

## Theoretical study of the ketonization reaction mechanism of acetic acid over SiO<sub>2</sub>

M. Fleisher, V. Stonkus, I. Liepiņa, K. Edolfa, D. Jansone, L. Leite, E. Lukevics

Latvian Institute of Organic Synthesis, 21 Aizkraukles Street, Riga LV1006, Latvia  
Mendel Fleisher [misha@osi.lv]

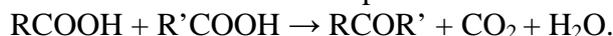
### Abstract:

The mechanism of ketonization of acetic acid over SiO<sub>2</sub> was investigated by semiempirical quantum chemical AM1 method using the cluster approach. It has been found that the adjacent acid-base pair of the catalytic sites provokes dissociative adsorption of the acetic acid molecules resulting in the formation of surface carboxylate species. The adsorption process proceeds spontaneously. After blocking the acid-base pairs of catalyst, the new portions of acetic acid molecules interact with active species in the gas phase, converting into acyl cations. The adsorbed carboxylate species is attacked from the methyl group side by the acyl cation resulting in the formation of an acetone molecule and CO<sub>2</sub> by bimolecular electrophilic substitution reaction.

**Keywords:** *Ketonization \* Acetic acid \* SiO<sub>2</sub> \* AM1*

### 1. Introduction

The ketonization of carboxylic acids over heated metal oxides is a reaction of wide applicability, and has been well known in organic chemistry for more than a century. The general reaction scheme is expressed as follows:



The target ketones are useful as intermediates in production of pesticides, herbicides, and pharmaceuticals, and as solvents. A large variety of oxides, such as Cr<sub>2</sub>O<sub>3</sub> [1], Al<sub>2</sub>O<sub>3</sub> [2-4], PbO<sub>2</sub> [2], Bi<sub>2</sub>O<sub>3</sub> [2], TiO<sub>2</sub> [3, 5 - 7], ZrO<sub>2</sub> [6, 8], CeO<sub>2</sub> [3, 8- 13], iron oxides [6, 14, 15], SiO<sub>2</sub> [11, 14], manganese oxides [2, 8, 11, 17], and MgO [18], catalyze the ketonization of carboxylic acids. Although much work has been done to determine the reaction pathways, the mechanisms are not yet completely understood. Good overviews on this subject are given by Rajadurai [19], Barteau [20], Dooley [21], and Renz [22]. Decarboxylation of an acid anhydride intermediate [4, 7], Claisen condensation to form β-keto acid followed by decarboxylation [4], and a concerted mechanism involving two monodentate carboxylates [23] have been proposed. Another possible mechanism consists of reaction of an adsorbed acyl carbenium ion (RCO<sup>+</sup>) with an adsorbed carboxylate to give ketonization products [15]. Some authors have proposed that the formation of ketones on oxides is a sequential reaction going through a "ketene intermediate" [1, 2, 9, 12, 14]. The surface ketene intermediate reacts with an adsorbed carboxylate to ultimately form the ketone, eliminating CO<sub>2</sub>, but the details of coupling step are not clear.

Apparently, further deeper study concerning the mechanisms of such reactions, apart from the experimental investigations, requires a wider application of theoretical approaches and computational modeling aimed to solving the problems on the molecular or atomic level.

### 2. Computational Details

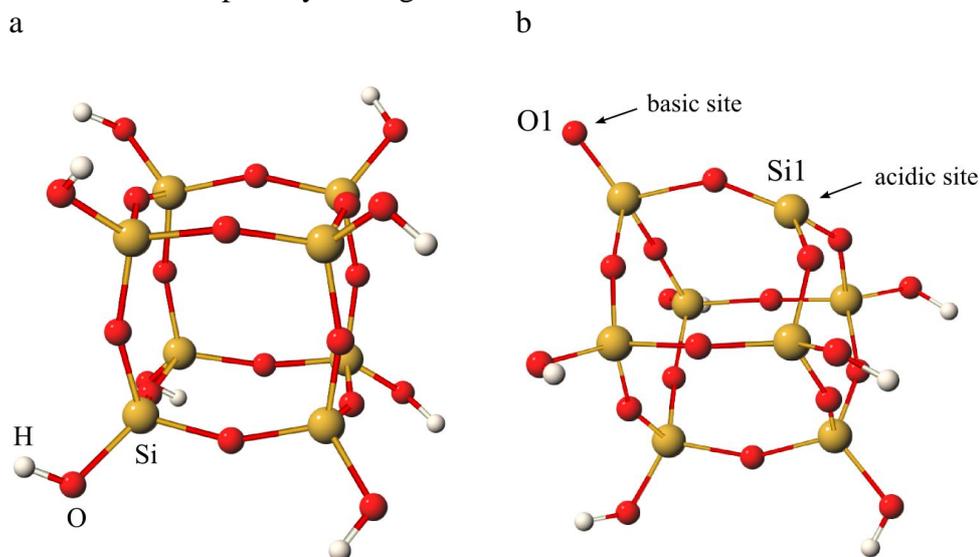
We have used the semiempirical AM1 quantum-chemical method [24]. The choice of method is due to its ability to calculate activation energy, proton affinity, and deprotonation enthalpy in good agreement with experimental data [25]. Besides, the AM1 method is successfully

applied to study the chemical and physical properties of metal oxides and different reactions with participation of oxide catalysts [26-28]. The calculations have been performed using the MOPAC 6.0 program package [29]. All structures (reactants, molecular clusters, reaction systems, and products) were fully optimized at the restricted Hartree-Fock level of theory. No constraint of symmetry was used. The nature of each stationary point was checked by diagonalization of the Hessian matrix. All stationary points were identified as minima on the potential energy surface. Computer design, postprocessing visualization and animation were performed using the JMol program [30].

### 3. Results and Discussion

#### 3.1. Cluster models of the active sites on the catalyst surface

Silicon dioxide  $\text{SiO}_2$  was chosen as an oxidic catalyst prototype because of its widespread application as a catalyst, adsorbent and carrier [11, 16, 31, 32]. One of the simplest representatives of carboxylic acids - acetic acid ( $\text{CH}_3\text{COOH}$ ), which is a traditional object for studying the mechanisms of catalytic ketonization [1 - 11, 15, 18], was chosen as a model compound. The fundamental structure of silica consists of three-dimensional tetrahedral  $\text{SiO}_4$  units arranged in a variety of siloxane structures, both linear and cyclic, with hydrophilic hydroxyls on the surface [26]. We have modeled the hydrated surface of the catalyst by a molecular electroneutral cluster  $\text{Si}_8\text{O}_{20}\text{H}_8$  as shown in Fig. 1a. The hydrogen atoms that are not involved in the surface hydroxyl groups are added to satisfy the valency of the  $\text{Si}-\text{O}$  bonds that were disrupted by cutting out the cluster from the surface/bulk of the catalyst.



**Figure 1.** a -  $\text{Si}_8\text{O}_{20}\text{H}_8$  cluster model of silica optimized by AM1 method; b - Cluster model representing acid-base pair sites of the  $\text{SiO}_2$  surface

Such cluster possesses a structural rigidity and avoids the artifacts connected with appearance of ‘unrealistic’ intra-molecular bonds during geometry optimization of the system.

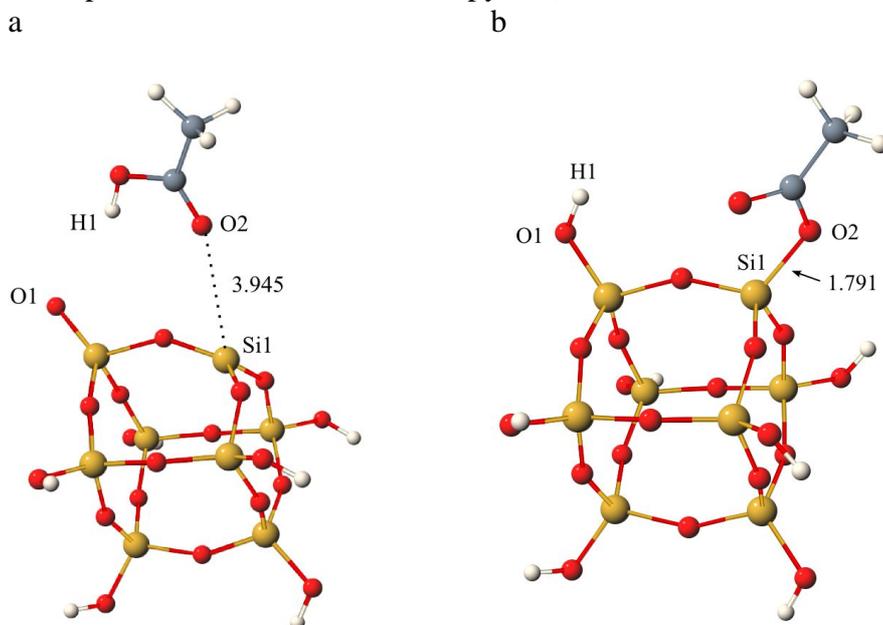
At high temperatures on the real catalysts surfaces, the condensation of hydroxyl groups takes place forming water molecules. In this process, so-called acid-base pair of the active sites originates on the catalyst surface: coordinatively unsaturated metal atom (Lewis acid site) and terminal oxygen atom (Lewis base site) [31, 33, 34].

The cluster  $\text{Si}_8\text{O}_{19}\text{H}_6$ , representing such an acid-base pair on the  $\text{SiO}_2$  surface, is depicted on the Fig. 1b. Indeed, inspection of the frontier molecular orbitals shows that the lowest unoccupied molecular orbital (LUMO) responsible for electron acceptor, i.e., for the acidic

properties of the system, is localized (approximately 67%) on the coordinatively unsaturated silicon atom Si1, while the highest occupied molecular orbital (HOMO), that characterizes the donor (basic) properties, is localized (approximately 83%) on the terminal oxygen O1.

### 3.2. Interaction of the acetic acid molecule with the acid-base pair sites

The modeling of interaction of the acetic acid molecule and the activated catalyst surface was started by setting the distance between the carbonyl oxygen O2 and silicon Si1 of the catalyst equal to 3.945 Å. (Fig. 2a). Results of the AM1 calculations show that the reaction is a barrierless process with a reaction enthalpy  $\Delta H_f = -434.3$  kJ/mol.



**Figure 2.** Interaction of acetic acid molecule with the acid-base pair sites on the SiO<sub>2</sub> surface. a - Starting position; b - Adsorption complex. Selected bond lengths in angstroms are indicated

The acid molecule gradually moves towards the acidic site of the catalyst surface (atom Si1), and, at the distance of O2–Si1 equal to 1.907 Å, the proton H1 transfer occurs from the molecule to the terminal oxygen O1 of the catalyst. Accordingly, during the adsorption process of the acetic acid molecule the filling of the coordination sphere of the acidic atom Si1 occurs (coordination number changes from three to four), and due to the nearby basic center O1 the dissociation of the adsorbing molecule happens.

The reaction outcome is the adsorbed carboxylate species and deactivated basic center of the catalyst. The optimized state of the system is represented in Fig. 2b. On adsorption the distance between O1 and Si1 was observed to be 1.791 Å.

It should be noted that the acid-base pairs as active sites for acetic acid conversion to acetone on MgO, TiO and SeO<sub>2</sub> are discussed as well [3, 18].

The adsorbed carboxylate species has a high negative charge equal to -0.470. The bond order between the carbonyl carbon atom and oxygen O2 is 1.103, but the bond order of the formed Si1-O2 bond is about 0.626. In so far as this value is considerably less than the bond order of the silicon-oxygen bond in the Si<sub>8</sub>O<sub>20</sub>H<sub>8</sub> cluster (0.820), apparently, under the reaction conditions the carboxylate species can be relatively easy desorbed into the gas phase and subsequently can take part in the dynamic processes over the catalyst surface.

### 3.3. Formation of the acyl cation

It is known that considerable amount of water is adsorbed at the room temperature on the oxide catalysts surface, including SiO<sub>2</sub> [2, 31]. Besides, as mentioned above, water is formed

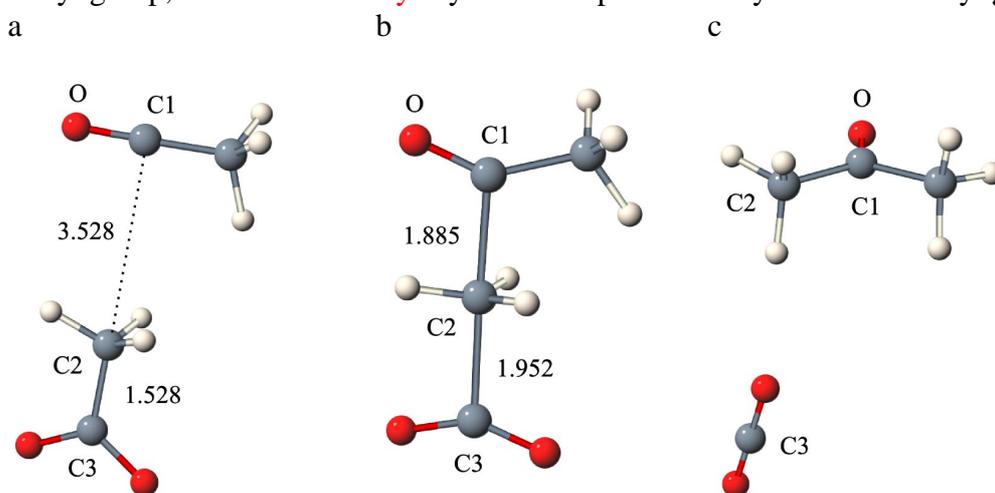
as a result of high temperature dehydroxylation process on the catalyst surface. It can be supposed that at the temperature range of the ketonization reaction being about 250-400 °C, water molecules on the oxide surface could serve as the source of protons and hydroxyl ions, and act as acid-basic catalyst [27, 35].

When the Lewis acid sites of the catalyst surface occur to be blocked by carboxylate species, the new portions of acetic acid molecules begin to interact with these active species located in the gas phase. The calculations show that the interaction of acetic acid molecule with an electrophile – a proton, proceeds spontaneously with the enthalpy of  $\Delta H_f = -506.2$  kJ/mol.

The proton attack is directed to the hydroxyl group oxygen atom having the highest  $\pi$ -electron density (4.896) in the molecule, and results in the formation of a water molecule and acyl carbenium ion ( $\text{H}_3\text{C-CO}^+$ ).

### 3.4. Interaction of carboxylate anion and acyl cation: formation of an acetone molecule

The reaction between the active species – carboxylate anion and acyl cation, had been studied. As the adsorbed carboxylate species is directed towards the catalyst surface by its carboxyl group, the attack on it by acyl cation is possible only from the methyl group side.



**Figure 3.** Reaction of carboxylate anion with acyl cation. a - Starting position; b - Intermediate state; c - Reaction products: acetone molecule and  $\text{CO}_2$ . Selected bond lengths in angstroms are indicated

At the initial state, the distance between the positively charged (0.445) atom C1 of acetyl cation and the negatively charged ( $-0.268$ ) atom C2 of carboxylate anion was set to 3.528 Å (Fig 3a). The reaction proceeds spontaneously with enthalpy  $\Delta H_f = -748.5$  kJ/mol.

The intermediate state of the system at the bond formation between the atom C1 of acyl cation and the atom C2 of the carboxylate methyl group is depicted in Fig. 3b.

The bond order of C1-C2 is 0.693, but the bond order of C2-C3 has decreased from 0.864 to 0.165. When the distance C1-C2 becomes equal to 1.713 Å, the bond C2-C3 disruption occurs, and a carbon dioxide molecule  $\text{CO}_2$  is released from the atom C2. The relaxed state of the system is represented in the Fig. 3c. Thus, the yield of this bimolecular electrophilic substitution reaction is a carbon dioxide molecule and the target product – an acetone molecule.

After desorption of the carboxylate species from catalyst surface, the exposed Lewis acid site captures a hydroxyl ion from the gas phase ( $\Delta H_f = -978.6$  kJ/mol). Thereby the hydroxyl cover of the catalyst surface is renewed, and the catalytic cycle is completed.

The possibility of ketonization reaction proceeding through a ketene molecule was also considered. The calculations indicate that under the conditions of acid-base catalysis the ketene easily forms by dehydration reaction of the acetic acid molecule. Interaction of ketene

molecule with carboxylate anion leads to formation of a weakly bonded complex ( $\Delta H_f = -11.7$  kJ/mol). Attack of this complex by a proton is directed at the negatively charged (-0.424) carbon atom of the methylene group. As a result, the ketene molecule turns into an acyl cation, and consequently, we can observe reaction (already discussed above) of the acetyl cation with the acetate anion leading to the formation of the acetone molecule.

#### 4. Conclusions

The following conclusions can be drawn from our calculation results:

- (1) Synergy of acid-base pairs of active catalytic sites, forming at high temperature, causes dissociative adsorption of an acetic acid molecule accompanied by formation of a surface carboxylate species. The reaction proceeds spontaneously with enthalpy  $\Delta H_f = -434.3$  kJ/mol.
- (2) When the Lewis acidic sites of the catalyst surface are blocked by the carboxylate species, the subsequent acetic acid molecules begin to interact with the  $H^+$  and  $OH^-$  ions in the gas phase, yielding acyl cation (or ketene).
- (3) Since the adsorbed carboxylate species is directed towards the catalyst surface by its carboxyl group, the attack on it by acyl cation is possible only from the methyl group side. The outcome of the subsequent reaction occurring by the bimolecular electrophilic substitution mechanism is an acetone molecule and a carbon dioxide.

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