Solketal - a Quantum Mecanics Study of the Reaction Mechanism of Ketalization

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The present paper describes the study of acetone-glycerol ketals synthesis, using the molecular modeling. As part of the introduction of sustainable fuels, along with biodiesel, the acetone - glycerol ketals represent a solution for the valorization of the continuously increasing amounts of glycerol generated as by-product in biodiesel manufacturing. The molecular modeling tasks regarded elucidation of the mechanism and of the transition states involved in the reaction of acetone with glycerol, using benzenesulfonic acid as a catalyst.

Keywords: acetone glycerol ketals, solketal, molecular modeling, biodiesel, fuel additives

The efforts of last years, made in the fuels research field were focused on trying to replace the crude oil distillates with renewable fuels, mostly biodiesel, in the endeavour to find a cheap, sustainable and environmental-friendly solution for the increasing demand of energy sources and fuels. The continuous menace driven by the reduction of petroleum resources and the environment degradation due to the increase of greenhouse gas concentration in the atmosphere have contributed to the development of the “biodiesel solution” as based on biomass exploitation, as a renewable available source, with multiple applications for other needs of the 21st century civilization.

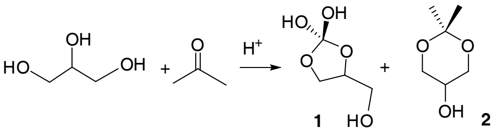
Biofuels, including biodiesel [1] (produced by transesterification of vegetable oils or animal fats), bioethanol, biomethanol (from natural sources), bioethers [2] (obtained by the addition of the above mentioned alcohols to butenes and amylenes) are presently an alternative to the fossil fuels.

But on the way of finding alternative fuels, the chemists encountered new problems, such as the valorization of the continuously increasing amounts of glycerol resulted in the biodiesel production via transesterification reactions. Absorption of the glycerol output on the market demanding efficient solutions, in order not only to promote a cheap, available and eco-friendly fuel additive, but also to convert it to value added chemicals, led to hydrogenolysis to propanediols, oxidation to various hydroxyaldehydes and hydroxyacids, dehydration to acrolein, polymerization to polyglycerols and polyglycerol esters, etc. [3-5].

Ketalization of acetone with glycerol [6] is a good candidate reaction for absorbing the huge amounts of glycerol, providing in the same time oxygenated structures with good combustion properties, improving biofuels’ viscosity, pour point, and particles emission, also ensuring oxidation protection of biodiesel. As a consequence, acetone-glycerol ketals were introduced as additives in the biodiesel formulation [7-10].

Reaction of carbonyl compounds (e.g. acetone) with alcohols (glycerol included) leads to acetals and ketals. The reaction is catalyzed by Lewis acids ($TiCl_4$), sulfonic acids in solution, but also by various heterogeneous phase acid catalysts, and other catalytic systems [11-16].

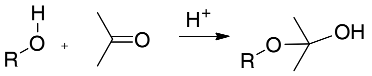
The glycerol acetone ketalization leads to two cyclic compounds, both branched, showing remarkable combustion properties, namely (2,2-dimethyl-[1,3] dioxane-4-yl)-methanol (solketal, **1**) and 2,2-dimethyl-[1,3]dioxane-5-ol **2**:



Scheme 1. Acid catalyzed reaction of acetone with glycerol

The acid catalyst is usually an aromatic sulfonic acid (p-toluenesulfonic or benzenesulfonic acid). In this case, the sulfonic acid catalyst must be removed at the end of the reaction by several washings with water, or with slightly alkaline solutions and water. This is the reason why for industrial scale synthesis the use of an acidic ion-exchange resin is preferred. Such resins possess active catalytic centers with sulfonic groups attached to an aromatic substrate. The use of acidic ion exchange resins allows a continuous process in a reactive distillation column. Unfortunately, such resins cannot be modeled using quantic methods, due to the too large number of atoms. Since the group effectively catalyzing the reaction is the sulfonic group, modeling can be achieved using benzenesulfonic acid, assimilating its SO_3H group with the same active group grafted on the resin skeleton. Therefore, we considered the benzenesulfonic acid molecule as a very good approximation for the real catalyst, acting in most industrial processes.

The first step in the ketalization process is a nucleophilic attack on the carbonyl performed by the alcohol, leading to a hemiketal (scheme 2):



Scheme 2. Hemiketal formation

În the second step, with a second alcohol molecule, a ketal is produced (scheme 3):

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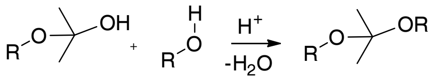
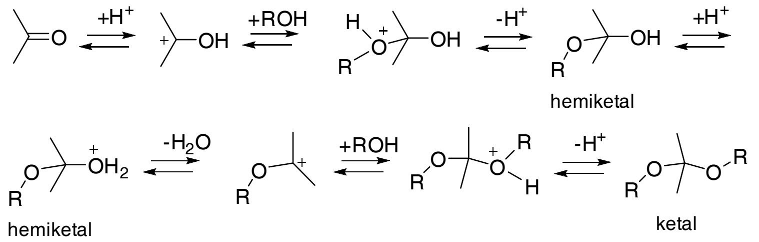


Scheme 3. Ketal formation



Scheme 4. The mechanism of hemiketal and ketal formation

The ketal formation is a sequence of equilibria, induced by a H^+ released by the catalyst.

Another mechanistic pathway for hemiketal occurrence was also reported [17, 18], based on experimental data that support a concerted process, in aqueous media, with water molecules acting both as proton donors and acceptors, as in scheme 5.

New information on the reaction mechanism is crucial for the optimization of reaction conditions in order to obtain high conversion of glycerol into ketals, and, last, but not least, improving the efficiency of biodiesel applications.

Since our research team has successfully used the quantum mechanics method for modeling the triglycerides involved in the biodiesel production [21], based on the experience already gained, the present study is reporting an original perspective for the mechanism of glycerol ketalization.

Results and discussions

Conditions and modeling parameters for the solketal synthesis

In order to study the ketalization reaction mechanism a quantum method is chosen. The level of theory used is DFT M11/KTZVP [22-24] under GAMESS [25]. Also the PCM method is used for the solvent effect [19, 20].

Modeling the hemiketalization step

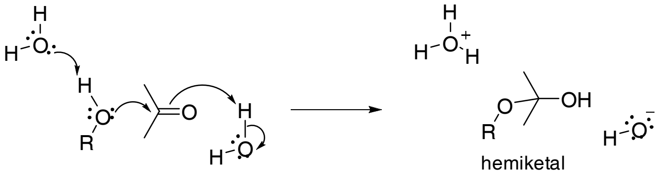
The Acetone-Benzenesulfonic acid complex

Any attempt to find a transition state for the proton transfer from benzenesufonic acid to acetone is unsuccessful, but a molecular association between acetone and benzenesulfonic acid is found to be formed spontaneously (fig. 1). As expected, a hydrogen bond is formed between the acid proton and the carbonylic oxygen. Hydrogen bond length is 1.63 Å, showing a strong interaction, but the length of the bond between the same hydrogen atom and the sulfonic group is 1.0 Å, just a little longer then the same bond in benzenesulfonic acid 0.95 A°. Also the partial formal charge of the sulfonic group is only -0.463 e showing a reduced tendency to transfer the proton to acetone.

Modeling the transition state of the hemiketalization step

The search of a transition state for hemiketalization led to a tri-molecular association, involving the acetone-benzenesulfonic acid association found in the previous step and a molecule of glycerol (fig. 2).

The transition state of the hemiketalization step presents a multitude of interactions between the catalyst (benzenesulfonic acid) and the reagents (acetone and glycerol).



Scheme 5.Concerted mechanism for hemiketal formation

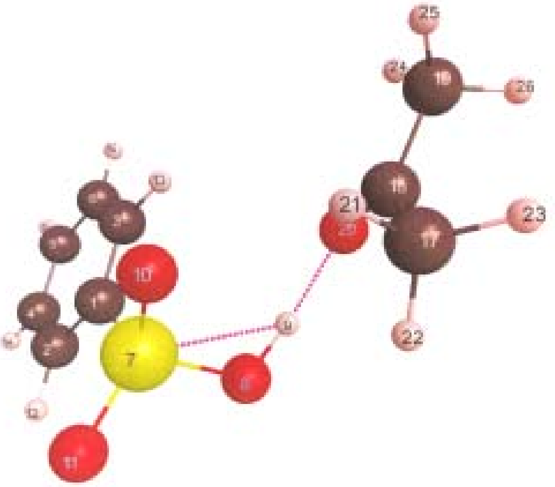


Fig. 1. The Acetone-Benzenesulfonic acid molecular association

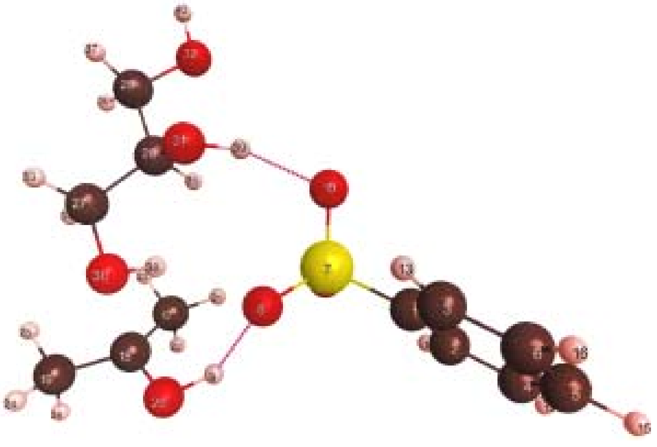


Fig. 2. Transition state for the formation of the hemiketal

The proton from the benzenesulfonic acid is almost completely transferred to acetone molecule. The distance between the hydrogen atom 9 and the carbonylic oxygen atom 20 is reduced to 1.0 A° while the distance between the same hydrogen atom and the oxygen 8 of the sulfonic group is increased from 1.0 to 1.61 Å. In the same time a new hydrogen bond (1.80 Å) is formed between the hydroxyl group in the middle position of the glycerol molecule and another oxygen atom from the sulfonic group. This stabilizes the molecular association of the three molecules. This demonstrates that the protonation of the acetone molecule is possible only with assistance of the alcohol molecule that solvates the sulfonic anion.

The total energy of the transition state is -1393.9516 Hartree.

Table 1
CHARGE DISTRIBUTION IN THE ACETONE-BENZENESUL FONIC ACID ASSOCIATION

ATOM	MULLIKEN POPULATION	CHARGE
1 C	6.429960	-0.429960
2 C	6.021212	-0.021212
3 C	5.980237	0.019763
4 C	6.168344	-0.168344
5 C	6.162930	-0.162930
6 C	6.184805	-0.184805
7 S	15.201073	0.798927
8 O	8.410264	-0.410264
9 H	0.638681	0.361319
10 O	8.462437	-0.462437
11 O	8.436855	-0.436855
12 H	0.774316	0.225684
13 H	0.786521	0.213479
14 H	0.804680	0.195320
15 H	0.806799	0.193201
16 H	0.806043	0.193957
17 C	6.570039	-0.570039
18 C	5.612366	0.387634
19 C	6.544461	-0.544461
20 O	8.452319	-0.452319
21 H	0.758313	0.241687
22 H	0.791564	0.208436
23 H	0.805031	0.194969
24 H	0.805820	0.194180
25 H	0.800828	0.199172
26 H	0.784101	0.215899

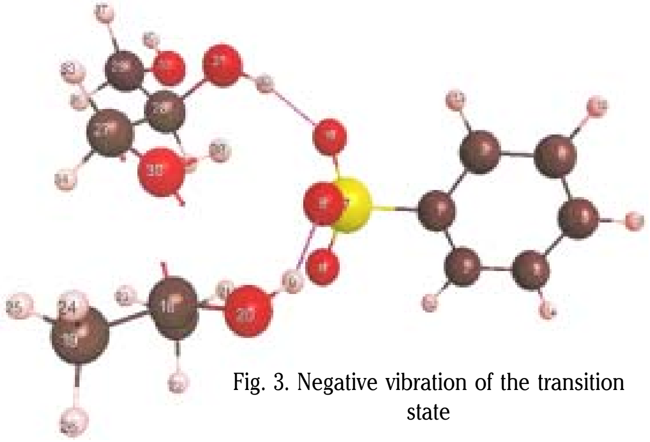


Fig. 3. Negative vibration of the transition state

In order to check the transition state structure, the vibrations are calculated and only one negative vibration is found. The vibration mode is shown in figure 3.

Since glycerol possesses two types of hydroxylic groups (two primary and one secondary) the hemiketalization can take place either with one of the two primary hydroxyl groups or with the secondary one.

Hemiketalization variants in respect with the participating OH group position

The product of the hemiketalization of acetone with a primary hydroxyl group from glycerol is shown in figure 4. It can be observed that the benzenesulfonic acid is reformed. There are three hydrogen bonds. One between the proton 27 of the benzenesulfonic acid and the etheric oxygen 19 the other between the oxygen atom 9 and hydrogen 28 in glycerol, and the third between the oxygen atom 10 of the sulfonic group and hydrogen atom 30 of the hemiacetal.

The hydrogen bonds in the product of hemiketalization with a primary hydroxyl group are not equivalent. The one involving the etheric oxygen 19 is the strongest with a length of 1.67 Å, the other two (between atoms 9-28 and 10-30) are little longer, of 2.0 and 1.94 Å respectively. Total energy is -1393.9657 Hartree which is by 37 kJ/mol lower than the one of the transition state.

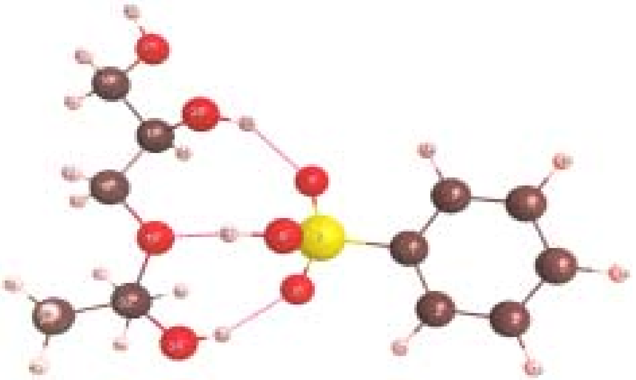


Fig. 4. Hemiketalization product obtained by reaction of the primary hydroxyl group

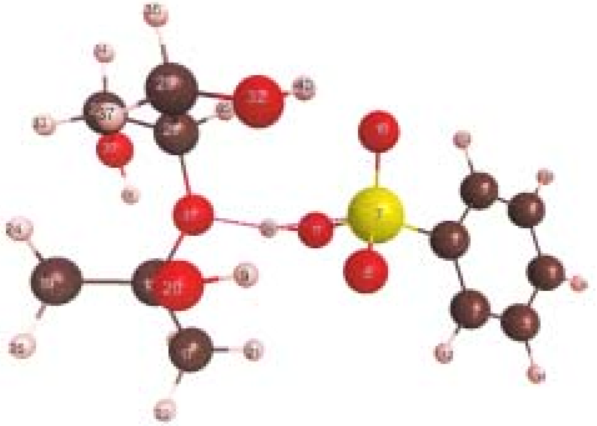


Fig. 5. Hemiketalization product obtained by reaction of the central hydroxyl group.

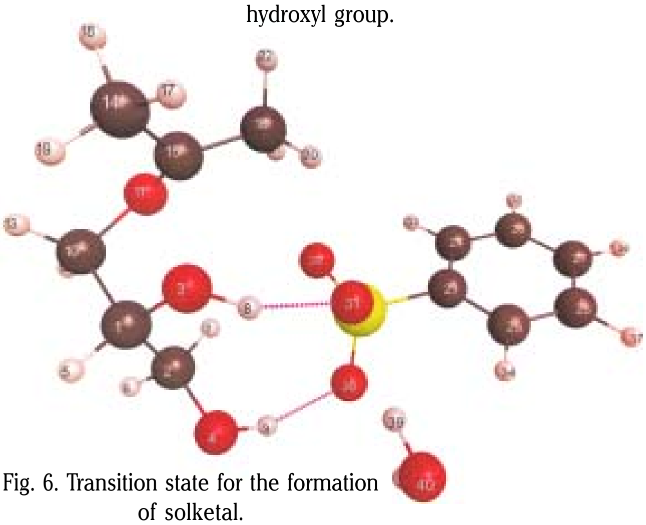


Fig. 6. Transition state for the formation of solketal.

When the hemiketalization reaction takes place with the secondary hydroxyl group, the product shown in figure 5 is obtained.

.Total energy is -1393.9655 Hartree which is 36.32 kJ/mol lower than the one of the transition state.

Resulting total energy is practically the same in both reactions showing that there is no thermodynamic factor favouring one of the products.

Solketal – the major output of the ketalization step

For the second step of the ketalization reaction a transition state is found (fig. 6).

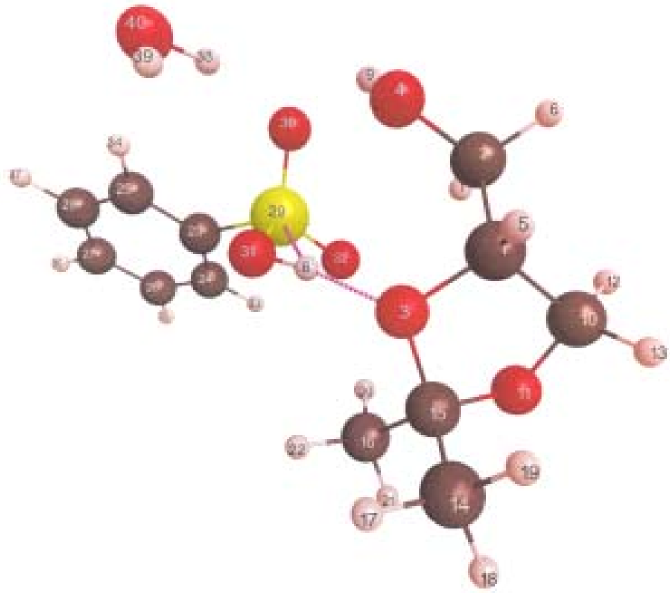


Fig.7. Solketal molecule in final state

The total energy is -1393.9441 Hartree. As it can be seen, the hydroxyl group of the hemiketal is eliminated, and a carbocation is formed. Also two hydrogen bonds are formed between the sulfonic group and the two hydroxyl groups in the glycerol.

The final product, as it is obtained from an IRC (Intrinsic Reaction Coordinate), also known as MEP (Minimum Energy Path), is presented in figure 7. Total energy is -1393.9695 Hartree.

Conclusions

The transition states for both steps are found and the calculated low energy barriers confirm the reversibility of the reactions involved.

In this case, the classical mechanism that involves the protonation of acetone is not confirmed by the QM study. Instead, a mechanism involving the assistance of glycerol molecule is confirmed, being presented in this paper, after our knowledge, for the first time in literature. In the final step of ketalization the presence of the water molecule formed by protonation-elimination of the –OH group of the hemiketal is essential.

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