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Electrostatic Molecular Potential Analysis of H_2AlOH and H_2AlCl Lewis Acidities

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The Electrostatic Molecular Potential approach is used to estimate the influence of the oxygen and chlorine valence electrons on the Lewis acidity of the aluminium atoms in H_2AlOH and H_2AlCl respectively. The potentials are computed using the electron density distribution arising from CNDO/2 wave functions.

Introduction

It is generally assumed that most of the chemistry of organoaluminium compounds is readily understood in terms of Lewis acidity of organoaluminium monomers [1]. In spite of the well-known tendency of organoaluminium monomers to self-association [1] the corresponding mechanisms are usually interpreted in terms of monomeric structures. A more sophisticated treatment should apparently include monomers, dimers or even higher associates of organoaluminium compounds. Nevertheless, to gain some insight into the reactivity problems of the organoaluminium chemistry even the consideration of simple flat monomers seems to be worthwhile.

It is the aim of this paper to give some theoretical background of the concept of the Lewis acidity of these compounds. The method of Electrostatic Molecular Potentials is applied to estimate the influence of the oxygen and chlorine valence electrons on the Lewis acidity of the aluminium atoms and on Al–H, Al–OH and Al–H, Al–Cl bonds in H_2AlOH and H_2AlCl monomers respectively. Further studies concerning other monomers and corresponding dimers of organoaluminium compounds are also being considered.

Description of the Method

The investigation of reactivity in terms of the Lewis acidity may be based on a concept of the electrostatic potential created by a molecule in the surrounding space [2]. Iso-energy maps for the interaction potential with an approaching unit charge (positive or negative) can be drawn, showing the existence of well-defined attractive and repulsive regions in the neighbourhood of a molecule. The Electrostatic Molecular Potential (EMP) arising from a given molecule is completely defined at every point of space by the electronic (wave function) and nuclear (geometry) charge distributions of a molecule. This method was successfully applied to describe protonation processes of *e.g.* formamide or purinic bases [2].

According to the first order perturbation theory the EMP gives an approximation of the interaction energy of a molecule with a unit point charge. Thus, EMP should provide an approximate picture of the capability of the molecule in question to interact with other chemical species. The picture is well suited for regions at medium or large distances from the molecule where the reaction channels begin to assume a definite shape. In these regions the approximations specific for this method do not interfere significantly.

Computational Details

The geometry of H_2AlOH and of the H_2Al fragment of H_2AlCl were taken from *ab initio* molecular orbital calculations [3]. The experimental value of terminal Al–Cl bond distance (2.06 Å) in $(AlCl_3)_2$ dimer was transferred to Al–Cl distance in H_2AlCl [4]. The geometries assumed have not been optimized during the molecular orbital calculations.

The computations were carried out within the CNDO/2 method for a Slater-type basis. The Electrostatic Molecular Potentials were computed owing to the electron density distribution arising from CNDO/2 wave functions [2]. The CNDO MO coefficients were treated as referring to the orthogonal basis set and before computing the Electrostatic Molecular Potentials the appropriate deorthogonalization (Löwdin) transformation was carried out following the most recommended treatment [2];

The integrals over Slater orbitals were computed by using Gaussian expansions (3-G) due to Huzinaga *et al.* [5].

EMP values were expressed in atomic units/mol, 1 a.u. = 628 kcal.

Results

Potential energy maps for H_2AlOH are shown in Figs. 1A, 1B, and 1C. Figs. 1A and 1B refer to the molecular (symmetry) plane and Fig. 1C to the plane perpendicular to the molecule containing Al and O atoms.

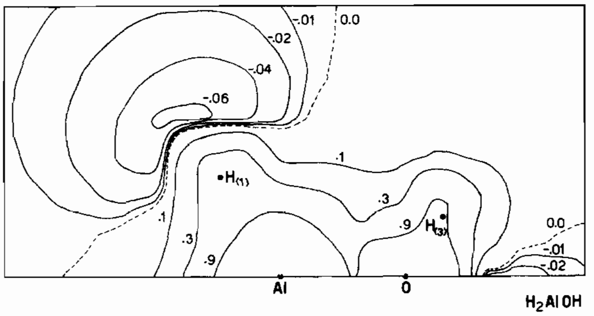


Fig. 1A. Electrostatic potential energy map for H_2AlOH in the molecular plane. Values are expressed in a.u./mol.

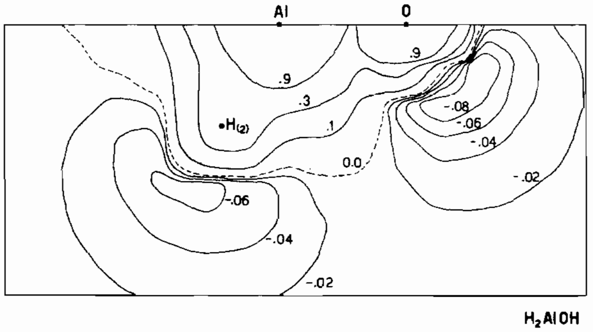


Fig. 1B. Potential energy map for H_2AlOH in the molecular plane.

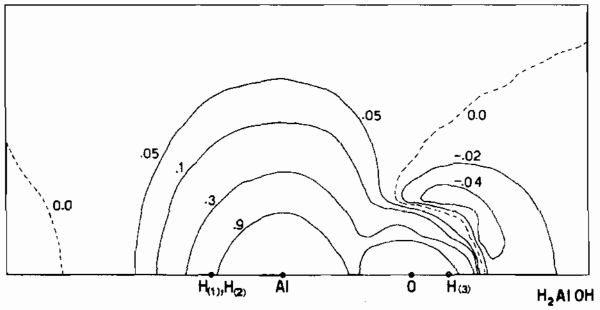


Fig. 1C. Potential energy map for H_2AlOH in the plane perpendicular to the molecular one and containing Al and O atoms.

Potential values are highly positive in the neighbourhood of atoms, where the nuclear charges are only partly shielded by the electron cloud. They are, however, very inaccurate in these regions and are not of primary interest.

On the side of the oxygen atom the EMP is strongly negative and reaches its minimum, so that the approach of a positively charged reactant to the oxygen atom is favoured. The shape of the EMP shows the presence of two electron lone pairs, placed symmetrically above and below the molecular plane.

On the side of hydrogens attached to the Al atom there are two negative regions, showing the other possible channel for electrophilic attack.

Figure 1C indicates the well-defined direction of nucleophilic attack towards the Al atom (in the plane perpendicular to the molecule) and also shows the presence of the oxygen lone pair electron density.

The EMP plot for H_2AlCl, referring to the molecular plane and to the second symmetry plane, perpendicular to the molecule is presented in Figs. 2A and 2B, respectively.

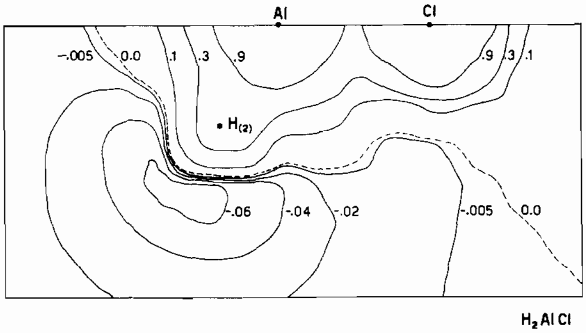


Fig. 2A. Potential energy map for H_2AlCl in the molecular plane.

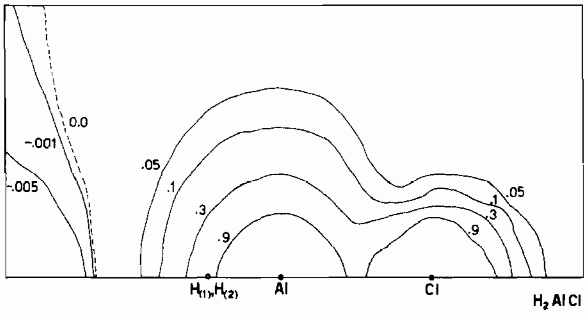


Fig. 2B. Potential energy map for H_2AlCl in the symmetry plane perpendicular to the molecular one.

The picture near the hydrogen atoms is similar to that of H_2AlOH, but the shape of the EMP on another side is different. In the molecular plane the chlorine atom is only weakly attractive for positively charged reactants, but in the perpendicular plane the Cl atom is electrophilic, though not so much as the Al atom. A comparison of EMP pictures for the molecules under consideration shows that the H_2AlCl molecule should be more attractive for negatively reactants (acidic in the Lewis sense) approaching in the perpendicular plane than the H_2AlOH monomer. The small difference between the electrophilic character of Al centres in these molecules should not offset the concerted electrophilic character of Al and Cl atoms in H_2AlCl.

It is also possible to order the hydrogens attached to Al in H_2AlOH and H_2AlCl according to growing basicity:

$$H_{(1)}(H_2AlOH) < H_{(2)}(H_2AlOH) < H_{(1)} = H_{(2)}(H_2AlCl),$$

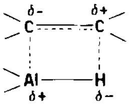
though the differences are rather small.

Discussion

The analysis of the Electrostatic Molecular Potentials for H_2AlOH and H_2AlCl supports the basic features of the generally accepted picture of charge distribution in these molecules.

The present data for EMP can be used for a discussion of some reaction mechanisms assumed in the organoaluminium chemistry. Howevcr it should be pointed out that this discussion is confined to the simplest possible model mechanisms dealing with monomeric reactants in a transition state.

As an example let us investigate the proposed mechanism for reactions of R_2AlH and R_2AlCl with olefins. It is believed that the following four-centre transition state is formed:



in which an olefinic double bond is polarized by the Al–H bond [1, 4, 6]. This mechanism assumes a polarising ability of the Al–H bond, which seems to be consistent with the EMP shape for H_2AlOH and H_2AlCl.

Although the Al–Cl bond has some dipole moment its ability to polarize a double bond should be considerably smaller than the Al–H polarizing power. Thus, interaction of the Al–Cl bond with the olefinic double bond in the transition state appears to be weaker than in the case of the Al–H bond, and indeed it was shown that the Al–Cl bond in R_2AlCl compounds does not react with olefins [7].

These arguments, based on EMP shape for organoaluminium monomers, may provide an explanation for the well-known difference in reactivity of R_2AlH and R_2AlCl with respect to olefins [1, 7].

Apparently, these arguments do not have a conclusive character and the validity of our explanation of the discussed reaction has to be confirmed by the study of more realistic models of organoaluminium compounds.

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