Figure 1).

In order to analyze the reactions, a pH measure that is independent of the solvent but related to the composition of the media is needed. The acidity is then thermodynamically defined according to the relation between the chemical potential μ_{H^+} and the activity a_{H^+}:

$$\mathrm{pH} = -\log a_{H^+} = \frac{\mu^\circ_{H^+} - \mu_{H^+}}{2.3RT}$$

where pH = 0 corresponds to the reference state (in general aqueous solutions).

In practice, experimental measurements lead only to approximations of pH through the acidity functions (see section IIB).

The acid character of the solvents HS enhances the basicity of a great number of compounds that are weak bases in water. In contrast, it is difficult to find strong acids in HS because of its low basicity: inorganic acids, such as HCl or $HClO_4$, which are strong acids in water, behave in HS solvents as weak acids.[43] The strongest acids are Lewis acids, such as SbF_5 and TaF_5, according to the acid–base equilibrium 5:

$$MF_n + HF \rightleftarrows MF_{n+1}^- + H^+ \qquad (5)$$

characterized by the acidity constant

$$K_A = \frac{a_{H^+}a_{MF_{n+1}^-}}{a_{MF_n}}$$

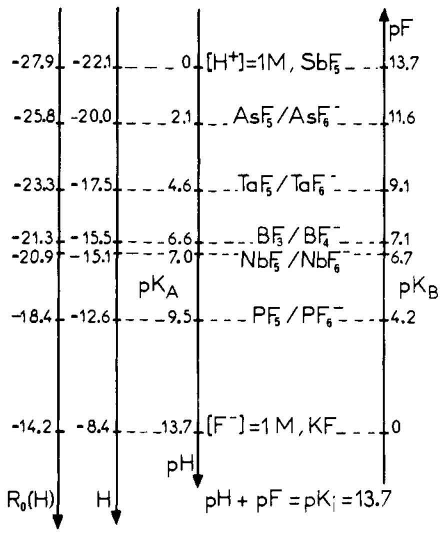


Figure 2. Acidity scale in anhydrous hydrogen fluoride: $pK_A = -\log [H^+][MF_{n+1}]/[MF_n]$ (= $pK_i - pK_B$). The acidity scale has been placed against the acidity functions H and $R_0(H)$ (see section IIB).

The determination of the strength of the Lewis acids MF_n has been carried out in the different solvents HS. Numerous techniques have been applied: conductivity measurements,[30,44–51] cryoscopy,[49,50] aromatic hydrocarbons extraction,[52,53] solubility measurements,[54–56] kinetic parameters determinations,[57–59] electroanalytical techniques (hydrogen electrode),[41,60–62] quinones systems as pH indicators,[22,40,43,63] or other electrochemical systems,[64,65] and acidity function H_0 determinations, with UV–visible spectroscopy[36–39,44,66–69] or with NMR spectroscopy.[70–73] The results were somewhat contradictory, but the order of the strength is now well established. The acidity scale in anhydrous hydrogen fluoride is presented in Figure 2, with the acidity constants of various Lewis acids allowed to buffer the medium to a pH value equal to

$$\mathrm{pH} = pK_A - \log \frac{a_{MF_n}}{a_{MF_{n+1}^-}} \quad (pK_A = -\log K_A)$$

or in diluted solutions pH = $pK_A - \log [MF_n]/[MF_{n+1}^-]$.

In hydrogen fluoride, the strength of the acids is decreasing in the order $SbF_5 > AsF_5 > TaF_5 > BF_3 > NbF_5$.

B. General Acidity Scale

A complete interpretation of the reactivity of alkanes needs a comparison between the acidity levels of the various superacid media. The general way is to translate the H^+ ion activity into pH_{aq}, which is a universal unit (Figure 1). Then, we can consider as an absolute acidity scale the chemical potential scale $\mu^\circ_{H^+}$ (HS) of H^+ ion (whatever the solvent is); the origin of the scale will be the standard chemical potential of H^+ in water $\mu^\circ_{H^+}(aq)$.[27,28] The value $\mu^\circ_{H^+}(HS) - \mu^\circ_{H}(aq)$ is equal to the free energy of H^+ ion transfer from the solvent HS to water:

$$\Delta G_t{}^{HS}{}_{aq} = \mu^\circ_{H^+}(HS) - \mu^\circ_{H^+}(aq) = 2.3RT \log \Gamma_{H^+}(HS)$$

where $\Gamma_{H^+}(HS)$ represents the activity coefficient of H^+ transfer.

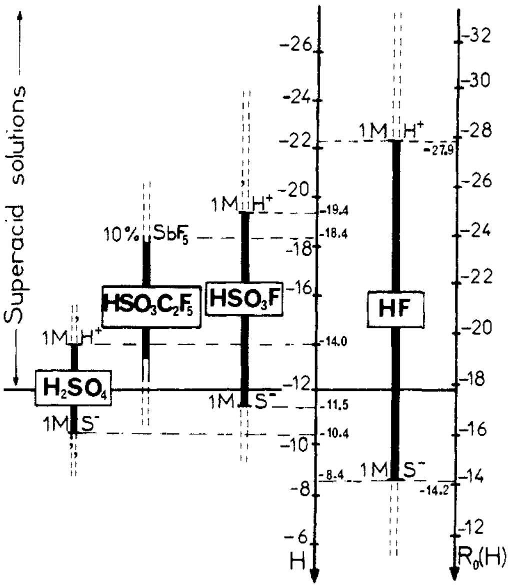


Figure 3. General acidity scale of the various superacid media (the acidity domains (pK_i) are represented by full lines).

According to this definition, a solution in HS whose acidity is equal to pH (HS) corresponds to an absolute acidity value, pH_{aq}, equal to

$$pH_{aq} = pH(HS) - \log \Gamma_{H^+}(HS)$$

As mentioned above, the experimental measurements lead only to approximations of pH_{aq} in the different solvents. Two principal methods have been developed whose characteristics have been widely discussed:[29,74,75] the Hammett acidity function H[76,77] and the Strehlow redox acidity function $R_0(H)$.[78-80]

The Hammett acidity functions in the various superacid media are well-known.[36-39,44,66-73,81] The H values of neat solvents and the values of the limits of the acidity domains ($[H^+] = 1$ M and $[S^-] = 1$ M) are reported in Table II, except for the perfluoroalkanesulfonic acids, whose autoprotolysis constants are not known.[81]

The acidity domains of the different solvents HS are represented by full lines in Figure 3. If we assume that the H function represents the H^+ activity in HS, the H value of a molar acidic solution (pH(HS) = 0) is calculated by the relation

$$H(pH(HS) = 0) = H(pH(HS) = pK_i(HS)) - pK_i(HS)$$

$H(pH(HS) = pK_i(HS))$ corresponding to a molar basic solution in HS ($[S^-] = 1$ M).

Therefore, the value of the neat solvent is evaluated in the same manner:

$$H(\text{neat HS}) = H(pH(HS) = pK_i(HS)) - 0.5pK_i(HS)$$

The differences between calculated and experimental H values may be attributed for the H_0 value of the neat solvent to the difficulties to get perfectly neat solvents (without H_2O, which is a strong base in these media) and for the acidic media to the method that requires a set of indicators (whose number increases with the value of pK_i) and the assumption on the equality of the indicators activity coefficients.

The Strehlow redox function $R_0(H)$ affords a simple means of the H^+ activity at any acid concentration from two emf measurements, in contrast to the laborious indicator procedure. Few data have been reported in literature on the determination of this redox function. $R_0(H)$ functions have been determined in $H_2O-H_2SO_4$[78,82,83] or R_FSO_3H[84] and in basic or slightly acidic hydrogen fluoride.[40,43,61]

In Figure 3, the $R_0(H)$ acidity scale has been placed against the H acidity scale with respect to the values of the H and $R_0(H)$ functions in a molar basic solution in hydrogen fluoride; that is:

$$H(\text{HF, KF 1 M}) = -8.4 \text{ (ref 66)}$$

$$R_0(H)(\text{HF, KF 1 M}) = -14.2 \text{ (ref 40, 43)}$$

Then, the values of H functions are translated into $R_0(H)$ functions: $R_0(H) = H - 5.8$. When the same procedure as above is used, the $R_0(H)$ values are calculated, whatever the acidity level, according to

$$R_0(H)(pH(HS)) = R_0(H)(pH(HS) = 0) + pH(HS)$$

Figure 3 shows the great interest of the media derived from hydrogen fluoride: first, its acidity range covers the acidity ranges of the other systems; second, it provides acidity levels which can be held to be the highest protonic levels (the use of highly concentrated SbF_5 mixtures or neat SbF_5 affords very high acidity levels up to $H_0 \simeq -26$[73] ($R_0(H) \simeq -32$), and third, the oxidizing action of SO_3 has not to be considered (see section IIC).

It can be seen that the acidity of superacid media runs from $H_0 \simeq -12$ ($R_0(H) \simeq -18$) up to $H_0 < -22$ ($R_0(H) < -28$); such highly negative values attest the exceedingly weak solvation energy of H^+ ion. Furthermore, the Gibbs free energy H^+ ion in any medium may be evaluated with respect to the free energy H^+ ion formation in water[85-88] according to the relation defined above:

$$\Delta G_t{}^{HS}{}_{aq} = 2.3RT \log \Gamma_H(HS)$$

Hence, in hydrogen fluoride, if we assume on one hand that the H function represents $-\log \Gamma_{H^+}(HS)$, transfer from water involves a change of about 29 units, which leads to a value of $\Delta G_f(H^+) \simeq 137$ kcal mol^{-1}; on the other hand, if the $R_0(H)$ function represents $-\log \Gamma_{H^+}(HS)$, transfer from water involves a change of about 35 units, which leads to a value of $\Delta G_f(H^+) \simeq 144$ kcal mol^{-1}.

C. Oxidizing Power of Superacid Media

Since the first paper reported on the formation of alkylcarbenium ions from alkanes,[12] according to the redox reaction

$$RH + H^+ \rightleftarrows R^+ + H_2 \qquad (6)$$

the claim that alkanes reacted by protonation followed by loss of hydrogen was clouded by the fact that the necessary quantity of H_2 was not always observed. It was suggested that other oxidizing agents must participate to the oxidation of alkanes. Larsen[89] proposed a thermochemical analysis of various oxidation processes according to superacid media.

In the superacid media derived from HSO_3F, the reduction of HSO_3F by hydrogen is exothermic[89] and thus may occur. Furthermore, the oxidation of alkanes in HSO_3F by SO_3 has been shown;[90-92] SO_3 is produced by the dissociation of HSO_3F into HF and SO_3,[33,34,93] the overall oxidation process being

$$RH + 3HSO_3F \rightarrow R^+ + SO_3F^- + SO_2 + 2HF + H_2SO_4 \quad (7)$$

In the mixtures $HSO_3F + SbF_5$, SbF_5 participates in the oxidation of alkanes[94] as was earlier observed in the oxidation of hydrocarbons by $SbCl_5$.[95]

In sulfuric acid, it has been established much earlier than the formation of carbenium ions from alkanes proceeds via the reduction of sulfuric acid into SO_2.[96,97]

In the media derived from hydrogen fluoride, the standard potential of the redox couple H^+/H_2 has been determined by the use of a hydrogen electrode:[22,60]

$$E°(H^+/H_2) = 0.226 \text{ V } (P_{H_2} = 1 \text{ atm})$$

(potentials are measured vs. the $Ag/AgSbF_6$ reference electrode[64]). It was also established that AsF_5 is a stronger oxidant than H^+ ion; indeed, in SbF_5 solutions, AsF_5 is slowly reduced by hydrogen (at 0 °C under atmospheric pressure) into AsF_3 while in basic media, where the predominating form of AsF_5 is AsF_6^-, reduction is not observed (or too slow to be noticeable).[22,60]

If the procedure of Larsen[89] is followed and one takes into account the formation enthalpies of the compounds,[98-100] the reduction of AsF_5 by H_2 is found to be highly exothermic (the solvation enthalpies are neglected):

$$\underset{-296}{AsF_5} + \underset{0}{H_2} \rightarrow \underset{-229}{AsF_3} + \underset{-72}{2HF} \quad (8)$$

$$\Delta H_8 = -77 \text{ kcal mol}^{-1}$$

In fact, taking into account the electrochemical reduction potential of AsF_5 and the standard redox potential of H^+/H_2, the free energy of reaction 8 is found to be about -5 kcal mol^{-1}. Thus, in such thermodynamical calculations, the solvation terms must not be neglected.

If we apply Larsen's procedure to the symmetrical reaction 9 in which solvation terms may cancel out AsF_5

$$\underset{-296}{AsF_5} + \underset{-219}{SbF_3} \rightarrow \underset{-229}{AsF_3} + \underset{-330}{SbF_5} \quad (9)$$

$$\Delta H_9 = -44 \text{ kcal mol}^{-1}$$

is found to be a higher oxidant than SbF_5.

With respect to the oxidizing power of SbF_5, the results are somewhat contradictory. An electrochemical study of the antimony system in HF did not lead to the standard potential of the redox couples because the electrochemical systems are irreversible.[101]

By application of classical thermodynamics, Larsen[89] calculated that the reduction of SbF_5 by H_2 is nicely exothermic:

$$\underset{-330}{SbF_5} + \underset{0}{H_2} \rightarrow \underset{-219}{SbF_3} + \underset{-72}{2HF} \quad (10)$$

$$\Delta H_{10} = -33 \text{ kcal mol}^{-1}$$

The calculated value of ΔH_{10} does not afford a definitive conclusion SbF_5 being a weaker oxidant than AsF_5 and taking into account the difference between calculations and experimental estimations.

The oxidation of alkanes or hydrogen by SbF_5 has been observed in various experiments:[94,102-105] hydrogen is oxidized by SbF_5 at room temperature under high pressure, $p_{H_2} = 50$ atm;[102-104] in highly concentrated solutions of SbF_5, neat SbF_5, or SbF_5 in SO_2 or SO_2ClF, alkanes are oxidized by SbF_5 according to reaction 11.[94]

$$RH + 5SbF_5 \rightarrow RSb_2F_{11} + HSb_2F_{11} + SbF_3 \quad (11)$$

This reaction, suggested in the oxidation of methane, would be followed in the oxidation of isobutane by

$$RH + HSb_2F_{11} \rightarrow RSb_2F_{11} + H_2 \quad (12)$$

In contrast, it has been shown that hydrogen is not oxidized by SbF_5 diluted in HF or HSO_3F.[90,106-108] Furthermore, a polarographic determination of SbF_3[109] in HF + SbF_5 mixtures (SbF_5 up to 4 M), in which n-pentane was previously isomerized under hydrogen pressure, did not lead to evidence for SbF_5 reduction in the process.[110]

The oxidizing power of SbF_5 is still ill-defined, SbF_5 behaving as a strong acid in diluted solutions; its predominating form is SbF_6^-.[64] Thus, as for AsF_5, the reduction of the anionic form may not occur (or is too slow), while in concentrated solutions or in neat SbF_5, free SbF_5 (or polymerized forms $Sb_nF_{5n+1}^-$[44,46,111,112]) may be slowly reduced by hydrogen or alkanes. However, if the oxidizing power of SbF_5 is not well established, one can see that the media derived from hydrogen fluoride offer the advantage over other media that the oxidizing action of SO_3 does not have to be considered. In the following sections, we shall consider that H^+ ion is the principal oxidant of alkanes.

III. Establishment of the Thermochemical Properties of Alkanes

The acidity range in superacid media runs from an H value of -12 to -26 (see section IIB), which means an increase of the H^+ activity of 10^{14} from the lower limit up to the higher one. Such an increase must change the redox properties of alkanes in these media; this is confirmed by studies of the chemical behavior of isopentane[23] and methylcyclopentane[24] in hydrogen fluoride. The reactivity of these two compounds is represented under the form of a potential acidity diagram (Pourbaix's type).

A. General Representation of Alkane Reactivity

The in situ determination of alkane concentration, by electrochemical methods, allowed quantitative analysis of the reactions in which the two hydrocarbons are involved. Different reactions were observed according to the acidity level, and their equilibrium constants were determined.[23,24]

1. Oxidation of RH into Carbenium Ion R^+

As expected, isopentane and methylcyclopentane undergo chemical oxidation by H^+ ion in acidic HF:

$$RH + H^+ \rightleftarrows R^+ + H_2 \quad (6)$$

characterized by the constant K_R:

$$K_R = \frac{[R^+]P_{H_2}}{[RH][H^+]} = R_R\frac{P_{H_2}}{[H^+]}$$

The oxidation process is the sum of the two electrochemical reactions:

$$2H^+ + 2e^- \rightarrow H_2,\ E°(H^+/H_2)$$

$$RH \rightarrow R^+ + H^+ + 2e^-,\ E°(R^+/RH)$$

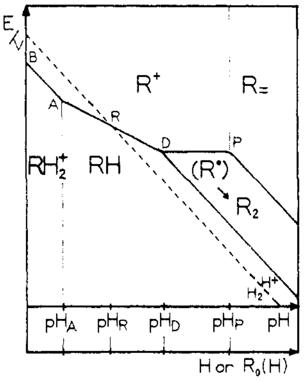


Figure 4. General potential-acidity diagram of an alkane RH in hydrogen fluoride. The potential-acidity diagram of RH (full lines) is placed against the H^+/H_2 system (dashed line).

Therefore, the constant K_R is related to the standard potentials of the redox couples R^+/RH and H^+/H_2 according to

$$\frac{2.3RT}{2F} \log K_R = E°(H^+/H_2) - E°(R^+/RH)$$

The experimental determination of the ratio R_R led to the calculation of K_R and $E°(R^+/RH)$, which allows one to plot the part B–D of the potential–acidity diagram (Figure 4) vs. the H^+/H_2 system.[22,60] The ensuing crossing ($pH_R = \log K_R$) of the two lines representing the H^+/H_2 and R^+/RH systems means that spontaneous oxidation of RH into R^+ runs almost to completeness at pH values lower than pH_R and no longer takes place when the acidity level is too low ($pH > pH_R$).

In SbF_5 solutions, the ratio R_R becomes independent of pH. This means that the oxidation process does not imply the H^+ ion; that is to say that RH is protonated into the carbonium ion, as follows:

$$RH + H^+ \rightleftarrows RH_2^+ \qquad (13)$$

which liberates H_2 to yield the carbenium ion R^+.

Reaction 13 renders an account of the basic nature of RH; point A represents the acidity level of RH protonation:

$$pH_A = pK_A\ (-\log K_A) = \log \frac{[RH_2^+]}{[RH][H^+]}$$

where K_A is the acidity constant of RH_2^+.

2. Alkylation of RH by R^+

In basic media, a different behavior has been observed: the addition of R^+ to a RH solution produces a decrease of the RH concentration. This is interpreted by the production of a redox reaction between R^+ (oxidation state +II) and RH (oxidation state 0), yielding the radical oxidation state (+ I, R·), which gives at first a dimer RR and then polymeric species, as follows:

$$R^+ + RH \rightleftarrows RR\ (2R\cdot) + H^+ \qquad (14)$$

Then

$$R^+ + R_xH \rightleftarrows R_{x+1} + H^+ \qquad (15)$$

or

$$R^+ + R_xH \rightleftarrows R_x^+ + RH \qquad (16)$$

TABLE III. Characteristics of Potential-Acidity Diagrams[a] of Isopentane[23] and Methylcyclopentane[24] in HF (at 0 °C)

alkane, RH	A RH_2^+/RH	R R^+/RH	D $RR/R^+,RH$	P $R^+/R_=$
i-C_5H pH (HF)	1.2	2.7	5.7	>13.7
H	−20.9	−19.4	−16.4	>−8.4
R_0(H)	−26.7	−25.2	−22.2	>−14.2
MCPH, pH (HF)	2.3	4.2	8.1	>13.7
H	−19.8	−17.9	−14.0	>−8.4
.R_0(H)	−25.6	−23.7	−19.8	>−14.2

[a] Acidity level of protonation of alkane (A), oxidation of alkane into carbenium ion (R), disproportionation of the dimer (D), and protonation of alkene (P). The conjugate bases (alkenes) of isopentyl and methylcyclopentyl ions are strong bases.[113,114]

Reaction 14 is the sum of the two electrochemical reactions:

$$2R^+ + 2e^- \rightarrow RR\ (2R\cdot),\ E°(R^+/RR)$$

$$2RH \rightarrow RR(2R\cdot) + 2H^+ + 2e^-,\ E°(RR/RH)$$

and, therefore, the equilibrium constant K_D of reaction 14

$$K_D = \frac{[RR][H^+]}{[RH][R^+]}$$

is related to the standard potentials of the redox couples R^+/RR and RR/RH according to

$$\frac{2.3RT}{2F} \log K_D = E°(R^+/RR) - E°(RR/RH)$$

Thus, the experimental determination of K_D led to the determination of the standard potentials of these two redox couples and to complete the potential–acidity diagram (Figure 4). The diagram shows the radical oxidation state domain, which is limited on the acid side by pH_D ($=pK_D = -\log K_D$). In basic media, alkene ($R_=$) becomes the predominating form of the R^+ oxidation state, according to

$$R^+ \rightleftarrows R_= + H^+ \qquad (17)$$

characterized by the acidity constant K_P

$$K_P = \frac{[R_=][H^+]}{[R^+]}$$

The acidity level of alkane protonation is represented by pH_P ($=-\log K_P = pK_P$).

The characteristics of the experimental potential–acidity diagrams of isopentane and methylcyclopentane are reported in Table III. The potential–acidity diagram of RH (Figure 4) shows that RH oxidation by H^+ directly gives the carbocation R^+, only in acidity levels higher than H_D; however, there is an equilibrium between the various species over the whole acidity range (ΔG's are slightly positive for $pH > pH_D$). In basic media, the formation of radicals enhances condensation reactions that can be followed by polymerization or cracking.

Such a potential–acidity diagram, which represents the variation of redox properties of hydrocarbon with acidity, should be established for other alkanes. In fact, most of them did not appear susceptible to the same experimental determinations because of side reactions: isomerization or high reactivity of the carbenium ions. Nevertheless, it is possible to calculate their equilibrium characteristics by estimating the differences between them and those pertaining to isopentane.

B. Standard Potentials of Redox Couples of Alkanes

The standard potentials of redox couples of alkanes (from methane to hexanes) are calculated at the temperature of 0 °C in HF; the general acidity scale permits transfer of the results in the other superacid media. The following abbreviations have been used to represent the alkanes: C_1H, methane; C_2H, ethane; C_3H, propane; n-C_4H, n-butane; i-C_4H, isobutane; n-C_5H, n-pentane; i-C_5H, isopentane; neo-C_5H, neopentane; n-C_6H, n-hexane; 2MPH, 2-methylpentane; 3MPH, 3-methylpentane; 22DMBH, 2,2-dimethylbutane; 23DMBH, 2,3-dimethylbutane.

The redox couples of alkanes that we consider are

$$R^+ + H^+ + 2e^- \rightarrow RH$$

$$2R^+ + 2e^- \rightarrow RR$$

$$RR + 2H^+ + 2e^- \rightarrow 2RH$$

and represented by the general electrochemical reaction

$$\mathrm{Ox}_i(\mathrm{RH}) + 2e^- \rightarrow \mathrm{Red}_i(\mathrm{RH}) \text{ with } i = 1, 2, \text{ or } 3$$

which is characterized by the standard potential $E°[\mathrm{Ox}_i(\mathrm{RH})/\mathrm{Red}_i(\mathrm{RH})]$.

The procedure is to calculate the Gibbs free energies of the redox reactions between the redox couples of isopentane, i-C_5H, (reference alkane), and those of the alkane RH,

$$\mathrm{Ox}_i(i\text{-}C_5H) + \mathrm{Red}_i(\mathrm{RH}) \rightleftarrows \mathrm{Red}_i(i\text{-}C_5H) + \mathrm{Ox}_i(\mathrm{RH}) \tag{18}$$

where $\Delta G_i(\mathrm{RH}) = \Delta G_{18} = \Delta G_f(\mathrm{Ox}_i(\mathrm{RH})) - \Delta G_f(\mathrm{Ox}_i(i\text{-}C_5H)) - |\Delta G_f(\mathrm{Red}_i(\mathrm{RH})) - \Delta G_f(\mathrm{Red}_i(i\text{-}C_5H))|$.

From the experimental determination of the standard potentials $E°(\mathrm{Ox}_i(i\text{-}C_5H)/\mathrm{Red}_i(i\text{-}C_5H))$,[23] the calculation of $\Delta G_i(\mathrm{RH})$ leads to the determination of the standard potentials $E°(\mathrm{Ox}_i(\mathrm{RH})/\mathrm{Red}_i(\mathrm{RH}))$ according to

$$E°(\mathrm{Ox}_i(\mathrm{RH})/\mathrm{Red}_i(\mathrm{RH})) = E°(\mathrm{Ox}_i(i\text{-}C_5H)/\mathrm{Red}_i(i\text{-}C_5H)) + \frac{\Delta G_i(\mathrm{RH})}{2F}$$

Such calculations are rigorous if the values of Gibbs free energies take into account the medium in which the reactions take place, either HF or any superacid media, that is, the free energies of solvation of the different species. Unfortunately, these values are not known. Then, we had to make a number of approximations and assumptions, some of which are open to just criticism. However, taking into account the symmetry of reaction 18, the calculations are based on the following hypothesis:[25] (i) the equality of the solvation energies of the different alkanes on one hand and those of the different alkenes on the other was admitted; (ii) the evaluation of the solvation energies of the carbocations ions was made according to a model of electrostatic interactions, developed by Franklin.[115]

The thermochemical properties of alkanes and alkenes are well-known.[116–118] In hydrogen fluoride or superacid media, the solubility determinations show that the alkanes solubility is weak and nearly independent of the hydrocarbon nature.[25,119–123] Thus, we can assume that the solvation energies are equal in the set of the considered hydrocarbons, which is nearly true in water.[124–128] The Gibbs free energies of formation of these species are reported in Table IV.

TABLE IV. Relative Gibbs Free Energies of Formation Redox Couples of Alkanes[a, b]

hydrocarbon	alkane, RH	dimer, R–R	carbenium ion, R^+	alkene $R_=$
C_1H	29.0	62.1	75	
C_2H	23.8	47.1	49	30.5
C_3H	16.3	30.7	25	19.8
n-C_4H	8.7	16.1	19	10.2
i-C_4H	7.6	15.9	8.4	9.1
n-C_5H	1.2	2.1	11	2.2
i-C_5H	0	0	0	0
neo C_5H	−1.2	−1.1	28	
n-C_6H	−6.3	−7.8	3.3	−6.0
2MPH	−7.4	−12.9	−7.8	−8.4
3MPH	−6.9	−10.9	−6.6	−7.9
22DMBH	−8.8	−8.4	−3.6	−2.6
23DMBH	−6.5	−8.1	−7.6	−8.1

[a] kcal mol^{-1}. [b] The Gibbs free energies of formation of isopentane (reference alkane) redox couples are RH −59.0, RR −97.4, R^+ 101.2, and $R_=$ −32.3 kcal mol^{-1}.

The thermochemical properties of carbenium ions R^+ are now well established in the gas phase.[129–140] Unfortunately, their solvation energies are not known in hydrogen fluoride or any superacid media. Arnett et al.[141–144] reported calorimetric measurements of ionization of alkyl halides by SbF_5; the experiments having been carried out in low dissociative solvents (SO_2, SO_2ClF...), the effects of solvation are negligible vs. the ones of Brønsted acids (HF, HSO_3F...). Therefore, the heats of R^+ formation derived from these measurements are of the same order of magnitude as in the gas phase.

A convenient way to evaluate the solvation terms is to proceed by calculation, derived from the Born equation.[115,145,146] The model, proposed by Franklin,[115] of electrostatic interactions leads to the evaluation of the solvation energies in water. We admit that the differences between the solvation terms of R^+ and i-C_5^+ (reference ion) are equal in water and hydrogen fluoride. Despite its easiness to handle,[25] this method has been shown to under estimate the solvation energies;[147] furthermore, in the set of considered cations the delocalization of the positive charge has to be taken into account.[148,149] In fact, as the calculation needs differences of Gibbs free energies of formation between R^+ and i-C_5^+, this method has been found to be satisfactory for parent cations of i-C_5^+ except for light cations ($<C_4^+$), where the solvation terms appeared to be underestimated.[25] Therefore, the solvation energies of these light cations are taken from the values, reported by Jorgensen,[149] derived from molecular orbital calculations. The relative Gibbs free energies of formation of alkylcarbenium ions are reported in Table IV.

The calculation of the Gibbs free energies of the redox reaction 18 for each redox couple of alkanes leads to the alkanes' standard potential in HF (which means at an acidity level of $H = -22.1$ or $R_0(\mathrm{H}) = -27.9$). These values are reported in Table V.

If we apply the calculated Gibbs free energies of formation of isopentane redox couples to the reactions whose constants have been experimentally deter-

TABLE V. Standard Potentials of Redox Couples of Alkanes in Hydrogen Fluoride ($H = -22.1$ or $R_0(\mathrm{H}) = -27.9$)[a]

alkane	$E°(\mathrm{R^+/RH})$	$E°(\mathrm{R^+/RR})$	$E°(\mathrm{RR/RH})$
C_1H	1.15	1.91	0.40
C_2H	0.70	1.10	0.30
C_3H	0.34	0.42	0.27
n-C_4H	0.38	0.48	0.28
i-C_4H	0.17	0.02	0.33
n-C_5H	0.37	0.43	0.30
i-C_5H	0.15[b]	0[b]	0.31[b]
neo-C_5H	0.78	1.24	0.34
n-C_6H	0.36	0.31	0.41
2MPH	0.14	−0.06	0.35
3MPH	0.16	−0.05	0.37
22DMBH	0.26	0.03	0.50
23DMBH	0.13	−0.15	0.41

[a] The potentials (V) are expressed vs. the $Ag/AgSbF_6$ reference electrode.[64] [b] Experimental standard potentials of isopentane redox couples.[23]

TABLE VI. Acidity Constants of Carbenium Ions in Hydrogen Fluoride ($\mathrm{p}K_\mathrm{p}$) and Acidity Levels of Alkene Protonation (H_p or $R_0(\mathrm{H_p})$)[a]

$\mathrm{R^+/R_=}$	$\mathrm{p}K_\mathrm{p}$	H_P	$R_0(\mathrm{H_P})$
$C_2^+/C_{2=}$	0.4	−21.7	−27.5
$C_3^+/C_{3=}$	11.0 (9.5[b])	−11.1	−16.9
n-C_4^+/n-$C_{4=}$	8.1	−14.0	−19.8
i-C_4^+/i-$C_{4=}$	15.8[a] (SB[b])	−6.3 (−8.5[c])	−12.1
n-C_5^+/n-$C_{5=}$	8.2 (8.4[b])	−13.9	−19.7
i-C_5^+/i-$C_{5=}$	15.2 (SB[b])	−6.9	−12.7
n-C_6^+/n-$C_{6=}$	7.8	−14.3	−20.1
$\mathrm{2MP^+/2MP_=}$	14.7	−7.4	−13.2
$\mathrm{3MP^+/3MP_=}$	14.2	−7.9	−13.7
$\mathrm{22DMB^+/22DMB_=}$	16.0	−6.1	−11.3
$\mathrm{23DMB^+/23DMB_=}$	14.8	−7.3	−13.1

[a] Acidity constant reported by Hogeveen et al.[150] when $\mathrm{p}K_\mathrm{p} > 13.7$ ($\mathrm{p}K_\mathrm{i}(\mathrm{HF})$), the alkene is a strong base (SB) in HF. [b] Experimental values from ref 113 and 114. [c] From ref 158, 159.

mined,[23] the Gibbs free energy of H^+ ion formation is thus evaluated: On one hand, reaction 6 in HF is exoenergetic ($\Delta G_6 = -2.3RT \log K_\mathrm{R} = -3.4$ kcal mol^{-1}):

$$\begin{array}{cccccccc} i\text{-}C_5H & + & H^+ & \rightleftarrows & i\text{-}C_5^+ & + & H_2 \\ -59.0 & & ? & & 101.2 & & -8.5 \end{array} \qquad (6)$$

Therefore, $\Delta G_\mathrm{f}(\mathrm{H^+}) \simeq 148$ kcal mol^{-1}. On the other hand, reaction 14 in HF is endoenergetic ($\Delta G_{14} = -2.3RT \log K_\mathrm{D} = 7.1$ kcal mol^{-1}):

$$\begin{array}{cccccccc} i\text{-}C_5H & + & i\text{-}C_5^+ & \rightleftarrows & C_{10} & + & H^+ \\ -59.0 & & 101.2 & & -97.4 & & ? \end{array} \qquad (14)$$

Therefore, $\Delta G_\mathrm{f}(\mathrm{H^+}) \simeq 145$ kcal mol^{-1}.

Taking into account the hypothesis required in the evaluation of the thermochemical properties of alkanes, one can notice a good agreement between these values and the ΔG_f H^+ value calculated from the $R_0(\mathrm{H})$ acidity function. Furthermore, the Gibbs free energies of reaction 6, which are calculated or derived from experimental results, may be compared. Thanks to the above calculations, the difference $\Delta G_6(i\text{-}C_4H) - \Delta G_6(i\text{-}C_5H)$ is found to be equal to 0.8 kcal mol^{-1}. Taking into account the equilibrium constant of oxidation of isobutane[150] and that of isopentane,[23] which have been experimentally determined in $HF-SbF_5$, the above-mentioned difference is found to be equal to 0.7 kcal mol^{-1}. Such a good agreement has been already observed for cycloalkanes where previous thermochemical calculations[25] and experimental determinations[24,151] are close.[25]

C. Acidity Constants of Carbenium Ions, R^+

Alkylcarbenium ions can be prepared in superacid media by dissolving the corresponding alcohols, alkyl halides, or alkenes.[152-155] The formation of R^+ ions comes from the basic nature of these latter compounds. In less acidic media, the carbenium ion leads to the corresponding alkene by a loss of H^+ ion, according to the acid-base equilibrium represented as follows:

$$R^+ \rightleftarrows R_= + H^+ \qquad (17)$$

Taking into account the acidity constant of i-C_4^+ reported by Hogeveen et al.[150] and the thermochemical properties of alkenes and carbenium ions, the acidity constant of any carbenium ion is calculated. The Gibbs free energy of the acid–base equilibrium 19 is evaluated as follows:

$$i\text{-}C_4^+ + R_= \rightleftarrows i\text{-}C_{4=} + R^+ \qquad (19)$$

characterized by the constant K_{19}

$$K_{19} = \frac{[i\text{-}C_{4=}][R^+]}{[i\text{-}C_4^+][R_=]} = \frac{K_\mathrm{P}(i\text{-}C_4^+)}{K_\mathrm{P}(R^+)}$$

$$\Delta G_{19} = \Delta G_\mathrm{f}(R^+) - \Delta G_\mathrm{f}(i\text{-}C_4^+) - (\Delta G_\mathrm{f}(R_=) - \Delta G_\mathrm{f}(i\text{-}C_{4=}))$$

The ΔG_{19} value leads to the calculation of $\mathrm{p}K_\mathrm{P}(R^+)$ according to

$$\mathrm{p}K_\mathrm{P}(R^+) = \mathrm{p}K_\mathrm{P}(i\text{-}C_4^+) - \frac{\Delta G_{19}}{2.3RT}$$

The values of $\mathrm{p}K_\mathrm{P}(R^+)$ are reported in Table VI.

Linear alkenes, conjugate bases of n-alkylcarbenium ions, behave as weak bases in HF. In contrast, alkenes that are protonated into tertiary carbenium ions behave as strong bases in HF ($\mathrm{p}K_\mathrm{P}(R^+) > \mathrm{p}K_\mathrm{i}(\mathrm{HF})$) or in superacid solvents because the acidity range of HF covers those of the different Brønsted acids (Figure 3). Thus, the latter alkenes are quantitatively protonated into carbenium ions.

From the values of the acidity levels of alkenes protonation (Table VI), one can see that every alkene is protonated in the "superacid" media except ethene, which is protonated only in highly superacid media ($H < -21$), that is, in $HF-TaF_5$[156,157] or $HF-SbF_5$ mixtures.[25,113] Recently, acid–base titrations of an acid (SbF_5 or TaF_5) by alkenes have been carried out in hydrogen fluoride, using quinonic redox systems as pH indicators. Good agreement is found between the calculated values and the determined ones from the titration curves,[113,114] as for the acidity level of alkene protonation in H_2SO_4[158,159] (see Table VI).

Therefore, if alkene intermediates have been suggested in aqueous H_2SO_4 or HF to explain alkylation or cracking reactions,[160,161] it is highly probable that in superacid media there will be no alkene formation. In contrast, the basic nature of alkenes is of great interest for hydrocarbon chemistry in superacid media because it provides a convenient preparation of carbenium ion solutions[155] for alkylation processes or isomerization initiations (see following sections).

TABLE VII. Acidity Constants of Carbonium Ions in HF (pK_A) or Acidity Levels of Protonation of Alkanes (H_A or $R_0(H)_A$)

RH_2^+/RH	pK_A	H_A	$R_0(H)_A$
$C_1H_2^+/C_1H$	~ -6	~ -28	~ -34
$C_2H_2^+/C_2H$	~ -5	~ -27	~ -33
$C_3H_2^+/C_3H$	~ 2	~ -20	~ -26
i-$C_4H_2^+/i$-C_4H	~ 1	~ -21	~ -27
i-$C_5H_2^+/i$-C_5H	1.2[a]	−20.9	−26.7
$MCPH_2^+/MCPH$	2.3[a]	−19.8	−25.6

[a] Experimental values from ref 23 and 24.

D. Acidity Constants of Carbonium Ions, RH_2^+

Because of the high activity of the H^+ ion, the protonation of alkanes[19,20] has been postulated to explain the chemical behavior of these compounds. No spectral evidence for RH_2^+ cations could be given except in the course of gaseous ionic reactions in the source of mass spectrometer.[162,163] The existence in solution of carbonium ions has been shown in studies of the oxidation equilibria of isopentane and methylcyclopentane[23,24] (reaction 13).

Taking into account the recently published values of heats of formation of a few carbonium ions (from methonium ion to isobutonium ion),[164,165] the acidity constants of these cations are estimated. Isopentane and isobutane behaving in the same manner in superacid media,[108] it is admitted that $K_A(i\text{-}C_4H_2^+) \simeq K_A(i\text{-}C_5H_2^+)$, which means that $pK_A(i\text{-}C_4H_2^+) \simeq 1$ ($-\log K_A$). Thus, the enthalpy of reaction 20 is calculated as follows:

$$RH_2^+ + i\text{-}C_4H \rightleftarrows RH + i\text{-}C_4H_2^+ \qquad (20)$$

characterized by the constant K_{20}

$$K_{20} = \frac{[RH][i\text{-}C_4H_2^+]}{[RH_2^+][i\text{-}C_4H]} = \frac{K_A(RH_2^+)}{K_A(i\text{-}C_4H_2^+)}$$

$$\Delta H_{20} = \Delta H_f(RH) - \Delta H_f(i\text{-}C_4H) - (\Delta H_f(RH_2^+) - \Delta H_f(i\text{-}C_4H_2^+))$$

The value of ΔH_{20} leads to estimate $pK_A(RH_2^+)$ according to the relation

$$pK_A(RH_2^+) - pK_A(i\text{-}C_4H_2^+) \simeq \frac{\Delta H_{20}}{2.3RT}$$

Such calculations should include the solvation heats, which are not known. Thus, as above described, (i) the equality of the solvation terms of the different alkanes and (ii) the equality of the solvation energies between carboniums ions and carbeniums ions, which have been estimated previously,[149] are admitted.

The pK_A values of a few carbonium ions are reported in Table VII.

The basic nature of alkanes explains the augmentation of their solubility when the acidity level is increased.[119,120,166,167] If the solubility is represented as

$$S(RH) = [RH] + [RH_2^+] = [RH]\left[1 + \frac{[H^+]}{K_A(RH_2^+)}\right]$$

one can see the influence of acidity on the solubility; the application of this relation to n-pentane solubility[120] leads to a $pK_A(n\text{-}C_5H_2^+)$ of about 1.1.

According to the $pK_A(RH_2^+)$ values reported in Table VII, it appears that methane and ethane are very weak bases. They must not be protonated in the acidity range of HF or in the highest superacid media HF + SbF_5. This weakly basic nature is confirmed by their electrochemical behavior in HF–SbF_5.[25,168] When alkanes are protonated, the voltammograms show, by linear sweep voltammetry, oxidation peaks whose characteristics are different from the ones attributed to the unprotonated alkanes. These oxidation peaks, corresponding to the carbonium ions, are observed for any alkane except methane and ethane.[25,168]

The other alkanes are protonated in HF–SbF_5 solutions, which means at acidity levels higher than $H \sim -20$ or $R_0(H) \sim -26$. The question "why has no spectral evidence been given?" may be answered by the kinetic parameters of the oxidation reaction 1:

$$RH + H^+ \underset{}{\overset{k_1}{\rightleftarrows}} RH_2^+ \overset{k_2}{\rightleftarrows} R^+ + H_2 \qquad (1)$$

It has been shown by kinetic analysis that the first reaction (protonation) is the limiting step, $k_1 << k_2$.[25,113] Thus, RH_2^+ concentration is always low vs. RH at the beginning of the oxidation or that of R^+ at the end of the process. When equilibrium is reached, the ratio RH_2^+/R^+ is equal to

$$[RH_2^+]/[R^+] = P_{H_2}/28$$

for isopentane[23] P_{H_2} in atm.

Therefore, in order to get the carbonium ion as the predominating form, the hydrogen pressure must be quite high.

Despite the uncertainties on the $pK_A(RH_2^+)$ values, the existence of RH_2^+ shall be taken into account in the establishment of the potential–acidity diagrams of alkanes. The pK_A values of the carbonium ions that could not be calculated are assumed to be of the same magnitude as that of the isopentonium ion: $pK_A(RH_2^+) \simeq 1$ for higher alkanes than butanes.

E. Potential–Acidity Diagrams of Alkanes

The calculation of the standard potentials of alkanes' redox couples (Table V) leads to the establishment of the potential–acidity diagrams in hydrogen fluoride. If the different species in the various superacid media are solvated in the same manner, these diagrams are easily transposable to any medium through the general acidity scale (Figure 3).

The electrochemical reactions are the following:

$$R^+ + H^+ + 2e^- \rightarrow RH, \; E^\circ(R^+/RH)$$

with

$$R^+ \rightleftarrows R_= + H^+, \; K_P(R^+)$$

The apparent potential $E^{\circ\prime}(R^+/RH)$ is related to the acidity (pH in HF) by

$$E^{\circ\prime}(R^+/RH) = E^\circ(R^+/RH) - \frac{2.3RT}{2F}\text{pH} - \frac{2.3RT}{2F}\log\left(1 + \frac{K_P(R^+)}{[H^+]}\right)$$

Taking into account the protonation of alkane:

$$RH_2^+ \rightleftarrows RH + H^+, \; K_A(RH_2^+)$$

the apparent potential is determined by the relation

$$E'^{\circ}(\mathrm{R^+/RH}) = E^{\circ}(\mathrm{R^+/RH}) - \frac{2.3RT}{2F}\,\mathrm{pH} - \frac{2.3RT}{2F}\log\left(1 + \frac{K_{\mathrm{P}}(\mathrm{R^+})}{[\mathrm{H^+}]}\right) + \frac{2.3RT}{2F}\log\left(1 + \frac{[\mathrm{H^+}]}{K_{\mathrm{A}}(\mathrm{RH_2^+})}\right)$$

The second electrochemical reaction is as follows:

$$2\mathrm{R^+} + 2\mathrm{e^-} \rightarrow \mathrm{RR},\ E^{\circ}(\mathrm{R^+/RR})$$

with

$$\mathrm{R^+} \rightleftarrows \mathrm{R_=} + \mathrm{H^+},\ K_{\mathrm{P}}(\mathrm{R^+})$$

The apparent potential $E'^{\circ}(\mathrm{R^+/RH})$ is related to the acidity pH in HF by

$$E'^{\circ}(\mathrm{R^+/RR}) = E^{\circ}(\mathrm{R^+/RR}) - \frac{2.3RT}{\mathrm{F}}\log\left(1 + \frac{K_{\mathrm{P}}(\mathrm{R^+})}{[\mathrm{H^+}]}\right)$$

Allowing for the protonation of alkane RR:

$$\mathrm{RRH^+} \rightleftarrows \mathrm{RR} + \mathrm{H^+},\ K_{\mathrm{A}}(\mathrm{RRH^+})$$

the apparent potential is determined according to

$$E'^{\circ}(\mathrm{R^+/RR}) = E^{\circ}(\mathrm{R^+/RR}) - \frac{2.3RT}{F}\log\left(1 + \frac{K_{\mathrm{P}}(\mathrm{R^+})}{[\mathrm{H^+}]}\right) + \frac{2.3RT}{2F}\log\left(1 + \frac{[\mathrm{H^+}]}{K_{\mathrm{A}}(\mathrm{RRH^+})}\right)$$

The third electrochemical reaction is as follows:

$$\mathrm{RR} + 2\mathrm{H^+} + 2\mathrm{e^-} \rightarrow 2\mathrm{RH},\ E^{\circ}(\mathrm{RR/RH})$$

The apparent potential $E'^{\circ}(\mathrm{RR/RH})$ is related to the acidity (pH in HF) by

$$E'^{\circ}(\mathrm{RR/RH}) = E^{\circ}(\mathrm{RR/RH}) - \frac{2.3RT}{F}\,\mathrm{pH}$$

Considering the protonation of alkanes RH and RR:

$$\mathrm{RRH^+} \rightleftarrows \mathrm{RR} + \mathrm{H^+},\ K_{\mathrm{A}}(\mathrm{RRH^+})$$

$$\mathrm{RH_2^+} \rightleftarrows \mathrm{RH} + \mathrm{H^+},\ K_{\mathrm{A}}(\mathrm{RH_2^+})$$

the apparent potential is determined according to

$$E'^{\circ}(\mathrm{RR/RH}) = E^{\circ}(\mathrm{RR/RH}) - \frac{2.3RT}{F}\,\mathrm{pH} + \frac{2.3RT}{F}\log\left(1 + \frac{[\mathrm{H^+}]}{K_{\mathrm{A}}(\mathrm{RH_2^+})}\right) - \frac{2.3RT}{2F}\log\left(1 + \frac{[\mathrm{H^+}]}{K_{\mathrm{A}}(\mathrm{RRH^+})}\right)$$

The variations of the redox properties of alkanes as a function of acidity are represented vs. the $\mathrm{H^+/H_2}$ system (dashed lines) in Figures 6, 7, 9, and 10 (see section V) in dotted lines taking into account carbonium ions and in full lines without carbonium ions formation.

The position of the redox couple $\mathrm{R^+/RH}$ vs. the $\mathrm{H^+/H_2}$ system leads to the calculation of the oxidation pH, $\mathrm{pH_R}$, or acidity level ($\mathrm{H_R}$ or $R_0(\mathrm{H})_{\mathrm{R}}$) for which the oxidation reaction 6 becomes quantitative (Figure 4):

$$\mathrm{RH} + \mathrm{H^+} \rightleftarrows \mathrm{R^+} + \mathrm{H_2} \qquad (6)$$

$$\mathrm{pH_R} = \frac{2F}{2.3RT}(E^{\circ}(\mathrm{H^+/H_2}) - E^{\circ}(\mathrm{R^+/RH}))$$

TABLE VIII. Acidity Levels of Oxidation of Alkanes into Carbenium Ions, $\mathrm{pH_R}$ in HF, H_{R} or $R_{\mathrm{o}}(\mathrm{H})_{\mathrm{R}}$

alkane	$\mathrm{pH_R}$	H_{R}	$R_{\mathrm{o}}(\mathrm{H})_{\mathrm{R}}$
$\mathrm{C_1H}$	−34	−56	−62
$\mathrm{C_2H}$	−17	−40	−46
$\mathrm{C_3H}$	−4.3	−26.4	−32.2
n-$\mathrm{C_4H}$	−5.6	−27.7	−33.5
i-$\mathrm{C_4H}$	2.0	−20.1	−25.9
n-$\mathrm{C_5H}$	−5.2	−27.3	−33.1
i-$\mathrm{C_5H}$	2.7[b]	−19.4	−25.2
neo-$\mathrm{C_5H}$	−21	−43	−49
n-$\mathrm{C_6H}$	−5.0	−27.1	−32.9
2MPH	3.0	−19.1	−24.9
3MPH	2.4	−19.7	−25.5
22DMBH	−1.5	−23.6	−29.4
23DMBH	3.5	−18.6	−24.4

[a] Reaction 6 becomes quantitative when the acidity level is higher than the one of point R ($\mathrm{H} < \mathrm{H_R}$). [b] Experimental value from ref 23.

TABLE IX. Acidity Levels of Disproportionation of the Radical Oxidation State RR(R·), $\mathrm{pH_D}$ in HF, H_{D}, or $R_{\mathrm{o}}(\mathrm{H})_{\mathrm{D}}$[a]

alkane	$\mathrm{pH_D}$	H_{D}	$R_{\mathrm{o}}(\mathrm{H})_{\mathrm{D}}$
$\mathrm{C_1H}$	−28	−50	−56
$\mathrm{C_2H}$	−15	−37	−43
$\mathrm{C_3H}$	−2.8	−24.9	−29.7
n-$\mathrm{C_4H}$	−3.6	−25.7	−31.5
i-$\mathrm{C_4H}$	5.7	−16.4	−22.2
n-$\mathrm{C_5H}$	−2.4	−24.5	−30.3
i-$\mathrm{C_5H}$	5.7[b]	−16.4	−22.2
neo-$\mathrm{C_5H}$	−17	−39	−45
n-$\mathrm{C_6H}$	1.9	−20.2	−26.0
2MPH	7.5	−14.6	−20.4
3MPH	7.8	−14.3	−20.1
22DMBH	8.7	−13.4	−19.2
23DMBH	10.5	−11.6	−17.4

[a] Reaction 14 becomes quantitative when the acidity level is lower than the value of point D ($H > H_{\mathrm{D}}$). [b] Experimental value from ref 23.

The values of $\mathrm{pH_R}$ in HF, H_{R}, and $R_0(\mathrm{H})_{\mathrm{R}}$ are reported in Table VIII. The alkanes methane, ethane, and neopentane, which are oxidized into primary carbenium ions, present very highly negative values of $\mathrm{pH_R}$. This means that the oxidizing power of $\mathrm{H^+}$ ion is not high enough to oxidize these alkanes into $\mathrm{R^+}$ in the acidity range of superacid media.

The potential–acidity diagrams show the existence domain of the radical oxidation state, characterized by the dimer R–R. The area of this domain are reduced when the stability of the corresponding carbenium ion increases. The upper limit ($\mathrm{pH_D}$, acidity level of disproportionation of the radical oxidation state) is calculated according to

$$\mathrm{pH_D} = \frac{F}{2.3RT}(E^{\circ}(\mathrm{RR/RH}) - E^{\circ}(\mathrm{R^+/RR}))$$

The values of $\mathrm{pH_D}$ in HF, H_{D} and $R_0(\mathrm{H})_{\mathrm{D}}$ are reported in Table IX. The negative values of $\mathrm{pH_D}$ mean that the radical oxidation state exists in the whole acidity range of HF; furthermore, according to the position of the $\mathrm{H^+/H_2}$ system, the oxidation of RH by $\mathrm{H^+}$ is endoenergetic and leads to the radical state RR; the carbenium oxidation state cannot be reached with $\mathrm{H^+}$ as the oxidizing agent.

We have to point out that (i) the isomerization of carbenium ion into a more stable ion displaces the $\mathrm{pH_D}$ value of the parent alkane toward lower acidic media—$\mathrm{pH_D}$ increases but is still lower than the $\mathrm{pH_D}$

TABLE X. Gibbs Free Energies in Hydrogen Fluoride of the Basic Reactions of Alkanes (kcal mol^{-1})

$RH + H^+ \rightleftarrows R^+ + H_2$, ΔG_R
$2RH \rightleftarrows R_2 + H_2$, ΔG_D
$RH + H^+ \rightleftarrows R_1H + R_2^+$, ΔG_C

alkane	ΔG_R	ΔG_D	ΔG_C
C_1H	43	8	
C_2H	22	3.3	35
C_3H	5.4	1.8	16
n-C_4H	7.0	2.3	18
i-C_4H	−2.5	4.6	0.9
n-C_5H	6.5	3.3	18
i-C_5H	−3.4	3.7	2.5
neo-C_5H	26	5.1	−7.0
n-C_6H	6.2	8.3	18
2MPH	−3.8	5.5	2.3
3MPH	−3.0	6.5	1.4
22DMBH	1.9	12.2	−7.8
23DMBH	−4.4	8.3	−4.7

value of the isomerized alkane;[25] (ii) the values of pH_D increase when the carbon atoms number of the alkane skeleton is increased, traducing the stability increase of the corresponding carbenium ions; (iii) the pH_D values are displaced toward lower acidity levels when the temperature decreases.[113]

IV. Thermodynamics of Oxidation of Alkanes by H^+

The potential–acidity diagrams of alkanes are restricted to the redox couples that are related to the reactivity of a C–H bond. In fact, the reactions of alkanes in superacid media lead to the formation of compounds with a lighter molecular weight than the initial alkanes. These cracking reactions, which are similar to the disproportionation reaction 14, are related to the reactivity of C–C bonds. This reactivity cannot be easily represented in the potential–acidity diagrams, but it is related to the thermochemical potential of the redox couples of alkanes. Therefore, these reactions can be estimated for any alkane in the considered set.

A. Oxidation of C–H Bonds

The potential–acidity diagrams of alkanes show two types of oxidation of the C–H bond according to the acidity level of the medium: oxidation of alkanes into carbenium ion; oxidation of alkanes into radical that gives at first dimer and then oligomers.

1. Oxidation into Carbenium Ion

The Gibbs free energy ΔG_R of reaction 6 is related

$$RH + H^+ \rightleftarrows R^+ + H_2 \qquad (6)$$

to the standard potentials of the redox couples H^+/H_2 and R^+/RH, according to the relation

$$\Delta G_R = -2F(E°(H^+/H_2) - E°(R^+/RH))$$

The ΔG_R values for the various alkanes are reported in Table X. As is expected according to the potential–acidity diagrams, the ΔG_R values decrease when the molecular weight of the alkane is increased. Tertiary alkanes present quite exoenergetic oxidation processes.

2. Oxidation into the Radical Oxidation State

When the acidity level of the medium in which RH is dissolved is too low ($H > H_D$ or $R_0(H) > R_0(H)_D$), the oxidation of RH by H^+ does not give the carbenium ion but stops at the radical oxidation state. The products are at first dimers and then oligomers. The initial oxidation reaction is expressed as follows:

$$2RH \rightleftarrows RR(2R\cdot) + H_2 \qquad (21)$$

This oxidation reaction is the sum of the electrochemical reactions

$$2RH \rightarrow RR(2R\cdot) + 2H^+ + 2e^-, E°(RR/RH)$$

$$2H^+ + 2e^- \rightarrow H_2, E°(H^+/H_2)$$

The Gibbs free energy ΔG_D of the condensation reaction 21 is related to the standard potentials of the redox couples RR/RH and H^+/H_2 according to

$$\Delta G_D = -2F(E°(H^+/H_2) - E°(RR/RH))$$

The ΔG_D values for the different alkanes are reported in Table X. They are positive for any hydrocarbon, which means that the radical dimerization is always endoenergetic.

B. Oxidation of C–C Bonds

In the processes of isomerization or alkylation of alkanes, a more or less important ratio of the hydrocarbon load is converted by cracking in low molecular weight products. The formation of such compounds has been explained by two principal reactions: the protolysis of alkanes by H^+ ion,[104,150,169,170] and the β scission of a carbenium ion.[166,167,171]

1. Protolysis of Alkanes

The protolysis is a C–C bond oxidation by H^+ ion that is similar to the reverse reaction of the alkylation (eq 14). The protolysis is represented as

$$R_3C{-}CR'_3 + H^+ \rightleftarrows R_3CH + R'_3C^+$$

that is, by the scheme

$$R_1R_2 + H^+ \rightleftarrows R_1H + R_2^+ \qquad (22)$$

Thermodynamically, this reaction is expressed by the sum of the chemical and electrochemical reactions

$$2R_1R_2 \rightleftarrows R_1R_1 + R_2R_2, \Delta G_E$$

and

$$R_1R_1 + 2H^+ + 2e^- \rightarrow 2R_1H, E°(R_1R_1/R_1H)$$

$$R_2R_2 \rightarrow 2R_2^+ + 2e^-, E°(R_2^+/R_2R_2)$$

The Gibbs free energy ΔG_C of the protolysis of R_1R_2 is calculated according to

$$\Delta G_C = {}^1/_2\Delta G_E - F(E°(R_1R_1/R_1H) - E°(R_2^+/R_2R_2))$$

Thus, taking into account this relation, the thermodynamic products of alkanes protolysis are determined. They are reported in Table XI with the corresponding values of ΔG_C (ΔG's are also reported in Table X).

Furthermore, the acidity levels of protolysis (pH_C in HF, H_C, and $R_0(H)_C$) are calculated by using the same procedure as for oxidation acidity levels (pH_R in HF, H_R, and $R_0(H)_R$; see section IIIE). The pH_C value is calculated by

$$2.3RT\ pH_C = -\Delta G_C$$

The values of pH_C, H_C, and $R_0(H)_C$ are reported in Table XII. The values represent the acidity levels that

TABLE XI. Protolysis of Alkanes in Hydrogen Fluoride[a]

$R_1R_2 + H^+ \rightleftarrows R_1H + R_2^+$ (22)

alkane, R_1R_2	ΔG_C	R_1H, R_2^+	ΔG_C	R_1H, R_2^+
C_2H	35	C_1H, C_1^+		
C_3H	16	C_1H, C_2^+		
n-C_4H	18	C_2H, C_2^+		
i-C_4H	0.9	C_1H, C_3^+		
n-C_5H	18	C_3H, C_2^+		
i-C_5H	2.5	C_1H, n-C_4^+	3.4	C_2H, C_3^+
neo-C_5H	−7.0	C_1H, i-C_4^+		
n-C_6H	18	n-C_4H, C_2^+		
2MPH	2.3	C_1H, n-C_5^+	3.3	C_3H, C_3^+
3MPH	1.4	C_1H, n-C_5^+	4.3	C_2H, n-C_4^+
22DMBH	−7.8	C_1H, i-C_5^+	−6.9	C_2H, i-C_4^+
23DMBH	−4.7	C_1H, i-C_5^+	2.4	C_3H, C_3^+

[a] Gibbs free energy of the protolysis (kcal mol^{-1}) and nature of the cracking products.

TABLE XII. Acidity Levels of Protolysis of Alkanes, pH_C in HF, H_C, and $R_0(H)_C$[a]

$R_1R_2 + H^+ \rightleftarrows R_1H + R_2^+$ (22)

alkane	pH_C	H_C	$R_0(H)_C$
C_2H	~−28	~−50	~−56
C_3H	~−13	~−35	~−41
n-C_4H	~−14	~−36	~−42
i-C_4H	−0.7	−22.8	−28.6
n-C_5H	~−14	~−36	~−42
i-C_5H	−2.0	−24.1	−29.9
neo-C_5H	5.6	−16.5	−22.3
n-C_6H	~−14	~−36	~−42
2MPH	−1.8	−23.9	−29.7
3MPH	−1.1	−23.2	−29.0
22DMBH	6.2	−15.9	−21.7
23DMBH	3.8	−18.3	−24.1

[a] Reaction 22 becomes quantitative when $H < H_C$ ($pH_C < pH_C$ or $R_0(H) < R_0(H)_C$).

must be reached in order to render the protolysis quantitative: when $H < H_C$ protolysis 22 is displaced toward the right.

Linear alkanes or light alkanes present highly positive ΔG_C values (Tables X, XI); thus, they will not be cracked by protolysis in superacid media. The oxidation of a C–C bond is enhanced when the size or the branching of the alkane is increased. This reaction can be quite exoenergetic; see, for example, neopentane or neohexane (22DMBH). The reactivity of these latter alkanes is characterized by protolysis (see section V).

2. *β Scission of Carbenium Ions*

The β scission of a carbenium ion is the breaking of the C–C bond, which is in β position vs. the positive charge, with formation of a new carbenium ion and an alkene:

$$R_3C{-}C{-}C^+ \rightleftarrows R_3C^+ + C{=}C$$

This reaction is represented as follows:

$$R_1R_2^+ \rightleftarrows R_1^+ + R_{2=} \qquad (23)$$

The Gibbs free energy ΔG_β of this reaction is calculated by the relation

$$\Delta G_\beta = \Delta G_f(R_1^+) + G_f(R_{2=}) - \Delta G_f(R_1R_2^+)$$

Through these calculations, the thermodynamic products of this reaction are determined; they are reported in Table XIII, with the corresponding values of ΔG_β.

TABLE XIII. β-Scission Reaction of Alkylcarbenium Ions in Hydrogen Fluoride[a]

$R_1R_2^+ \rightleftarrows R_1^+ + R_{2=}$, ΔG_β
$H^+ + R_1R_2^+ \rightleftarrows R_1^+ + R_2^+$, $\Delta G_\beta'$

carbenium ion, $R_1R_2^+$	ΔG_β	R_1^+	$R_{2=}$	$\Delta G_\beta'$	R_1^+	R_2^+
C_3^+	48	C_1^+	$C_{2=}$	47	C_1^+	C_2^+
nC_4^+	44	C_1^+	$C_{3=}$	30	C_1^+	C_3^+
iC_4^+	54	C_1^+	$C_{3=}$	40	C_1^+	C_3^+
nC_5^+	28	C_2^+	$C_{3=}$	14	C_2^+	C_3^+
iC_5^+	33	C_3^+	$C_{2=}$	32	C_1^+	i-C_4^+
$neoC_5^+$	24	C_1^+	i-$C_{4=}$	5	C_1^+	i-C_4^+
nC_6^+	33	C_2^+	n-$C_{4=}$	23	C_2^+	n-C_4^+
$2MP^+$	23	C_3^+	$C_{3=}$	10	C_3^+	C_3^+
$3MP^+$	33	C_2^+	n-$C_{4=}$	23	C_2^+	n-C_4^+
$22DMB^+$	19	i-C_4^+	$C_{2=}$	18	i-C_4^+	C_2^+
$23DMB^+$	29	C_3^+	$C_{3=}$	15	C_3^+	C_3^+

[a] Gibbs free energies of reactions (kcal mol^{-1}) and nature of the products.

In superacid media, it has been shown that most alkenes are protonated into carbenium ions (see Table VI, section IIIC). Hence, the β-scission reaction has to be represented as follows:

$$R_1R_2^+ + H^+ \rightleftarrows R_1^+ + R_2^+ \qquad (24)$$

The Gibbs free energy of this reaction is then expressed by

$$\Delta G_\beta' = \Delta G_f(R_1^+) + \Delta G_f(R_2^+) - \Delta G_f(R_1R_2^+) - \Delta G_f(H^+)$$

which is also related to the above calculated ΔG_β according to the relation

$$\Delta G_\beta' = \Delta G_\beta + 2.3RT(-22.1 - H_p(R_{2=}))$$
$$= \Delta G_\beta + 2.3RT(-27.9 - R_0(H)\ p(R_{2=}))$$

where −22.1 (or −27.9) is the acidity level H (or $R_0(H)$) of hydrogen fluoride ($[H^+] = 1$ M, standard reference) and $H_P(R_{2=})$ (or $R_0(H)_P$ ($R_{2=}$ protonation)).

The different calculations of $\Delta G_\beta'$ lead to the determination of the thermodynamic products, which are reported in Table XIII with the corresponding $\Delta G_\beta'$ values.

According to the ΔG values of protolysis (Table XI) and β scission (Table XIII), the protolysis reaction is more exoenergetic than the β-scission one. This result may be traduced in terms of oxidation state: The protolysis, which is similar to the disproportionation of the radical oxidation state, is an oxidation of $R_2\cdot$ into R_2^+ and a reduction of $R_1\cdot$ into R_1H.

The β-scission (reaction 24) may be represented by the electrochemical reactions

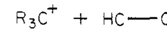
$$R_3C\cdot \rightarrow R_3C^+ + e^-,\ E°(R_3C^+/R_3C\cdot)$$

$$\cdot C{-}C^+ + H^+ + e^- \rightarrow HC{-}C^+,\ E°(\cdot C{-}C^+/HC{-}C^+)$$

whose sum is, of course, the β-scission reaction:

$$R_3C{-}C{-}C^+ + H^+ \rightarrow R_3C^+ + HC{-}C^+$$

Therefore, this reaction may be regarded as a disproportionation, but at a higher oxidation state than the protolysis, that is, an oxidation by H^+ of the C–C bond in β vs. the positive charge:



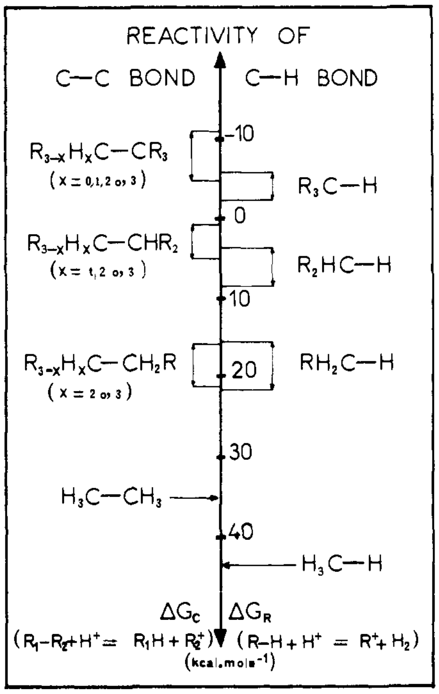


Figure 5. Thermodynamic reactivity scale of C–C and C–H bonds as a function of the alkane structure.

This high oxidation intermediate explains the fact that the cracking of carbenium ions is only observed in superacid media for cations having at least five carbon atoms.[15,16,104,170] The principal product is the i-C_4^+ cation, which is very stable at this acidity level.

In contrast, when alkanes are dissolved in superacid media, the cracking goes through a protolysis of the C–C bond[94,103,104,170,172–174] that can be quite exoenergetic (Table XI). The best example is the protolysis of neopentane in superacid media ($H < -19$) according to

$$\text{neo-}C_5H + H^+ \rightarrow i\text{-}C_4^+ + C_1H \tag{25}$$

In superacid solutions of carbenium ions with reducing agents such as H_2 or RH, the cracking of these cations may go through a reduction into alkane, followed by a protolysis. These two steps prevent to go through the high oxidation state (radical cation $\cdot C—C^+$) involved in the β-scission reaction. In this way, the cracking of the methylcyclopentane ring has been shown to proceed via a protolysis of MCPH and not through the β scission of MCP^+ [24] as was suggested.[175,176]

When no reducing agents are present, the cracking of carbenium ions has to process via the β scission. H^+ is then the oxidant, and, with respect to its oxidizing power, such a cracking is weak. Its importance increases with the size of the cations or by raising the temperature.[15,16]

C. Reactivity Scale of C–H and C–C Bonds

According to the calculated values of ΔG_R, the Gibbs free energy of C–H bond oxidation, a thermodynamic scale of the C–H bond reactivity as a function of the substituents is represented in Figure 5. When the same procedure is used and the calculated values of ΔG_C, protolysis of a C–C bond, are considered, a thermodynamic scale of the C–C bond is placed against one of the C–H bond in Figure 5.

As expected, the reactivities of C–C and C–H bonds are the highest when their oxidations lead to the formation of tertiary carbenium ions that are very stable in superacid media. The reactivity for an alkane is related to the electron density in the skeleton that causes basic sites. These "negative" places constitute the targets of the electrophilic reactions in superacid media. The scale presented in Figure 5 is in good agreement with the experimental reactivity order, reported by Olah et al.[102,103]

The conclusions must be moderated by the kinetic parameters and steric hindrance that can modify the occurrence of any reaction, that is, the thermodynamic reactivity order.

V. *Chemical Behavior of Alkanes*

Despite the uncertainties on the establishment of the thermochemical properties of alkanes, an examination of the potential–acidity diagrams leads to interesting conclusions concerning the behavior of alkanes in superacid media that depends on their nature and the acidity level of the medium.

The potential–acidity diagram shows, as a function of the acidity level, the alkane oxidation state that is reached by oxidation. This oxidation state is determined by the oxidizing power of the involved redox couple that we limited to the H^+/H_2 system. It stands to reason that a higher oxidation state can be reached when oxidants higher than H^+ are involved, such as SO_3 in HSO_3F,[91] alkylcarbenium ion,[177–179] or fluoranil[183] in HF.

The established diagrams are restricted to the initial reactions of alkanes. Thus, the condensation products, for example, being much more reactive than the starting compounds, react according to their diagrams and complicate the overall process. Therefore, kinetic data are needed for the description of the reactions, and they are briefly summarized.

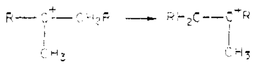
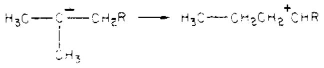
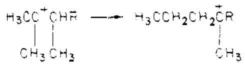
A. Typical Kinetic Parameters of the Basic Processes

The mechanism of acid-catalyzed hydrocarbon conversions has been the subject of numerous studies. It is generally agreed that the overall processes comprise two basic reactions, namely, (1) a redox reaction, oxidation of C–H or C–C bonds to yield carbenium ions or the reverse, and (2) skeleton rearrangements of the carbenium ions.

Much work has been devoted to the measurements of the rate constants of the various reactions: NMR spectroscopy has been shown to be suitable for the study of skeleton rearrangements;[14–16,181,182] rate constants of the redox reactions have been determined in HF–SbF_5[25,108,150,166,167,169] and related media,[25,171] R_FSO_3H media (neat or SbF_5 mixtures),[183,184] HSO_3F,[57,185] or less acidic media.[57,174] Typical values of rate constants for the different basic reactions in highly superacid media ($H < -20$) are reported in Table XIV. They vary, of course, with the particular skeleton structures of the species involved. As expected, the rate constants of H^+ oxidation increase when the acidity level is raised.[25,57,183,184] Furthermore, when a different oxidant is involved, such as SO_3 in HSO_3F, the oxidation rate constant of alkanes is quite increased.[185]

The mechanisms of rearrangement of the carbenium ions were paid considerable attention in the literature,

TABLE XIV. Kinetic Parameters of Reactions of Alkane in Superacid Media ($H < -20$)[a]

redox reaction[a]	rate constant k at 0 °C
$H^+ + RH \rightarrow R^+ + H_2$	10^{-5}–10^{-3} L mol^{-1} s^{-1}
$H_2 + R^+ \rightarrow RH + H^+$	10^{-3}–10^{-2} atm^{-1} s^{-1}
$R_1R_2 + H^+ \rightarrow R_1H + R_2^+$	10^{-5}–10^{-3} L mol^{-1} s^{-1}
$t\text{-}R_1H + t\text{-}R_2^+ \rightarrow t\text{-}R_1^+ + t\text{-}R_2H$	>10 L mol s^{-1}
$sec\text{-}R_1H + t\text{-}R_2^+ \rightarrow sec\text{-}R_1^+ + t\text{-}R_2H$	10^{-2} L mol s^{-1}
rearrangement reaction[b]	**rate constant at 0 °C**
$R_2XC{-}C^+R_2 \rightarrow R_2C^+{-}CR_2X$ ($X = H$ or CH_3)	$>10^3$ s^{-1} at −80 °C
 $R{-}C^+(CH_3){-}CH_2R \rightarrow RH_2C{-}C^+(CH_3)R$	10 s^{-1}
 $H_3C{-}C^+(CH_3){-}CH_2R \rightarrow H_3C{-}CH_2CH_2{}^+CHR$	10^{-2}–2 s^{-1}
 $H_3CC^+(CH_3)CH(CH_3)R \rightarrow H_3CCH_2CH_2C^+(CH_3)R$	6×10^{-2} s^{-1}

[a] See section VA. [b] Reference 122.

in particular the question of knowing whether primary ions can occur as intermediates and whether cyclic intermediates such as protonated cyclopropanes are involved.[121,122,186–193] The formation of protonated cyclopropanes would explain the fact that in HF–SbF$_5$ n-butane is not isomerized because the pathway implies going through a primary ion.[121] In less acidic media, the isomerization of primary ions such as neopentyl cation has been explained by a bimolecular process.[187–189]

Whatever the mechanisms of skeleton rearrangements are, Table XIV shows that they are faster than the redox reactions that are the rate-determining steps of the overall processes. In the acid-catalyzed alkane isomerization, represented as follows:

$$n\text{-RH} + H^+ \rightarrow n\text{-R}^+ + H_2 \qquad (1)$$

$$n\text{-R}^+ \rightarrow i\text{-R}^+ \qquad (2)$$

$$i\text{-R}^+ + n\text{-RH} \rightarrow n\text{-R}^+ + i\text{-RH} \qquad (3)$$

The process is rate determined by reaction 1 during the induction time, which corresponds to the acid phase formation.[120,166,167,181] Once the acid phase is saturated with n-R$^+$ and i-R$^+$ cations, reaction 3 completes the isomerization cycle and rate determines the process. Thus, the conditions of carbenium ion formation are of prime importance in the isomerization process of alkanes.

B. Isomerization of Alkanes

The alkanes considered in this reaction are the hydrocarbons from butanes up to hexanes. Their principal reactivity concerns the isomerization of normal alkanes into tertiary alkanes, which is of great interest for upgrading of motor fuels. Numerous processes have been reported in highly superacid media: HF, HSO$_3$F, or R$_F$SO$_3$H/SbF$_5$ or TaF$_5$ mixtures,[194–200] which means that $H < -18$.

According to the general schematic representation of the isomerization process (reactions 1–3), the carbenium ion formation has to be enhanced. Then, when the potential–acidity diagrams of these alkanes are considered, the direct oxidation of RH into R$^+$ only takes place in media of acidity levels higher than the one of the radical oxidation state dismutation, point D in the diagrams, which means that $H < H_D$ or $R_0(H) < R_0(H)_D$ (see Table IX).

The values of H_D or $R_0(H)_D$ reported in Table IX for n-alkanes are calculated without taking into account the isomerization of the n-R$^+$ ion. This reaction displaces H_D or $R_0(H)_D$ toward positive values;[25] the upper limit is the H_D or $R_0(H)_D$ values of the corresponding tertiary alkanes.

Furthermore, the direct oxidation of RH into R$^+$ becomes quantitative when the acidity level of the medium is higher than the oxidation one, point R in the diagrams, which means $H < H_R$ or $R_0(H) < R_0(H)_R$ (see Table VIII).

In contrast, when the acidity level of the medium is too low ($H > H_D$ or $R_0(H) > R_0(H)_D$), the H$^+$ oxidation of RH does not lead to the carbenium ion but stops at the radical oxidation state, yielding at first the dimer RR. This oxidation is slightly endoenergetic (ΔG_D; see Table X), and the process is complex, yielding condensation and cracking products. In this way, a radical initiation of n-alkane isomerization in low acidic media has been reported. The isomerization of n-pentane[201] and n-butane[202] is carried out in neat perfluoroalkanesulfonic acids, whose acidity levels ($H \sim -14$) are, of course, higher than the H_D values of these alkanes (Table IX).

The dimer, being much more reactive than the initial compound, is oxidized into the carbenium ion RR$^+$ as follows:

$$RR(H) + H^+ \rightarrow RR^+ + H_2 \qquad (26)$$

which is isomerized into different cations

$$RR^+ \rightarrow RR'^+ \qquad (27)$$

From that point, two pathways leading to the same products may be suggested,[201,202] namely (1) β scission of the carbenium ion and (2) protolysis of RR′(H) resulting from the reduction of RR′$^+$.

(1) The β scission of RR′$^+$ yields the isocarbenium ion i-R$^+$ and an alkene or cracking products, as follows:

$$RR'^+ \rightarrow i\text{-}R^+ + R_= \xrightarrow{+H^+} R^+ \qquad (28)$$

or

$$RR'^+ \rightarrow R_1^+ + R_{2=} \xrightarrow{+H^+} R_2^+ \qquad (29)$$

These new carbenium ions are then reduced to yield the corresponding alkanes.

(2) The protolysis route implies an initial reducing step that can be quite fast (Table XIV); for example:

$$RR'^+ + RR(H) \rightarrow RR'(H) + RR^+ \qquad (30)$$

The next step is the protolysis of the alkane into the isoalkane i-RH and a carbenium ion or cracking products, as follows:

$$RR'(H) + H^+ \rightarrow i\text{-}RH + R^+ \qquad (31)$$

or

$$RR'(H) + H^+ \rightarrow R_1H + R_2^+ \qquad (32)$$

From the thermodynamic point of view (section IV), the protolysis reactions are more exoenergetic than the β-scission reactions. Thus, it is highly probable that isomerization in low acidic media ($H > H_D$) proceeds through dimerization and protolysis. Anyhow, such isomerizations give bad yields and wide product distribution (cracked, isomerized, and condensation products).

Taking into account the two basic processes, the chemical behavior of these alkanes can be reviewed.

1. Butanes (Figure 6)

The behavior of *n*-butane is one of the most striking and controvertible. In highly superacid media, HF or HFO_3F/SbF_5, $H < -18$, *n*-butane was claimed to be isomerized[104,170,192] into isobutane, while other works gave evidence of the oxidation process only.[121,203,204] In fact, if the carbenium ion rearrangements are assumed to proceed through protonated cyclopropanes, *n*-butyl ion cannot be isomerized into *tert*-butyl ion and leads only to carbon scrambling in the skeleton.[121] These different behaviors may be explained by taking into account the acidity level of the medium: the oxidation of *n*-butane into *n*-butyl ion takes place in the highest superacid media, $HF-SbF_5$,[121] which means that $H < H_D$ (*n*-C_4H); the isomerization of *n*-butane is observed in less acidic media, such as HSO_3F-SbF_5[104,170] or R_FSO_3H.[202] In these latter media, the process is initiated by radicals and goes through dimers.[202] Then, the acidity level is lower than the radical dismutation one: $H > H_D$ (*n*-C_4H), which is in good agreement with the calculated H_D values.

In contrast with the probable "radical" isomerization of *n*-butane, the *n*-butyl ion isomerization, where *n*-C_4^+ results from acid–base reactions of RX with H^+,[192] may be explained by a bimolecular cationic reaction.[187–189]

In contrast, the behavior of isobutane is quite clear. In superacid media, $H < H_D$ (*i*-C_4H), the oxidation of *i*-C_4H into *i*-C_4^+ takes place and is nearly quantitative in the highest acid media, $HF-SbF_5$.[120,150] The carbenium ion *i*-C_4^+ is one of the most stable cations.[104,108,170] In a solvent where $H > H_D$ (*i*-C_4H), isobutane is alkylated by carbenium ions for the synthesis of motor fuels (see section VD).

2. Pentanes (Figure 7)

The isomerization of *n*-pentane has been studied in various media: $HF-SbF_5$,[120,166,167] HSO_3F-SbF_5,[104,170,205–207] HSO_3F,[185] and R_FSO_3H (neat or with SbF_5).[181,182,201,207] According to the product distribution, the two basic processes are observed. Typical product distributions are represented in Figure 8 for two media: $HF-SbF_5$, $H \sim -22.7$, and $C_2F_5SO_3H$, $H \sim -14$.

In $HF-SbF_5$, the oxidation of *n*-C_5H directly gives the *n*-C_5^+ cation which is isomerized into *i*-C_5^+ ion. The overall process corresponds to the general scheme (reactions 1–3) and leads to a thermodynamic *n*-C_5H conversion.[166,167] No condensation products result, but a few cracked products (up to 1%) are formed, probably through the protolysis of isopentane (see Table XI). Thus, the acidity level of $HF-SbF_5$ corresponds to $H < H_D(C_5H)$.

In $C_2F_5SO_3H$, the *n*-C_5H conversion is very slow, and large amounts of condensation products are recovered. The process goes through the radical oxidation state and can be radically initiated.[201] The initial formation of the dimer leads to complex reactions; a wide product distribution is obtained and the conversion ratio is very low. The acidity level corresponds, of course, to $H > H_D(C_5H)$.

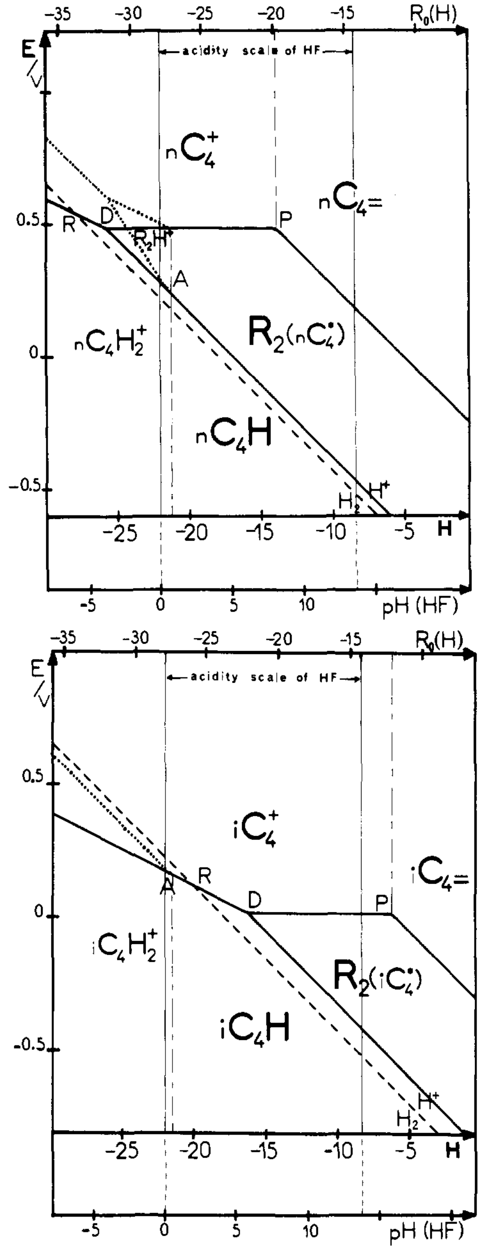


Figure 6. Potential–acidity diagrams of butanes (*n*-C_4H and *i*-C_4H) in superacid media. The diagrams are plotted vs. the H^+/H_2 system (dashed line); dotted lines considering the protonation of the alkane and full lines without carbonium ion formation. The acidity scale in HF (pH(HF)) is plotted against the H and R_0(H) acidity functions (Figure 3, section IIB).

The two media mentioned above represent the utmost media in which the two basic processes are separately involved. HSO_3F-SbF_5 mixtures yield products similar to those in $HF-SbF_5$. The other solvents, whose acidity levels stand between the ones of the two media mentioned above, lead to the occurrence of the two processes. The conversion ratio is nearly thermodynamic, but a few condensation products, and consequently cracked compounds, are recovered.

As for isobutane, the oxidation of isopentane yields the corresponding carbenium ion *i*-C_5^+ in a wide acidity range.[23] The *i*-C_5^+ cation is very stable at room temperature; by increasing the temperature, above 100 °C, it is converted into the *tert*-butyl cation *i*-C_4^+.[104,170]

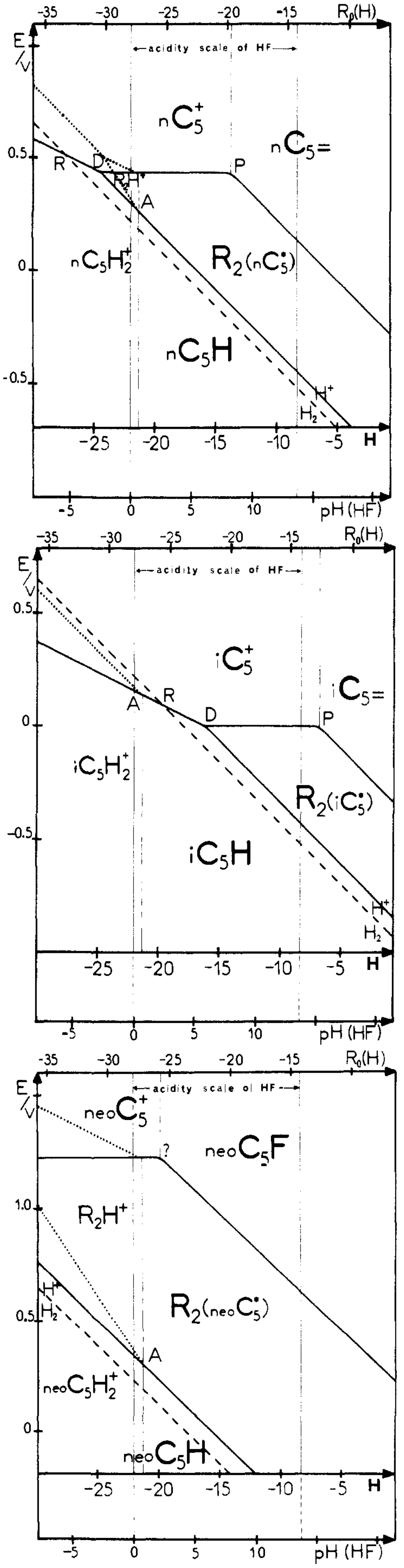


Figure 7. Potential-acidity diagrams of pentane in superacid media: n-C_5H, n-pentane; i-C_5H, isopentane; neo-C_5H, neopentane; see Figure 6.

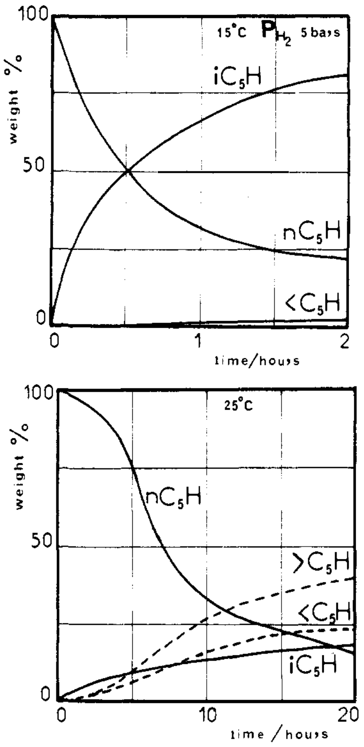


Figure 8. Isomerization of n-pentane (n-C_5H) in superacid media: (A) in HF–SbF$_5$ ($H \sim -22.7$) (reprinted with permission of R. Bonifay[120]); (B) in $C_2F_5SO_3H$ ($H \sim -14$) (reprinted with permission of P. Ortega[184]).

The chemical behavior of neopentane is quite surprising. In very superacid media, HF–SbF$_5$ or HSO$_3$F–SbF$_5$, neopentane undergoes conversion into *tert*-amyl cation i-C_5^+ at low temperature ($T < -50$ °C),[104,170] and it is cracked by protolysis at room temperature[102,104,150,169,170] according to thermochemical calculations (section IVB, Tables X, XI). The dimer process may be suggested to explain the isomerization at low temperature. The H^+ oxidizing power is too low to initiate the cationic isomerization through the primary neo-C_5^+ ion (Figure 7). In contrast, when neopentyl ion neo-C_5^+ is produced from neopentyl halide, the isomerization into i-C_5^+ cation is observed but proceeds by a bimolecular reaction.[189]

3. Hexanes (Figure 9)

According to the potential–acidity diagrams of hexanes, their isomerization requires less acidic media than the ones needed for the isomerization of pentane. Hexanes are isomerized through the carbenium ion route in solvents such as HF–BF$_3$,[171] or HF–TaF$_5$.[208] In the highest superacid media (HF–SbF$_5$ or HSO$_3$F–SbF$_5$), the amount of cracking products becomes important.[120,166,167,203,209] The isomerization process of hexanes is represented as follows:[170,171,203]

$$\begin{tikzcd}
 & & 2MPH \arrow[d, shift left] & & \\
 & & 2MP^+ \arrow[u, shift left] \arrow[dd, shift left] & 23DMBH \arrow[d, shift left] & \\
nC_6H \arrow[r, phantom, "\rightleftarrows"] & nC_6^+ & \arrow[r, phantom, "\rightleftarrows"] & 23DMB^+ \arrow[u, shift left] \arrow[r, phantom, "\rightleftarrows"] & 22DMB^+ \arrow[d, shift left] \\
 & & 3MP^+ \arrow[uu, shift left] \arrow[d, shift left] & & 22DMBH \arrow[u, shift left] \\
 & & 3MPH \arrow[u, shift left] & &
\end{tikzcd}$$

The first products of n-hexane conversion are the monobranched alkanes 2MPH and 3MPH, whose carbenium ions are converted into the 23DMB$^+$. This carbenium ion is the most stable cation of the hexyl

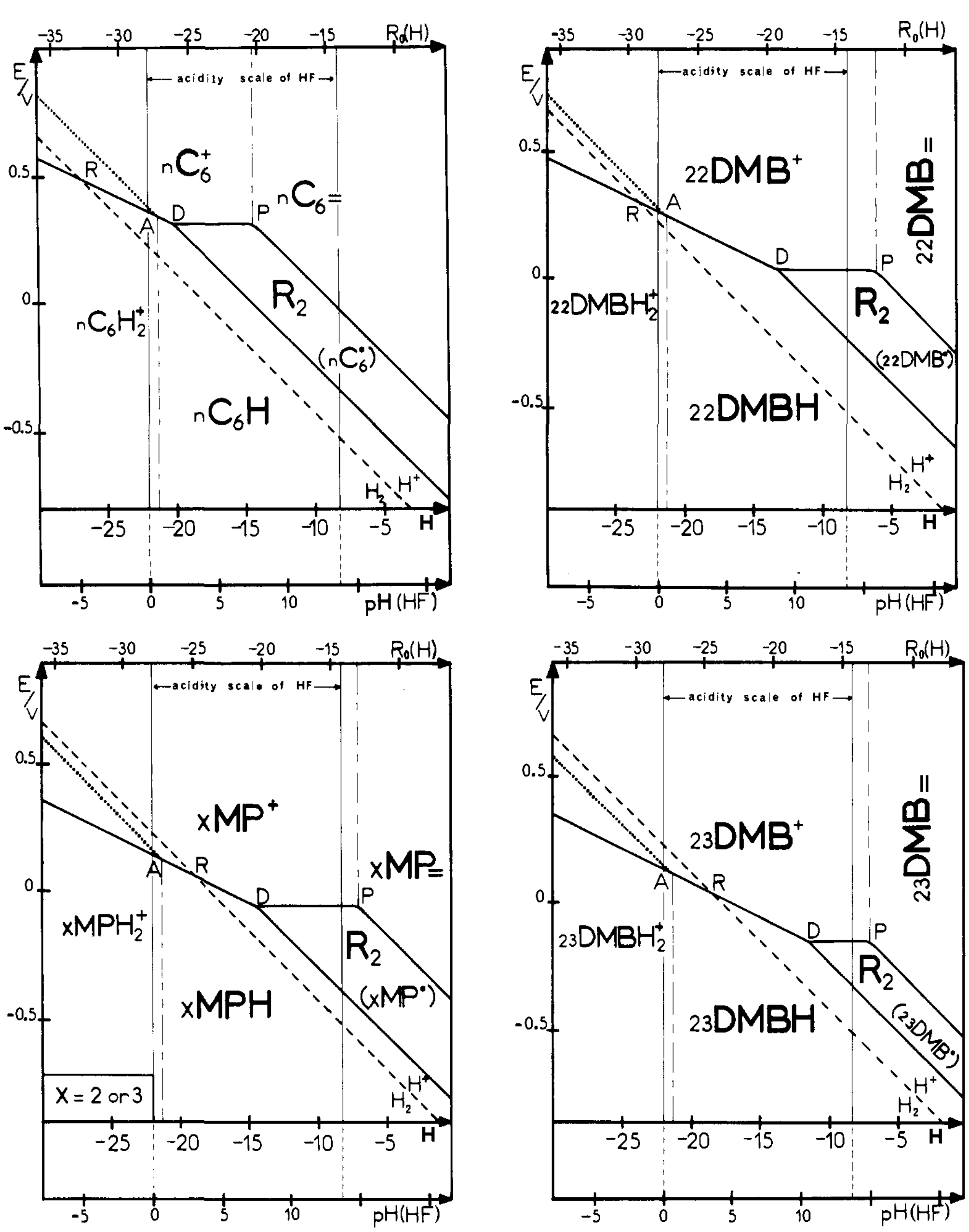


Figure 9. Potential–acidity diagrams of hexanes in superacid media: n-C_6H, n-hexane; 22DMBH, 2,2-dimethylbutane; 23DMBH, 2,3-dimethylbutane; 2MPH (2-methylpentane), 3MPH (3-methylpentane), presenting the same behavior, are represented by XMPH; see Figure 6.

ions[14-16] and yields, of course, the corresponding alkane 23DMBH by reduction. In a last step, the 23DMB$^+$ cation is isomerized into the 22DMB$^+$ cation, which is easily reduced into neohexane, 22DMBH.

This latter step, formation of the 22DMBH structure, would explain the occurrence of cracking products by protolysis of neohexane. Taking into account the ΔG_C values of hexanes' protolysis (Tables X, XI), the protolysis of neohexane (22DMBH) is the most exoenergetic reaction and yields either isobutane and ethane or isopentane and methane. This is in good agreement with experimental results where the product distribution analysis shows that the amount of cracking products is related to the 22DMBH fraction.[120,171] The other tertiary hexanes may be cracked (Table XI); but, according to the oxidation equilibria K_R, their predominating forms are the carbenium ions, which are not easily cracked. In contrast, 22DMB$^+$ is easily reduced (Table X) into 22DMBH, which undergoes a protolysis.

In low acidic media, the isomerization of hexanes has been initiated by alkyl halide/BF_3,[177] but the product distribution is wide: cracked, condensation, and isomerized compounds are recovered. This isomerization may proceed through a condensation process in which the oxidant is the alkylcarbenium ion, according to the reactions

$$RF + BF_3 \rightarrow R^+ + BF_4^-$$

$$R^+ + C_6H \rightarrow RC_6 + H^+$$

The alkylated hexane leads to numerous products by oxidation, isomerization, and cracking.

Through the examples mentioned above, highly superacid solutions appear quite suitable for the isomerization of alkanes. In contrast, the lower acidic solutions ($H > H_D$ of alkanes) present inconvenient properties: they induced wide product distribution resulting from the condensation route. In each case, a good agreement between the calculated previsions and experimental results is observed. Thus, the examination of the diagrams presented for the selected alkanes leads to the choice of the appropriate medium for the isomerization.

The increase of the acidity level is a convenient way to enhance the isomerization of alkanes, but it also induces protolysis reactions yielding cracked products. According to the thermochemical calculations and through the examples presented, it is highly probable that the cracking is restricted to protolysis reactions in isomerization processes. The β-scission reaction, which involves an oxidation state higher than the carbenium ion state, would only take place in solvents where oxidants stronger than H^+ are involved.

Thus, an equilibrium in the choice of the acidity level has to be found in order to enhance isomerization and to prevent cracking. Generally, high hydrogen pressures or addition of aromatic compounds are used to prevent the side reactions. In fact, both procedures decrease the H^+/H_2 redox potential, according to the Nernst law and the basic nature of aromatic compounds. Then, the amount of cracked products is decreased, but isomerization is also inhibited.[166,167,171] According to the protolysis reactions that yield light alkanes, a simplest way to inhibit these reactions may be the use of methane or ethane, under high pressure, which acts on the protolysis only because of their very weak reactivities.

C. Light Alkanes (Figure 10)

Alkanes from methane to propane present weak reactivities; the ΔG values of any reaction are positive in any medium (Table X). According to their potential–acidity diagrams, the oxidizing power of H^+ is too low to yield the corresponding carbenium ions.

In HSO_3F–SbF_5 (1:1), oxidation of propane yields *tert*-butyl ion i-C_4^+ and *tert*-hexyl ions.[104] This may be interpreted by dimer formation:

$$2C_3H \rightarrow C_6H + H_2$$

followed by the isomerization of hexanes and the protolysis of 22DMBH, which yields i-C_4^+.

The two lightest alkanes, methane and ethane, show practically no reactivity at low or room temperature. In HF–SbF_5 or HSO_3F–SbF_5 mixtures, hydrogen–deuterium exchanges have been observed at room temperature, according to the acid–base reaction.[169,173,210]

$$RD + H^+ \xrightarrow{k} RH + D^+$$

In HSO_3F–SbF_5 (1:1), the oligocondensation of methane and ethane is observed by increasing the temperature and the alkane pressure.[104,170,172,173] Methane yields the *tert*-butyl cation while ethane yields i-C_4^+ (90%) and 23DMB$^+$ (10%). To explain these reactions a cationic pathway was suggested, as follows:

$$C_1H + H^+ \rightarrow C_1H_2^+ \rightarrow C_1^+ + H_2$$

$$C_1H + C_1^+ \rightarrow C_2H_2^+ \rightarrow C_2^+ + H_2$$

$$C_1H + C_2^+ \rightarrow C_3H_2^+ \rightarrow C_3^+ + H_2$$

$$C_1H + C_3^+ \rightarrow C_4H_2^+ \rightarrow i\text{-}C_4^+ + H_2$$

The oligocondensation of methane stops at the very stable i-C_4^+ carbenium ion.

When the H_D values (Table IX) and the potential–acidity diagrams of methane and ethane (Figure 10) are

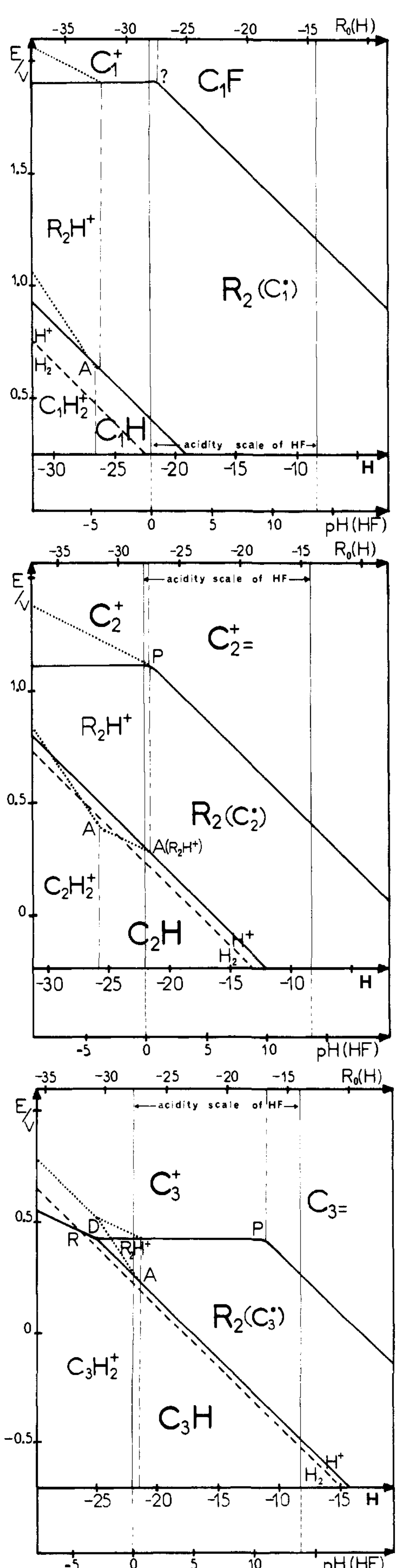


Figure 10. Potential–acidity diagrams of light alkanes in superacid media: C_1H, methane; C_2H, ethane; C_3H, propane; see Figure 6.

TABLE XV. Gibbs Free Energies of the Basic Reactions between Methyl Ion and Alkanes in Hydrogen Fluoride (kcal mol^{-1})

$C_1^+ + R'H \rightleftarrows C_1H + R'^+$, redox
$C_1^+ + R'H \rightleftarrows C_1R' + H^+$, alkylation
$C_1^+ + R'H \rightleftarrows R_1H + R_2^+$, cracking

alkane, R'H	ΔG	nature of the reaction	ΔG	nature of the reaction
C_1H	−33	alkylation		
C_2H	−35	alkylation	−21	redox
C_3H	−37	alkylation	−37	redox
n-C_4H	−37	redox	−36	alkylation
i-C_4H	−45	redox	−37	alkylation
n-C_5H	−37	alkylation	−36	redox
i-C_5H	−46	redox	−37	alkylation
neo-C_5H	−42	cracking	−36	alkylation
n-C_6H	−38	alkylation	−36	redox
2MPH	−46	redox	−35	alkylation
3MPH	−46	redox	−36	alkylation
22DMBH	−42	cracking	−41	redox
23DMBH	−47	redox	−40	cracking

taken into account, the H^+ activity is not high enough to yield the corresponding carbenium ions. The redox potential of the oxidant has to be very high in order to get the methyl ion from $E° > 1.2$ V, Table V. In this way, ozone is not a sufficient oxidant because its reaction with methane leads to C_3 or C_4 alkoxycarbenium ions,[211] whose formation may be interpreted by first steps of condensation. The resulting C_3 or C_4 alkane is then oxyfunctionalized. Therefore, the oligocondensation may go through the dimerization pathway involving the radical oxidation state, according to the reactions

$$2C_1H \rightarrow C_2H + H_2$$

$$C_2H + C_1H \rightarrow C_3H + H_2$$

$$C_3H + C_1H \rightarrow i\text{-}C_4H + H_2$$

At these acidity levels, isobutane is oxidized into i-C_4^+ ion:

$$i\text{-}C_4H + H^+ \rightarrow i\text{-}C_4^+ + H_2$$

The oligocondensation of ethane yields the C_6^+ cations by trimerization and oxidation of the resulting C_6H, and the i-C_4^+ cation by cracking of 22DMBH or dimerization and oxidation of the resulting butane.

According to the thermochemical properties of radicals,[212–215] whose heats of formation are lower than those of carbenium ions, it may be suggested that the oligocondensation proceeds through a radical process, as follows:

initiation by H^+ oxidation

$$RH + H^+ \rightarrow RH^{+\cdot} + H\cdot$$

$$RH^{+\cdot} \rightarrow R\cdot + H^+$$

propagation

$$R\cdot + RH \rightarrow RR + H\cdot$$

$$H\cdot + RH \rightarrow H_2 + R\cdot$$

chain breaking

$$R\cdot + H\cdot(R\cdot) \rightarrow RH\ (RR)$$

Such radical pathways may be suggested for the isomerization of n-butane and n-pentane in neat $C_2F_5SO_3H$,[201,202] whose acidity level is, of course, lower than those of D points ($H > H_D(RH)$).

If the oxidation by H^+ of the light alkanes does not lead to the carbeniums ions in superacid media, these cations are produced from the alkyl halides or alkenes by acid–base reactions, according to[216–222]

$$RX + H^+ \rightarrow R^+ + HX$$

or

$$R_= + H^+ \rightarrow R^+$$

According to the calculated redox potentials (Table V), these carbenium ions are powerful oxidants. Thus, they are used as initiators in isomerization processes[177–179] or as alkylating agents.[219–222] So, with respect to their oxidizing power, they react on alkanes as H^+ ion does,[221,222]

by redox reaction:

$$R^+ + R'H \rightarrow RH + R'^+ \qquad (33)$$

by alkylation

$$R^+ + R'H \rightarrow RR' + H^+ \qquad (34)$$

by cracking (protolysis reaction):

$$R^+ + R'H \rightarrow R_1H + R_2^+ \qquad (35)$$

Following the same procedure as the one presented in section IV, the Gibbs free energies of these basic reactions have been calculated[113] according to the relations

$$\Delta G_{33} = -2F(E°(R^+/RH) - E°(R'^+/R'H))$$

$$\Delta G_{34} = -2F(E°(R^+/RR) - E°(R'R'/R'H)) + \Delta G_F$$

$$\Delta G_{35} = -F(E°(R^+/RR) + E°(R_2R_2/R_2H) - E°(R'R'/R'H) - E°(R_1^+/R_1R_1)) + \Delta G_G$$

where ΔG_F and ΔG_G are correction terms (see section IVB).

The most exoenergetic reactions between alkanes and methyl, ethyl, and propyl cations in hydrogen fluoride are reported in Tables XV, XVI, and XVII.

Taking into account the values reported in Table XV, methyl ion appears to be a very high oxidant. Its formation requires highly superacid media, such as HF–SbF_5 or HSO_3F–SbF_5 mixtures, to yield CH_3SbF_6 complex.[216–220] Its redox potential is so high that methyl ion reacts on free CH_3F at room temperature; the principal product is the *tert*-butyl ion i-C_4^+.[218] The methyl ion is a good alkylating agent,[218–220] but it leads also to redox reactions[220] with alkanes heavier than propane, according to the calculated ΔG values. Considering the ΔG values reported in Tables XV, XVI, and XVII, a thermodynamic pathway of the methane alkylation by methyl ion is presented in Figure 11. The most exoenergetic reactions are expressed in full lines. The overall process is the sum of three alkylations (eq 33), yielding isobutane, which is oxidized into the stable ion i-C_4^+ [218–220] as follows:

$$3C_1F + C_1H \rightarrow i\text{-}C_4H + 3HF$$

Isobutane may be oxidized by H^+ ion or methyl ion, according to

$$i\text{-}C_4H + H^+ \rightarrow i\text{-}C_4^+ + H_2$$

or

$$i\text{-}C_4H + C_1^+ \rightarrow i\text{-}C_4^+ + C_1H$$

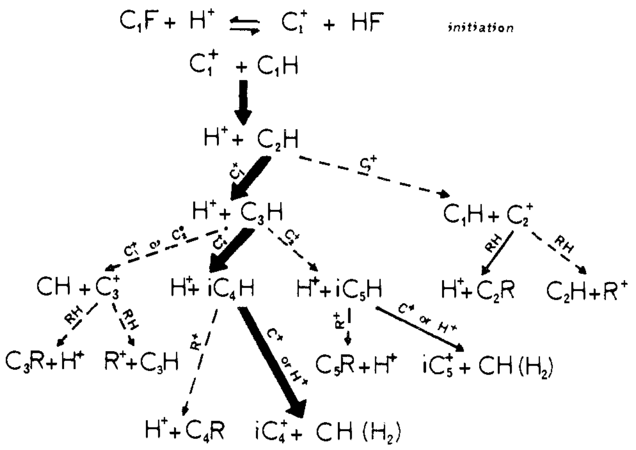


Figure 11. Schematic representation of methane alkylation by methyl fluoride in $HF-SbF_5$ or HSO_3F-SbF_5 ($H < -20$).

TABLE XVI. Gibbs Free Energies of the Basic Reactions between Ethyl Ion and Alkanes in Hydrogen Fluoride (kcal mol^{-1})

$C_2^+ + R'H \rightleftarrows C_2H + R'^+$, redox
$C_2^+ + R'H \rightleftarrows C_2R' + H^+$, alkylation
$C_2^+ + R'H \rightleftarrows R_1H + R_2^+$, cracking

alkane, R'H	ΔG	nature of the reaction	ΔG	nature of the reaction
C_1H	−15	alkylation		
C_2H	−17	alkylation		
C_3H	−18	alkylation	−17	redox
n-C_4H	−18	alkylation	−15	redox
i-C_4H	−24	redox	−18	alkylation
n-C_5H	−18	alkylation	−15	redox
i-C_5H	−25	redox	−17	alkylation
neo-C_5H	−23	cracking	−16	alkylation
n-C_6H	−17	alkylation	−16	redox
2MPH	−26	redox	−17	alkylation
3MPH	−25	redox	−17	alkylation
22DMBH	−24	cracking	−20	redox
23DMBH	−26	redox	−24	cracking

Thus, the overall process is equivalent to the self-condensation of methyl fluoride:[218]

$$4C_1F + H^+ \rightarrow i\text{-}C_4^+ + 4HF$$

or to a single alkylation of methane:

$$3C_1F + C_1H + H^+ \rightarrow i\text{-}C_4^+ + H_2 + 3HF$$

The ethyl cation (Table XVI) presents the same reactivity as that of methyl ion; nevertheless, the reactions are less exoenergetic and the carbenium ion C_2^+ can be produced in less acidic media, such as $HF-TaF_5$, by dissolving ethene.[156,157] However, the acidity levels of these media are the limit to yield the ethyl ion from ethene because in $HF-TaF_5$ (10:1) the alkylation ratio is high,[156] resulting from a quantitative protonation of ethene, while in $HF-TaF_5$ (1.5 mol %) the alkylation ratio is low.[157] This is confirmed by the calculated acidity level of ethene protonation (Table VI).

The ethyl ion is still a good alkylating agent.[156,157,220] Its reaction on butanes, for example, in HSO_3F-MF_n[223] or in $HF-TaF_5$,[156,224,225] leads to the formation of hexanes with good yields. However, as mentioned above for the reactions induced by methyl ion, there is a competition between the basic reactions[220] (Table XVI).

The oxidizing power of the propyl ion is far below the ones of the former carbenium ions, ethyl and methyl cations (Tables V, XVII). However, it is high enough to initiate isomerization processes[177-179] or to yield alkylation products with low molecular weight alkanes.[221,222] The nearly strong basicity in hydrogen fluoride of propene (Table VI) allows the use of low acidic media to promote the propyl ion formation.

TABLE XVII. Gibbs Free Energies of the Basic Reactions between Propyl Ion and Alkanes in Hydrogen Fluoride (kcal mol^{-1})

$C_3^+ + R'H \rightleftarrows C_3H + R'^+$, redox
$C_3^+ + R'H \rightleftarrows C_3R' + H^+$, alkylation
$C_3^+ + R'H \rightleftarrows R_1H + R_2^+$, cracking

alkane, R'H	ΔG	nature of the reaction	ΔG	nature of the reaction
C_1H	−1	alkylation		
C_2H	−2	alkylation		
C_3H	−2	alkylation		
n-C_4H	−2	alkylation	2	redox
i-C_4H	−8	redox	−1	alkylation
n-C_5H	−2	alkylation	1	redox
i-C_5H	−9	redox	−1	alkylation
neo-C_5H	−7	cracking	1	alkylation
n-C_6H	−1	alkylation	1	redox
2MPH	−9	redox	0	alkylation
3MPH	−8	redox	−1	alkylation
22DMBH	−9	cracking	−4	redox
23DMBH	−10	redox	−9	cracking

The calculated ΔG values of the reactions 33–35 in hydrogen fluoride decrease rapidly when the molecular weight of the involved carbenium ion is increased.[113] The occurrence of any reaction is related to the potential–acidity diagrams of the selected hydrocarbons, which means to the oxidation state. Thus, the alkylation reactions are related to the existence domain of the radical oxidation state (see potential–acidity diagrams); a quantitative alkylation reaction is then observed when the acidity level of the medium is settled in the range D–P of the reagents involved (see next section).

D. Alkylations in Low Acidic Media

These reactions, so-called "alkene–alkane alkylations", consist of the condensation of an alkane with an alkene, yielding high molecular weight hydrocarbons. These products present high octane numbers and are of great interest for the synthesis of motor fuels. Thus, a great number of alkylation processes has been reported in the literature during the last decade.

The selected alkanes generally are butanes, but also pentanes or hexanes, and the chosen alkenes are mainly propene or isobutene, and occasionally butenes or pentenes. The reactions are carried out in low acidic media vs. the superacid media such as $HF-SbF_5$. The selected media are neat Brønsted acids or mixtures: HF,[226-231] $HF-HSO_3H$,[232] $HF-CF_3SO_3H$,[233] $HF-H_2SO_4$,[234] HSO_3F,[235] $FSO_3H-H_2SO_4$,[236,237] or $CF_3SO_3H-H_2SO_4$.[238,239] Taking into account the general acidity scale (Figure 3) and the basic nature of alkenes, the acidity levels of these media are lower than that of pure sulfuric acid, which means $H > -12$.

Two basic processes have been suggested for the understanding of these alkylation reactions: the alcoylation reaction on one hand, and the alcoylolysis on the other hand.

The alcoylation reaction results from the acid–base reaction between an alkene and an alkylcarbenium ion.[171,187-189] The carbenium ion is produced by oxidation of the parent alkane; the overall process is represented by eq 36–38.

$$R_1H + H^+(Ox) \rightleftarrows R_1{}^+ + H_2(Red) \qquad (36)$$

$$R_1{}^+ + R_{2=} \rightleftarrows R_1R_2{}^+(R^+) \qquad (37)$$

$$R^+ + H_2(R_1H) \rightleftarrows RH + H^+(R_1{}^+) \qquad (38)$$

According to eq 36–38, the process involves the oxidation of R_1H into the carbenium ion and the condensation of $R_1{}^+$ with the alkene $R_{2=}$, the reverse of β scission (section IVB). In fact, allowing for the potential–acidity diagrams of alkanes, the acidity level of the media is too low for a direct oxidation of alkane R_1H into the carbenium ion: $H > H_D(R_1H)$. Furthermore, considering the basic nature of alkenes (Table VI), the alkene (generally propene or isobutene) is protonated. Thus, the alcoylation reaction does not appear satisfactory.

The alcoylolysis reaction is similar to the condensation reaction 14 and results from the oxidation of an alkane by a carbenium ion.[172,173,221,222] This reaction is then related to the basic nature of alkene, and the overall process is represented by the reactions

$$R_{2=} + H^+ \rightarrow R_2{}^+ \qquad (39)$$

$$R_2{}^+ + R_1H \rightarrow R_1R_2(RH) + H^+ \qquad (40)$$

The redox reaction 40 is the sum of the electrochemical reactions

$$R_2{}^+ + e^- \rightarrow R_2(R_2R_2)\cdot,\ E^\circ(R_2{}^+/R_2R_2)$$

$$R_1H \rightarrow R_1(R_1R_1)\cdot + H^+ + e^-,\ E^\circ(R_1R_1/R_1H)$$

Therefore, ΔG_{40} is related to the standard potentials of the redox couples $R_2{}^+/R_2R_2$ and R_1R_1/R_1H, which means the radical oxidation state domain. Then, taking into account the potential–acidity diagrams of alkanes, the H_D values (Table IX) and the H_p values (Table VI), the necessary conditions of occurrence of the alkylation reaction are as follows: the acidity level of the medium has to be higher than that of alkene protonation, meaning that $H < H_p(R_{2=})$; the acidity level of the medium has to be lower than that of the radical dismutation, which means that $H > H_D(R_1H)$ and $H > H_D(R_2H)$.

In short, the alkylation conditions are $H_D(R_1H)$ and $H_D(R_2H) < H < H_p(R_{2=})$.

In the isobutene–butanes alkylation processes, the alkylation conditions are expressed by $-16.4 < H < -6.3$, which is in good agreement with the acidity levels of the media used for this alkylation process ($H \sim -12, -10$).

In contrast, if the acidity level is much too high ($H < H_D$), the alkylation does not take place. The redox exchange may occur, depending on the standard potentials of the redox couples $R_2{}^+/R_2H$ and $R_1{}^+/R_1H$, as follows:

$$R_2{}^+ + R_1H \rightleftarrows R_2H + R_1{}^+ \qquad (41)$$

Such reactions occur in alkylation processes involving ethene or methyl fluoride[220] (section VC) because the acidity of the solvent has to be high enough to yield the carbenium ion, but it is too high, with respect to the H_D value of the alkane, to be alkylated. Furthermore, if the acidity level is much too low ($H > H_p(R_{2=})$), the alkene is not protonated and then cannot oxidize the alkane; no reaction takes place.

VI. Conclusion

Thermodynamics appear to be a good tool for the description of the reactivity of alkanes in various superacid media. The potential–acidity diagram (Pourbaix's type) represents the variations of the potentials of the alkane redox couples as a function of the acidity level. Its use is quite simple and provides a rational understanding of the occurrence of the basic processes in any superacid media. One of the most important characteristics of the diagram is the disproportionation of the radical oxidation state: H_D). According to the H_D values of alkanes, the medium may be chosen in order to enhance or inhibit any kind of reaction: simple cationic isomerization of alkanes occurs at acidity levels higher than the disproportionation ones of the corresponding radical oxidation states, which means that $H < H_D(RH)$; condensation or alkylation reactions are observed at acidity levels lower than the disproportionation ones of the radical oxidation state of the selected hydrocarbons, meaning that $H > H_D(RH)$.

Nevertheless, such diagrams are based on the approximations of the thermochemical properties of alkane redox couples in superacid media. Therefore, the determination of these values is an open field for the future. However, the uncertainties are not very large: for light alkanes, the errors in the evaluation of Gibbs free energies are lower than 10 kcal mol^{-1} while they are reduced to a few tenths kcal mol^{-1} for tertiary alkanes.[25] Thus, the reactivity of an alkane may be well defined among the basic reactions, according to the acidity level of the solvent. The validity of the reactivity model described has been checked through the examples discussed in section V. By following the procedure presented in this review, the previsions are easily widened to any case.

In addition to the thermodynamic analysis, the kinetic parameters cannot be forgotten. The reactions described constitute the initial steps of complex pathways. The condensation products are indeed more reactive than the initial compounds, and their reactivities are then described according to their thermochemical properties. Thus, kinetic and thermochemical data must be collected in order to reach a complete description of the chemical behavior of alkanes in superacid media. However, the framework presented here provides a trial of rationalization and a new point of view on the chemistry of alkanes in superacid media.

VII. Acknowledgments

We thank our co-workers, Dr. Ben Hadid, P. Capron, and F. Bedioui. They deserve the credit for the experiments from our research group that have contributed to the field of investigations of nonaqueous solvents. Several people have helped us enter the chemistry of alkanes in superacid media. In particular, we are grateful to Professor A. Commeyras, Dr. A. Germain, and Dr. D. Brunel of U.S.T.L. (University of Montpellier, France), Professor J. Sommer (University of Strasbourg), and Dr. B. Torck (Institut Français du Pétrole, Rueil-Malmaison, France) for continuing helpful discussions. The "Délégation Générale de la

Recherche Scientifique et Technique" and the "Centre National de la Recherche Scientifique" have provided financial support.

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