TAME – a Quantum Mechanics Study of the Reaction Mechanism for Methoxylation of Isoamylenes

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The present paper describes the quantum mechanics study regarding a tertiary-alkyl methyl ether synthesis mechanism. As octane number boosters, ethers such as TAME (2-methoxy-2-methylbutane) represent a solution for increasing the amount of oxygen in gasolines and for decreasing their isoamylenes content, for more environmentally-friendly fuels. The quantum mechanics modeling targeted the elucidation of the isoamylenes methoxylation mechanism, defining the transition states involved in the reaction of 2-methyl-2-butene (2M2B) with methanol, using benzenesulfonic acid to simulate cation-exchange resins catalytic involvement.

Keywords: TAME, 2-methoxy-2-methylbutane, molecular modeling, oxygenates, fuel additives

For the last decades the environment has constantly degraded due to various causes, among which pollution induced by fuels combustion is one of the most responsible ones. As a result, emission regulations and strict requirements for fuels on the market were enforced by both the US and EU.

On the other side, the more and more powerful engines demand higher octave fuels (although the lead alkyl antiknock additives have been banned for more than one decade), with increased butane content, gasolines with higher vapor pressure. Meanwhile, amendments and regulations for fuels impose reduction of components vapor pressure and of their aromatic content, along with compulsory minimum oxygen content. This requirement can be achieved by using oxygenated agents, and/or inferior alcohols added to the “usual” fuel, and a certain percentage (about 30%) is imposed to be supplied by renewable sources.

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The general reaction of alkenes with alcohols in acidic catalysis [6-11] is exothermic and occurs even at moderate temperatures, being selective to alkenes (not affecting other hydrocarbons in the fuel if applied to olefin fraction in gasolines).
As Au(I), Pd, Au(III)–CuCl₂ [16-20] were reported as metals, their salts and/or their complex combinations, such as organic sulfonic acids [12,13] and sulfonated macroporous styrene divinylbenzene co-polymers, which assure high conversion rates without temperature support [14,15]. It is proven that the ion exchange resin displays an activity higher than soluble anhydrous p-toluenesulfonic acid [3, 4]. Other systems, based on transitional noble metals, their salts and/or their complex combinations, such as Au(I), Pd, Au(III)–CuCl₂ [16-20] were reported as catalysts.

Al-montmorillonite also proved to catalyze methoxylation of olefins [21].

Studies dedicated to isoamylenes methoxylation – concerning both the thermodynamic and the kinetic aspects – published along the last about forty years after TAME launching were carried out in proper reactors at various temperatures, mainly between 40-80°C, on cation-exchange resins.

A system of chemical equations consisting of the two isoamylenes etherification and their reciprocal equilibrium interconversion is taken into account (The only reactive alkenes were those with the double bond attached to the tertiary carbon atom, i.e. 2M1B and 2M2B, scheme 1). The 3-methyl-1-butene does not react at all. These results suggest that a carbocation can be the common intermediate and that olefin protonation is a more important kinetic step than the interaction with the nucleophile. The observed high order on SO₃H groups can be related to a nonlinear dependence of protonating power of the resin on the concentration of sulfonic groups [4].

At lower temperatures the reaction rates were controlled by kinetic factors, but at temperatures above 60°C both reactions were affected by thermodynamic equilibria [22].

For example, it is determined that the two isoamylenes react at different rates, i.e. TAME synthesis from 2M1B is faster than TAME synthesis from 2M2B since the reported activation energies were 88.1 and 102.1 kJ/mol for the etherification of 2M1B and 2M2B, respectively [11,15, 23,24].

Piccoli and Lovisi [25] studied the kinetics and thermodynamics of liquid-phase etherification of isoamylenes with methanol on ion exchange catalyst in a batch reactor operating under 1013 kPa and 323-353 K. Based on the kinetic equation, they have advanced a surface mechanism when methanol adsorbs and completely covers the active sites, and the isoamylenes react in the acidic site after having migrated through the liquid layer formed by the alcohol around the catalyst.

Our present study supports in a great extent this suggested mechanism. Generally, literature does not provide data on the chemistry and the mechanism of isoamylenes methoxylation. This research presents original results, attempting to support a better understanding of the way this reaction proceeds, for further improvements to manufacturing process.

Since our results already published for the application of quantum mechanics method to modeling the biodiesel-triglycerides [26] and for modeling the synthesis of acetone-glycerol ketals [27] are successful, the present study is completing those results in the field, reporting an original outcome for the mechanism of alkenes methoxylation.

**Results and discussions**

**Conditions and modeling parameters for the TAME synthesis**

The mechanism for the TAME formation is studied using a quantum method. Modeling is performed on a 12 nodes 96 cores cluster running CentOS Linux. Quantum mechanical calculations were performed with GAMESS 2013 software package [28]. All the calculations were performed using M11 DFT and KTZVP basis set [29-31]. The modern M11 functional is more suitable for long distance interactions than the classical B3LYP. Also the PCM method is used for the solvent effect considering pentene as solvent [32, 33].

As the usual catalysts for this reaction are sulfonated copolymers of styrene and divinyl benzene, the catalyst is modeled by benzenesulfonic acid as the computational effort is more cost effective in terms of computer power. Also, this model is used for other reactions involving ion-exchange resins [34, 35].

The transition states were verified by running a hessian to ensure that only one imaginary frequency is present. Also this allows the calculation of zero point energy (ZPE) which is included in the final energy of the transition states and of the stable molecules. Since in the initial and final reaction states there is a difference between the sum of the individual molecules energies and the energy of the same molecules considered as an assembly, the energies used were those of the molecular assemblies. The energy used is the M11/KTZVP + ZPE.

**Modeling the reaction steps**

It has been long ago admitted that the addition of alcohols to olefins double bonds has an electrophilic mechanism: in the first step, the attack on the catalyst proton performed by the p doublet of the alkene leads to the predominance of the most stable carbenium ion that isoamylene can provide (scheme 2).

The alcohol nucleophilic molecule attacks the carbocation to generate an oxonium ion that further stabilizes by proton elimination (scheme 3). The addition regioselectivity is the expected one and the alkohol reactivity for the addition to double bonds decreases as follows: primary alcohols > secondary alcohols > tertiary alcohols.
In order to elucidate the mechanism for alcohol addition to alkenes in acid catalysis we have attempted the modeling of the electrophilic attack on the alkene considering the reaction between the sulfonic acid and the alkene as a first step, leading to the intermediate carbenium ion (scheme 4).

In this case neither a transition state nor a carbenium ion could be found. This result is somehow expected, since acids ionization is practically impossible in the absence of a proton acceptor (it is well known that anhydrous hydrochloric acid does not react with iron, and thus can be deposited in iron recipients). Since the organic sulfonic acids are considerably weaker than hydrochloric acid, the lack of evidence for their ionization in the absence of a sufficiently nucleophilic proton acceptor is perfectly acceptable.

Despite a considerable volume of attempts, no evidence for the “classical” intermediates in the sulfonic acids catalyzed addition of methanol to isoamylens is found. Therefore, we tried to model the addition of the sulfonic acid to the alkene leading to a sulfonate 1 to further act as alkylation agent for the alcohol (scheme 5).

Not even this hypothesis is supported by finding a transition state. We concluded that without the assistance of any supplemental favoring factors / circumstances the reaction in Scheme 5 does not occur (anyway, such a reaction should be stepwise, the initial step being the protonation of the double bond).

The Methanol-Benzencesulfonic acid complex

Since the attempt to find a transition state for the protonation product of isoamylene by the sulfonic acid failed, the solvation of the benzene sulfonic acid is considered (scheme 6).

As expected, the final geometry (fig. 1) shows a hydrogen bond between the sulfonic group and methanol. The solvation energy is -53.14 kJ/mol showing a strong hydrogen bond between the benzencesulfonic acid and the methanol molecule.

The subsequent attack of the solvated benzencesulfonic acid at the alkene p bond did not provide a transition state leading to a carbenium ion. The transition state 2 is underlined to be the one preceding the final ester expected from an addition of the sulfonic acid to the isoamylene.

The reaction is endothermic and the reaction energy is 90.8 kJ/mol. If the ZPE is considered, the reaction energy is 82.8 kJ/mol. The amount of 8.0 kJ/mol is below the expected error in this type of QM calculations.

One can easily observe that the H1-atom – alkene bond length (1.22 Å) is larger than a normal C – H bond (approximately 1 Å). It is also obvious that the sulfonic moiety proton is transferred to the methanol molecule, replacing the proton additioned to the alkene partner. Figure 3 presents the unique imaginary vibration mode of this transition state (-252.84 cm⁻¹).

Quite unexpectedly, this transition state evolves into a benzencesulphonate with the reformation of the methanol molecule (scheme 8, fig. 4). The methanol molecule is still captive in the solvent cage.

The reaction energy is -110.5 kJ/mol (-94.97 kJ/mol considering ZPE) showing that this ester is more stable (by about -15.5 kJ/mol) than the solvated starting materials.

The slightly increased distances (> 2 Å) between the sulfonic oxygen atoms and the H in the methanol hydroxy
The group suggests that the weak interaction between the isoamyl benzenesulfonate and the methanol molecule, both still in the solvent cage, facilitates the next step. The methanol molecule attack “from behind” on the isoamyl benzenesulfonate 1 appears to be quite probable. Modeling this step has demonstrated the transition state 3 for such an attack (fig. 5). The transition state 3 is already “advanced”, i.e. the sulfonate moiety leaves ester 1, withdrawing from the isoamyl chain, while the methanol approaches from the opposite direction (related to the sulfonate position) (scheme 9).

The activation energy is 128.03 kJ/mol (120.5 kJ/mol with ZPE).

Transition state 3 progresses to an oxonium salt of TAME (4, fig. 6) presented in scheme 10. The reaction is endothermic, 119.2 kJ/mol, i.e. 111.7 kJ/mol considering ZPE, due to the weak basicity of TAME.

The oxonium salt of TAME (4)
Scheme 11. Deprotonation of the oxonium salt 4

If the ZPE is considered, formation of this oxonium salt (4) is endothermic by 1.25 kJ/mol compared to the transition state 3, and in this case the oxonium salt 4 is not an intermediate stage in the reaction mechanism. By deprotonation, the oxonium salt 4 leads to TAME (scheme 11).

The quantum mechanics study of the reaction mechanism in isomylhenes methoxylation, namely in TAME synthesis allowed to evidence the energetic profile for the global reaction including the energy levels for the intermediate transition states, presented in figure 7.

The final product is a little endothermic compared to the isoamyl benzenesulfonate. The reaction energy is 20.1 kJ/mol. If the ZPE is considered, the reaction energy is 19.2 kJ/mol.

Conclusions

The reaction mechanism of formation of TAME from methanol and isomylamine, catalyzed by benzene sulfonic acid is modeled using QM methods at an elevated level of theory (KTZVP/M11). The results show a multiple stages reaction involving a solvation of the benzene sulfonic acid by methanol. This stage is essential, since the classical mechanism involving the protonation of the alkene leading to a carbocation is not confirmed by QM model. Also, the formation of the isoamyl benzenesulfonate is quite unexpected according to classical mechanism. But the QM model shows that this stage is essential for the reaction. Formation of an oxonium salt of TAME is unclear, as the QM model shows that this stage is essential for the reaction. If the ZPE is considered, formation of this oxonium salt leads to TAME (19.12.1995), cf.


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