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In situ ^{13}C NMR study of "conjunct polymerisation" of 1-pentene in 95% sulfuric acid

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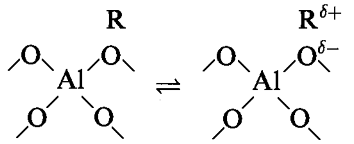
^{13}C NMR study of "conjunct polymerisation" of 1-pentene in 95% sulfuric acid demonstrated that this is a carbenium ion reaction, where the esters are the precursors of carbenium ions. In the first step of the reaction a complicated mixture of primary and secondary mono- and dipentyl esters is formed. In an excess of the acid the esters are decomposed yielding aliphatic carbenium ions, which are then involved in secondary reactions resulting in the final products. Similar to heterogeneous catalysis on zeolites, the steady state concentration of the aliphatic carbenium ions during the reaction is, however, too low for their direct detection by NMR.

Keywords: NMR; acid catalysis; pentene

1. Introduction

Acid catalysed transformations of olefins both in homogeneous and in heterogeneous systems are traditionally considered to be classical examples of carbenium ion reactions [1,2]. Modern ideas about the mechanism of these processes were formulated as early as the 30's, mainly from the stereochemistry of the reaction products, their composition and from observed kinetic regularities of the corresponding reactions. However, direct spectroscopic evidence for aliphatic carbenium ion formation has never been reported, excepting the observation of a low temperature interaction between olefins and "magic acid" by NMR [3,4].

Considerable progress in the understanding of the nature of aliphatic carbenium ion intermediates has recently been achieved for catalytic transformations of olefins on zeolites. Results obtained by quantum chemical calculations [5–7], from ^{13}C NMR studies of active intermediates [8,9], and from IR [10] measurements of proton transfer from surface Brønsted acid sites to adsorbed hydrocarbons clearly indicate that the adsorbed carbenium ions are the highly chemically active, unstable species. They are formed from the much more stable surface alkoxides as highly energetically excited ion pairs by stretching of C–O bonds [10,11]:



(1)

This results in separation of electric charges and in formation of "zwitterions", which contain the unstable short-lived adsorbed carbocations. The subsequent reactions of these species follow the rules of carbenium ion chemistry and result in the corresponding final products. However, due to the extremely high reactivity of such excited adsorbed intermediates, they are formed from the more stable surface alkoxides in amounts which are much below the sensitivity of any spectral technique currently available.

The progress in the understanding of the real nature of aliphatic carbenium ions in homogeneous systems, except of the low temperature reactions in superacids, is more modest. There is certainly no doubt that in solutions these species are similar to those adsorbed on zeolites and are stabilised by interaction with solvating molecules or with dissolved anions. Similar to surface alkoxides, this should convert them into esters, ion pairs or oxonium structures.

Most interesting in this connection are the recent results reported by Albright et al. [12–14] concerning the sulfuric acid catalysed alkylation of isobutane with olefins. The authors demonstrated that this classical carbenium ion reaction could be carried out in two separate steps. The first of them represented the interaction of the acid with olefins. It was performed with 95% sulfuric acid at low temperature of about −30°C and resulted in formation of dialkyl sulfates, which were relatively stable at room temperature and below. On the other hand, in presence of an excess of 95% acid, these intermediates decomposed into a complicated mixture of branched paraffins. Simultaneously cyclopentenes were formed, which were dissolved in the acid. When the reaction mixture contained isobutane in addition to olefin, the reaction mainly resulted in isooctane alkylate.

In the present work a similar two-step approach was used for the ^{13}C NMR study of the "conjunct polymerisation" of 1-pentene in 95% sulfuric acid. This reaction results in formation of paraffinic branched oligomers and in substituted cyclopentenes dissolved in the acid and is usually considered as a classical example of carbenium ion chemistry [2,15]. Earlier ^{13}C NMR was already applied to investigate the interaction of tert-butanol with sulfuric acid and has proved to be a highly informative technique [15]. Below, both the ^{13}C NMR spectra of pentyl sulfuric acid esters and the results of the in situ NMR study of their decomposition in an excess of the acid are reported.

2. Experimental

The mixture of the pentyl sulfuric acid esters was prepared at 0°C by slow addition of 1-pentene to the cooled 95% sulfuric acid. To avoid heating of the solution during preparation it was kept in an ice bath with constant temperature control. The second reagent was added in small portions in such a way that the temperature increase never exceeded a few degrees.

The composition of the hydrocarbon final products was analysed by NMR and chromato mass spectral analysis. The latter was carried out with a Perkin Elmer Chromass 910 instrument supplied with a capillary column using He as a carrier gas. The assignment of the reaction products was made from the parent masses in the mass spectra and from the fragmentation patterns of the parent ions. In addition, a mass balance of the final products was performed at the end of the reaction from the amount and density of resulting hydrocarbons.

The high resolution ^{13}C NMR measurements were performed at room temperature with $CDCl_3$ as an external reference using a Perkin Elmer Gemeny 300 spectrometer operating at 300 MHz for protons. No enrichment of 1-pentene in ^{13}C was used. Typically, between 40 and 96 scans were performed during NMR measurements. The spectra, unless otherwise indicated, were recorded with ^{13}C–H decoupling. The chemical shifts were referred to the TMS standard.

For in situ ^{13}C NMR study of the active intermediates, the ampoule with the mixture of the esters was immediately transferred after preparation to the cavity of the NMR spectrometer. During the course of the experiment only the spectrum of the heavier lower part of the solution was recorded, as the growing upper layer of the hydrocarbon final products was outside the NMR coil. The kinetics of the decomposition of the esters then followed both from the accumulation of the resulting hydrocarbons in the upper part of the ampoule and from the decrease of the NMR lines from the esters dissolved in the acid. The latter was done with help of the KIND (Kinetic Decrease) program.

Sulfuric acid (95%) was of analytical grade. 1-pentene from Fluka contained less than 1% of impurities.

3. Results

After addition of the very first portions of 1-pentene to 95% sulfuric acid at 0°C the solution became opaque and separated into two layers: the higher density layer contained a mixture of sulfuric acid and sulfuric acid esters, whereas the upper layer contained 1-pentene, if 1-pentene was there in excess. With increasing amount of the added olefin the solution gradually became more uniform and at the composition of the reaction mixture, which corresponded to about two moles of olefin per one mole of the acid, it became clear with a slightly yellowish colour. As will be shown below, with high resolution ^{13}C NMR, this corresponds to formation of a mixture of dipentyl sulfuric acid esters.

At room temperature the esters were rather stable, but in the presence of an excess of the acid they gradually started to decompose again resulting in formation of two separate layers. The upper layer contained the hydrocarbon final products, whereas the lower dark orange or red heavier layer represented the remaining sulfuric acid-ester solution. The amount of the upper layer increased with time. This was used to estimate both the conversion of the esters and the reaction rate. For this purpose, the reaction mixture was placed in a calibrated cylinder and accumulation of the resulting hydrocabons was gradually followed by measurement of the volume.

Fig. 1a represents a ^{13}C NMR spectrum of the mixture of pentyl sulfuric acid esters prepared according to the above mentioned procedure. The lines with chemical shifts in the region of 10–40 ppm are produced by aliphatic carbon atoms of alkyl groups, whereas those with the shifts in the region of 80–90 ppm by primary carbon atoms connected with oxygen in R–O–S oxo-fragments of the esters. The very weak lines in the region of chemical shifts of 115–140 ppm should be ascribed to carbon atoms at the double bonds in unreacted initial olefin [3] (the lines with the shifts of 114 and 139 ppm are connected with 1-pentene, whereas those with shifts of 123 and 133 ppm with 2-pentene, thus indicating the double bond shift in 1-pentene).

The partial isomerisation of 1-pentene during preparation of the esters was also confirmed by the compli-

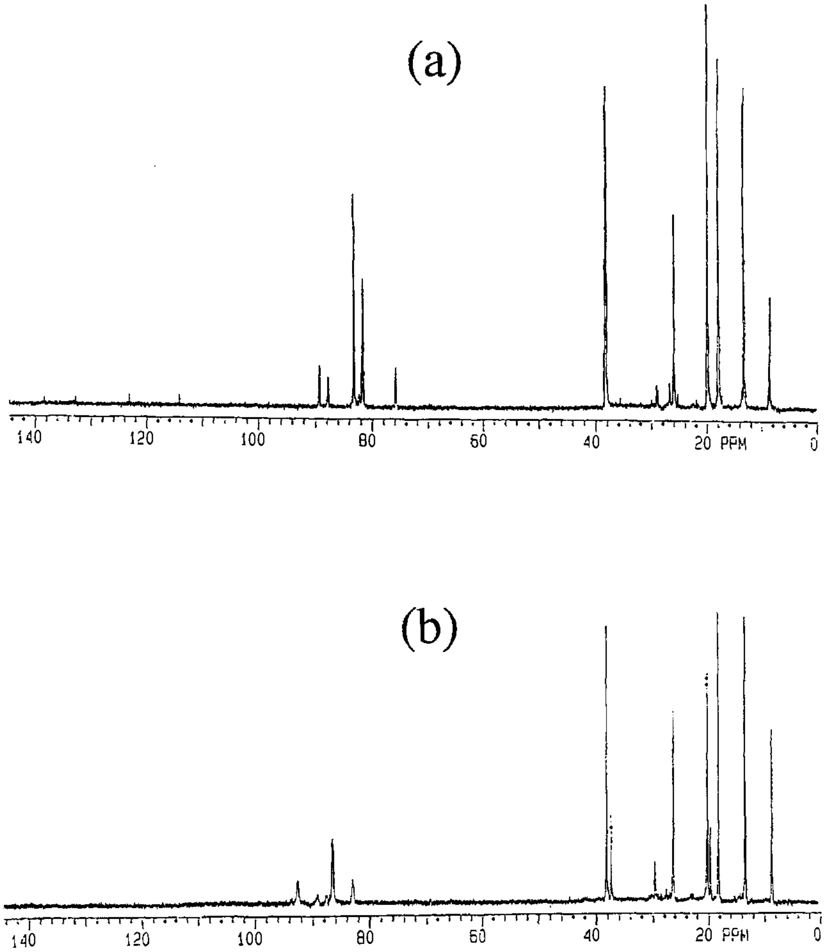


Fig. 1. (a) ^{13}C NMR spectrum of pentyl esters of sulfuric acid recorded at room temperature. (b) The NMR spectrum of the same mixture in presence of an excess of sulfuric acid (1 : 1 esters to 95% acid molar ratio).

cated nature of the resulting NMR spectrum in the region of C–O chemical shifts, where the lines from at least five different species are evident. They could be separated into two doublets and one singlet. Since the ^{13}C shifts of the diesters are usually slightly larger than those of the monoesters [3], the most intense lines in each of the doublets with the shifts of 90 and 84 ppm should be attributed to the dipentyl esters, and those with the smaller shifts of 88 and 82 ppm to the monopentyl esters. Finally, the single line with the lowest chemical shift of 76 ppm is probably connected with oxonium ions, which are formed by partial hydrolysis of the esters due to 5% water content in sulfuric acid. Such an assignment is also supported by the low value of the chemical shift of this line, which is too small for the sulfuric acid esters. In addition, as will be shown below, the corresponding species are not transformed into hydrocarbon final products upon decomposition of the esters.

At room temperature the NMR spectrum was practically constant for several hours. This indicates that the esters are relatively stable. In addition, the solution remained clear and its yellowish colour was unchanged. This also confirms the absence of reaction. On the other hand, as was already mentioned in the Introduction, in an excess of concentrated acid (more than about one mole of 95% acid per mole of the ester) the mixture of the esters started to decompose resulting in the colourless upper layer of hydrocarbon final products and in an opaque dark orange or red heavier layer of the sulfuric acid containing residual.

Without stirring the solution, the reaction was completed within several to ten hours depending on the excess of the acid. However, if the ampoule containing the reaction mixture was rotated inside the NMR cavity, the decomposition of the esters was much faster and was completed in only 10–20 min.

Fig. 2 depicts a mass-chromatogram and a ^{13}C NMR spectrum of the resulting hydrocarbons. The reaction products represent a very complicated mixture of C_9–C_{12} branched paraffins with odd and even number of carbon atoms (fig. 2a). This is consistent with the ^{13}C NMR spectrum of fig. 2b, where only the lines from aliphatic carbon atoms on the background of a broad line from oligomers are seen, whereas the lines from carbon atoms at double bonds are absent.

The amount of resulting hydrocarbons was always about half that of the initial olefin used for preparation of the esters, whereas the amount of residual solution

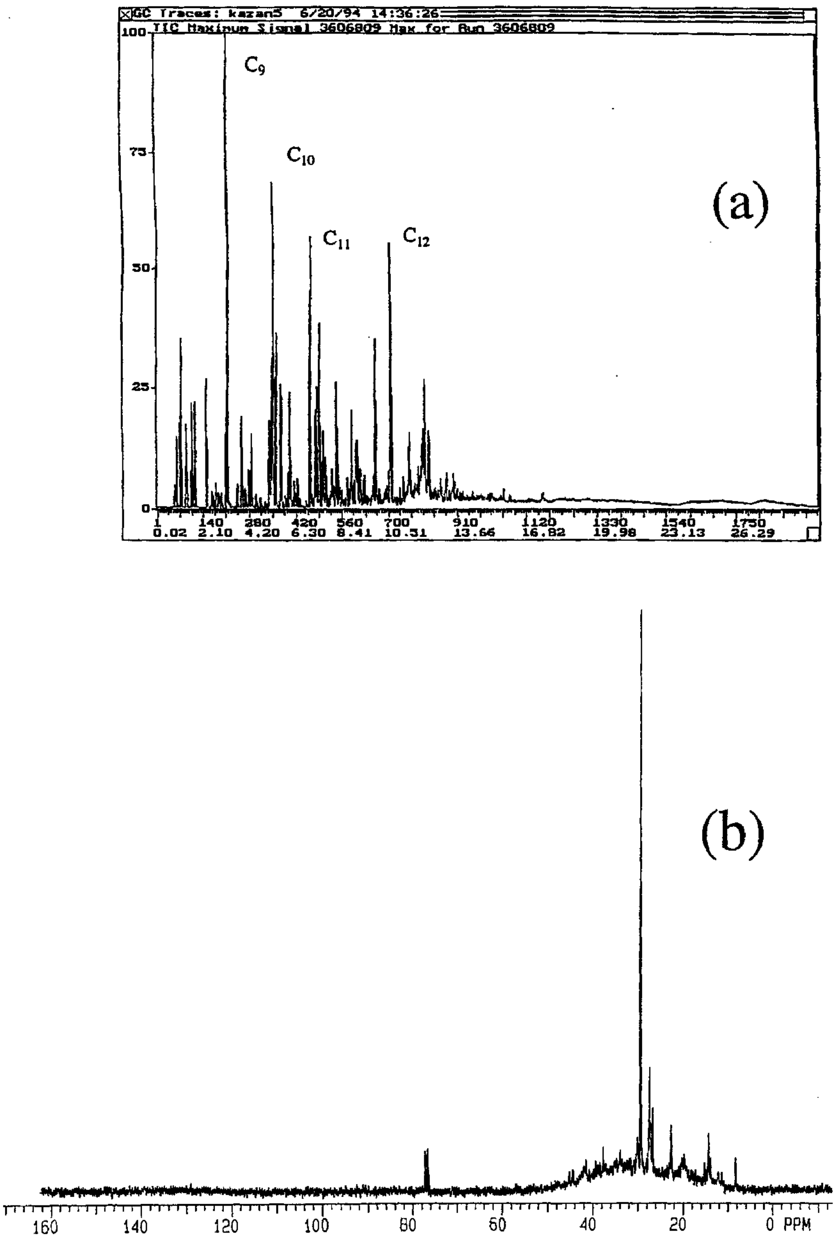


Fig. 2. Mass-chromatogram of hydrocarbon products resulting from decomposition of pentyl sulfuric acid ester at room temperature. The composition of the reaction mixture corresponded to 1 : 1 esters to 95% acid molar ratio.

was about twice that of the initial acid. In addition, the colour of the heavier part of the reaction mixture changed during the reaction to dark red. This means that after reaction some part of hydrocarbon final products remained dissolved in sulfuric acid.

These results are in excellent accordance with the reaction mechanism of "conjunct polymerisation" of olefins in an excess of 95% sulfuric acid proposed by Deno et al. in ref. [15]. According to these authors, the reaction starts with protonation of olefins resulting in formation of aliphatic carbenium ions. These species are then involved in oligomerisation, which yields the branched olefinic oligomers. The consequent hydride transfer between these olefins and the aliphatic carbenium ions results in branched paraffinic oligomers and in dienes or substituted cyclopentenes dissolved in the acid. This explains the red colour of the solution at the end of the reaction.

Such "conjunct polymerisation" of olefins represents a classical example of the acid catalysed carbenium ion reaction. Therefore, we attempted an in situ observation of these active intermediates during decomposition of pentyl sulfuric acid esters in an excess of the acid by ^{13}C NMR. The results obtained in one such experiment are depicted in figs. 1b and 3.

The NMR spectrum of fig. 1b was recorded immediately after addition of about one mole of 95% acid to one mole of esters at room temperature. It differs from that of fig. 1a in two respects. Firstly, the intensity of the lines from the primary carbon atoms in diesters decreased

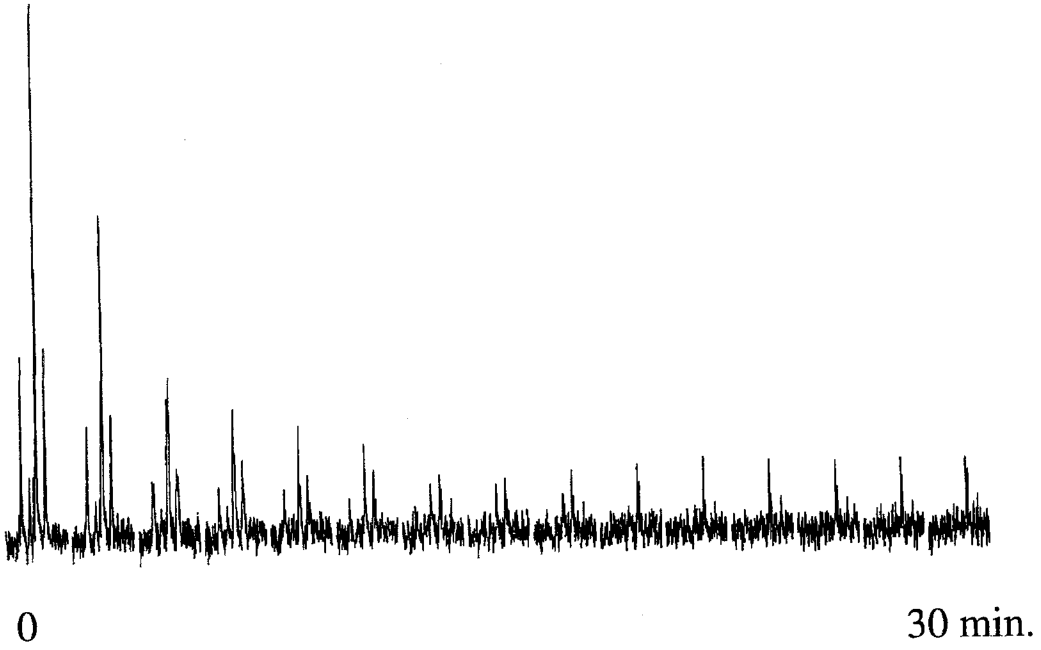


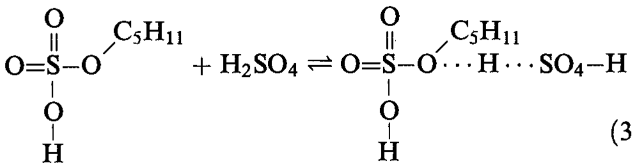
Fig. 3. Kinetics of decomposition of pentyl sulfuric acid esters in an excess of the acid at room temperature (1 : 1 esters to 95% acid molar ratio). Only the peaks in the region of 80–95 ppm with chemical shifts from primary carbon atoms of alkyl groups were followed.

almost to zero, whereas the remaining lines in this spectral region became somewhat broader. Secondly, all of the chemical shifts from primary carbon atoms of the monoesters in the region of 70–90 ppm increased by 5–10 ppm, whereas the shifts from aliphatic carbon atoms of alkyl groups remained unchanged.

The most reasonable explanation of both these effects is a predominant formation of pentyl sulfuric monoesters in an excess of the acid, whereas the increase of the chemical shifts from primary carbon atoms of alkyl fragments most likely results from strong hydrogen bonding of the esters with sulfuric acid as it was earlier reported in ref. [16] for tert-butyl oxonium ions:

$$(C_5H_{11})_2SO_4 + H_2SO_4 \rightleftharpoons 2(C_5H_{11})OSO_3H \qquad (2)$$

and then



$$HO{-}S(=O)_2{-}O{-}C_5H_{11} + H_2SO_4 \rightleftharpoons HO{-}S(=O)_2{-}O(C_5H_{11})\cdots H \cdots SO_4{-}H \qquad (3)$$

The mobility of such larger hydrogen bonded aggregates is certainly lower than that of the non-solvated esters. This explains the experimentally observed broadening of the NMR lines.

Immediately after addition of an excess of 95% sulfuric acid, the esters started to decompose resulting in the decrease of the intensity of the corresponding NMR lines. This happened in parallel with the formation of the hydrocarbon final products. Their mass-chromatogram and the ^{13}C NMR spectrum completely coincided with those depicted in fig. 2.

The kinetics of the reaction, as followed from the diminishing of the NMR lines in the region of chemical shifts of 70–90 ppm, is depicted in fig. 3. The decomposition of the esters was completed in about 25 min, whereas only the line with the smallest chemical shift of 82 ppm, which was earlier attributed to oxonium structures, remained unchanged. On the other hand, all our attempts to observe the ^{13}C NMR lines from aliphatic carbenium ion intermediates with chemical shifts in the range of above 300 ppm failed.

4. Discussion

There is no doubt that "conjunct polymerisation" of olefins can be performed in two separate steps. The first step represents synthesis of sulfuric acid esters in the presence of an excess of the olefin. In the second step, which should be carried out in an excess of concentrated acid, the esters are decomposed into branched paraffins and substituted cyclopentenes which remain dissolved in the acid. This is certainly a carbenium ion reaction, since the final products are well explained by the classical carbenium ion mechanism, which involves polymerisation, cracking and hydride transfer as elementary steps. The above results also clearly indicate that sulfuric acid esters are the precursors of carbenium ions.

The most simple way to explain the latter conclusion is to assume that, similar to heterogeneous acid catalysis in presence of zeolites, the carbenium ions in solution are also formed by heterolytic dissociation of the esters:

$$R_2SO_4 \rightleftharpoons R^+ + RSO_4^- \qquad (4)$$

or

$$RHSO_4 \rightleftharpoons R^+ + HSO_4^- \quad (5)$$

Both these reaction are endothermic. Therefore, the resulting carbenium ions should be formed as excited states in amounts much below the limit of the ^{13}C NMR detection.

Although eqs. (4) and (5) reasonably explain both the carbenium ion mechanism of "conjunct polymerisation" of olefins and the failure of our attempt of direct observation of these active intermediates by ^{13}C NMR, the role of the excess of 95% sulfuric acid in the decomposition of esters, and in the formation of carbenium ions remains unclear. These points could be clarified, if one considers the possibility of protonation of the esters in the similar way as the well known self-protonation of the concentrated sulfuric acid [17].

Due to the very high dielectric constant of sulfuric acid ($\varepsilon = 110$ [18]) the ion product of its autoprotolysis according to the reaction

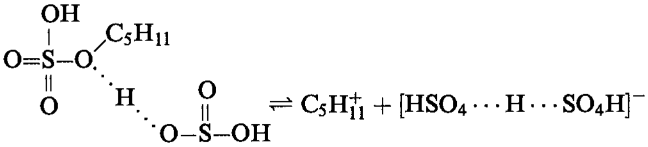
$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^- \quad (6)$$

is equal to $K = 1.7 \times 10^{-4}$ mol^2 kg^{-2} [17]. Such heterolytic dissociation is also favoured by strong solvation of the HSO_4^- anions with molecules of non-dissociated acid:

$$HSO_4^- + H_2SO_4 \rightleftharpoons [HSO_4\ H\ SO_4H]^- \quad (7)$$

In other words, the 100% H_2SO_4 contains about 1% of $H_3SO_4^+$ ions, which are the strongest acids possible in pure H_2SO_4 and certainly possess much stronger acid properties than the non-dissociated sulfuric acid.

Due to the stronger basic properties of the esters in comparison with sulfuric acid, similar protonation and consequent heterolytic dissociation of these species is even more favourable than the self-dissociation of the acid. The protonation of the esters at first involves a strong hydrogen bonding according to eq. (3), as has been supported above by the higher ^{13}C chemical shifts and by the broadening of the NMR lines in an excess of the acid. In the second step of the reaction, the hydrogen bonded complexes are decomposed into aliphatic carbenium ions and $[HSO_4\cdots H\cdots SO_4H]^-$ anions:



$$HO{-}S(=O)_2{-}O(C_5H_{11})\cdots H{-}O{-}S(=O)_2{-}OH \rightleftharpoons C_5H_{11}^+ + [HSO_4\cdots H\cdots SO_4H]^- \quad (8)$$

This certainly occurs more easily than the heterolytic dissociation of the non-protonated esters according to eqs. (4) and (5), since reaction (8) represents substitution by a proton instead of splitting off the alkyl group. Thus, the role of an excess of 95% sulfuric acid in "conjunct polymerisation" of olefins consists of assisting the easier decomposition of monoesters into carbenium ion intermediates, whereas the most general form of the mechanism of this reaction is the following:

$$\text{olefin} + H_2SO_4 \rightarrow R_2SO_4$$

$$R_2SO_4 + H_2SO_4 \rightarrow 2RHSO_4$$

$$RHSO_4 + H_2SO_4 \rightleftharpoons R^+ + H_3(SO_4)_2^-$$

$$R^+ + \text{olefin} \rightarrow \text{final products} + H^+$$

$$H^+ + H_3(SO_4)_2^- \rightleftharpoons 2H_2SO_4 \quad (9)$$

The carbenium ion intermediates of these reactions, similar to those involved in acid-catalysed transformations of olefins on zeolites, are short-lived and are formed by excitation (heterolytic dissociation) of the esters. This conclusion once more confirms the similarity of these active intermediates and of the reaction mechanisms both in homogeneous and in heterogeneous acid catalysis.

5. Conclusion

The ^{13}C NMR in situ study of "conjunct polymerisation" of 1-pentene in an excess of 95% sulfuric acid demonstrated that this reaction proceeds in two steps. In the first step the dialkylsulfates are formed, which are then transformed in the excess of the acid into monoalkyl esters. In addition, the excess of the acid favours the heterolytic dissociation of the esters, which results in formation of aliphatic carbenium ions. The steady state concentration of these highly chemically active species is, however, much below the limit of NMR detection. On the other hand, the subsequent reactions of such invisible carbenium ions well explain the final reaction products of "conjunct polymerisation". These results confirm the similar nature of carbenium ion active intermediates both in homogeneous acid catalysis and in acid-catalysed transformations of olefins on zeolites, where carbenium ion-like active species were also not detected by NMR.

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