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*Mendeleev Commun.*, 1994, **4(4)**, 144–146
Mendeleev Communications

# Quantum Chemistry of Chemisorption of Ethylene at the Active Site of Alumophenylsiloxane

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Quantum chemical calculations provide support for reaction mechanisms suggesting chemisorption of the ethylene molecule on the $AlO_4$ site of alumophenylsiloxane accompanied by π-bond rupture and the creation of cation-radicals.

Studies of elementary chemical processes occurring on alumosilicate compounds are of importance due to the great significance of these species as catalysts in the conversion of oil fractions.[1] Along with well-known solid alumosilicates related soluble substances, in particular alumophenylsiloxane (APS), possess similar structural properties and are viewed as potential catalysts as well.[2] Recent experimental studies[3] show that in the presence of APS in a liquid reaction volume an efficient ethylene–benzene interaction occurs yielding ethylbenzene. It is suggested that one of the stages of the process may be related to the chemisorption of unsaturated hydrocarbons on APS accompanied by the creation of cation- and anion-radicals.

Considerable efforts are being performed in order to clarify the mechanisms of catalytic activity of alumosilicates, starting from different viewpoints. According to the theory developed by one of the authors[4] the active sites in alumosilicate compounds are the tetrahedrons $\{AlO_4\}$ and $\{SiO_4\}$. This work presents a quantum-chemical contribution which provides some support for this idea, taking the ethylene–APS system as an example.

All calculations described here have been carried out with the GAMESS package.[5] We have considered the interaction of the ethylene molecule with APS within a cluster approach,[6–10] *i.e.* by representing the local chemisorption site as a group of atoms. Namely, the $\{AlO_4\}$ fragment has been selected as an active species in environments simulating the original APS complex. Special attention has been paid to such parameters as partial charges on atoms, effective electronic configurations and compositions of bonding orbitals. Application of the natural bond orbital formalism[11] for the analysis of electron distributions is an important step forward in studies of reaction mechanisms compared to the previously used approaches.[6,7,12,13]

In the preliminary stages the structure of APS, $[Ph(HO)_2SiO]_2Al[OSi(OH)_2Ph]$, was studied by using molecular mechanics and semiempirical AM1 quantum chemistry techniques[14] followed by *ab initio* MO LCAO calculations with the 3-21G basis set. According to these approaches the central part of the APS may be considered as a distorted $AlO_4$ tetrahedron with two Al–O bonds directed

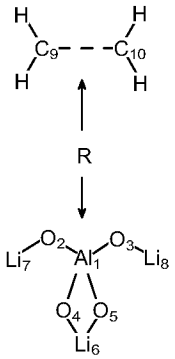


**Fig. 1** Geometry configuration of the $C_2H_4 + AlO_4Li_3$ reaction complex.

towards the $Si(OH)_2Ph$ fragments and two Al–O bonds forming a well-known aluminum–oxygen–silicon cycle with a bridged OH group. A partial electronic charge on aluminum is estimated as +2.0, on oxygen as –1.2 (on average) and on silicon as +2.4. The composition of the bonding Al–O orbital may be described in terms of natural bond orbitals[11] as 0.35 $sp^{2.3}$(Al) + 0.95 $sp^{1.3}$(O) indicating that the orbital is polarized towards the oxygen hybrid. A strongly ionic character of the compound is consistent with the data common to many aluminum oxide molecules.[15,16]

To simulate an active site of APS, namely, the $\{AlO_4\}$ fragment, several neutral clusters representing a reduced version of APS have been considered: $AlO_4Li_3$, $Al(OH)_4$, $Al(OSiN)_2O_2Li$, $Al(OH)_2(OSiH_3)$. In all cases the tetrahedral arrangement of oxygen atoms around the aluminum centre has been assumed. Detailed results will be presented below for the interaction $C_2H_4$ + $AlO_4Li_3$ although most important qualitative conclusions are similar for all species.

The lithium atoms here play the role of "pseudoatoms" often used in attempts to select a finite cluster from an extended system when studying complicated processes like chemisorption.[6–10] In the $AlO_4Li_3$ moiety partial charges on atoms (+1.5 on Al and –1.0 on O) resemble those calculated for APS (+2.0 and –1.2) as well as effective electronic configurations ($3s^{0.5}3p^{1.0}$ in $AlO_4Li_3$ *versus* $3s^{0.35}3p^{0.65}$ in APS for aluminum and $2s^{1.9}2p^{5.0}$ in $AlO_4Li_3$ *versus* $2s^{1.8}2p^{5.4}$ in APS for oxygen). A composition of the bonding Al–O orbitals in $AlO_4Li_3$ [0.34 $sp^{2.3}$(Al) + 0.94 $sp^{1.6}$(O)] also nicely reproduces that of APS. We conclude that the local electronic properties of the $AlO_4$ site are reproduced successfully by the $AlO_4Li_3$ molecule.

Fig. 1 shows the geometry of the entire reaction complex $C_2H_4 + AlO_4Li_3$. We have considered configurations with the fixed geometry parameters of reagents and varied a distance, *R*, between Al and the centre of the C–C bond. Qualitative MO considerations lead to the conclusion that for the most favourable arrangements (in the sense of minimal energy of the entire reaction complex) the atoms $C_9$, $C_{10}$, $O_2$, $O_3$ and $Al_1$ should form a plane. Pilot calculations have been carried out which confirm that the total energies of other structures are substantially higher. Under this restriction three slightly different geometries of the $AlO_4Li_3$ site have been considered.

The first one (denoted Geometry 1 in Table 1) corresponds to the perfect $AlO_4$ tetrahedron with Al–O bond lengths of 1.72 A, the value known from experimental studies of alumosilicates. Two other structures present consequent steps towards the APS geometry found by quantum chemistry calculations. In Geometry 2 the perfect $AlO_4$ tetrahedron structure has been kept but the Al–O distances have been reduced to 1.71 A. In Geometry 3 the tetrahedral arrangement has been partly distorted – new values for the $O_4Al_1O_2$ and $O_5Al_1O_4$ bond angles are 116° and 77°, respectively (instead of 109°), and for the $O_4Al_1O_2O_3$ and $O_5Al_1O_4O_2$ torsion angles –153° and 108° instead of –120° and 120°.

**Table 1** Interaction energies ($\Delta E$/kJ mol$^{-1}$) for the $C_2H_4 + AlO_4Li_3$ system and total charges ($Q$) on the $C_2H_4$ fragment *versus* intermolecular distance ($R$/A) calculated at the RHF/3-21G approximation.

| | Geometry 1 | | Geometry 2 | | Geometry 3 | |
|---|---|---|---|---|---|---|
| *R* | $\Delta E$ | *Q* | $\Delta E$ | *Q* | $\Delta E$ | *Q* |
| 25.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5.0 | 3.2 | 0.0 | 5.3 | 0.0 | 6.6 | 0.01 |
| 4.0 | 15.5 | –0.01 | 23.4 | –0.01 | | |
| 3.0 | –213.0 | 0.62 | –45.6 | 0.36 | 153.6 | 0.05 |
| 2.75 | –361.0 | 0.65 | –166.4 | 0.42 | 190.2 | 0.27 |
| 2.5 | –416.9 | 0.66 | –190.5 | 0.48 | 222.5 | 0.48 |
| 2.25 | | | 78.0 | 0.54 | 506.0 | 0.55 |
| 2.0 | 726.6 | 0.67 | | | | |

Within the natural bond orbital formalism[11] the electronic structure of $C_2H_4$ is described as a configuration with doubly occupied bonding orbitals: $[Core]\sigma^2(C–C)[\sigma^2(C–H)]^4\pi^2(C–C)$. When interacting with the $AlO_4$ site of APS or related reduced systems specific changes in the electronic structure of $C_2H_4$ are expected. For the goals of the present study the most important is a process of π-bond rupture in $C_2H_4$ which should be reflected by a substantial reduction of population of the π(C–C) orbital.

Indeed, for all three geometry arrangements (as well as for all other model systems) we found that along the reaction pathway the population of the π-orbital of $C_2H_4$ reduced from 2.00 to a boundary value of 1.50 generally accepted as a critical value for regularly occupied MOs[11] at distances *R* between 5 and 4 A. We can interpret this result as π-bond rupture in this region. An analysis of electron density in terms of natural orbitals showed that instead of the π(C–C) orbital the $\sigma(C_9–O_2)$ and $\sigma(C_{10}–O_3)$ orbitals were becoming populated which resulted in a cycle extending over the coplanar atoms $–C_9–O_2–Al_1–O_3–C_{10}–$ at distances $R < 4$ A.

Table 1 shows interaction energies for the $C_2H_4$ + $AlO_4Li_3$ system and gross natural electronic charges attributed to the ethylene fragment along the reaction coordinate computed at the RHF/3-21G level of the theory. We see that unlike the results of population analysis an energy profile is extremely sensitive to the site geometry. For the perfect $C_{2v}$ symmetry of the reaction complex the interaction $C_2H_4$ + $AlO_4Li_3$ leads to a strongly bound system at a distance *R* of about 2.5 A. For an asymmetric tetrahedron the reactants follow along the repulsive energy curve.

The computed energy profiles do not correspond to the true reaction pathways since no geometry optimization along the chosen reaction coordinate is performed. The sound conclusions that can be drawn from the numbers presented in Table 1 are as follows. For a perfect tetrahedral $\{AlO_4\}$ site there should be an activated complex in the vicinity of the potential barrier and a bound complex at the region of the energy minimum. In the case of distorted tetrahedral sites no interesting stationary points on the potential energy surface are found. Estimations of the precise positions of stationary points and energies require considerably more elaborate techniques including geometry optimizations, basis set superposition energy and correlation energy calculations. However, all these efforts may add a small contribution to a general understanding of the reaction mechanism especially taking into account that this model ignores solvation effects.

A total natural charge on the ethylene fragment increases from zero to values from 0.5 to 0.7 depending on the pathway indicating that reaction mechanisms which assume the creation of cation-radicals gain some support by these quantum chemical simulations.

In conclusion, the present study confirms that the $\{AlO_4\}$ tetrahedron may serve as an active site in the alumophenylsiloxane complex. According to the quantum chemical model calculations the ethylene molecule reacts efficiently with this site yielding a singly bonded cation-radical as an intermediate species.

Appreciation is expressed to Dr. M. Schmidt and Professor F. Weinhold for use of their programs. A. V. Nemukhin wishes to thank the National Science Foundation for granting the funds for a personal computer. The generous assistance of Professor J. Almlof is greatly acknowledged.

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*Received: Moscow, 3rd February 1994*
*Cambridge, 21st March 1994; Com. 4/00755G*