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Solvation as a main factor that determines the strength of liquid superacids and the selectivity of the acid-catalyzed reactions of olefins

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Abstract

Analysis of literature and *ab initio* quantum chemical calculations indicates that the solvation of protons in anhydrous H_2SO_4 or HF is considerably weaker than in aqueous solutions. This results in very low constants of autoprotolysis of anhydrous superacids. In contrast, hydration of protons in moderately concentrated acids is much stronger, resulting in higher dissociation constants. Therefore, the strength of superacids is connected to the high chemical activity of the weakly solvated protons, rather than to the amount of protons. In a similar way, solvation of protonated active intermediates of the acid-catalyzed transformations of olefins in anhydrous superacids is also weaker than in aqueous solutions. This results in the real carbenium ion mechanisms of the isoparaffin–olefin alkylation or “conjunct oligomerization” of olefins. In contrast, solvation with water in moderately concentrated or dilute sulfuric acid transforms alkyl carbenium ions into oxonium ions. Therefore, cationic polymerization of olefins in moderately concentrated sulfuric acid is not a real carbenium ion reaction. Similar to the acid-catalyzed transformations of olefins on zeolites, it involves oxonium ions as the stable active intermediates and alkyl carbenium ions as transition states. © 2002 Published by Elsevier Science B.V.

Keywords: Superacids; Solvation; Protons; Acid catalysis; Olefins; Alkylation

1. Introduction

The mechanism of acid-catalyzed transformations of hydrocarbons has originally been suggested by Broensted [1]. According to his theory, the active intermediates of acid-catalyzed reactions are the protonated forms of the substrates, which are more reactive than the initial molecules. The main disadvantage of this classic approach, however, is the very formal description of the protonated species without taking their real molecular structure into account or their interaction with surrounding molecules of an acid or a solvent. In other words, a more realistic mechanism of acid-catalyzed reactions requires a molecular description of the reaction intermediates with account of solvation effects.

Seventy years ago, when Broensted formulated his theory of acids and acid catalysis, this was certainly impossible. However, since that time considerable progress has been achieved in the molecular description of reactions in liquids. In this paper, we will discuss the dissociation of strong acids and superacids taking the solvation of resulting protons and anions at a molecular level into account. In a similar way, we will also consider the role of the solvation in the mechanism of the acid-catalyzed transformation of olefins.

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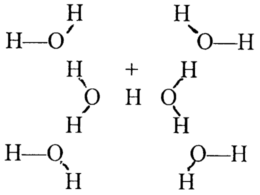
2. Solvation of protons in the strong acids and superacids

2.1. *Nature of hydrated protons in aqueous solutions and the acidic strength*

Hydrated protons are usually considered to be H_3O^+ hydroxonium ions. On the other hand, it is well known that in liquid water they are solvated by many water molecules. For instance, according to the model supported by Zundel [2] or Librovich and coworkers [3], the simplest form of a hydrated proton corresponds to a $H_5O_2{}^+$ ion, whereas Eigen [4] advocated the bigger $H_9O_4{}^+$ complexes. This point of view is currently prevailing [5]. The numerous theoretical calculations also confirm that in liquid water protons are solvated by at least four water molecules [6,7]. However, the most convincing arguments in favor of proton solvation by many water molecules were found with the high-pressure mass spectroscopy [8].

The results obtained by Lau and Kebarle [8] indicated that the heat of the stepwise proton hydration depends on the number of solvating water molecules (Table 1). For the addition of the first water molecule, the solvation energy is equal to 166 kcal/mol, but decreases to 41 kJ/mol for solvation with the seventh and the eighth molecules. The latter figure coincides with the heat of water vapor condensation. This means that the seventh and the eighth solvating H_2O molecules do not feel the presence of the proton in the hydrated cluster. Thus, the specific hydration of the proton corresponds to the composition of the solvated clusters H^+ $6H_2O$ [9,10].

The total energy of proton hydration can then be obtained as a sum of the proton hydration with six water molecules. It is equal to 1085.9 kJ/mol. This is in excellent agreement with the experimental proton hydration energy in liquid water of 1090 kJ/mol [11]. Thus, according to high-pressure mass spectrometry, the most probable structure of a hydrated proton in any moderately concentrated strong acid is the following:


(1)

This cluster represents the central $H_5O_2{}^+$ ion with two shortest hydrogen bonds as the simplest form of a hydrated proton that is at any moment surrounded by four more weakly bonded water molecules.

It is also quite clear that, if the molar water to acid ratio is higher than 6, such hydrated clusters represent the protons of any acid in an aqueous solution. This critical water to acid ratio approximately corresponds to the concentration of the strong acids of 5–10 mol/l. Under this critical concentration, the structures of the hydrated protons in aqueous solutions of all strong acids are identical to each other, because the difference between the strong and the weak acids consists only in the number of hydrated species. This conclusion agrees well with the generally accepted method to measure the strength of the moderately concentrated acids by the K_a, pK_a or pH values.

In contrast, if the water to acid ratio in a very concentrated acid is less than 6, then the number of water molecules is not sufficient for a complete solvation of the protons. In this case, the solvation with water is partially replaced by solvation with the acid. This results in considerably lower heats of proton hydration than in a more dilute water solution. Indeed, heterolytic self-dissociation of the very concentrated sulfuric acid is endothermic by only 18.8 kJ/mol. In contrast, for a dilute acid it is exothermic with 83.6 kJ/mol. Such less favorable energetics also influences the dissociation constant of sulfuric acid. For the anhydrous acid it is as low as 10^{-4} mol/kg, but it is very high in an aqueous solution.

The unusual behavior of protons in sulfuric acid with concentrations higher than about 80% has been

Table 1
Heats of the stepwise solvation of protons by water molecules in the gas phase according to Lau and Kebarle [8]

n H_2O	1	2	3	4	5	6	7	8
ΔH of hydration (kJ/mol)	696	132	81.5	74.8	53.1	48.5	41	41

discussed in literature many times [12]. It is evident from the nonlinear increase of the Hammett acidity function [13] or from an extremely high chemical activity of protons.

2.2. *Solvation of protons by superacids*

The acids that are able to protonate even very weak bases are known as superacids. The number of liquid superacids is rather limited. All of them are certainly anhydrous acids, since otherwise the protons would protonate water instead of the substrates. The most important superacids are the anhydrous sulfuric and perchloric acids, the liquefied anhydrous hydrogen fluoride or the 100% sulfuric and hydrofluoric acids modified by addition of Lewis acids such as SO_3, BF_3 or SbF_5.

The strength of different acids is usually measured either with the Hammett acidity function H_0 or with the constants of their heterolytic dissociation. However, for superacids the latter approach is not effective, as they are only very weakly dissociated. For instance, the K_a value of anhydrous 100% sulfuric acid is equal to 10^{-4}, whereas that one for anhydrous 100% HF it is only 10^{-10}, etc. [14].

At the first glance, this looks like it is in contradiction with the 100% dissociation of strong acids in aqueous solutions. However, similar to the very concentrated sulfuric acid, the strength of superacids is determined not by degree of their dissociation, but by the unusual properties of the weakly solvated protons. In this connection, let us compare the energy of heterolytic dissociation of anhydrous superacids with their dissociation in aqueous solutions.

2.3. *Solvation of protons in anhydrous sulfuric acid*

The simplest analog of the hydroxonium ion in anhydrous sulfuric acid is the $H_3SO_4^+$ cation. *Ab initio* quantum-chemical calculations of the energy of its solvation with liquid anhydrous acid as well as that of the solvation of the HSO_4^- anion were carried out in two steps. First, we calculated the structures and the formation energies of the above mentioned cations and anions solvated by one or two molecules of sulfuric acid in the gas phase. Then these clusters were immersed into liquid sulfuric acid and the additional contribution to the total solvation energy due to the interaction of the clusters with the surrounding molecules of liquid acid was estimated in the framework of the electrostatic continuous PCM model. The acid was modeled as a continuous medium with a high dielectric constant. The *ab initio* quantum-chemical calculations were carried out with the 6-31++G* basis set and complete optimization of geometry of solvated species taking into account the zero point energy corrections and using GAMESS or GAUSSIAN programs [15].

The calculated structures of $H_3SO_4^+$ cations solvated with one or two molecules of sulfuric acid are depicted in Fig. 1. For the $H_3SO_4^+$ H_2SO_4 dimer, the calculated interaction energy was equal to 115.4 kJ/mol. The addition of the next molecule of sulfuric acid to the dimeric complex takes place from the side of the first solvating H_2SO_4 molecule giving rise to the linear $H_3SO_4^+$ H_2SO_4 H_2SO_4 solvated complex of Fig. 1b. The calculated formation energy of this complex in the gas phase from $H_3SO_4^+$ cation and two sulfuric acid molecules is equal to 224.9 kJ/mol.

To obtain the solvation heats of the dimeric or trimeric cationic complexes in the liquid acid, two more contributions to the total solvation energy were taken into account. The first results from the electrostatic interaction of the positively charged clusters with the surrounding molecules of the liquid acid. It was estimated in the frame of the continuum PCM model. The second contribution corresponds to evaporation heat of liquid H_2SO_4 which is equal to

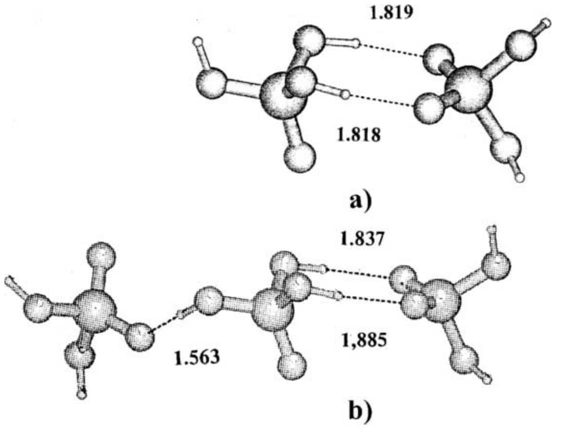


Fig. 1. $H_3SO_4^+$ ion solvated by one (a) or two (b) molecules of sulfuric acid. Bond lengths in Å.

ca. +50 kJ/mol [16]. The energy balance of the solvation of trimeric cationic clusters in anhydrous H_2SO_4 is the following:

$$\begin{array}{l}
2\,H_2SO_{4L} \rightarrow 2\,H_2SO_{4G} + 100\ \text{kJ/mol (evaporation heat of the acid)} \\
H_3SO_4{}^{+}{}_{G} + 2\,H_2SO_{4G} \rightarrow (H_3SO_4{}^{+}\,2H_2SO_4)_G - 224.9\ \text{kJ/mol} \\
(H_3SO_4{}^{+}\,H_2SO_4)_G + H_2SO_{4L} \rightarrow H_3SO_4{}^{+}{}_{L} - 200.2\ \text{kJ/mol (PCM contribution)} \\
\hline
H_3SO_4{}^{+}{}_{G} + H_2SO_{4L} \rightarrow H_3SO_4{}^{+}{}_{L} - 325.1\ \text{kJ/mol}
\end{array} \qquad (2)$$

Taking into account the PCM contribution and the evaporation heat of the acid we also carried out similar calculations for solvation of HSO_4^- anion. For dimeric and trimeric clusters, the obtained solvation heats were found to be −334.4 and −321.0 kJ/mol, respectively.

To check, how precise were the obtained values of solvation energies, we used them for calculation of the self-dissociation heat of anhydrous sulfuric acid using the experimental energy of its self-dissociation in the gas phase of 589.4 kJ/mol [17]. The obtained heats of autoprotolysis for dimeric and trimeric complexes were equal to +21.3 and +43.9 kJ/mol, respectively. This is close to the experimental value of +15 kJ/mol [18] and obviously, points out the rather high accuracy of our calculations. A possible source of disagreement between calculated and experimental values could be connected to the experimental value of the evaporation heat of sulfuric acid of about 50 kJ/mol that is not very precise.

The estimation of the solvation energy of a proton with liquid sulfuric acid was carried out in the similar way. First a proton was added to one molecule of sulfuric acid in the gas phase. This corresponds with the experimental value of the proton affinity of −720.2 kJ/mol [19]. Then the resulting $H_3SO_4^+$ cation was solvated by the liquid acid with the above calculated energy gain of −(321–334) kJ/mol.

The obtained total energy of the proton solvation with anhydrous sulfuric acid of about 1003 kJ/mol is approximately 90 kJ/mol less than the experimental value of the proton affinity in liquid water of 1090 kJ/mol. This evidently points to specific properties of protons in anhydrous sulfuric acid.

2.4. Solvation of protons in liquid HF

Another example of a superacid, with a strong hydrogen bonding, is liquid HF. Energies of proton and F^- anion solvation with liquid HF were calculated in a similar manner taking into account the electrostatic interaction with surrounding HF molecules and correcting the obtained values for the heat of the acid evaporation equal to 30 kJ/mol.

The results of the calculations indicated that the energies of the proton solvation are gradually approaching the limiting value of about 920 kJ/mol for solvation with five HF molecules. The structure of the corresponding cluster in the gas phase is shown in Fig. 2. The obtained limiting value of the solvation energy is about 85 kJ/mol less than the solvation

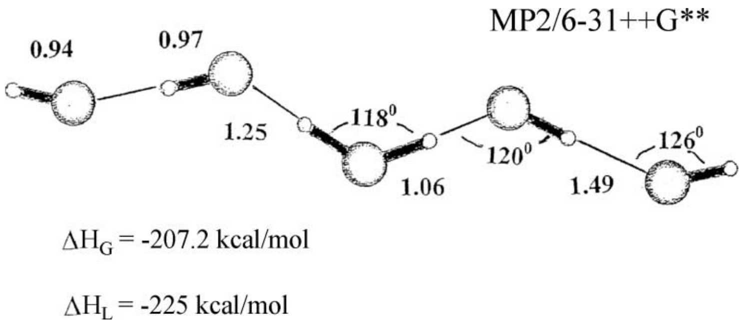


Fig. 2. Structure of the cluster, representing proton solvated by five molecules of HF.

energy of proton by sulfuric acid and by 170 kJ/mol less than for solvation of the proton with liquid water. In contrast, the calculated solvation energy with liquid HF of the F^- anion is higher than for water. For tetrahedral or octahedral solvated clusters it is close to 606 kJ/mol in comparison to 505.8 kJ/mol for the aqueous solution [10].

The obtained solvation heats of protons and F^- ions were then used to calculate the heat of autoprotolysis of liquid HF. With the experimental value of the energy of heterolytic dissociation of HF in the gas phase equal to +1541.6 kJ/mol, the corresponding energy balance is as follows:

$$\begin{array}{l} \mathrm{HF_L} \leftrightarrow \mathrm{HF_G} + 30\ \text{kJ/mol (evaporation of liquid HF).} \\ \mathrm{HF_G} \rightarrow \mathrm{H^+_G} + \mathrm{F^-_G} + 1541.6\ \text{kJ/mol (hetrolytic dissociation of free HF)} \\ \mathrm{H^+_G} + \mathrm{HF_L} \rightarrow \mathrm{H^+_L} - 920\ \text{kJ/mol} \\ \mathrm{F^-_G} + \mathrm{HF_L} \rightarrow \mathrm{F^-_L} - 606\ \text{kJ/mol} \\ \hline \mathrm{HF_L} \leftrightarrow \mathrm{H^+_L} + \mathrm{F^-_L} + 40.6\ \text{kJ/mol} \end{array} \tag{3}$$

The moderate endothermicity of this reaction looks quite reasonable, thus also indicating a rather high accuracy of our calculations.

The obtained results confirmed our earlier conception, according to which the specific properties of superacids are associated with the lower energy of proton solvation in comparison with that one in aqueous solutions [10,19]. In contrast, the basic negatively charged anions are solvated by very concentrated strong acids and superacids stronger than by water.

This conclusion is illustrated by comparison of the solvation heats of protons and anions in anhydrous H_2SO_4 and HF with those in water solution presented in Table 2. The weaker solvation of protons by anhydrous acids than by the more basic water certainly appears to be quite natural. In contrast, negatively charged basic anions are solvated more strongly by superacids than by water. Therefore, superacids represent a compromise between the weakest possible solvation of protons and the strongest possible solvation of anions. The former requirement results in a high chemical activity of protons, while the latter provides a satisfactorily good entire energetic of heterolytic dissociation.

In this context it should also be underlined that, although solvation is an absolutely necessary requirement for the heterolytic dissociation of any acid, it simultaneously lowers the chemical activity of the proton. In this connection, the lowering of the proton solvation energy in 100% sulfuric acid by about 100 kJ/mol or by 170 kJ/mol in the anhydrous HF is quite appreciable, since at room temperature one pK_a unity corresponds to the energy difference of only about 6 kJ/mol.

On the other hand, the stronger solvation of the negatively charged anions by superacids is also quite important. For instance, it explains the unusual properties of the "magic acid" by Olah (a mixture of hydrofluoric acid with Lewis acids, such as SbF_5 or BF_3). Indeed, according to the above arguments, the superacidic properties of these mixtures are connected to the stronger solvation of F^- anions by SbF_5 or BF_3 than by HF:

$$\mathrm{HF_L} + \mathrm{SbF_5} \leftrightarrow \mathrm{H_L}^+ + \mathrm{SbF_{6L}}^- \quad \text{or}$$
$$\mathrm{HF_L} + \mathrm{BF_3} \leftrightarrow \mathrm{H_L}^+ + \mathrm{BF_{4L}}^- \tag{4}$$

Table 2
Comparison of the heats of solvation of protons, HSO_4^- and F^- anions with superacids and water

The acid	ΔH of proton solvation (kJ/mol)		ΔH of anion solvation (kJ/mol)	
	Water solution	100% acid	Water solution	100% acid
H_2SO_4	−1090	−1003	−301	−292.6
HF	−1090	−920	−505.8	−606

This additional stabilization of the negatively charged anions favors a higher degree of HF dissociation, but does not decrease the high chemical activity of the weakly solvated protons. Therefore, the very low dissociation constant of liquid HF of 10^{-10}, increase strongly. Thus, the magic acid represents a combination of a higher dissociation degree with the high chemical activity of protons. This results in the range of H_0 Hammett acidity functions of up to −20 or −25 instead of −12.1 for liquid HF.

3. Acid-catalyzed transformations of olefins

The difference in the solvation of protons and protonated active intermediates in superacids and strong acids certainly has a strong influence on the selectivity of acid-catalyzed transformations of olefins. The following alternatives for reactions catalyzed by sulfuric or hydrofluoric acids should be considered and discussed in connection to

1. "Conjunct oligomerization" of olefins or the isoparaffin–olefin alkylation in the anhydrous sulfuric or hydrofluoric acids resulting in the branched *paraffinic* oligomers.
2. Cationic polymerization of isoolefins catalyzed by moderately concentrated 75–65% sulfuric acid, resulting in the selective formation of *unsaturated olefinic* oligomers.
3. Hydration of olefins in a strongly dilute 30–50% sulfuric acid, resulting in the formation of alcohols.

Starting with the classic works of Whitmore [20], all of these reactions are believed to involve the quasi-free carbenium ion active intermediates. It is also postulated that these reactions start via a reversible proton addition to the double bond of an olefin resulting in R^+ alkyl carbenium ion.

$$C{=}C + H^+ \leftrightarrow R^+ \tag{5}$$

Consequently, the initial alkyl carbenium ion is converted into the larger $R_1{}^+$ carbenium ion via a reaction with the next olefin molecule:

$$R^+ + C{=}C \rightarrow R_1{}^+ \tag{6}$$

Abstraction of the proton from the $R_1{}^+$ carbenium ion yields the products of cationic polymerization:

$$R_1{}^+ \rightarrow R_1{}^= + H^+,\ \text{etc.} \tag{7}$$

To explain the formation of saturated R_1H oligomers as the main products of the isoparaffin–olefin alkylation or of conjunct oligomerization, one more step of the hydride transfer from the isoparaffin or olefin to the alkyl carbenium ion is added to this reaction scheme:

$$R_1{}^+ + i\text{-RH} \rightarrow R_1H + i\text{-R}^+ \tag{8}$$

The similar reaction of the hydride transfer from the olefin to the carbenium ion also explains the formation of dienes and cyclopentenes as byproducts of the conjunct oligomerization:

$$R^+ + R^= \rightarrow RH + \text{dienes and cyclopentenes dissolved in the acid} \tag{9}$$

Finally, in the hydration of olefins, the alkyl carbenium ion reacts with water resulting in the abstraction of a proton:

$$R_{aq}{}^+ + H_2O \rightarrow ROH + H_{aq}{}^+ \tag{10}$$

Whitmore [20], Schmerling [21] and Deno et al. [22] proposed these reaction schemes more than 50 years ago. Since then they have remained unchanged. However, it is absolutely unclear, why the same alkyl carbenium ions react differently in 95% or in a moderately concentrated sulfuric acid resulting in *saturated paraffinic* oligomers in conjunct oligomerization of olefins and the isoparaffin–olefin alkylation, but yield *unsaturated olefinic* oligomers in cationic polymerization. This discrepancy can be quite naturally explained with the difference in solvation of protonated species either by anhydrous superacids or by water in the moderately concentrated or dilute acid resulting in the different active intermediates.

3.1. Solvation of alkyl carbenium ions in anhydrous H_2SO_4 and HF and the mechanism of the isoparaffin–olefin alkylation and conjunct oligomerization of olefins

According to the composition of the resulting final products, both the isoparaffin–olefin alkylation and conjunct oligomerization of olefins definitely are the carbenium ion reactions. This conclusion follows from formation of paraffins with even and odd numbers of carbon atoms, indicating the participation of carbenium ions in hydride transfer and cracking reactions. This is also consistent with the weak solvation of alkyl carbenium ions by anhydrous H_2SO_4 or HF that follows from the results of our quantum chemical calculations. For instance, the calculations indicated that the interaction of a *tert*-butyl carbenium ion with the first molecule of sulfuric acid results in a weak ion–molecular pair with an interaction energy of only about 60 kJ/mol [23]. Thus, in the anhydrous or in a very concentrated sulfuric acid, the properties of *tert*-butyl carbenium ions resemble those of the free species.

On the other hand, such weak solvation makes the formation of alkyl carbenium ions energetically unfavorable. Therefore, in reality, the interaction of olefins with anhydrous sulfuric acid results in alkyl sulfates instead of alkyl carbenium ions. This conclusion is consistent with the general experience in organic chemistry. Recently, this was also confirmed directly by our ^{13}C NMR study of the products resulting from interactions of propylene or 1-pentene with 95% H_2SO_4 [24–26].

The ^{13}C NMR data also indicated that alkylsulfates are the precursors of alkyl carbenium ions, which are formed via protonation of the monoesters in a large excess of anhydrous sulfuric acid. As follows from quantum-chemical calculations, the resulting protonated species are identical to the weakly solvated carbenium ions:

$$\begin{aligned} &H_2SO_{4L} + C{=}C \rightarrow RHSO_{4L}, \\ &RHSO_{4L} + H_2SO_{4L} \rightarrow R^+H_2SO_{4L} + HSO_{4L}^- \qquad (11) \end{aligned}$$

The subsequent reaction of such weakly solvated carbenium ions with isoparaffin results in the final products of alkylation, while the reaction of these species with the nonprotonated esters yields the products of conjunct oligomerization. Thus, the isoparaffin–olefin alkylation or conjunct oligomerization of olefins are in reality the consecutive reactions involving monoesters as the stable intermediates and alkyl carbenium ions as the highly reactive ionic species [24–26].

However, the concentration of alkyl carbenium ions in the excess of the acid is very low. ^{13}C NMR, therefore, detects these species only in an indirect way via increasing chemical shifts from the carbonyl groups of the protonated esters in excess of anhydrous sulfuric acid. Application for the quantitative interpretation of the ^{13}C NMR results of the rapid exchange model between protonated and the nonprotonated esters, indicated that the concentration of the resulting carbenium ions in the reaction mixture is about 100 times lower than that of alkylsulfates [25].

3.2. Solvation of alkyl carbenium ions in aqueous solutions

According to the results of our quantum-chemical calculations, the solvation of alkyl carbenium ions with the first water molecule results in the formation of oxonium ions. These species are identical to those resulting from the protonation of alcohols. The calculations also indicated that the second water molecule is hydrogen bonded to one of the protons of the oxonium ion instead of the hydrophobic alkyl group.

Similar to the solvation of protons, the corresponding experimental data on the heats of the stepwise hydration of alkyl carbenium ions in the gas phase via many water molecules were also obtained by Kebarle and coworkers [27,28] with the high-pressure mass spectrometry. The results of this study indicated that hydration energy of methyl, ethyl or propyl cations, becomes equal to 41 kJ/mol after solvation by five water molecules. Therefore, following a similar logic as for the proton case, we also concluded that the specific hydration of alkyl carbenium ions corresponds to the formation of hydrated $R^+ \, 5H_2O$ clusters.

The charge distribution in such clusters can be analyzed by comparing of the experimental data on proton affinities of alcohols and water. Let us do so for the case of the *tert*-butyl carbenium ion.

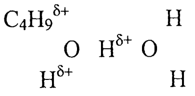
As follows from Table 3, the proton affinity of isobutene molecule of 817.2 kJ/mol is considerably

Table 3
Comparison of proton affinities of *iso*-butene, *tert*-butanol and water [29]

Molecules	Proton affinity (kJ/mol)
H_2O	664.6
i-C_4H_8	817.2
t-C_4H_9OH	827.6
$2H_2O$	828
$3H_2O$	909.6
Liquid H_2O	1090

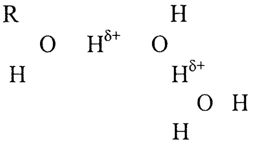
higher than that of water (696 kJ/mol). Therefore, in the complex of the *tert*-butyl carbenium ion with the first water molecule, the positive charge mainly remains at the alkyl fragment.

In contrast, the proton affinities of isobutene and of two water molecules (828 kJ/mol) are practically equal. Therefore, in the complex solvated by two water molecules, the positive charge is distributed between the *tert*-butyl fragment and the water molecule resulting in a structure that resembles a *tert*-butyl oxonium ion solvated with the water molecule:



$$\begin{array}{lllll} C_4H_9^{\delta+} & & & & H \\ & O & H^{\delta+} & O & \\ H^{\delta+} & & & & H \end{array} \qquad (12)$$

Moreover, the proton affinity of three water molecules of 909.6 kJ/mol is considerably higher than both affinities of isobutene and *tert*-butanol. Therefore, in the complex solvated with three water molecules, the tendency of the positive charge migration towards water is even stronger:



$$\begin{array}{llllll} R & & & H & & \\ & O & H^{\delta+} & O & & \\ H & & & H^{\delta+} & & \\ & & & & O & H \\ & & & H & & \end{array} \qquad (13)$$

Finally, the proton affinity of water is equal to 1090 kJ/mol. This is very much higher than of isobutene. Protonation of the latter, therefore, results in the weakly perturbed *tert*-butanol.

Thus, the hydrated *tert*-butyl carbenium ion only resembles a free *tert*-butyl carbocation if it is weakly solvated with the first water molecule. By contrast, hydration with several water molecules results in the *tert*-butyl oxonium ion or even in a weakly perturbed *tert*-butyl alcohol with the chemical properties that are quite different from those of the free *tert*-butyl carbocation.

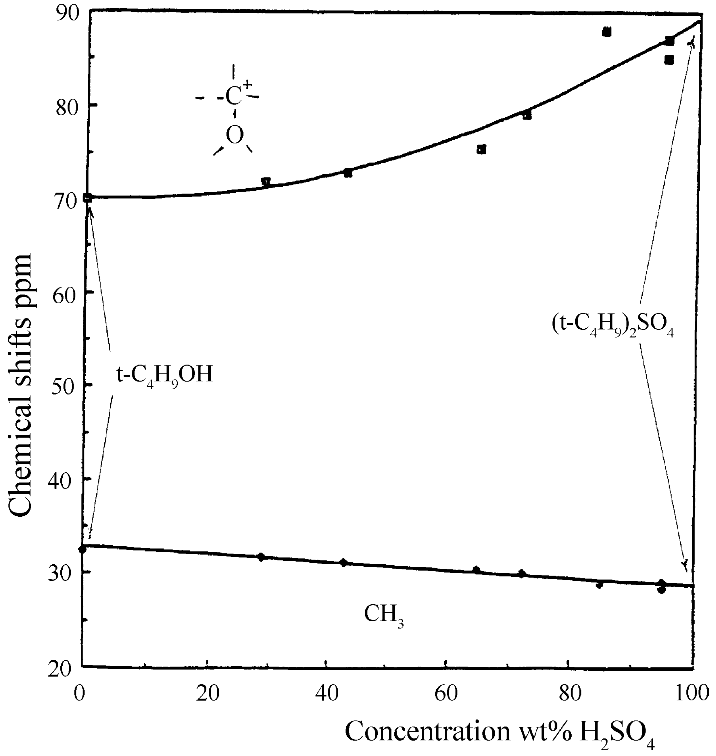


Fig. 3. ^{13}C NMR shifts of *tert*-butanol in mixtures with H_2SO_4 of different concentrations.

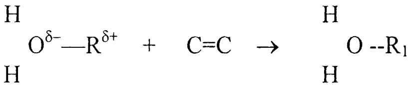
These conclusions are supported with our ^{13}C NMR study of *tert*-butanol–sulfuric acid solutions of different concentrations reported in Ref. [30]. As one can see from Fig. 3, upon dilution of 95% sulfuric acid with water, the ^{13}C chemical shifts of the NMR lines resulting from the central carbon atom of the *tert*-butyl alcohol decrease from 90 to 70 ppm. The first of these figures corresponds to the ^{13}C chemical shift at the central carbon atom of a *tert*-butyl oxonium ion, whereas the latter is very close to the corresponding chemical shift in pure *tert*-butanol. In [31], a similar effect was reported for the mixtures of ethanol with sulfuric acid of different concentrations. Thus NMR data also confirm that upon dilution of sulfuric acid–alcohol solution with water, the positive charge migrates from the alkyl group towards many water molecules resulting in instead of carbenium ions in alkyl-oxonium ions or even in alcohol weakly perturbed by hydrogen bonding with the protonated water.

3.3. Cationic polymerization of olefins in moderately concentrated sulfuric acid

As already mentioned earlier, the products of a cationic polymerization of olefins in a moderately concentrated sulfuric acid are quite different from those of conjunct oligomerization. Indeed, oligomerization of 1-pentene in 65% sulfuric acid results in the selective formation of olefinic dimers and trimers instead of paraffins in conjunct oligomerization of olefins or in isoparaffin–olefin alkylation [20–22]. This obviously indicates the absence of hydride transfer and cracking, i.e. of reactions that are typical of alkyl carbenium ions.

Taking into account of the above discussion on solvation of carbenium ions with water, this result looks quite natural. Indeed, 60% sulfuric acid corresponds to 3:1 water to acid ratio and is completely dissociated. Therefore, in the moderately concentrated sulfuric acid, olefin interacts with hydrated protons instead of the nondissociated acid. The protonation of olefin then results in the formation of hydrated oxonium ions, while the properties of alkyl fragments in these species are quite different from those of the weakly solvated alkyl carbenium ions. Therefore, the oxonium ions are not involved in such typical carbenium ion reactions such as cracking or hydride transfer. Instead, the cationic polymerization of olefins in the moderately concentrated sulfuric acid results in the selective formation of the olefinic dimers and trimers.

In other words, cationic polymerization is not a real carbenium ion reaction. Instead, it most likely proceeds via an interaction of olefins with the positively charged polarized alkyl groups of oxonium ions:



$$\begin{matrix}\mathrm{H} & \\ & \mathrm{O}^{\delta-}\text{—}\mathrm{R}^{\delta+} \\ \mathrm{H} & \end{matrix} \quad + \quad \mathrm{C{=}C} \quad \rightarrow \quad \begin{matrix}\mathrm{H} & \\ & \mathrm{O}\text{--}\mathrm{R}_1 \\ \mathrm{H} & \end{matrix} \qquad (14)$$

Similar to alkoxy groups in zeolites [32,33], this reaction requires an additional activation of the alkyl groups. In liquid acids this also most likely occurs by formation of the carbenium-ion-like transition states via stretching and polarization of the C–O chemical bond. The resulting more strongly positively charged alkyl group of the oxonium ion is then involved in the subsequent cationic oligomerization.

An important feature of hydrated oxonium ions is that these species can never dissociate into alkyl carbenium ions and water. Indeed, in accordance with the above discussion, the proton affinity of several water molecules is higher than that of olefin. Therefore, after some critical stretching of the C–O bond, proton is transferred back from the alkyl fragment to water resulting in abstraction of olefin instead of formation of carbenium ion (Fig. 4). This explains the different selectivity of cationic polymerization in comparison with conjunct oligomerization.

Neither the positive charge of the alkyl group in such transition states, nor the strength of the carbenium-ion-like fragments as a Lewis acid are as high as for the weakly solvated or free alkyl carbenium ions. Therefore, in moderately concentrated sulfuric acid the alkyl groups are neither involved in cracking nor in the hydride transfer from olefins. This explains the different selectivity of cationic polymerization in comparison with conjunct oligomerization or isoparaffin–olefin alkylation.

3.4. Hydration of olefins in dilute sulfuric acid

The sulfuric acid-catalyzed hydration of ethylene has been quite recently used in the chemical industry. This reaction was performed in the following two steps. At first, ethylene was dissolved in the

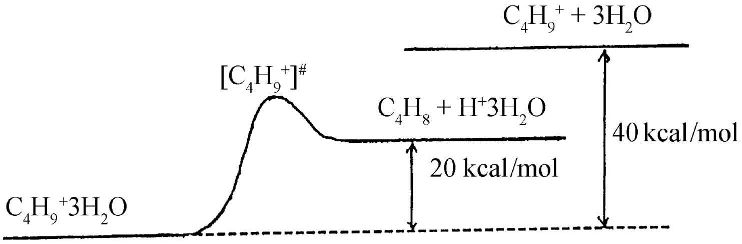


Fig. 4. Energy diagram illustrating decomposition of hydrated *iso*-butyl oxonium ion in water solution.

concentrated sulfuric acid resulting in the formation of mono-alkylsulfates. Then the water was added to the reaction mixture and the ethyl alcohol resulting from hydrolysis of the ester was separated by distillation.

In accordance with the earlier discussion, the mechanism of the second step of this reaction should be represented in the following way. Due to the higher affinity of many water molecules, the proton migrates from the acid–alkylsulfate solution towards water upon dilution. As follows from ^{13}C NMR spectroscopy [31], this results in the formation of alcohol that is only weakly perturbed by hydrated protons:

$$\begin{matrix} H \\ \\ H \end{matrix}\; O^{\delta-}\text{--}R^{\delta+} \quad + \quad n\,H_2O \quad \rightarrow \quad ROH \quad + \quad H^+\,nH_2O \tag{15}$$

4. Conclusion

This paper demonstrates that the strength of superacids mainly depends not on the high concentration of protons, but on their weak solvation resulting in the unusually high chemical activity of these species. In a similar way, solvation also determines the nature of protonated active intermediates in the acid-catalyzed transformations of hydrocarbons. Depending on the nature and concentration of the acids, or on the solvents, the properties of protonated species are changing in a broad range. In superacids this are the almost free alkyl carbenium ions, whereas in aqueous solutions the carbenium-ion-like alkyl species are only formed as transition states.

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