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]:

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\begin{align*}
\text{C-O} &\rightarrow \text{C=O} \\
\text{O} &\rightarrow \text{O} \\
R &\rightarrow R^+ \\
\end{align*}
\]

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 isoctane alkylate.

In the present work a similar two-step approach was used for the 13C 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 13C 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 13C 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 chromatoo 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 13C NMR measurements were performed at room temperature with CDC13 as an external reference using a Perkin Elmer Gemeny 300 spectrometer operating at 300 MHz for protons. No enrichment of 1-pentene in 13C was used. Typically, between 40 and 96 scans were performed during NMR measurements. The spectra, unless otherwise indicated, were recorded with 13C–H decoupling. The chemical shifts were referred to the TMS standard.

For in situ 13C 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 13C 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 hydrocarbons was gradually followed by measurement of the volume.

Fig. 1a represents a 13C 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-