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In situ ^{13}C NMR study of tert-butanol interaction with moderately concentrated sulfuric acid

V.B. Kazansky

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
Leninsky Prospect, 117334 Moscow, Russia

F. Figueras and L.C. de Ménorval

Laboratoire de Chimie Organique Physique et Cinètique Chimique Appliquées,
URA 418 du CNRS, ENSCM, 8 Rue Ecole Normale, 34053 Montpellier Cedex 1, France

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An in situ NMR study of tert-butanol dehydration in 95 and 85% sulfuric acid did not indicate the formation of tert-butyl cations as active reaction intermediates. Instead, only NMR lines from oxonium ions under the condition of fast exchange with water and the acid were observed. It is most likely that, in the concentrated acid, the active intermediates of this reaction are represented by tert-butyl sulfuric ester which probably is a precursor of invisible tert-butyl carbenium ions representing short-lived excited or transition states.

Keywords: NMR; tert-butanol; sulfuric acid; carbenium ions

1. Introduction

Acid-catalyzed dehydration of tert-butanol is traditionally considered as a classical example of reactions involving carbenium-ion active intermediates. This was first concluded for homogeneous catalysis by concentrated sulfuric acid about sixty years ago in refs. [1–3]. Later, these ideas were generally accepted [4,5] and transferred to heterogeneous acid catalysis by amorphous silica–aluminas, zeolites etc.

On the other hand, very recent ^{13}C NMR MAS studies of tert-butanol decomposition on ZSM-5 zeolite did not confirm the formation of adsorbed tert-butyl carbenium ions, since no NMR lines with chemical shifts above 300 ppm were reported [6,7]. Instead, only shifts of about 80 ppm from surface ethers of adsorbed tert-butanol were observed. Nevertheless, some indirect evidence in favor of the carbenium ion mechanism was still provided.

In this connection, we present below the data on a reinvestigation of the tert-butanol interaction with moderately concentrated sulfuric acid using ^{13}C NMR for studying the active intermediates of the reaction. Our aim was to compare the homogeneous and heterogeneous tert-butanol dehydration to explore the similarities and distinctions in behaviour of both these systems.

2. Experimental

The reaction mixture was prepared by slow addition of tert-butanol to sulfuric acid of different concentrations at room temperature with intensive stirring of the resulting solution. To avoid heating in the case of concentrated acid, the solution was cooled during preparation in an ice bath with constant temperature control. In most of our experiments, equimolar 1 : 1 sulfuric acid to alcohol ratios were used.

In concentrated acid, the reaction started immediately. This resulted in gradual formation of two well-separated layers: an upper, colorless layer of hydrocarbon final products and a lower, heavier layer of the reacting alcohol–sulfuric acid solution. The amount of the upper layer increased with time. Therefore, this was used to estimate both the conversion of initial alcohol and the reaction rate.

For in situ ^{13}C NMR study of active intermediates, the reaction mixture was immediately after preparation transferred to the cavity of the NMR spectrometer. During NMR measurements, only the spectra of the heavier lower part of the solution were recorded, whereas the growing upper layer of the final products was outside the NMR coil. Their chemical composition was studied separately after completion of the reaction by chromato-mass spectrometry and NMR.

The ^{13}C NMR spectra were recorded at room temperature using WP 200 SY and AC 250 Bruker spectrometers operating for protons at 200 and 250 MHz respectively. The sample volume was about 2 cm^3. No enrichment of tert-butanol in ^{13}C was used. The typical number of scans during NMR measurements was within 48–96. The spectra, if not specially indicated, were recorded with ^{13}C–H decoupling. The chemical shifts were referred using TMS as an external standard.

The chromato-mass spectrometric analysis of resulting hydrocarbons was carried out with a Hewlett-Packard 5890/5972 gas chromato-mass spectrometer with CH_2Cl_2 as a solvent. 95% sulfuric acid was of the analytical grade. The concentrations of 85, 75, and 65% aqueous solutions approximately corresponded to 1 : 1, 1 : 2, and 1 : 3 H_2SO_4-to-H_2O molar ratios. Tert-butyl alcohol contained less than 0.5% of water.

3. Results

3.1. THE REACTION PRODUCTS

Slow mixing of 95 or 85% sulfuric acid with equimolar amounts of tert-butanol at constant temperature of 25°C first resulted in a homogeneous yellow opaque solution that was gradually transformed into the above described separated layers: the upper one from the final hydrocarbon products and the lower heavier layer of the tert-butanol–sulfuric acid reacting mixture. For 95% acid, the reaction was completed without stirring in 30–40 min quantitatively yielding a complicated mixture of hydrocarbons and diluted H_2SO_4. With stirring or shaking or, if the reaction was carried out in the NMR spectrometer, with sample rotation, the transformation was faster and required only 15–20 min. After keeping the reaction mixture at room temperature for several days, the color of the heavier layer first turned to orange and then to dark-red.

In more diluted acid the reaction was slower and the coloration of sulfuric acid was weaker or even absent. For instance, in 85% acid, the reaction was completed at room temperature without stirring in about 1–2 h, while in 75% acid, in about 50 h. With further dilution, no hydrocarbons were formed at room temperature at all.

The mass-chromatograms of the final products for stoichiometric 1 : 1 molar mixtures of tert-butanol with 95 or 85% sulfuric acid confirmed the conclusion of refs. [1–3] that the reaction quantitatively yields a complicated mixture of olefinic dimers, trimers, and tetramers. 2,4,4-trimethylpentene-1 and, in somewhat smaller amount, 2,4,4-trimethylpentene-2 are the predominating dimers.

Such composition of final products is also confirmed by the ^{13}C NMR spectra represented in fig. 1, where the peaks from CH_2 at the double bond with chemical shifts of 115 and 118 ppm, those from CH groups at the double bond with shifts of 140 and 145.7 ppm, and from $=C<$ groups with a shift of 132.4 ppm are evident. This assignment is supported by the non-decoupled NMR spectra depicted in fig. 1b and by the literature data [8].

Thus, our results confirmed the earlier conclusion that at room temperature the interaction of stoichiometric amounts of tert-butanol and concentrated sulfuric acid represents a combination of dehydration with subsequent oligomerization of alkyl fragments into branched di-, tri-, and tetra-olefinic oligomers:

$$n\ t\text{-}C_4H_9OH + H_2SO_4 \rightarrow n\ i\text{-}C_4H_8 + H_2SO_4\ nH_2O\,. \qquad (1)$$

In case of stoichiometric mixtures, the yield of oligomers was practically quantitative. There is also no doubt that the reaction proceeded without intermediate formation of free isobutene, since no gaseous products were evolved.

3.2. NMR SPECTRA

Our first experiments already demonstrated that NMR spectra of tert-butanol dissolved in concentrated sulfuric acid are gradually changing with time. This is in agreement with the above observation that in 95% acid the reaction is completed within 15–20 min. Therefore, we will start with a more simple case of catalysis by

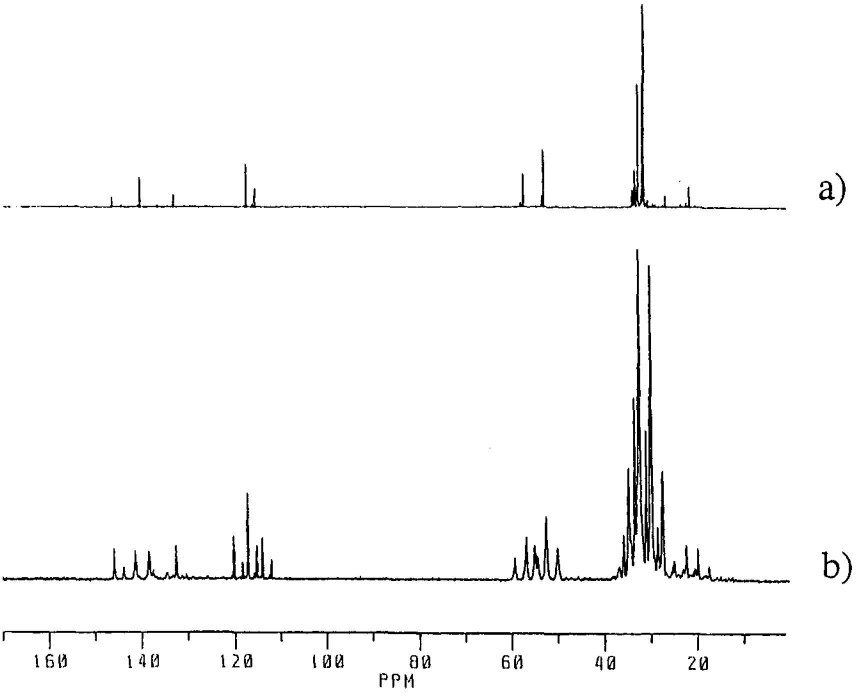


Fig. 1. ^{13}C NMR spectra of reaction products. (a) Recorded with C–H decoupling. (b) Recorded without C–H decoupling.

diluted sulfuric acid, where the reaction rate was lower and ^{13}C NMR lines did not change their positions and intensities with time.

For all of such reaction mixtures of very different compositions, we observed neither the lines with chemical shifts in the region of 300 ppm from tertiary carbon atoms of tert-butyl carbenium ions, nor those with a shift of 48.3 ppm from their methyl groups [8]. Instead, only the chemical shifts of 70–90 and 29–32 ppm were evident (figs. 2 and 3). Neither of them coincides with chemical shifts in pure tert-butanol of 32.7 and 69.9 ppm. Therefore, the observed spectra can obviously be attributed to some reaction intermediates different both from tert-butyl carbonium ions and from pure tert-butanol.

A remarkable feature of the NMR spectra is the dependence of chemical shifts and signal amplitude ratios on the composition of the solution. This is clearly seen from fig. 2, where are presented the spectra of 0.5 : 1, 1 : 1 and 2 : 1 molar mixtures of tert-butanol with 75% sulfuric acid. The shift of the line from the tertiary carbon atom decreases in this sequence from 80.2 to 75.2 ppm approaching at higher alcohol concentration the chemical shift of 69.9 ppm for pure tert-butanol. Simultaneously the chemical shift from the methyl group increases from 29.4 to 30.9 ppm also approaching the corresponding shift in pure tert-butanol of 32.7 ppm.

Another remarkable feature of the spectra is the unusual ratio of signal amplitudes from methyl groups and tertiary carbon atoms. Indeed, their theoretical

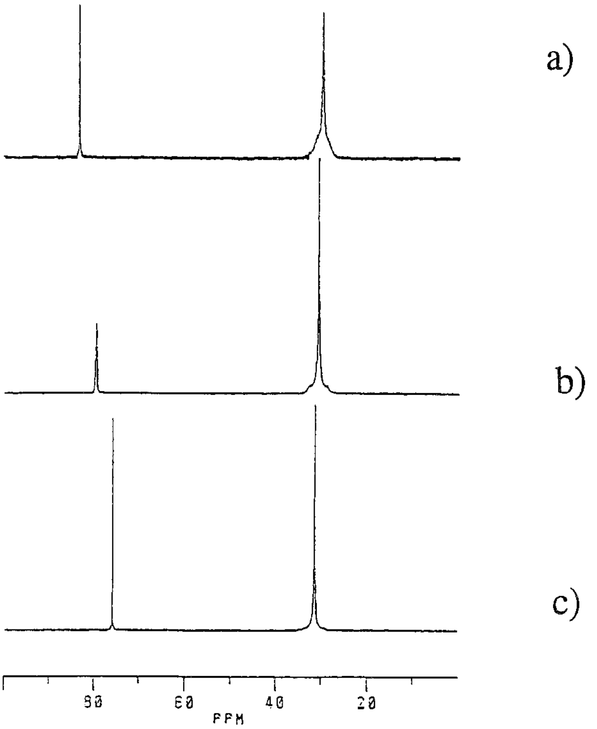


Fig. 2. ^{13}C NMR spectra of tert-butanol solutions in 75% H_2SO_4. (a) H_2SO_4 : ROH molar ratio 1 : 0.5. (b) H_2SO_4 : ROH molar ratio 1 : 1. (c) H_2SO_4 : ROH molar ratio 1 : 2.

3 : 1 ratio is evident only for spectrum (b), whereas in spectra (a) and (c), this ratio is close to one. This indicates that the linewidths of the signals from tertiary and primary carbon atoms are influenced in a different way by the composition of the solution.

The chemical shifts are also dependent on the concentration of the acid (fig. 3). Indeed, in more diluted sulfuric acid, the similar tendency as for dilution with alcohol is evident: the lines approach the positions characteristic for pure tert-butanol.

Such a behavior is absolutely unusual for the NMR spectra of individual chemical compounds. However, it can be easily explained by the coexistence in the solution of several intermediates with different chemical shifts in the state of rapid exchange with each other [9].

In this case, the NMR line represents the average of the lines from individual compounds. Its position is both dependent on the chemical shifts δ of the solution components and on their mole fractions N. For instance, for the mixture of two components with mole fractions N_1 and N_2 the resulting chemical shift is equal to the sum of the products of the individual shifts and mole fractions:

$$\delta = \delta_1 N_1 + \delta_2 N_2 \,. \tag{2}$$

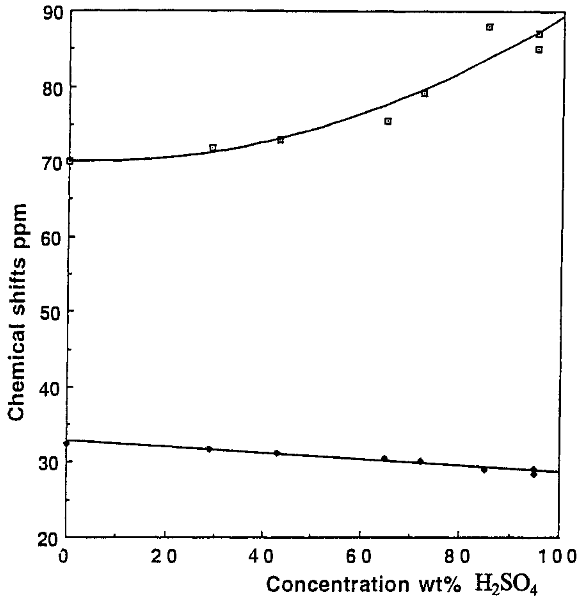


Fig. 3. Dependence of ^{13}C chemical shifts on the concentration of H_2SO_4 in the molar mixtures with tert-butanol.

Thus, the averaged line approaches the position characteristic for the major component with the increase of its amount in the solution.

In our case, one of the components is certainly tert-butanol with a chemical shift of the tertiary carbon atom of 69.9 ppm (table 1). The other possible components are tert-butyl ether or mono and di tert-butyl esters. The chemical shift of the former is equal to 73.6 ppm, while at room temperature, tert-butyl esters are unstable [10], and the corresponding shifts are unknown. However, they should be of the same order of magnitude as for other esters listed in table 1, i.e. about 70–75 ppm.

This is considerably lower than the largest value of the tert-carbon atom chemical shift of almost 90 ppm obtained in this work for the most concentrated sulfuric acid solution (fig. 2). Therefore, the reaction intermediates are likely represented by protonated ether or esters with larger chemical shifts than those of protonated alco-

Table 1
^{13}C chemical shifts of primary carbon atoms in different alcohols and related compounds [8]

Alkyl fragments	^{13}C chemical shifts on primary carbon atoms (ppm)		
	ROH	ROR	RSO_4R
CH_3	50.5	61.2	59.1
C_2H_5	58.4	66.9	69.6
$2\text{-}C_3H_7$	64.7	69.2	?
$t\text{-}C_4H_7$	69.9	73.6	?

hol. Indeed, as it was shown in a special experiment, the dissolution of diethyl ether in a large excess of concentrated sulfuric acid, presumably resulting in ethyl oxonium ions, shifted the ^{13}C NMR line from the primary carbon atom from 66.9 to 77.5 ppm, i.e. increases the chemical shift upon protonation by more than 10 ppm.

Let us now discuss in more detail the NMR spectra of tert-butanol dissolved in more concentrated sulfuric acid. The minimal time required in our experiments for accumulation and recording of NMR spectra was about 15 min. Therefore, for 95% acid, in situ measurements were hardly possible. However, for 85% acid, the reaction was slower and, even with sample rotation, completed in about half an hour. Therefore, the spectra were recorded in the course of the reaction at least twice. Fig. 4 represents one such example.

The upper spectrum (a) of this figure was recorded immediately after mixing the reaction components. The most intensive line with a chemical shift of 29 ppm belongs to methyl groups and the one with a shift of 88 ppm is attributed to the ter-

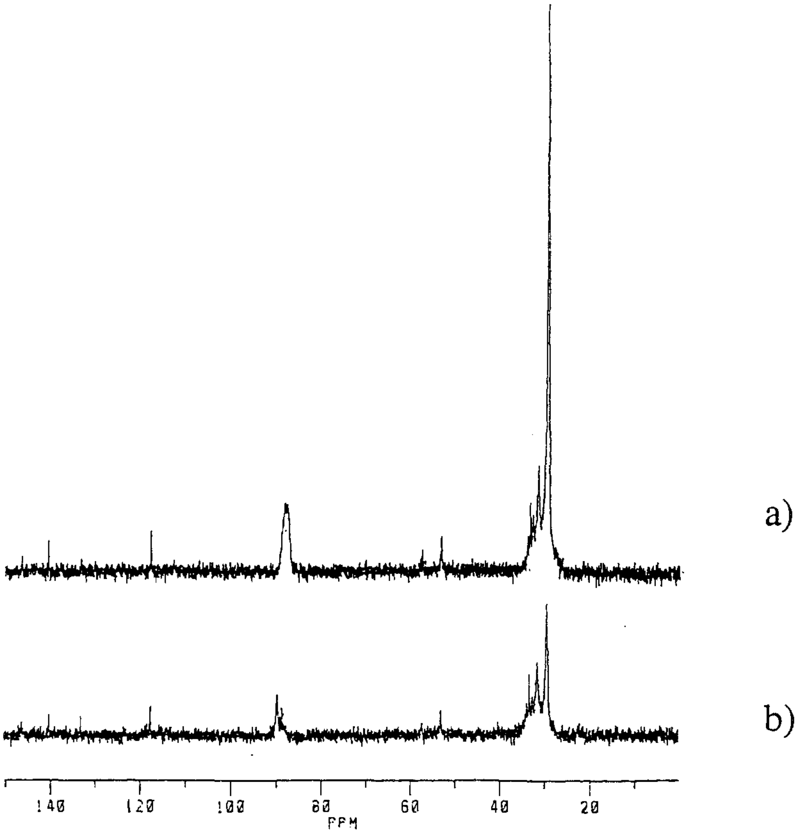


Fig. 4. ^{13}C NMR spectra recorded at room temperature during the reaction of 85% H_2SO_4 with tert-butanol in a 1 : 1 molar ratio: (a) NMR spectrum recorded immediately after the beginning of the reaction. (b) 15 min after the beginning of the reaction. The conversion of tert-butanol at the end of this experiment was about 70%.

tiary carbon atom of an iso-butyl fragment, which enters the composition of some reaction intermediates involved in the rapid exchange. The shape of this line is quite unusual. Its flat maximum represents a classical example of a moderately fast exchange [9]. The positions of multiple weaker lines in the regions of 30, 50–60, and 110–130 ppm practically coincide with those in ^{13}C NMR spectra of final products shown in fig. 1. Therefore, they belong to some steady state concentration of olefinic oligomers dissolved during the reaction in sulfuric acid.

The spectrum (b) presented in fig. 4 was recorded with the same amplification as (a) at about 15 min after the beginning of the reaction, when the conversion was approximately 50–70%. The intensities of the weaker lines from the final products changed insignificantly, whereas those from active intermediates strongly decreased. In addition, the line from the tertiary carbon atom became sharper with the normal 1 : 3 ratio of amplitudes relative to the line of the methyl groups. This probably indicates a higher content of a certain more stable intermediate with the largest shift of 89 ppm from the tertiary carbon atom that we ever observed. On the other hand, no lines from butyl carbenium ions with a chemical shift of 330 ppm were detected.

It is also remarkable that the chemical shift from methyl groups in the most concentrated sulfuric acid solutions tends to decrease instead of increase and approach the value of 48.3 ppm, as it should be expected for tert-butyl cations (fig. 3). This is one more argument in favor of the absence of tert-butyl cations in the reaction mixture.

4. Discussion

The most surprising result of this paper is the discrepancy between the data on the catalytic dehydration of tert-butanol and those of the ^{13}C NMR study of the reaction intermediates. Indeed, the composition of the final products is in excellent agreement with the original publication of Whitmore and coworkers [1–3], which resulted later in the creation of the carbenium ion theory of acid catalysts [4,5]. In contrast, our NMR measurements did not confirm the formation of carbenium ions as active intermediates.

For moderately concentrated sulfuric acid used in our study this conclusion is, however, quite natural. Indeed, 85% sulfuric acid corresponds to the 1 : 1 H_2SO_4 : H_2O molar ratio, whereas for 75% and 65% acid these ratios are 1 : 2 and 1 : 3 respectively. In addition, one more water molecule is released during the reaction. Therefore, the equilibrium of tert-butyl cation hydration was presumably always shifted toward oxonium structures, and we always observed the oxonium ions instead of carbenium ions. In this connection, it should be stressed that the ^{13}C NMR spectra of aliphatic carbenium ions reported by Olah and coworkers in "magic acid" were observed only in absolutely anhydrous conditions [8,11].

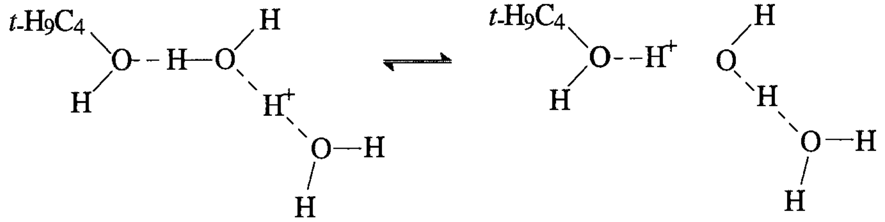
Earlier, the state of protons in concentrated sulfuric acid has been extensively studied by IR and Raman spectroscopy in refs. [12–14]. It was concluded that in 90–100% acid only self-dissociation takes place according to the following equation:

$$H_2SO_4 + H_2O \rightarrow [H_2O\ HSO_3OH_2]^+ + HSO_4^- \qquad (3)$$

At acid concentration below 90%, the interaction with a second water molecule results in subsequent dissociation of the $[H_2O\ HSO_3OH_2]^+$ cation and in the formation of protons solvated with two water molecules:

$$[H_2O\ HSO_3OH_2]^+ + H_2O \rightarrow H_2SO_4 + [H_2O\ H\ OH_2] \qquad (4)$$

Such species also represent the hydrated protons in aqueous solutions of other acids. Therefore, it is most likely that in 85% and more diluted sulfuric acid the protonation of tert-butyl alcohol also occurs with participation of hydrated protons:

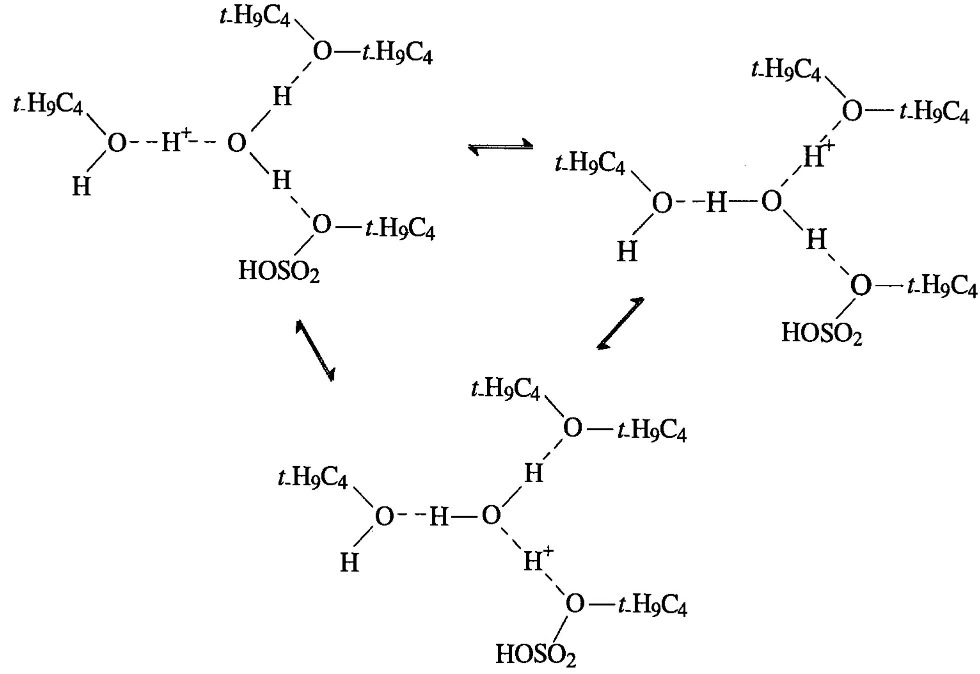


(5)

According to proton NMR study [9], such protonation results in hydrated oxonium ions with fast exchange of protons between oxygen atoms of water and alcohol. This should average the NMR lines of non-protonated and protonated species (structures (5)) thereby increasing the chemical shift of the tert-carbon substituted with oxygen up to 10 ppm. In its pure form, the equilibrium (5) most likely corresponds to the range of chemical shifts 70–80 ppm or to the concentrations of sulfuric acid below 70% (fig. 3).

On the other hand, the chemical shifts above 80 ppm in more concentrated sulfuric acid should be attributed to the additional formation of some other moieties, for instance, tert-butyl esters of sulfuric acid or tert-butyl ether. These intermediates can certainly also participate in similar equilibria with hydrated protons as tert-butanol, resulting in even larger shifts than those presented in table 1.

It is also remarkable that, instead of three or four doublets representing the rapid exchange equilibria of alcohol, ether, and esters with their protonated forms, we always observed only two averaged lines, which change their positions depending on the composition of the solution. Therefore, we have also to postulate in addition to rapid exchange of protons between protonated species and water also an exchange between ester, ether, and alcohol. It likely takes place in the following triple or even more complicated mixed complexes, when proton migrates around the central oxygen atom of the oxonium ion:



(6)

Such an exchange is possible only if the activation barriers and enthalpies of corresponding equilibria are low enough and close to each other. In other words, this means close proton affinities of all the above intermediates.

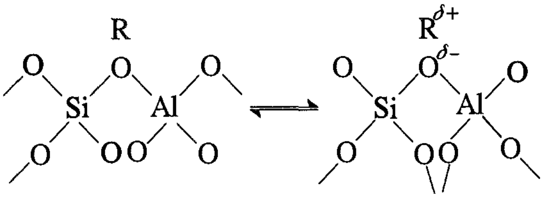
Let us now bring together the results of the NMR study of active intermediates with catalysis. There is certainly no doubt that the most catalytically active system corresponds to the most concentrated sulfuric acid. Therefore, the catalytic activity should be related to some intermediates with chemical shifts of tertiary carbon atoms of about 85–90 ppm (fig. 3). In accordance with the above discussion, these species are most likely the protonated esters which are hydrolyzed easier than ethers and therefore exist only in very concentrated acid. In addition, 95% acid is also known as a catalyst of isobutene oligomerization with very similar final products. In this case obviously no ether or protonated alcohol can be formed. Therefore, the active intermediates of the sulfuric acid catalyzed transformations of olefins and alcohols are most likely similar and are represented by tert-butyl ester, which probably is a precursor of tert-butyl carbenium ions. Their steady-state concentration in the reaction mixture is, however, far below the limit of detection by NMR.

Earlier [6], the ^{13}C NMR MAS spectra of selectively labelled $(CH_3)_3{}^{13}COH$ alcohol adsorbed on HZSM-5 zeolite were studied in the broad temperature range from 10 to 373 K. Like in the present paper, no resolvable spectral features could be distinguished from the background in the region expected for carbenium ions, though the chemistry of adsorbed intermediate transformations was in excellent agreement with the formation of these species. Therefore, the similar conclusion was made that the steady-state concentration of adsorbed carbenium ions during tert-butanol decomposition on ZSM-5 zeolite is very low or that their lifetime is very short.

Instead of adsorbed carbenium ions, the authors observed the formation of adsorbed tert-butyl alkoxides with a chemical shift of the tertiary carbon atom bonded to the surface oxygen of the zeolitic framework equal to 77 ppm and another line at 29 ppm from aliphatic carbon of methyl groups. After heating to 373 K, the oligomerization of hydrocarbon fragments occurs resulting in the appearance of additional lines with somewhat smaller chemical shifts in this spectral region.

All these conclusions were essentially confirmed in a later publication [7] which was also devoted to the study of dehydration of selectively ^{13}C labelled tert-butyl alcohol on a HZSM-5 zeolite. Similar to ref. [6], no signals from adsorbed tertiary butyl carbenium ions were observed. Instead, only those from ^{13}C tertiary carbon atoms in the surface tert-butyl-silyl ether or corresponding oligomeric silyl ether were detected. The silyl ether intermediates were stable within the temperature range of 296–373 K and were decomposed at 448 K to produce an additional amount of butene oligomers. Another important feature of the reaction was the scrambling of the ^{13}C label among the reaction products. The authors also supposed that the reaction proceeded through the adsorbed carbenium ions, which did not represent really existing intermediates, but should be rather considered as short-lived invisible species.

The nature of these species was discussed in our papers [15–19], where it was shown that the carbenium-ion-like transient species may result from stretching or vibrational excitation of carbon–oxygen bonds in surface esters:



(7)

Such "vibrational polarization" results in separation of charges and in formation of an excited $R^{\delta+}$ fragment that can further react according to the rules of carbenium-ion chemistry.

This conclusion was based on the general idea, that in most cases the stretched chemical bonds are more polar than those in corresponding ground states [15]. This was also supported by a spectral study of proton transfer from surface Brønsted acid sites to adsorbed molecules [16–19].

In our opinion, it is highly probable that the similar "vibrational polarization" is also effective for activation of alkyl fragments in protonated esters in homogeneous catalysis by concentrated sulfuric acid. Such excitation should result in positive charging of the isobutyl group, which can further react according to the S_N2 mechanism:

$$RSO_4R \rightleftharpoons \overset{\delta+}{R}\ \overset{\delta-}{SO_4R}\,. \tag{8}$$

In the case of complete C–O bond dissociation, the real carbenium ions can be also formed as short-lived excited states in parallel with splitting off the sulfuric acid and water molecules. Then, the reaction follows the S_N1 mechanism:

$$RSO_4R \rightleftharpoons R^+ + SO_4R^-\,. \tag{9}$$

Of course, at the moment, these ideas are still of a quite preliminary character and require additional arguments and confirmation. This probably will be done in our following publications.

5. Conclusion

The results of the present study showed that solutions of tert-butanol in moderately concentrated sulfuric acid represent a highly dynamic system with multiple fast equilibria between different protonated ionic species. They mainly involve the oxonium structures, whereas the ^{13}C NMR spectra of tert-butyl carbenium ions were not observed.

It is most likely that tert-butyl cations represent the activated complexes or short-lived excited states, which are probably formed in a very low concentration via vibrational excitation of protonated tert-butyl sulfuric acid ester. Similar to heterogeneous transformation of tert-butanol on zeolites the amount of such species is, however, too low for their NMR detection. In this connection, it is surprising that the interaction of tert-butanol with moderately concentrated sulfuric acid is still considered as a classical example of the carbenium-ion chemistry, whereas it rather represents the case of oxonium-ion chemistry.

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