NMR study of the role of isopropylsulfates in the two-step "conjunct oligomerization" of propylene and isopentane–propylene alkylation catalyzed by 95% sulfuric acid

V.B. Kazansky [a], H.C.L. Abbenhuis [b], R.A. van Santen [b] and M.L.V. Vorstenbosch [b]

[a] *Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, Leninsky prospect 47, Moscow 117334, Russia*
[b] *Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands*

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"Conjunct oligomerization" of propylene or the isopentane–propylene alkylation catalyzed by an excess of 95% sulfuric acid was performed in two consecutive steps. First di-isopropylsulfate was prepared by interaction of sulfuric acid with propylene. The ester was then either decomposed at room temperature in the presence of the 5–10 molar excess of 95% acid or was used in the acid-catalyzed alkylation of isopentane. *In situ* ^{1}H and ^{13}C NMR study of the reaction mixture of "conjunct oligomerization" indicated that the diester participates in two equilibria with sulfuric acid. The first one transforms the diester into a monoester. The second equilibrium corresponds to protonation of the monoester with an excess of sulfuric acid. This converts a minor fraction of the mono-alkylsulfate into isopropyl carbenium ions that are only weakly solvated with sulfuric acid: $C_3H_7HSO_4 + H_2SO_4 \rightleftharpoons C_3H_7^+ H_2SO_4 + HSO_4^-$. The subsequent reactions of alkyl carbenium ions with the non-protonated alkylsulfate result in final products of "conjunct oligomerization" while in the presence in the reaction mixture of isopentane, alkylation with the predominant formation of C_8 branched paraffins takes place. A very low yield of propane indicates a minor role of hydride transfer in alkylation. Another unexpected result is the absence in both reaction mixtures of propylene. These findings are in contradiction with the classical mechanism of isoparaffin–olefin alkylation by Schmerling. Therefore, an alternative mechanism of this reaction is suggested via a direct alkylation of isopentane with the mono-alkylsulfate.

Keywords: alkyl carbenium ions, isoparaffin–olefin alkylation, ^{1}H NMR, ^{13}C NMR

1. Introduction

Catalytic transformations of olefins in 95% sulfuric acid are usually considered as classical carbenium ion reactions. It is also generally believed that generation of alkyl carbenium ions occurs via addition of a proton to an olefin:

$$H^+ + C{=}C \rightarrow R^+ \tag{1}$$

However, our recent ^{13}C NMR studies of the interaction of 1-pentene with 95% acid led us to challenge this traditional approach [1,2]. In agreement with extensive chemical experience we concluded that interaction of 1-pentene with the 95% acid results in a complicated mixture of monoesters and diesters of sulfuric acid instead of carbenium ions. Provided that there is no excess of the acid, these compounds are stable at room temperature. In contrast, if the 95% sulfuric acid is used in five- to ten-fold excess, the alkylsulfates are transformed into products of "conjunct oligomerization". The latter are represented by saturated oligomers with the odd and even numbers of carbon atoms indicating the occurrence of such typical carbenium ion reactions as oligomerization, cracking and hydride transfer. Dienes or cyclopentenes dissolved in the acid are concommitantly formed [1,3].

In previous papers we explained the generation of alkyl carbenium ions from alkylsulfates by protonation of the esters by an excess of the acid. This reaction is similar to the well-known self-dissociation of sulfuric acid. As has been shown by our quantum chemical calculations in [2], protonation of the esters results in formation of alkyl carbenium ions which are only weakly solvated with the acid:

$$RHSO_4 + H_2SO_4 \rightleftharpoons R^+ H_2SO_4 + HSO_4^- \tag{2}$$

The subsequent reactions of these species with monoesters or diesters result in products of "conjunct oligomerization". In [4] a similar mechanism of generation of alkyl carbenium ions via protonation of alkyl sulfates with a large excess of 95% sulfuric acid was also discussed for the acid-catalyzed isoparaffin–olefin alkylation.

Below we report results of an NMR study of the role of isopropylsulfates in the "conjunct oligomerization" of propylene and in the alkylation of isopentane with propylene. Following Albright et al. [5–7], both of these reactions were carried out in two separate steps. At first we prepared di-isopropylsulfate from propylene and 95% sulfuric acid. Then "conjunct oligomerization" or alkylation of isopentane with di-isopropylsulfate was carried out in the presence of an excess of the acid. According to the Markovnikov rule, interaction of sulfuric acid with propylene resulted only in formation of isopropylsulfates. Thus, the NMR study of propene "conjunct oligomerization" and isopentane–propene alkylation was much easier and was more informative than for the previously studied transformation of 1-pentene.

2. Experimental

Di-isopropylsulfate or a mixture of di- and mono-isopropylsulfates was prepared by reaction of propylene with 95% sulfuric acid at 0 °C. The reaction was carried out in a glass autoclave containing a magnetic stirrer. The amount of sulfuric acid was equal to 5–6 g. The autoclave containing the acid was evacuated and then filled with propene at the pressure of 2–4 atm. The reaction started with intense stirring of the acid that was continued during the experiment. Propylene absorption was complete in approximately 30 min. Formation of the diester at the end of the reaction was indicated by the stoichiometry of propylene absorption. For preparation of monoester, the reaction was interrupted at the moment when the amount of absorbed propylene was 50% less.

"Conjunct oligomerization" of propylene was also carried out at room temperature also with intense stirring of the reaction mixture. In this case the diester was added to a 5–10 molar excess of sulfuric acid. At the end of reaction the upper layer of resulting hydrocarbons was separated from the heavier layer of sulfuric acid with dissolved conjugated hydrocarbons and analyzed with a Carlo–Erba GC-6000 gas chromatograph equipped with a capillary column and a flame ionization detector. Assignment of the peaks in the gas chromatograms was made with a Shimadzu class 5000 gas chromatograph/Mas spectrometer.

Alkylation of 2-methylbutane with isopropylsulfate was carried out in a similar way to that discussed above. Five- to ten-fold molar excesses of isoparaffin and of 95% acid relative to the diester were used. The resulting hydrocarbons were analyzed with the same chromatograph that was used for analysis of liquid products of the "conjunct oligomerization".

^{13}C NMR spectra of mono- and di-isopropylsulfates and of mixtures of these esters with 95% sulfuric acid were measured with a Varian Gemini 300 spectrometer operating at the frequency of 300 MHz for protons and 75 MHz for ^{13}C with TMS as an external standard. The chemical shifts were referred to TMS. The relative amounts of diester and monoester in the final products were estimated after integration of corresponding lines in proton non-decoupled NMR spectra. The experiments were performed with propylene and isopentane from Aldrich Chem. Co. with the natural ^{13}C isotope content. 95% sulfuric acid from "Merck" was of the analytical grade.

3. Results

3.1. NMR spectra of isopropylsulfates

^{13}C NMR spectra of both mono- and di-isopropylsulfates contain two groups of resonances. Those with chemical shifts of 75–85 ppm belong to the –CH– fragments in isopropyl groups. The lines with chemical shifts of 20–22 ppm originate from carbon atoms in methyl groups. For a mixture with a higher concentration of diester this interpretation is supported by the ^{13}C proton non-decoupled spectra shown in figure 1. Three doublets with ^1J(C,H) 120 Hz correspond to –CH– fragments in the propyl groups (figure 1(a)). The most intense doublet with a larger chemical shift of about 80.5 ppm belongs to diester while the weaker doublet centered at about 78.7 ppm to monoester. Each of the components of those doublets are additionally resolved into seven lines due to interaction with six protons of two equivalent methyl groups. The much weaker doublet with a much lower chemical shift of 72.2 ppm most likely belongs to isopropyl oxonium ions that are formed from protonated water which is contained in the initial sulfuric acid in amount of 5 wt% or about 25 mol%. ^{13}C non-decoupled spectra of methyl groups of both monoester and diester correspond to quadruplets centered at 22.2 ppm (figure 1(b)). The lines from methyl groups of mono- and diester in this spectrum practically coincide with each other.

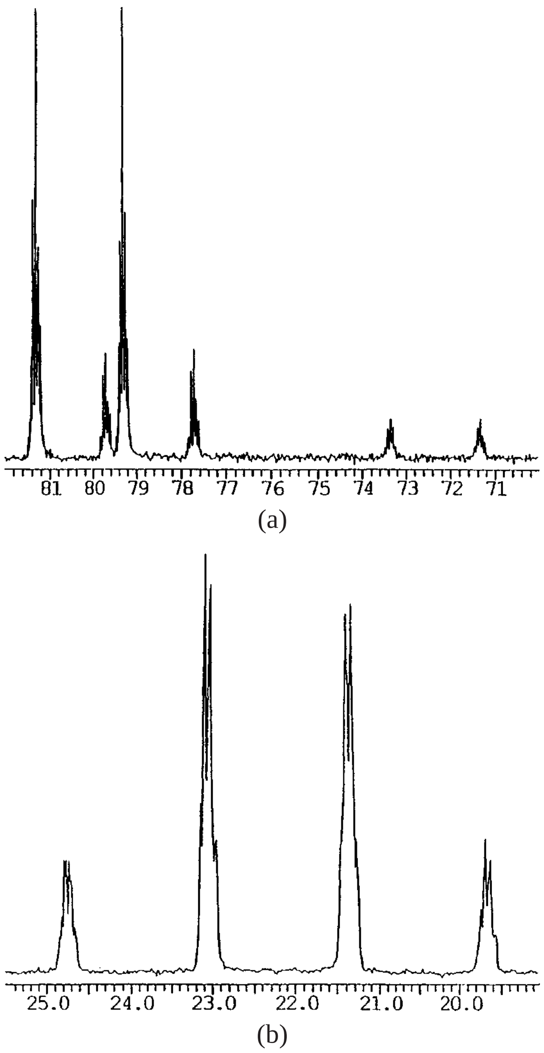

Figure 1. A proton non-decoupled ^{13}C NMR spectrum of –HCO– oxo-fragment (a) and of methyl groups (b) in di-isopropylsulfate.

The proton spectrum of the same sample is depicted in figure 2. The line with the chemical shift of 10.8 ppm belongs to protons of water. It may be also partially con-

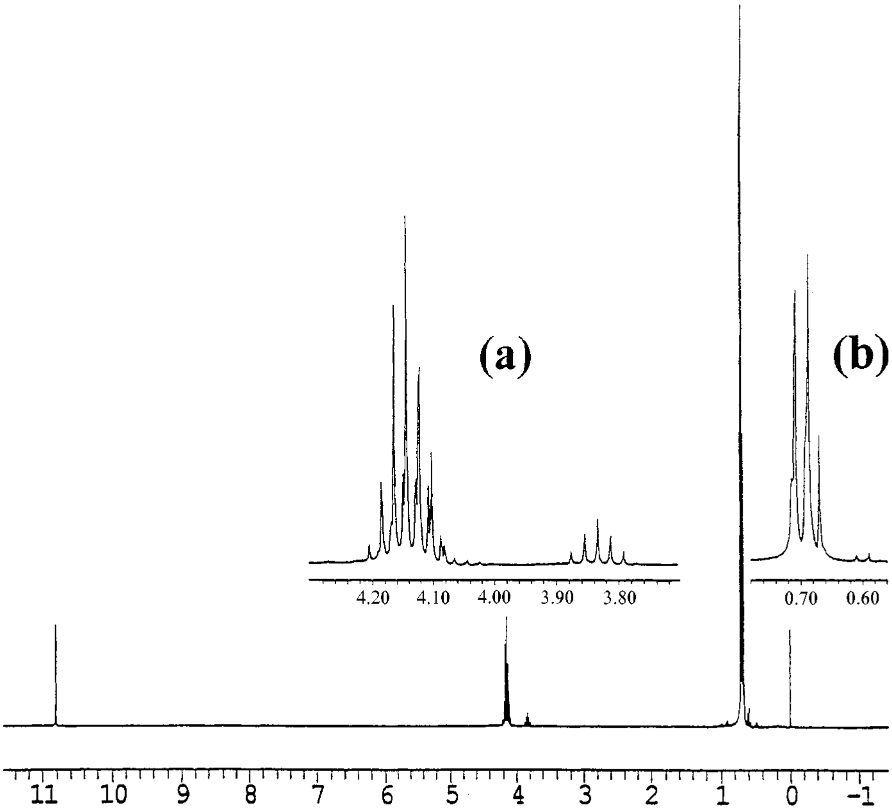

Figure 2. A proton NMR spectrum of the same di-isopropylsulfate as in figure 1.

nected with protons of the residual sulfuric acid or with HSO_4 groups in monoester. The peak with higher intensity and a larger chemical shift equal to 4.15 ppm belongs to diester. A much weaker pattern with almost identical chemical shift originates from monoester. Both resonances are resolved into seven components due to interaction of –HCO– protons with six equivalent protons of two methyl groups. In the similar way the heptet at 3.83 ppm should be ascribed to –CH– fragments in isopropyl oxonium ions. Finally, the group of lines with a chemical shift close to 0.7 ppm belongs to protons of methyl groups in monoesters and diesters. Each of these signals represents a doublet resulting from coupling with the HCO fragment.

This interpretation is consistent with the ratio of intensities of proton lines from the methyl groups and those from –CHO– fragments that is close to the theoretical value of 6. The integrated intensities of the lines from di- and mono-isopropylsulfates in the non-decoupled proton NMR spectra indicated that the yield of diesters in different experiments was 80–85%.

Formation of the monoester upon the lower propylene absorption by the acid was less selective. This follows from the ^{13}C proton non-decoupled NMR spectrum of the final products obtained in an experiment where the amount of propene absorbed by the acid corresponded to a stoichiometric formation of monoester (figure 3). The yield of monoester estimated from intensities of corresponding proton NMR lines was only about 60% in comparison with the greater than 80% yield of diester observed in a similar experiment in which twice the amount of propylene was absorbed by the acid.

Another more important feature of both the proton and the ^{13}C NMR spectra of the monoester and the diester is a dependence of chemical shifts on the ratio of these products in solution. For instance, the chemical shift of the carbon atom in the –HCO– group in the diester in figure 1 is equal to 80.5 ppm while the corresponding shift of the lines in figure 3 is equal to 82.2 ppm. In a similar way the chemical shift of a carbon atom in this group in the monoester is also different depending on the composition of the solution: 78.7 ppm in figure 1 and 81.2 ppm, respectively. The dependence of ^{13}C NMR chemical shifts of the lines from methyl groups in the monoester and in the diester on the composition of the solution is much weaker but is still considerable. As a result the corresponding ^{13}C spectrum of methyl groups in figure 3(b) becomes well resolved into two quadruplets.

Earlier we reported a similar phenomenon for the mixtures of sulfuric acid of different concentrations with pentylsulfates [1,2] or with ethyl [8] or tertiary butyl [9] alcohols. The increase of ^{13}C chemical shifts in the presence of excess of sulfuric acid was explained in these references by protonation of the ester or alcohols by excess of the acid and by a fast proton exchange between protonated species with the higher chemical shift and the non-protonated alkylsulfates or alcohols with the lower shifts. A similar argument can be also used to explain the results of the present study.

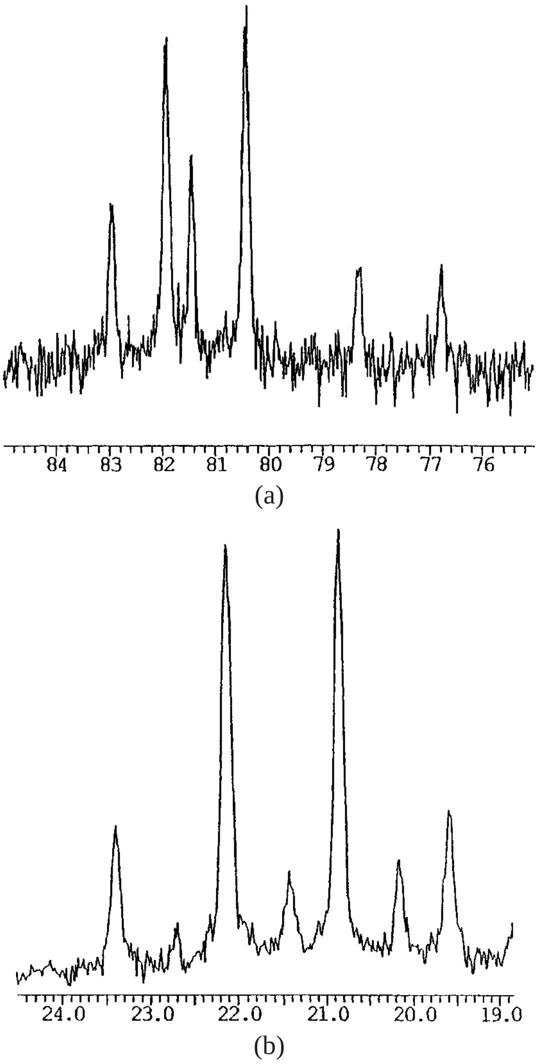

Figure 3. A proton non-decoupled ^{13}C NMR spectrum of –HCO– oxo-fragment (a) and of methyl group (b) in the mono-isopropylsulfate–di-isopropylsulfate mixture.

Indeed, in the case of the diester, the sulfuric acid was almost completely neutralized by olefin. In contrast, for the monoester, some amounts of sulfuric acid remained in solution at the end of the reaction resulting in protonation of alkylsulfates and in an increase of the observed ^{13}C chemical shifts. This suggestion is supported by comparison of intensities of proton NMR lines from acidic protons that in the case of the monoester were about 2.5 times more intense than for the diester.

Nevertheless, to check this explanation directly, we measured the ^{13}C NMR chemical shifts for different mixtures of di-isopropylsulfate with 95% sulfuric acid. Some of the proton-decoupled ^{13}C NMR spectra obtained are depicted in figure 4. Values of the chemical shifts for a broader range of isopropylsulfate–sulfuric acid ratios are collected in table 1. They indicate that increase of chemical shifts induced by the large excess of 95% sulfuric acid is as high as about 10 ppm.

Another effect resulting from an excess of the acid is the redistribution of intensities of the NMR lines of the diester, monoester and of the isopropyl oxonium ions in favor of two last species for a larger amount of 95% sulfuric acid in solution. In a mixture with a three-fold excess of sulfuric acid the amount of diester strongly decreased while at higher sulfuric acid content the intensities of corresponding NMR lines were much lower. This should be explained by the shift of the following equilibria between diester and sulfuric acid or diester and hydroxonium ions upon increasing amount of 95% sulfuric acid towards the right:

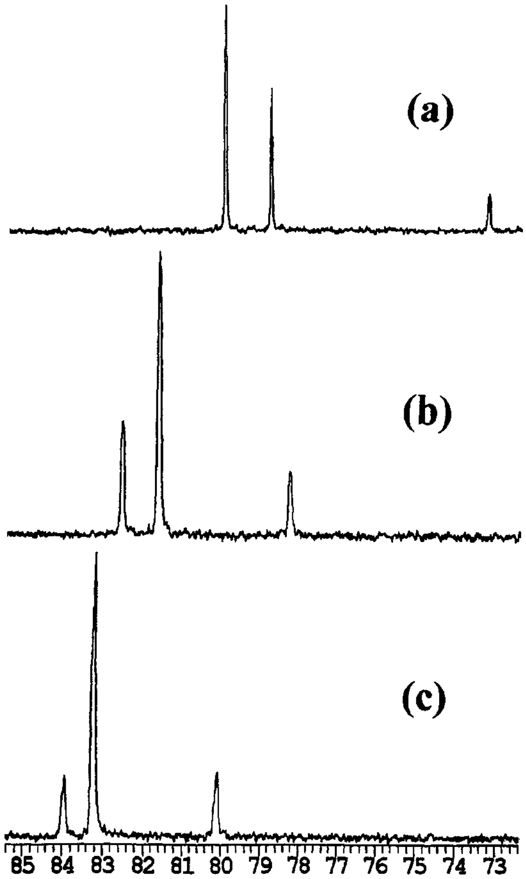

Figure 4. Proton decoupled ^{13}C NMR spectra of –HCO– oxo-fragments in the mixtures of different composition of di-isopropylsulfates with 95% sulfuric acid: (a) di-isopropylsulfate, (b) 1 : 1 and (c) 3 : 1 molar mixtures with 95% H_2SO_4.

$$R_2SO_4 + H_2SO_4 \rightleftharpoons 2RHSO_4 \tag{3}$$

$$R_2SO_4 + H_3O^+ \rightleftharpoons RHSO_4 + ROH_2^+ \tag{4}$$

3.2. Two-step “conjunct oligomerization” of propylene

Di-isopropylsulfate is a colorless homogeneous liquid with a density of 1.22 g/cm^3. At room temperature the ester is rather stable, but starts to decompose in an excess of 95% sulfuric acid. At the beginning this results in a dark yellow or orange coloration of the solution. Then the color turns red. This is well consistent with our previous observations reported in [1] and with results by Deno et al. [3] who explained the appearance of the red color by formation of substituted cyclopentenes and dienes dissolved in the acid as by-products of “conjunct oligomerization”.

Table 1

^{13}C chemical shifts in the mixtures of isopropyl sulfates with 95% sulfuric acid.

H_2SO_4 to alkylsulfate ratio	Di-isopropylsulfate		Mono-isopropylsulfate		Propyl oxonium ion	
	CH– group	CH_3– group	CH– group	CH_3– group	CH– group	CH_3– group
[a]	80.1	22.2	78.6	22.2	72.2	–
	80.3	22.2	78.7	22.2	72.3	
	80.6	22.1	79.4	22.0	72.3	–
	80.7	22.1	79.4	21.9	72.9	
1 : 1[b]	82.2	21.4	81.2	21.6	78.3	?
	82.2	?	81.2	?	78.6	?
2 : 1	84.6	20.0	83.8	21.6	80.7	?
3 : 1	–	–	84.1	21.5	?	20.8
	–	–	84.3	?	81.2	?
5 : 1	–	–	85.2	21.4	82.1	20.7
10 : 1	–	–	85.9	21.4	?	20.60

[a] The spectrum depicted in figure 1.

[b] The spectrum depicted in figure 4.

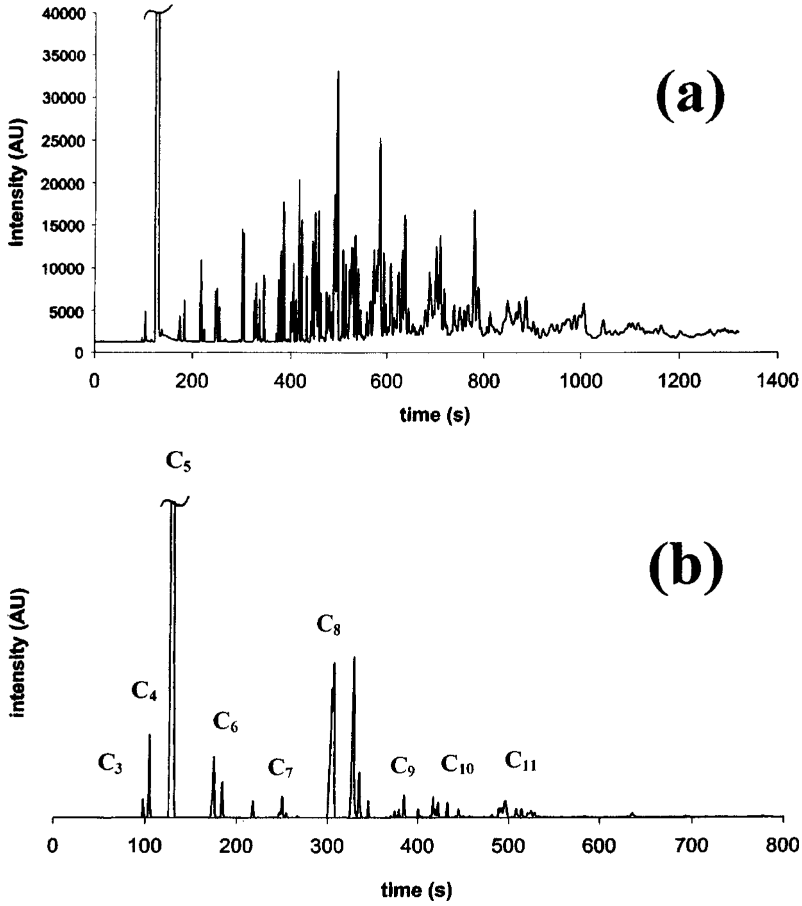

Figure 5. Gas chromatograms of the final products of the two-step "conjunct oligomerization" (a) and of the two-step alkylation of propylene with isopentane (b).

For a larger excess of the acid the solution gradually became opaque due to formation of hydrocarbons and for acid-to-ester ratios higher than 3 gradually separated into two layers. The upper colorless layer corresponds to the hydrocarbon final products. The lower dark red heavier layer represents the remaining sulfuric acid–ester solution with dissolved dienes and cyclopentenes. The amount of the upper colorless layer increased with time. This was used to estimate both the extent of the isopropylsulfates conversion and the reaction rate.

Figure 5(a) depicts a gas chromatogram of the resulting hydrocarbons. It corresponds to a very complicated

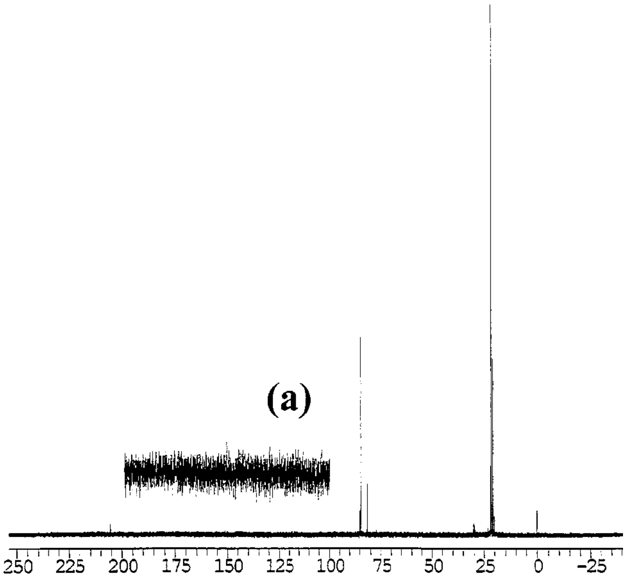

Figure 6. A broad-range ^{13}C proton decoupled NMR spectrum recorded in the course of the "conjunct oligomerization" of propylene. (a) The spectrum in the range of chemical shifts of propylene at much higher amplification.

mixture of C_6–C_{15} branched paraffins with odd and even numbers of carbon atoms. This obviously indicates the classical carbenium ion reactions of oligomerization, skeletal isomerization and cracking combined with participation of alkyl carbenium ions in the hydride transfer.

We also made several attempts of the *in situ* observation of alkyl carbenium ion active intermediates. However, no ^{13}C NMR lines from aliphatic carbenium ions with chemical shifts above 300 ppm were observed in those experiments. We also did not observe the lines from propylene or other olefins with chemical shifts of 120–140 ppm that are believed to be involved in "conjunct oligomerization" of olefins (figure 6). On the other hand, the NMR lines from the esters gradually decreased in intensity indicating participation of these species in the reaction that most likely involves the following sequence of elementary steps:

$$\begin{aligned} &2\mathrm{C{=}C} + n\mathrm{H_2SO_4} \rightarrow \mathrm{R_2SO_4} + (n-1)\mathrm{H_2SO_4} \\ &\quad \rightleftharpoons 2\mathrm{RHSO_4} + (n-2)\mathrm{H_2SO_4} \rightarrow \\ &\begin{array}{c}\text{alkyl carbenium ion}\\ \text{active intermediates}\end{array} \rightarrow \begin{array}{l}\text{saturated hydrocarbon oligomers}\\ \text{and dienes and cyclopentenes}\\ \text{dissolved in the acid}\end{array} \end{aligned} \tag{5}$$

3.3. Two-step alkylation of isopentane with propylene

A chromatogram of the final products resulting from alkylation of di-isopropylsulfate with isopentane is depicted in figure 5(b). The composition of the resulting alkylate is also presented by table 2. The conversion of di-isopropyl ester was close to 50%. The similar final products were also formed from decomposition of mono-isopropylsulfate but in the about twice less amount.

Table 2

Composition of liquid alkylate resulting from reaction of 3 g of di-isopropylsulfate with 7 g of 2-methylbutane at 20 °C in presence of 7.05 g of 95% sulfuric acid.

Fraction	Hydrocarbons	Retention times (s)	Compostion (wt%)
C_3	Propane	98	1.1
C_4	Isobutane	104	5.8
C_6	2-methylpentane	175	7.6
	3-methylpentane	184	3.6
			$\sum_{C_6} = 11.2$
C_7	2,2-dimethylpentane	218	1.7
	2,3-dimethylpentane	251	2.3
			0.5
			$\sum_{C_7} = 4.5$
C_8	2,5-dimethylhexane	304	22.5
	2,4-dimethylhexane	328	27.0
	2,3,4-trimethylpentane	334	5.7
	3,3-dimethylhexane	345	1.5
			$\sum_{C_8} = 56.7$
C_{8+}	C_9–C_{11} hydrocarbons		$\sum_{C_{8+}} = 20.7$
			Total = 100%

It follows both from table 2 and figure 6 that the distribution of paraffins resulting in isopentane–isopropylsulfate alkylation is much narrower than in the case of "conjunct oligomerization". As one can see from table 2, the yield of octane isomers in the alkylate was about 60%. About 15% of lower C_6–C_7 paraffins were formed in parallel. The heavier paraffins were mainly represented by C_9–C_{11} isomers (about 20%). The most surprising result was only a very small amount of propane formation (2.5%). This obviously indicates only a minor role of hydride transfer, because otherwise the reaction of isopropyl carbenium ions with isopentane would mainly result in formation of propane:

$$i\text{-}\mathrm{C_3H_7^+} + i\text{-}\mathrm{C_5H_{12}} \rightarrow \mathrm{C_3H_8} + t\text{-}\mathrm{C_5H_{11}^+} \tag{6}$$

Another difference with "conjunct oligomerization" is a much weaker coloration of the sulfuric acid–ester solution at the end of the reaction. This obviously also indicates a lower extent of hydride transfer from the ester to alkyl carbenium ions than in the case of "conjunct oligomerization".

4. Discussion

The results of the present study confirm that similar to isoparaffin–olefin alkylation the "conjunct oligomerization" of olefins can be also performed in two consecutive steps. The first step represents the synthesis of alkylsulfates. In the second step, that needs at least a five-fold molar excess of 95% sulfuric acid, the esters are decomposed into branched paraffins and substituted cyclopentenes which remain dissolved in the acid. According to the composition of final products, the "conjunct oligomerization" is definitely a carbenium ion reaction. Thus, the above results clearly indicate that alkylsulfates are precursors of carbenium ions. However, the amount of these species in the reaction mixture is below the limit of a direct ^{13}C NMR detection.

Our result also demonstrated that alkylsulfates are involved in two following equilibria with excess of sulfuric acid. The first one converts di-isopropylsulfate into mono-isopropylsulfate:

$$(C_3H_7)_2SO_4 + H_2SO_4 \rightleftharpoons 2(C_3H_7)HSO_4 \qquad (7)$$

The second equilibrium transforms the mono-alkylsulfate into propyl carbenium ions that are weakly solvated with sulfuric acid:

$$(C_3H_7)HSO_4 + H_2SO_4 \rightleftharpoons C_3H_7^+\,H_2SO_4 + HSO_4^- \qquad (8)$$

The subsequent reactions of isopropyl carbenium ions with the non-protonated esters result then in formation of the final products of "conjunct oligomerization".

Equilibrium (8) also explains the dependence of ^{13}C chemical shifts of the alkylsulfates on excess of sulfuric acid by a fast proton exchange between the major part of non-protonated and a small amount of protonated species. Indeed, our previous quantum chemical calculations demonstrated that the protonated mono-alkylsulfate in reality is identical to an alkyl carbenium ion that is only weakly solvated with sulfuric acid [2]. Therefore, the ^{13}C NMR chemical shift of the lines of the carbon atom in the –OCH– oxo-fragment of these species should be close to the value that is typical of free aliphatic carbenium ions, i.e., to 300 ppm. Then the averaging of chemical shifts of the protonated and non-protonated mono-alkylsulfates by a fast proton exchange results in the experimentally observed dependence of ^{13}C chemical shifts on concentration of sulfuric acid that could be described by the following well-known expression [10]:

$$\delta_{av} = \delta_e N_e + \delta_{pe} N_{pe}. \qquad (9)$$

Here δ_{av} is the experimentally observed NMR chemical shift, δ_e and δ_{pe} are the chemical shifts of carbon atoms in –HCO– fragments of the non-protonated and protonated mono-alkylsulfates, N_e and N_{pe} are the mole fractions of the non-protonated and protonated esters in solution.

The concentration of protonated monoester (i.e., of the weakly solvated carbenium ions) in excess of sulfuric acid estimated from this equation is equal only to several percents. Thus, our results explain well the experimentally observed ^{13}C chemical shifts, their dependence on the concentration of sulfuric acid and a very low concentration of the weakly solvated alkyl carbenium ions in solution. They also contribute to a better understanding of the mechanism of isoparaffin–olefin alkylation that has been proposed more than fifty years ago by Schmerling [11,12] and since that time remained unchanged.

Indeed, according to Schmerling [11] the most important steps of isopentane–propylene alkylation are the following:

$$\begin{aligned}
&C_3H_6 + H^+ \rightarrow C_3H_7^+\\
&C_3H_7^+ + C_3H_6 \rightarrow t\text{-}C_6H_{13}^+\\
&t\text{-}C_6H_{13}^+ + i\text{-}C_5H_{12} \rightarrow i\text{-}C_6H_{14} + t\text{-}C_5H_{11}^+\\
&t\text{-}C_5H_{11}^+ + C_3H_6 \rightarrow t\text{-}C_8H_{17}^+\\
&t\text{-}C_8H_{17}^+ + i\text{-}C_5H_{12} \rightarrow i\text{-}C_8H_{18} + t\text{-}C_5H_{11}{}^+ \text{ etc.} \qquad (10)
\end{aligned}$$

The main features of this chain mechanism include:

(i) Formation of alkyl carbenium ions by protonation of olefin.

(ii) A subsequent cationic oligomerization via interaction of these species with the next olefin molecule.

(iii) A fast hydride transfer from the isoparaffin to alkyl carbenium ion that explains the high selectivity in formation of C_8 paraffins. A fast hydride transfer also explains propagation of reaction chains.

The first contradiction of this mechanism with our previous works [1,2] and with results of the present study concerns the nature and mechanism of generation of alkyl carbenium ions. According to our results, these active intermediates are formed by protonation of mono-alkylsulfates instead of protonation of olefins. In other words, generation of alkyl carbenium ions in the presence of an excess of 95% sulfuric acid is a consecutive reaction involving the following elementary steps:

$$\begin{aligned}
&2C{=}C + 2H_2SO_4 \rightarrow 2RHSO_4 \rightleftharpoons R_2SO_4 + H_2SO_4\\
&RHSO_4 + H_2SO_4 \rightleftharpoons R^+\,H_2SO_4 + HSO_4^- \qquad (11)
\end{aligned}$$

In addition, our results on the two-step isopentane–propylene alkylation definitely indicate that alkylation itself represents rather an alkylation of isoparaffin with mono-alkylsulfate than with olefin. This conclusion is also strongly supported by a very low concentration of propylene in excess of 95% sulfuric acid that is below the limit of detection with ^{13}C or proton NMR (see figure 6). This result is, however, quite natural because 95% sulfuric acid has been for a long time used in gaseous chemical analysis for absorption of olefins. Therefore, in the presence of excess of 95% acid the concentration of propylene dissolved in the reaction mixture is certainly extremely low. In this context, it is worthwhile to remind that the isoparaffin–olefin alkylation was accidentally discovered by Pines and Ipatiev in the early thirties when they tried to find an explanation of a source of errors in analytic detection of olefins by absorption by 95% sulfuric acid in the presence of isoparaffins [13].

One more contradiction of our results with the classical mechanism of alkylation consists in a very small yield of propane in the propylene–isopentane alkylation. In contrast to the mechanism by Schmerling, this obviously indicates only a minor role of hydride transfer. Finally, the classical mechanism of alkylation does not discuss the role of excess of sulfuric acid.

To explain all these contradictions, we propose the following new alternative mechanism of the two-step isoparaffin–olefin alkylation via direct interaction of isoparaffins with protonated monoesters.

The reaction starts with formation of mono-alkylsulfate from olefin and 95% sulfuric acid. Protonation of alkylsulfate in the presence of excess of the acid results then in a small amount of alkyl carbenium ions weakly solvated with the acid. These active intermediates are involved in the following two new reactions. First of them is a formation of the non-classical carbonium ion from isoparaffin and the protonated ester:

$$i\text{-R}_1\text{H} + \text{R}^+\,\text{H}_2\text{SO}_4 \rightleftharpoons [\text{R}_1\text{HR}]^+\,\text{H}_2\text{SO}_4 \qquad (12)$$

This reaction is an analog of the well-known interaction of carbenium ions with paraffins in the gas phase that normally results in a hydride transfer upon subsequent dissociation of the non-classical carbonium ion [14]:

$$\text{R}_1^+ + \text{HR} \rightleftharpoons [\text{R}_1\text{HR}]^+ \rightleftharpoons \text{R}_1\text{H} + \text{R}^+ \qquad (13)$$

However, acording to the above results in the case of sulfuric-acid-catalyzed isopentane–propylene alkylation the rate of the hydride transfer is rather low. This indicates a relatively high stability of the non-classical carbonium ion intermediates and the relatively long lifetime of these species. Therefore, there is some probability of their recombination with the negatively charged HSO_4^- anions. This results in a direct alkylation of isoparaffin with the protonated ester:

$$\text{HSO}_4^- + [\text{R}_1\text{HR}]^+\,\text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{SO}_4 + \text{R}_1\text{R} \qquad (14)$$

As is schematically shown in figure 7, formation of 2,4- and 2,5-dimethylhexane as the main products of isopentane–propene alkylation corresponds then to predominant abstraction of protons from different methyl groups of the isopenthyl fragment in the non-classical isooctyl carbonium ion with subsequent recombination of the resulting electroneutral isopropyl and isopentyl radicals. In the similar way, formation of minor amount of 2,3,4-trimethylpentane corresponds to proton abstraction from the CH_2 group of the isopentyl fragment, while formation of 3,3-dimethylhexane from CH_3 groups of the isopropyl fragment of the non-classical octyl carbonium ion. Repetition of alkylation of isopropylsulfate by the resulting isooctanes explains formation of heavier paraffins, while their cracking formation of the lower C_3, C_4, C_6 and C_7 paraffins.

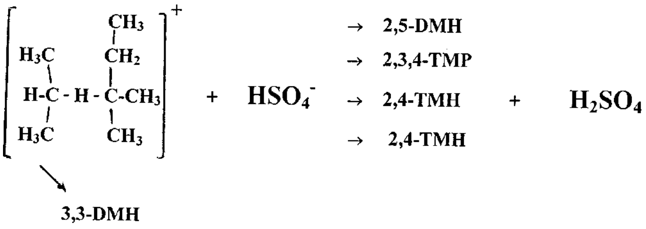

Figure 7. Formation of different isooctanes via recombination of non-classical isooctyl carbonium ion with HSO_4^- anion.

Reaction (14) is a reverse of the well-known protolytic cracking of paraffins that has been well proven both for the liquid superacids and zeolites [14–18]. Earlier the similar reaction of direct alkylation of light paraffins by the primary carbenium ions in liquid superacids was also discussed and experimentally proven in [19,20]. However, for the sulfuric-acid-catalyzed alkylation of isoparaffins with olefins such a possibility has been never before considered.

Thus, the central point of the above alternative mechanism of the two-step isoparaffin–olefin alkylation is a *suggestion that this reaction involves a direct alkylation of isoparaffins by protonated esters via intermediate formation of the non-classical carbonium ions*. This explains the role of excess of sulfuric acid and the composition of reaction products without assumption on a predominant role of reactions of carbenium ions with olefin and on the fast hydride transfer from isoparaffin to the alkyl carbenium ion. It is quite possible that a similar alternative mechanism is also true for the coventional isoparaffin–olefin alkylation.

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