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 octane 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.

The scientific community, the fuel producers, the specialists and the users had to face also the perspective of a dramatic shortage of crude oil resources in the future and have focused on gradually replacing common fuels by biodiesel, also optimizing the quality of biofuels, to gradually replace traditional fuels. The ultimate complementary goal is to reduce conventional CO_2, CO, nitrogen oxides (NO_x), volatile organic compounds (VOCs) and other toxic particles emissions.

As an alternative to classic fuels different types of biofuels were developed (bioethanol produced by fermentation of plants with high content of starch and sugars, biodiesel, etherified bioethanol (ETBE), biogas produced by anaerobic fermentation of organic matter, bioethanol produced from biomass, etc.) whose sustainability is based on the advantageous renewable raw material sources.

Nevertheless, additives are needed to cope with the engine operating parameters, to improve fuel quality and to change its volatility and combustion properties. The octane number of gasoline can be increased by adding a certain percentage of oxygenates such as MTBE (methyl *tert*-butyl ether, i.e. 2-methoxy-2-methylpropane), ETBE (Ethyl tert-butyl ether, i.e. 2-ethoxy-2-methylpropane), TAME (*tert*-amyl methyl ether, i.e. 2-methoxy-2-methylbutane), or TAEE (*tert*-amyl ethyl ether, i.e. 2-ethoxy-2-methyl-butane). The use of such high octane gasoline blending components also solves the problem of the presence of isoamylenes in gasoline (isoamylenes are a major component in gasolines, atmospherically reactive hydrocarbons with a high RVP (Reid vapor pressure), inducing a potential risk of tropospheric ozone formation and their use in the manufacturing of TAME and TAEE significantly reduces the above inconveniences.

Fuel ethers- mostly those produced out of the C4 and C5 olefins with methanol and/or ethanol [1] are therefore an environmentally-friendly solution, as blending components obtained from renewable alternative sources, whose addition to fuel ensures a clean and complete burning, engine protection and improved performances, reduced exhaust emissions, while meeting the EU Renewable and Fuel Quality objectives [2]

Scheme 1 presents the main oxygenates obtained from C4-C5 olefins, isobutene and isoamylenes: isobutene (2-methylpropene), 2-methylbutene (2M1B) and 2-methyl 2-butene (2M2B, 2-methyl but-2-ene).

The manufacturing of all these compounds is studied in detail: the reaction mechanism of the alcohols addition to tertiary olefins catalyzed by a macroporous sulfonic acid resin is proven to vary according to the molar ratios of the reactants [3]. The conclusions are based on experimental kinetic data while reducing the alcohol: olefin molar ratio. In such conditions the authors advanced the idea of a concerted reaction on the associated network of sulfonic groups. Other reports reveal relative reactivities of primary alcohols in their addition to butenes and significant differences in reactivity of isobutene toward specific alcohols (methanol versus butanol), the addition being catalyzed by a macroporous sulfonic acid resin. [4].

Literature reported the activation energy values for the simultaneous etherification and hydration of isoamylenes [5].

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).

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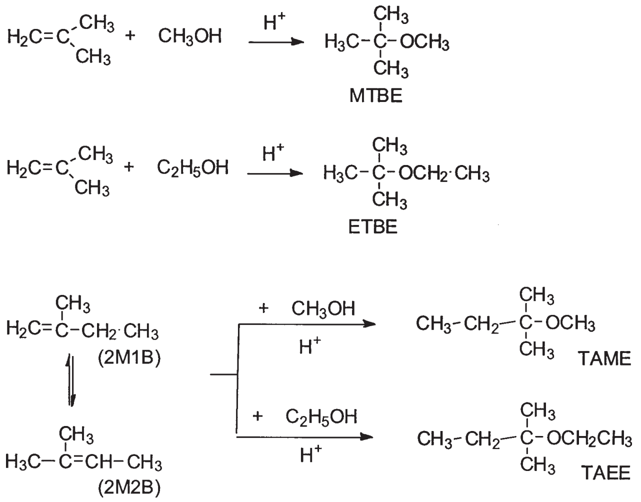


Scheme 1. Tertiary ethers obtained out of C4 and C5 olefins

For manufacturing octane boosting ethers various acid catalysts besides strong inorganic acids (e.g. sulfuric acid) were tested, such as organic sulfonic acids [12,13] and sulfonated macroporous styrene divinylbenzene copolymers, 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)–$CuCl_2$ [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 carbenium ion 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 SO_3H 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.

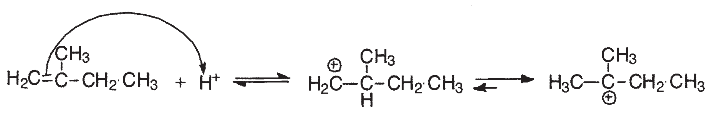
Modeling the reaction steps

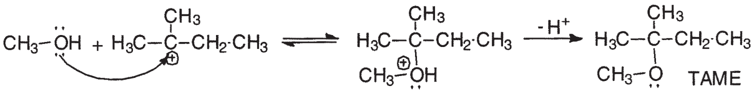
It has been long ago admitted that the addition of alcohols to olefins double bonds has an electrophilic mechanism: in the first step, the attack on the catalyst proton performed by the p doublet of the alkene leads to the predominance of the most stable carbenium ion that isoamylene can provide (scheme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

The alcohol nucleophilic molecule attacks the carbocation to generate an oxonium ion that further stabilizes by proton elimination (scheme 3).

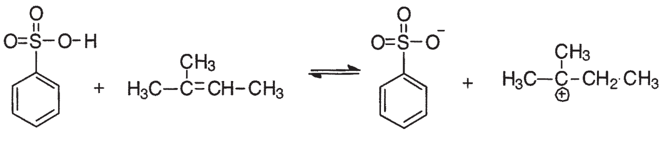
The addition regioselectivity is the expected one and the alkohol reactivity for the addition to double bonds decreases as follows: primary alcohols > secondary alcohols > tertiary alcohols.

Scheme 2 Isoamylene protonation





Scheme 3 The nucleophilic attack of the alcohol leading to the final ether

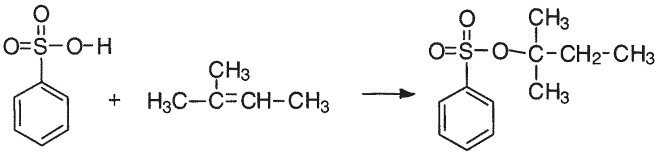


Scheme 4 Reaction between isoamylene and the benzenesulfonic acid

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 isoamylenes 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).



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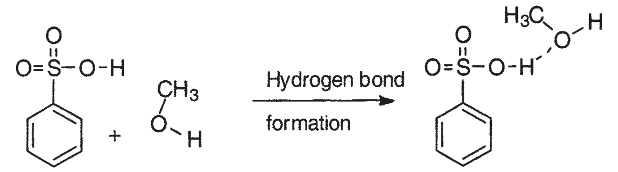
Scheme 5. Reaction between the benzenesulfonic acid and the alkene to produce sulfonate **1**

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-Benzenesulfonic 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).



Scheme 6. Solvation of the catalyst

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 benzenesulfonic acid and the methanol molecule.

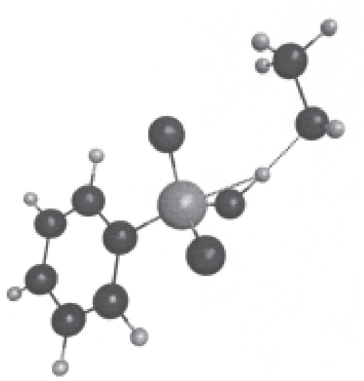
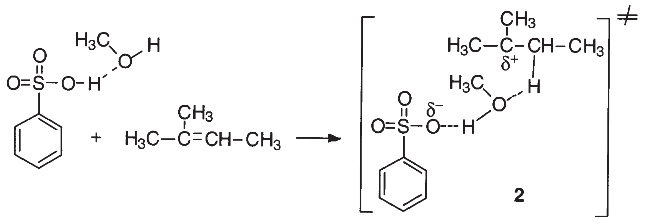


Fig. 1. The solvated benzenesulfonic acid

The subsequent attack of the solvated benzenesulfonic acid at the alkene p bond did not provide a transition state leading to a carbenium ion. The transition state **2** (scheme 7) is underlined to be the one preceding the final ester expected from an addition of the sulfonic acid to the isoamylene.



Scheme 7. The solvated sulfonic acid attacks the isoamylene to generate the transition state **2**

The structure of transition state **2** is shown in figure 2.

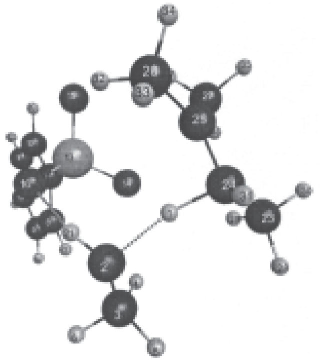


Fig. 2. Transition state **2** of the isoamylene protonation

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 A^{o}) is larger than a normal C – H bond (approximately 1 A^{o}). 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 benzenesulfonate 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 A^{o}) between the sulfonic oxygen atoms and the H in the methanol hydroxy

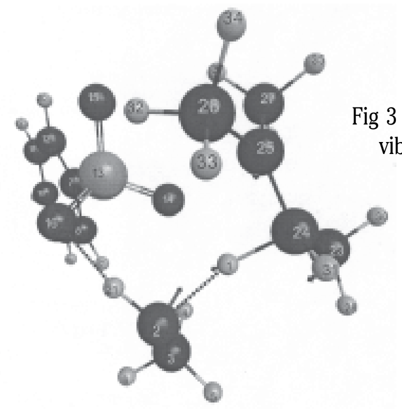


Fig 3 The unique imaginary vibration mode of the transition state **2**

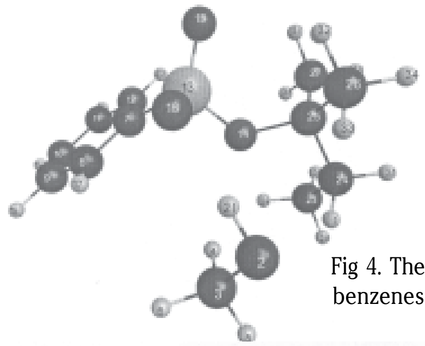


Fig 4. The isoamyl benzenesulfonate

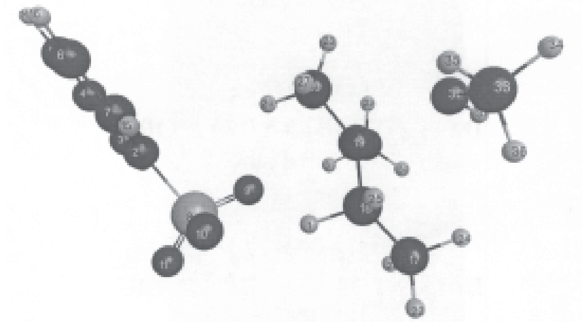
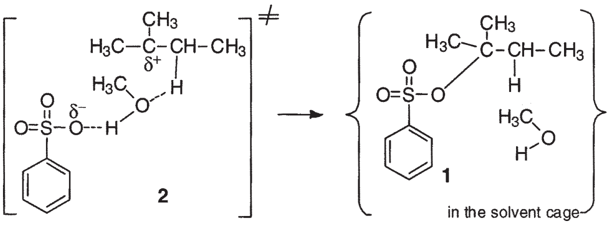


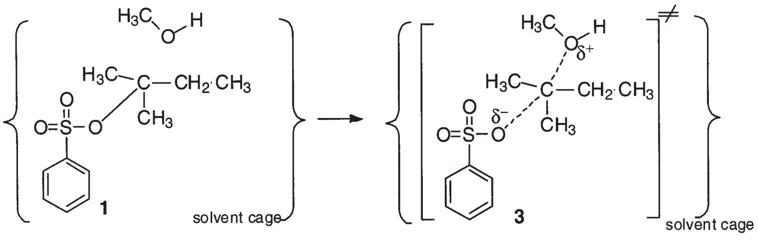
Fig 5 Transition state **3** for the methanol attack in the solvent cage

group suggests that the weak interaction between the isoamyl benzenesulfonate and the methanol molecule, both still in the solvent cage, facilitates the next step.

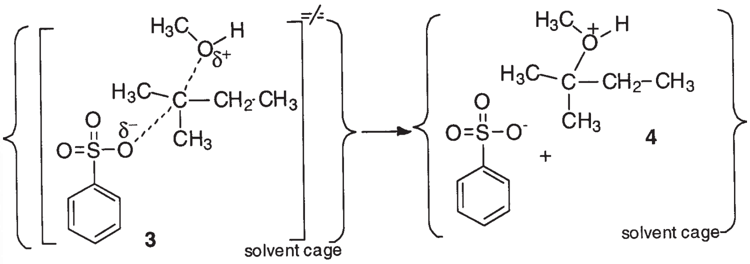
The methanol molecule attack "from behind" on the isoamyl benzenesulfonate **1** appears to be quite probable. Modeling this step has demonstrated the transition state **3** for such an attack (fig. 5). The transition state **3** is already "advanced", i.e. the sulfonate moiety leaves ester **1**, withdrawing from the isoamyl chain, while the methanol approaches from the opposite direction (related to the sulfonate position) (scheme 9).



Scheme 8. Ester **1 (isoamyl benzenesulfonate)** formation in the solvent cage



Scheme 9. Formation of transition state **3** in the solvent cage



Scheme 10. Evolution of transition state **3** to the oxonium salt **4**, in the solvent cage

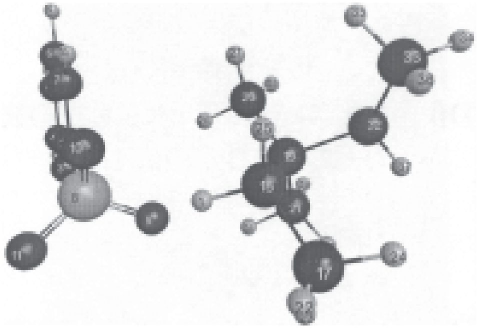


Fig. 6 The oxonium salt of TAME (**4**)

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.

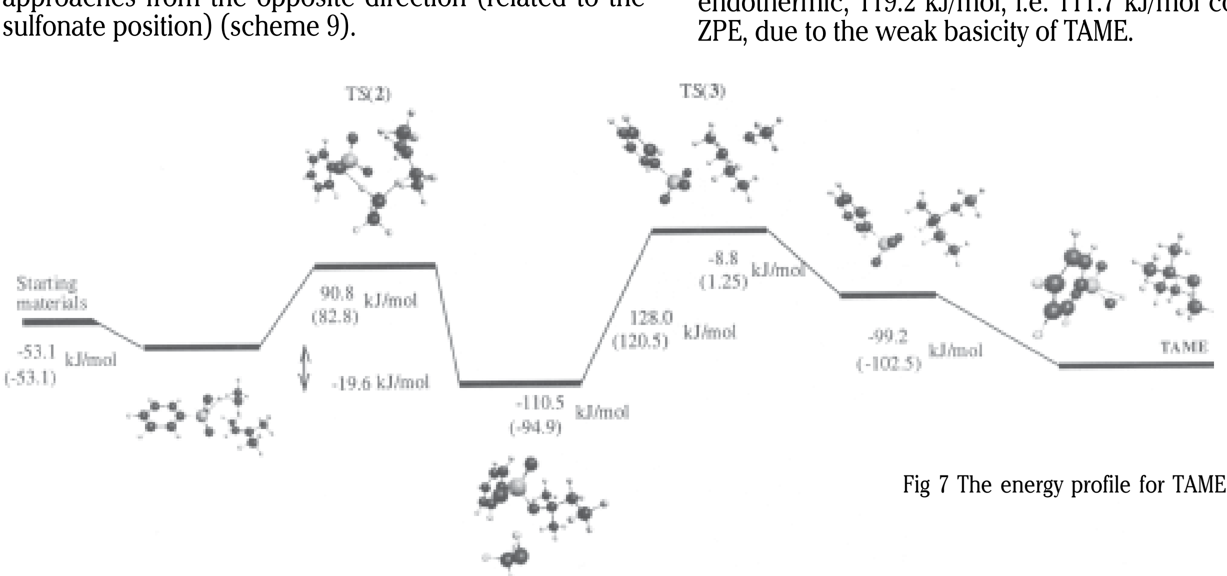
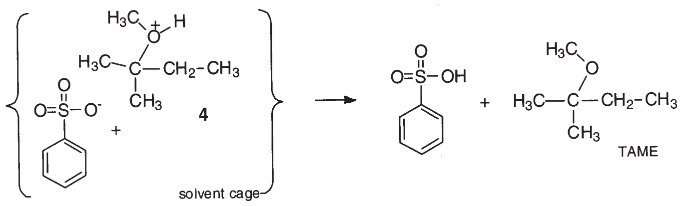


Fig 7 The energy profile for TAME synthesis



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 isoamylenes methoxylation, namely in TAME synthesis allowed to evidentiate 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 isoamylene, 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 effect of ZPE shows that this intermediate is thermodynamically not possible. Generally, the effect of ZPE is very small and in most cases less than 8.4 kJ/mol, which is below the errors of the methods that were used for modeling this reaction.

The QM calculations show that the reaction is reversible and the rate determining step is the transformation of the isoamyl benzenesulfonate in TAME. Also the previous studies based on kinetic and thermodynamic studies of liquid-phase etherification of isoamylenes with methanol on ion exchange resin as catalyst showed an initial stage involving adsorbtion of methanol on the surface of the ion exchange resin, which is consistent with our findings. The activation energy involving the highest transition state is 108.4 kJ/mol (100.8 kJ/mol with ZPE), consistent with literature data (102.1 kJ/mol [11, 15, 23, 24])

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References

1. STRUCKMANN, L.K, Acta Polytech. Scand., Chem. Technol., **246**, 1997, p. 43.
2. SOTO, R., FITÉ, C., RAMÍREZ, E., BRINGUÉ, R., CUNILL, F., Chem. Eng. Res. Des., **92**, no. 9, 2014, p. 644.
3. ANCILLOTTI, F., MASSI MAURI, M., PESCAROLLO, E., ROMAGNONI, L, J. Mol. Catal., **4**, no. 1, 1978, p. 37.
4. ANCILLOTTI, F., MASSI MAURI, M., PESCAROLLO, E., J. Catal., **46**, no. 1, 1977, p. 49.
5. LINNEKOSKI, J.A., KRAUSE, A.O.I., STRUCKMANN, L.K., Appl. Catal., A, **170**, no. 1, 1998, p. 117.
6. HAMID, H., ASHRAF ALI, M., (editors), Handbook of MTBE and Other Gasoline Oxygenates, CRC Press, New York, 2004.
7. HARANDI, M. N., OWEN, H., US Pat US4988366 A, (29.01.1991), cf. http://www.uspto. gov/patents-application-process/search-patents, consulted 3rd June 2015.
8. EVANS, T. W., EDLUND, K. R., Ind. Eng. Chem., **28**, no. 10,1936, p. 1186.
9. HUTCHINGS, G. J., NICOLAIDES, C. P., SCURRELL, M. S., Cat. Today, **15**, 1992, p. 23.
10. TAU, L.M., DAVIS, B.H., Appl. Catal., **53**, 1989, p. 263.
11. RANDRIAMAHEFA, S., GALLO, R., RAOULT, G., MULARD, P., J. Mol. Catal., **49**, 1988, p. 85.
12. VERSTEEG, G.F., IJBEN, P., WERMINK, W.N., KLEPACOVA, K., VAN LOO, S., KESBER, W., The GTBE Company N.V., Pat. US 20110098510 (28.04.2011), cf http://patft.uspto.gov/netacgi/nph-Parser?Sect1= PTO2&Sect2=HITOFF&p=1 &u=%2Fnetahtml% 2FPTO%2Fsearch-bool.html&r=1&f=G&l=50&co1= AND&d=PTXT&s1= 20110098510& OS= 20110098510&RS=20110098510, consulted 3rd June 2015.
13.GUPTA, V.F., Arco Chemical Technology, L.P., Pat. US 5476971 (19.12.1995), cf. http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO2&Sect2= HITOFF&p=1 &u=%2Fnetahtml %2FPTO%2Fsearch-bool.html&r= 1&f=G&l=50&co1=AND&d=PTXT&s1=5476971&OS= 5476971&RS=5476971, consulted 3rd June 2015
14. McNULTY, J.T., Chem. Eng. **104**, no. 6, 1997, p. 94.
15. OOST, C., SUNDMACHER, K., HOFFMANN, U., Chem. Eng. Technol., **18**, 1995, p. 110.
16. KOROBITSYNA, I.K., RODINA, L.L., SUSHKO, T.P., J. Org. Chem. USSR, **4**, 1968, p.175.
17. JONES, JR., M., ANDO, W., J. Am. Chem. Soc., **90**, 1968, p. 2200.
18. LEE, Y.R., SUK, J.Y., KIM, B.S., Tetrahedron Lett., **40**, 1999, p. 8219.
19. WISKUR, S.L., FU, G.C., J. Am. Chem. Soc., **127**, 2005, p. 6176.
20. SCOTT, A.P., PLATZ, M.S., RADOM, L., J. Am. Chem. Soc., **123**, 2001, p. 6069.
21. ADAMS, J. M., CLEMENT, D. E., GRAHAM, S. H., Clays Clay Miner., **31**, 1983, p.129.
22. KRAUSE, A.O.I., HAMMARSTROM, L.G., Appl. Cat. **30**, no. 2, 1987, p. 313.
23. WEI MAO, XIAOLEI WANG, HUA WANG, HEYING CHANG, XIANGWEN ZHANG, JINYU HAN, Chem. Eng. Process., **47**, 2008, p. 761.
24. MUJA, I., TOMA, A., POPESCU, D. C., IVANESCU, I., STANISTEANU, V., Chem. Eng. Process., **44**, 2005, p. 645.
25. PICCOLI, R.L., LOVISI, H.R, Ind. Eng. Chem. Res. **34**, no. 2, 1995, p. 510.
26. MARTON, G., PLESU, V., MARTON, A., BERCARU, M.T., Chemical Engineering Transactions, **21**, 2010, p. 1351.
27. MARTON, G.I., IANCU, P., PLESU, V., MARTON, A,. SORIGA, S.G., Rev. Chim. (Bucharest), **66**, no. 5, 2015, p. 750.
28. SCHMIDT, M.W., B.ALDRIDGE, K.K., BOATZ, J.A., ELBERT, S.T., GORDON, M.S., JENSEN, J.J., KOSEKI, S., MATSUNAGA, N., NGUYEN, K.A., SU, S., WINDUS, T.L., DUPUIS, M., MONTGOMERY, J.A., J. Comput. Chem., **14**, 1993, p.1347.
29. PEVERATI, R., TRUHLAR, D.G., J. Phys. Chem. Lett., **2**, 2011, p. 2810.
30. SCHAEFER, A. HORN, H. AHLRICHS, R., J. Chem. Phys., **97**, 1992**,** p. 2571.
31. SCHAEFER, A, HUBER, C., AHLRICHS, R., J. Chem. Phys., **100**, 1994, p. 5829.
32. POMELLI, C.S., LI, H., JENSEN, J.H., Theoret. Chim. Acta, **109**, 2003, p. 71.
33. MARENICH, A.V., CRAMER, C.J., TRUHLAR, D.G., J.Phys.Chem. B, **113**, 2009, p. 6378.
34. MA, Q., CHAKRABORTY, D., FAGLIONI, F., MULLER, R. P., GODDARD, W. A., HARRIS, T., CAMPBELL, C., TANG, Y., J. Phys. Chem. A., **110**, 2006, p. 2246.
35. NAMUANGRUK, S., PANTU, P., LIMTRAKUL, J., J. Catal. **225**, 2004, p. 523

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