The reaction between aluminium and dimethyl ether Comparative study of density functional theory and EPR results

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Stationary points on the surface describing the reaction between aluminium and dimethyl ether (DME) have been located using density functional theory at the B3LYP level with a 6-31G(d,p) basis set. Hyperfine coupling constants (HFCC) of Al and the proton attached to it, as well as total energies, were computed at all stable structures using the B3LYP and BP86 functionals and density functional theory at the B3LYP level with a 6-31G(d,p) basis set. Hyperfine coupling constants (HFCC) of Al and the other atom have been reported. The most stable products are the cis and trans conformers of an open chain C=O insertion product which lie 58–65 kcal mol⁻¹ below the reactants in energy. Among the C=O insertion products the most stable ones are cyclic cis and trans structures, which are found to lie 9–10 kcal mol⁻¹ below the reactants.

Several experimental investigations of reactions between aluminium atoms and small organic molecules such as ethylene, acetylene, buta-1,3-diene, propyne, benzene and several ethers have been presented during the last 25 years. Also a number of theoretical works on the above-mentioned reactions and/or its products have been performed, cf. ref. 11–16.

Recently, Chenier et al. studied the reaction of ground-state aluminium atoms with dimethyl ether on inert hydrocarbon surfaces at 77 K, using EPR techniques. From the Al hyperfine coupling constants (HFCC) obtained, they suggest an assignment to four possible products (I–IV): (i) a mono-ligand complex between Al and a DME molecule, with Al binding to the DME oxygen atom; (ii) a di-ligand complex between two Al atoms and two DME, similar to (i); (iii) a product complex formed by the insertion of an Al atom into a C=O bond of the ether; and finally (iv) a second transition state. A reaction product resulting from Al insertion into a C=H bond. Chenier et al. reported one proton HFCC for only one of the suggested products, for the other three products no proton HFCC were resolved. The most and second most intense sextets observed in the EPR spectra were tentatively assigned to the C=O insertion product and the mono-ligand complex, respectively.

A subsequent theoretical investigation of the reaction, using ab initio calculations at the Hartree–Fock and MP2 levels has been reported by Sakai. In this study a mono-ligand complex, a complex where one of the hydrogens has migrated to the Al atom, whereafter a more stable C=H insertion structure is reached through a second transition state. A second reaction path leading to two C=O insertion products, starting from the addition complex, is also described. The most stable products are the cis and trans conformers of an open chain C=O insertion product which lie 58–65 kcal mol⁻¹ below the reactants in energy. Among the C=H insertion products the most stable ones are cyclic cis and trans structures, which are found to lie 9–10 kcal mol⁻¹ below the reactants.

**Methods**

**Geometries**

In all calculations the program systems Gaussian 92,17 and Gaussian 9418 were used. The functional used in the optimizations, referred to as B3LYP, is based on Becke's three-parameter adiabatic connection method (ACM) approach,19 and consists of a combination of Slater,20 Hartree–Fock and Becke22 exchange, and the Vosko, Wilk and Nusair (VWN) local23 and Lee, Yang and Parr (LYP)24 non-local correlation functional. The split valence 6-31G(d,p)25,26 basis set was used in all optimizations.

**Energies**

To obtain more reliable total energies at the different stationary points on the PES, single point calculations were carried out using the 6-31G(d,p)27–31 basis set, using the B3LYP and the BP86 functionals. The latter functional is constructed from the non-local exchange functional by Becke22 together with Perdew's gradient corrected correlation functional.32

**Isotopic hyperfine coupling constants**

Magnetic interactions between the nuclear spin (\(I\)) and the electronic magnetic moments, caused by the electron spin (\(S\)), give rise to hyperfine splittings in molecular EPR spectra. The splittings can be divided into an isotropic and an anisotropic part, where the isotropic part is given by a contact interaction term (Fermi contact)33,34 in the spin Hamiltonian:

\[
\hat{H}_{\text{spin}}^{(1)} = A_{N}^{(\text{iso})} (\hat{I} \cdot \hat{S})
\]

(1)

For a particular nucleus \(N\) (assuming a doublet radical) \(A_{N}^{(\text{iso})}\) is:

\[
A_{N}^{(\text{iso})} = \frac{8\pi}{3} g_{N} g_{\beta} \beta_{N} \rho^{\alpha - \beta}(r_{N})
\]

(2)

where \(\rho^{\alpha - \beta}(r_{N})\) is the spin density at the position of the nucleus, \(\beta\) is the Bohr magneton, \(\beta_{N}\) is the nuclear magneton and \(g\) and \(g_{N}\) are the electronic and nuclear \(g\) values, respectively.
The isotropic hyperfine coupling constants (HFCCs) are thus related to the spin density at a particular nucleus, which can be acquired from a calculated wavefunction. Hence, comparisons with measured hyperfine splittings give a good indication of the quality of the calculated wavefunction and the ability of the method in question to accurately describe the system under study. Here, we reported HFCCs for the Al atom and the hydrogens, at those points on the potential-energy surface believed to represent possible reaction products. Results are presented from the B3LYP and BP86 calculations, using the 6-311 + G(2df,p) basis set.

Results

Potential-energy surface

The PES turned out to be extremely corrugated and a large number of stationary points were found at the computational level presently employed.

Altogether 23 points of interest have been located on the potential-energy surface: one addition complex (AC), one di-ligand complex, eleven transition states, eight C—H insertion products and two C—O insertion products. Table 1 lists the relative energies of the B3LYP/6-31G(d,p) optimized structures, obtained from single point calculations using the B3LYP and BP86 functionals in conjunction with the larger 6-311 + G(2df,p) basis. Fig. 1–4 depict the geometries of the optimized stationary points.

The products and transition states were verified to be true energy minima and saddle points of first order, respectively, in frequency calculations performed at the B3LYP/6-31G(d,p) level.

To verify the relevance of the transition states found, intrinsic reaction coordinate IRC53,36 calculations were performed starting from the different transition states.

Addition complexes. In both complexes the structures of the DME fragments differ only slightly from the geometry of the free DME molecule (cf. Fig. 1 and 2). The weak interaction between the constituents can also be seen in the rather large Al—DME bond distances, around 2.2 Å for the mono-ligand and 2.4 Å for the di-ligand complexes. In the addition complex the aluminium, oxygen and carbon atoms are all in one plane. The di-ligand complex is non-planar, close to C2, symmetry, with an O—Al—O angle of 87° (cf. Fig. 1).

The energies of the addition complex and the di-ligand complex are 5.9 and 11–15 kcal mol⁻¹ below that of the free reactants, respectively, depending on method used. This corresponds reasonably well with the experimentally determined gas phase value of the binding energy for the mono-ligand complex of 9.2 kcal mol⁻¹.8

C—H Insertion products. In the eight C—H insertion compounds the aluminium atom binds to the oxygen and one hydrogen atom (C1-cis and C1-trans); to the oxygen, one of the carbon and one of the hydrogen atoms (C2-cis and C2-trans); and to one of the carbon and one of the hydrogen atoms, in the last case forming both planar (C3-cis, C3-trans) and non-planar compounds (C3-cis and C3-trans), cf. Fig. 2, 3 and 4.

A transition state (TS1), in which a hydrogen has started to migrate to the aluminium atom, connects the addition complex with C1-trans. This transition state is 21.3–25.8 kcal mol⁻¹ above the reactants giving a barrier for the insertion of the aluminium atom into the C–H bond of 30.4–32.9 kcal mol⁻¹, with the largest barrier observed at the B3LYP/6-31G(d,p) level and the lowest at the BP86 level (cf. Fig. 2 and Table 1). C1-trans, on the other hand, is a very high lying metastable minimum.

C1-trans is also connected with the more stable compound C2-trans through a second transition state (TS2-trans) in which the aluminium atom interacts also with one of the carbon atoms, cf. Fig. 2. TS2-trans is located 20–26 kcal mol⁻¹ above the reactants in energy giving an energy barrier of 29.8 kcal mol⁻¹ for the passage to C2-trans, cf. Fig. 2. This compound together with the corresponding cis conformer (C2-cis) are the most stable C—H insertion products, 6.2–10.5 kcal mol⁻¹ below the reactants in energy, with the cis compound slightly lower in energy of the two (Fig. 3 and Table 1). A transition state similar in shape to the C2 product struc-

Table 1 Energies in kcal mol⁻¹ given relative to the reactants dimethyl ether and the aluminium atom

<table>
<thead>
<tr>
<th>Method</th>
<th>B3LYP/6-311 + (2df,p) / B3LYP/6-31G(d,p)</th>
<th>BP86/6-311 + (2df,p) / B3LYP/6-31G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>addition complex</td>
<td>−4.9 (−4.1)</td>
<td>−9.1 (−8.3)</td>
</tr>
<tr>
<td>di-ligand complex</td>
<td>−10.9</td>
<td>−13.3</td>
</tr>
<tr>
<td>TS1</td>
<td>25.8 (20.7)</td>
<td>21.3 (16.2)</td>
</tr>
<tr>
<td>C1-cis</td>
<td>21.6 (17.0)</td>
<td>21.2 (16.6)</td>
</tr>
<tr>
<td>C1-trans</td>
<td>21.4 (17.0)</td>
<td>20.6 (16.2)</td>
</tr>
<tr>
<td>TS2 (cis)</td>
<td>22.3 (21.4)</td>
<td>21.9 (17.1)</td>
</tr>
<tr>
<td>TS2 (trans)</td>
<td>25.7 (21.2)</td>
<td>19.6 (15.1)</td>
</tr>
<tr>
<td>C2-cis</td>
<td>−7.4 (−10.2)</td>
<td>−10.5 (−13.2)</td>
</tr>
<tr>
<td>C2-trans</td>
<td>−6.8 (−9.7)</td>
<td>−9.9 (−12.8)</td>
</tr>
<tr>
<td>TS2 (cis-trans)</td>
<td>−2.9 (−6.1)</td>
<td>−6.3 (−9.5)</td>
</tr>
<tr>
<td>TS2 (cis-cis)</td>
<td>−3.6 (−7.0)</td>
<td>−6.8 (−10.2)</td>
</tr>
<tr>
<td>TS2 (trans)</td>
<td>−2.9 (−6.5)</td>
<td>−6.3 (−9.9)</td>
</tr>
<tr>
<td>TS3 (cis-trans)</td>
<td>−4.3 (−8.0)</td>
<td>−6.7 (−10.4)</td>
</tr>
<tr>
<td>TS3 (trans-transp)</td>
<td>−2.7 (−6.6)</td>
<td>−5.4 (−9.3)</td>
</tr>
<tr>
<td>TS3 (trans-cis)</td>
<td>−4.8 (−8.5)</td>
<td>−7.1 (−10.8)</td>
</tr>
<tr>
<td>C3-cis</td>
<td>−4.9 (−8.7)</td>
<td>−7.4 (−11.2)</td>
</tr>
<tr>
<td>C3-trans</td>
<td>−5.4 (−9.1)</td>
<td>−7.9 (−11.6)</td>
</tr>
<tr>
<td>C3-cis</td>
<td>−4.2 (−7.6)</td>
<td>−7.4 (−10.8)</td>
</tr>
<tr>
<td>C3-trans</td>
<td>−4.4 (−7.9)</td>
<td>−7.7 (−11.2)</td>
</tr>
<tr>
<td>TS4</td>
<td>6.0 (4.1)</td>
<td>0.1 (1.8)</td>
</tr>
<tr>
<td>C4-cis</td>
<td>−60.7 (−62.6)</td>
<td>−61.7 (−63.6)</td>
</tr>
<tr>
<td>C4-trans</td>
<td>−62.1 (−63.9)</td>
<td>−63.3 (−65.1)</td>
</tr>
<tr>
<td>TS4 (cis-trans)</td>
<td>−60.5 (−62.7)</td>
<td>−61.2 (−63.4)</td>
</tr>
</tbody>
</table>

* ZPE corrections, calculated at the B3LYP/6-31G(d,p) level, are included for the values in parentheses. * Energy (E₀) of reactants: Al −242.386 697, DME −155.084 672, total −397.471 369. * Energy (E₀) of products: Al −242.383 618, DME −155.077 005, total −397.460 623.
Fig. 2 Energy reaction profile for the C—H and C—O insertion reactions as well as geometrical structures of the C—H and C—O insertion products and transition states, optimized at the B3LYP/6-31G(d,p) level.

Fig. 3 Reaction profile for isomerization between different C—H insertion products and optimized structures of products and transition states.

Fig. 4 Reaction profile for isomerization between different C—H insertion products and optimized structures of products and transition states.
trans forms of C2 (atoms in one plane (TS2–kcal mol to the transferred hydrogen and one of the carbons for the low barrier between C1–lowest at the BP86 level. The same trend was also observed barrier again obtained at the B3LYP/6-31G(d,p) level and the
È observed to be separated by small energy barriers of 2.6
~1

The roman numbers correspond to the experimentally observed species (cf. Table 4).

Table 2 Isotropic HFCC in gauss for possible products in the reaction between dimethyl ether and an aluminium atom.* Method: BP86/6-311 + G(2df,p)//B3LYP/6-31G(d,p)

<table>
<thead>
<tr>
<th>compound</th>
<th>Al</th>
<th>H1</th>
<th>H2</th>
<th>H3</th>
<th>H4</th>
<th>H5</th>
<th>H6</th>
</tr>
</thead>
<tbody>
<tr>
<td>addition complex</td>
<td>21.9</td>
<td>0.0</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>di-ligand complex</td>
<td>22.6</td>
<td>0.0</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>C1–cis</td>
<td>1.3</td>
<td>0.2</td>
<td>–9.6</td>
<td>–13.2</td>
<td>2.7</td>
<td>3.6</td>
<td>0.5</td>
</tr>
<tr>
<td>C1–trans</td>
<td>4.5</td>
<td>6.1</td>
<td>–9.2</td>
<td>–12.4</td>
<td>3.4</td>
<td>1.8</td>
<td>–0.3</td>
</tr>
<tr>
<td>C2–cis</td>
<td>306.5(II)</td>
<td>57.6(II)</td>
<td>3.3</td>
<td>–1.4</td>
<td>0.7</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>C2–trans</td>
<td>287.6</td>
<td>58.6</td>
<td>3.8</td>
<td>0.1</td>
<td>–0.2</td>
<td>–0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>C3–cis</td>
<td>1954</td>
<td>43.3</td>
<td>–0.5</td>
<td>–1.5</td>
<td>0.1</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>C3–trans</td>
<td>205.0</td>
<td>40.9</td>
<td>6.0</td>
<td>3.1</td>
<td>1.1</td>
<td>2.7</td>
<td>–0.1</td>
</tr>
<tr>
<td>C3–cisp</td>
<td>220.2</td>
<td>52.4</td>
<td>–1.9</td>
<td>–1.9</td>
<td>–0.3</td>
<td>–0.3</td>
<td>0.9</td>
</tr>
<tr>
<td>C3–transp</td>
<td>253.1</td>
<td>50.9</td>
<td>1.9</td>
<td>1.9</td>
<td>0.1</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>C4–cis</td>
<td>333.9</td>
<td>–3.0</td>
<td>1.9</td>
<td>1.4</td>
<td>–0.7</td>
<td>–0.7</td>
<td>–0.4</td>
</tr>
<tr>
<td>C4–trans</td>
<td>269.8(IV)</td>
<td>5.0</td>
<td>–2.7</td>
<td>–2.3</td>
<td>–0.1</td>
<td>0.0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

* The roman numbers correspond to the experimentally observed species (cf. Table 4).

butions with the aluminium, oxygen and the two carbon atoms in one plane (TS2–cis–trans) connects the cis and trans forms of C2 (cf. Fig. 3). The barrier corresponding to this cis–trans–interconversion is 3.6–4.7 kcal mol
~1
, with the largest barrier again obtained at the B3LYP/6-31G(d,p) level and the lowest at the BP86 level. The same trend was also observed for the low barrier between C1–trans and C2–trans, which vanishes at the BP86/6-311 + G(2df,p)//B3LYP/6-31(d,p) level (cf. Table 1 and Fig. 2).

The local minima where the aluminium atom binds solely to the transferred hydrogen and one of the carbons (compounds denoted C3) are reached from C2–cis and -trans. The planar trans compound, C3–transp, is connected with C2–cis through an open chain transition state (TS3 cis–transp) in which the Al–O bond is broken. C3–trans is reached from C2–trans through TS3 trans–trans in which again the Al–O bond is broken (cf. Fig. 3). The C2 and C3 structures are observed to be separated by small energy barriers of 2.6–4.7 kcal mol
~1
.

Finally, two of the C3 compounds, C3–transp and C3–trans, are connected through TS3 trans–trans with an energy barrier varying between 2.5 and 3.0 kcal mol
~1
depending on method (Fig. 3).

The remaining energy minima, C1–cis, C3–cis and C3–cisp can all be reached from C2–cis (cf. Fig. 4). Breaking the Al–C

bond in C2–cis, C1–cis is reached through TS2–cis with an energy barrier of about 30 kcal mol
~1
. Finally, breaking the Al–O bond C3–cis and C3–cisp are reached from C2–cis through two open chain transition states TS2 cis–cis and TS3 cis–cisp. The energy barriers are in the order of 2.6–4.7 kcal mol
~1
with the barrier leading to the C3–cisp structure slightly lower (cf. Fig. 4).

The different C3 compounds are all found at 2.7–7.9 kcal mol
~1
below the reactants, and hence lie a few kcal mol
~1
above the two C2 compounds (cf. Table 1).

C–O Insertion products. Two C–O insertion products, one cis (C4–cis) and one trans (C4–trans), were located (cf. Fig. 2). The addition complex is connected to the cis form of the C–O insertion compounds (C4–cis), which is 56.5–61.7 kcal mol
~1
below the reactants in energy, through a transition state (TS4) with an elongated O–C bond. TS4 is located 0.1–6.4 kcal mol
~1
above the reactants in energy giving a barrier for the C–O insertion ranging from 9.2 to 13.5 kcal mol
~1
depending on the method. Just as for the Al insertion into the C–H bond, the B3LYP/6-31(d,p) method predicts the highest and BP86 the lowest energy barrier. C4–cis is further connected to the most stable stationary point encountered at the PES, the trans C–O insertion product (C4–trans), through a transition state with a close to linear C–O–Al fragment (TS4 cis–trans), cf. Fig. 2. C4–trans is 58.1–63.3 kcal mol
~1
more stable than the reactants, depending on method. The small barrier separating the cis from the trans conformers is calculated to be between 0.2 and 0.8 kcal mol
~1
.

Zero point vibrational energy corrections. Zero point vibrational energy corrections (ZPE) were calculated for all stationary points at the B3LYP/6-31(d,p) level. The corrections stabilize all transition states and product structures by 1.8 to 5.1 kcal mol
~1
and destabilize the addition complex by ca. 0.8 kcal mol
~1
. All energy barriers are thus lowered somewhat, from a few tenths of a kcal mol
~1
up to 2.7 kcal mol
~1
, when

Table 4 Experimental isotropic HFCC (in G) for the reaction between dimethyl ether and an aluminium atom*.

<table>
<thead>
<tr>
<th>Species</th>
<th>Al</th>
<th>H1</th>
<th>H2</th>
<th>H3</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>357.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>II</td>
<td>294.7</td>
<td>58.9</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>III</td>
<td>318.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>IV</td>
<td>269.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* The experimental values are from the work by Chenier et al.10

the ZPE corrections are included. The one exception is the barrier separating the addition complex from C1-trans for which a somewhat larger lowering of ca. 6 kcal mol\(^{-1}\) is observed when the correction is included. Owing to the small basis set superposition errors observed in a previous study of the Al + propene system, using similar methods as those employed here,\(^{33}\) no such corrections were calculated in the present paper.

**Hyperfine coupling constants**

The isotropic HFCC are reported for the hydrogens and the aluminium atom of the addition complex, the di-ligand complex and the insertion products from single point calculations employing the larger basis set. The calculated and experimentally observed couplings are presented in Tables 2-4.

Very good agreement with the experimental spectrum (II) is observed at the BP86 level for the cis structure of the most stable C—H insertion product (C2-cis) [cf. Fig. 3 and Tables 2 and 4]. The deviations between calculated and experimental values for the aluminium atom and the migrated proton, H1, are less than 4.5%. Also at the B3LYP level good agreement between experimental and calculated values is observed, with deviations between calculated and experimental values of less than 10.5% for the Al HFCC and less than 12.5% for the proton HFCC. The agreement between experimental and calculated values is even somewhat better for the trans compound. However, the assignment that the cis conformer of C2 corresponds to the observed C—H insertion product is supported by the calculated energetic stability of the products for which C2-cis 0.5-3.8 kcal mol\(^{-1}\) more stable compared to the other C—H insertion products. The calculated HFCC for the remaining protons, H2—H6, for both the cis and trans conformers of compound 2 are less than 4.5 G irrespective of method used, which suggests why no β proton HFCCs were resolved in the experimental EPR spectra.

The experimentally observed sextet with a splitting of 269.4 G (IV) was previously assigned to either an addition or a di-ligand complex.\(^{10}\) Considering the extremely poor agreement with the calculated HFCC for the complexes, [cf. Tables 2-4], we suggest a reassignment of the observed splitting to one of the C—O insertion products. The observed experimental value agrees excellently with the calculated Al HFCC for the most stable C—O insertion product, C4-trans, at the BP86/6-311 + G(2df,p)//B3LYP/6-31G(d,p) level. The calculated value deviates 0.2 and 6% from the experimental value at the BP86 and B3LYP levels, respectively. The maximum calculated proton HFCC for the C—O insertion products was again very small; 5.2 G (cf. Tables 2 and 3 and Fig. 2). The calculated energetic stability of the products supports the assignment of C4-trans to one of the experimentally observed species.

The assignment of the observed proton and Al HFCC for C2-cis and C4-trans using the HFCC calculated at the BP86/6-311 + G(2df,p)//B3LYP/6-31G(d,p) level and, shown in parentheses, at the B3LYP/6-311 + G(2df,p)//B3LYP/6-31G(d,p) level, are as follows [cf. Fig. 2 and 3 and Tables 2-4]. cis Structure of the C—H insertion product (C2-cis): Al: experimental value 294.7 G, computed 306.5 G (324.2 G); H1: experimental value 58.9 G, computed 57.6 G (66.0 G); trans structure of the C—O insertion product (C4-trans): Al: experimental value 269.4 G, computed 269.8 G (285.5 G).

The two remaining sextets observed experimentally, with splittings of 318.6 and 357.5 G can not be uniquely assigned to any of the stationary points found. From the very poor agreement between the calculated values for the two addition complexes and the two experimentally observed splittings we conclude that neither of the latter corresponds to an addition or di-ligand complex. Both the calculated relative energies and the calculated HFCC clearly exclude the possibility that C1-cis and -trans have been observed in the experiment. Neither of the remaining C2 or C3 compounds could clearly be identified with the two unassigned species because of their large calculated proton HFCC.

**Discussion and Summary**

Stationary points have been located for the reaction between aluminium and dimethyl ether at the B3LYP and BP86 levels. Both methods give qualitatively the same results although the barriers differ slightly depending on method. In general the relative energies are predicted to be lowest at the BP86/6-311 + G(2df,p)//B3LYP/6-31G(d,p) level with the one exception of the di-ligand complex which is observed to be lowest in energy at the B3LYP/6-31G(d,p) level.

Possible reaction paths for both the Al C—H and C—O insertion reactions are outlined. Based on the results in this theoretical investigation, the Al atom breaks a C—H bond in the methyl group to eventually form a (H)Al product in which the aluminium atom binds to both the carbon and oxygen atoms. The reaction path involves an Al—O addition complex, a first transition state leading to a structure in which one hydrogen has migrated to the Al atom, whereafter a more stable C—H insertion structure is reached through a second transition state. When the C—O insertion product is formed, the Al atom instead breaks one of the C—O bonds to form the insertion product. This second reaction path involves, except for the addition complex, a first transition state leading to a cis form of an open chain C—O insertion structure, whereafter the more stable trans form is reached through a second transition state. The ZPE corrected barriers for the C—H and C—O insertion reactions were calculated to be 24.5–27.0 and 6.5–10.8 kcal mol\(^{-1}\), respectively, depending on method. Both barriers were calculated to be lowest at the BP86/6-311 + G(2df,p)//B3LYP/6-31G(d,p) level and highest at the B3LYP/6-31G(d,p) level.

The hyperfine coupling constants for the possible products have been determined using the 6-311 + G(2df,p) basis in conjunction with the B3LYP and BP86 functionals. There is good agreement between the computed and experimental HFCC for two of the products found, namely the cis structure of the most stable C—H insertion product and the trans-C—O insertion product. This supports the two suggested reaction paths towards a HAICH\(_2\)CH\(_2\)O complex as one of the final products and the C—O insertion product CH\(_3\)AIOCH\(_3\) as a second. Best overall agreement between calculated and experimental HFCC is obtained at the BP86/6-311 + G(2df,p)//B3LYP/6-31G(d,p) level of theory in which the calculated values differ at most 4.5% and at average 2.2% from the experimental values. Two experimentally observed sextets with splittings of 318.6 and 357.5 G were not possible to uniquely assign to any of the stationary points found. None of the points located in the present paper was clearly possible to identify as the carrier of the two experimentally observed sextets, either due to calculated relative stability and energy barriers and/or due to poor agreement between calculated and experimental HFCC values.

The unassigned sextets might correspond to complex formation between DME and some of the found product structures.

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References


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