Ab initio investigation of triethylaluminum complexes with fluorine and chlorine anions

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Computational methods

The geometry optimization of the dimer of trimethylaluminum and its complexes under consideration were performed using the PC GAMESS v7.0 quantum chemical package and taking the second-order Möller-Plesset perturbation theory to evaluate the effect of the electron correlation correction. Pople's split-valence double-zeta 6-31G basis set augmented by one set of *d*-polarization functions on heavy atoms and *p*-polarization function on hydrogens [6–31G (d,p)] was used in the calculations. For every optimized structure vibrational analyses were performed. The ChemCraft program v1.4 was used to visualize the molecular structures of the compounds under consideration.

The spatial structure of the complexes

Complexation of trialkylalanes with halogen-anions was examined on the example of interaction of $AlEt_3$ with F- and Cl-anions to form of 1:1 and 2:1 complexes.

Geometrical parameters of complexes of triethylaluminum with halogen-anions have been calculated. In all cases the central atom (Al) is four-coordinated. The arrangement of ligands corresponds to trigonal pyramid with halogen anion situated in its vertex and halogen anion being shared in case of 2:1 complexes.

Due to change the hybridization character ($sp^2 \rightarrow sp^3$) of aluminum atom the Al–C bond in complexes with halogen anions is slightly longer than in case of $AlEt_3$, the interaction of $AlEt_3$ with halogen anions being manifested to a smaller degree in 2:1 complexes.

Thermodynamic parameters of complex formation

Organoaluminum compounds are known to be inclined to dimerization and complexation with Lewis bases. Therefore, the following possible ways of $AlEt_3$ interaction with F- and Cl-anions in gas phase are considered and thermodynamic parameters of dimerization of trimethylaluminum and its complexation with F- and Cl-anions are calculated:

$2\ AlEt_3 = Al_2Et_6$ (**1**)

$AlEt_3 + F^- = AlEt_3 \cdot F^-$ (**2**)

$AlEt_3 + Cl^- = AlEt_3 \cdot Cl^-$ (**3**)

The calculated thermodynamic parameters of dimerization of triethylaluminum and its complexation with F- and Cl-anions are presented in Table 1.

Table 1. Thermodynamic parameters of reactions **1-3**

	1	**2**	**3**
$\Delta_rH^0_{298}$, kJ/mol	–90.833	–553.292	–238.529
$\Delta_rS^0_{298}$, J/mol · K	–255.933	–123.691	–112.197
$\Delta_rG^0_{298}$, kJ/mol	–14.527	–516.413	–205.077

According to the calculated values of Δ_rH^{298}, in case of triethylaluminum complexation with halogen anions is more preferable process form thermodynamic viewpoint in comparison with its dimerization that leading to decomposition of dimer of triethylaluminum in the presence of halogen anions.

[1] The author would like to thank her supervisors, Prof. Ass. Vakulin I.V. and Prof. Talipov R.F. for guidance and fruitful discussions.