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Mechanisms for reactions of trimethylaluminum with molecular oxygen and water

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ABSTRACT

$(CH_3)_3Al$ (TMA) has been employed for preparation of various thin films. It is also known to be hypergolic in the air. To unveil the hypergolic phenomenon, the mechanism for the reaction of TMA with O_2 and/or H_2O molecules is studied using computational quantum methods. Our results show that TMA reacts with water much faster than with O_2, and water is not an efficient catalyst to help O_2 reacting with TMA. The reactions of TMA with water and oxygen molecules can undergo subsequent ones in the air. However, the barrier predicted for production of CH_3 was found to be too high for combustion initiation under the ambient condition.

1. Introduction

The group III–VI materials have been the subject of significant interest, in part due to the fact that they are wide-gap semiconductor materials for potential photovoltaic or optoelectronic applications [1–5]. Trimethylaluminum (TMA) is well known as an aluminum source used in semiconductor fabrication to grow thin films, such as Al_2O_3 and aluminum nitride (AlN) via different processes of atomic layer deposition (ALD) or metal organic chemical vapor deposition (MOCVD) [6–11]. The role of Al_2O_3 thin films is important as insulator and passivating layers in many different applications and it was the first dielectric oxide deposited by ALD, though the precursors in that process are $AlCl_3$ and water [12]. The reason for using TMA to fabricate Al_2O_3 thin films is that trimethylaluminum is a thermally stable high vapor pressure (8.4 Torr) liquid at room temperature and easily reacts with water to produce Al_2O_3. The interesting features of aluminum nitride (AlN) include a range of unique physical properties from a large band gap (6.2 eV) and high electrical resistivity, to low dielectric loss and high thermal conductivity [13]. Consequently, thin films of AlN have a wide range of applications in electronics, such as insulating layers in metal–insulator–semiconductor devices [14], in microelectronics packaging [15] and in surface-acoustic wave devices for chemical sensors [16]. In fabricating a light emitting element using this nitride semiconductor, growing a crystal of a nitride semiconductor thin film by a metal–organic chemical vapor deposition (MOCVD) method is the mainstream. This technique is thus carried out, and in fact trimethylaluminum (TMA) is one of effective compounds to produce aluminum nitride thin films, due to the fact that it could be deposited from the reaction between TMA and ammonia [17]. Beside the part of supplying aluminum source to fabricate thin film, trimethylaluminum is also known as one of the industrially important organometallic compounds [18]. It is used to play the role of co-catalyst for polymerization of alkenes in conjunction with homogeneous Ziegler–Natta catalysts such as halides of titanium or vanadium [19]. Research work over the last decades showed that alkylaluminums are also active as co-catalysts along with aluminoxanes in polymerization reactions catalyzed by metallocenes [20,21].

Another application of trimethylaluminum is that it can be used as an ignitor for jet and rocket engines. In this regard, TMA has been considered as a pyrophoric colorless liquid compound. In fact this liquid spontaneously bursts into flames if exposed to air, and reacts explosively with water. Thus, an atmosphere of dry nitrogen or argon is required for handling and storage of TMA. In this context, a major goal of the present research is about how it happens when it is in contact with the air containing a considerable amount of oxygen and water. To understand the underlying mechanisms,

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our strategy for the present work is to search for elementary reactions in which a large amount of energy is release, together with reactive radical products such as CH_3 are generated to initiate a chain process. The reactions investigated include $(CH_3)_3Al + O_2$, $(CH_3)_3Al + H_2O$ and $(CH_3)_3Al + H_2O + O_2$. Beside these reactions, we have also considered another important reaction between dimethylaluminum (DMA) with water, because DMA is one of the intermediate decomposition products formed from these processes. The results of this work are presented herein.

2. Quantum chemical methods

All electronic structure calculations were performed using the Gaussian 03 suite of programs [22]. Geometrical parameters of the structures considered were initially optimized using the MO methods at the Hartree–Fock (HF) level and the stationary points were subsequently characterized by harmonic vibrational analyses. Geometries of the relevant equilibrium structures and transition structures were then re-optimized using the density functional theory (DFT) with the popular hybrid B3LYP functional in conjunction with the polarized plus diffuse functions 6-311++G(3df,2p) basis set. The zero-point energy (ZPE) corrections to the relative energies were also obtained at the latter level, but applying a scaling factor of 0.97. The unrestricted formalism is used for open shell systems (UHF, UB3LYP...). In order to further improve the relative energies between stationary structures, single-point electronic energy calculations were finally computed using the coupled-cluster theory, incorporating all the single and double excitations plus perturbative corrections for the triple excitations, (U)CCSD(T) with the 6-311+G(d,p) and 6-311+G(3df,2p). Spin contamination was not high as was judged by the expectation values of S^2.

3. Results and discussion

3.1. Reactions of trimethylaluminum $(CH_3)_3Al$ with O_2

Trimethylaluminum (TMA) is formed when one Al atom binds three methyl groups. As each of these bonds contains a pair of electrons, then it is surrounded by six electrons. TMA has a planar structure but with small rotational energy barriers of the methyl groups. This implies that one Al 3*s* and two Al 3*p* orbitals hybridize to form three sp^2 orbitals bonding with $-CH_3$ ligands, and an empty *p* orbital is left on the Al atom [23]. The C–Al bond length is 1.965 Å (move up from the next section). Although the carbon atoms of the methyls are surrounded each by four neighbors, they have eight electrons in their outer shells. This electron-deficiency causes TMA to be very reactive with respect to any substance that may offer electrons. It readily undergoes exchanges of methyls for others groups and/or atoms bearing more electrons. This property makes TMA an excellent methylation agent.

$(CH_3)_2AlO_2$ is a potential product of the addition of TMA with molecular oxygen. From its doublet state, the CH_3 radical is generated, which in turns may initiate a chain reaction in the air. A transition structure and an intermediate formed from this process are both in the triplet state. The detail of the release of CH_3 is described in Fig. 1.

Portions of the potential energy surface (PES) corresponding the reaction of the singlet TMA and the triplet O_2 is displayed in Fig. 1, along with the selected parameters of the optimized geometries of the reactants, transition structures, intermediates and products obtained at the CCSD(T)/6-311+G(3df,2p)//B3LYP/6-311++G(3df,2p) level. The $(CH_3)_3AlO_2$ intermediate is formed by attachment of both atoms of the molecular oxygen, simultaneously bound to a TMA aluminum center through $\mathbf{TS_{1a}}$, giving rise to a bridged adduct. This transition structure is about 16.9 kcal/mol higher in energy than the reactants (values at CCSD(T)/6-311+G(3df,2p) + ZPE). The intermediate and product $(CH_3)_2AlO_2 + CH_3$ are also predicted to be slightly higher in energy than the reactants, by 5.8 and 8.2 kcal/mol, respectively.

The predicted geometries provide useful information on the reaction mechanism. The O–O bond and one of the Al–C bonds are elongated by 0.084 Å and 0.154 Å in going from the reactants and the transition state. The two Al···O distances are calculated to be about 2.0 and 2.176 Å in the $\mathbf{TS_{1a}}$ structure. The bond length changes in Al–C, O–O and Al–O, suggest that this step is clearly defined as the critical motions of the transition state. The $(CH_3)_3AlO_2$ intermediate obtained is a three-membered ring triplet compound, in which the O–O and two Al–C bond lengths are 1.344, 1.925 and 1.958 Å, respectively. This indicates that an Al–C bond is much weaker than the other two Al–C counterparts. The distance is estimated at ~2.611 Å. To form the final products, namely $(CH_3)_2AlO_2 + CH_3$, one of the CH_3 groups needs to be ejected from $(CH_3)_3AlO_2$, and in fact, the CH_3 group is expelled from the most elongated Al–C bond. As seen in the PES, this Al–C bond is very weak, and it is broken to form the free methyl radical product by a small dissociation energy of ~2.4 kcal/mol. No transition structure has been found for this simple bond cleavage. In the final product, the Al–C bond length is shortened to 1.947 Å in $(CH_3)_2AlO_2$, and the Al–O distance is also decreased to 1.890 Å. In this regard, the Al–O bond is stronger in $(CH_3)_2AlO_2$ than in $(CH_3)_3AlO_2$, as one would expect. The O–O bond length is now increased to 1.348 Å in the $(CH_3)_2AlO_2$ product.

In summary, the reaction between TMA and O_2 is characterized by a barrier height of 16.9 kcal/mol, which is the rate-determining step (Fig. 1). The intermediate is not stable giving rise to the final products $(CH_3)_2AlO_2 + CH_3$ by simple bond cleavage. After these products are formed, then they can lead to subsequent reactions in the air.

3.2. Reactions of trimethylaluminum $(CH_3)_3Al$ with H_2O

Similar to the $(CH_3)_3Al + O_2$ reaction, we explore in detail the mechanism for the reaction of $(CH_3)_3Al + H_2O$ using two different methods B3LYP and CCSD(T). All the geometries were optimized at the B3LYP/6-311++G(3df,2p) level, and in order to further improve the relative energies between stationary structures, single-point energy calculations were subsequently computed at the CCSD(T)/6-311+G(3df,2p) level and corrected for ZPEs. Profile of the potential energy illustrating the reaction, and selected optimized geometries are shown in Fig. 2.

Starting from the reactants $Al(CH_3)_3 + H_2O$, the empty *p* orbital of TMA can interact with the incoming H_2O lone pair electron [23] to form a stable adduct $(CH_3)_3Al{:}OH_2$ (Fig. 2). This intermediate is easily formed by a strong interaction between strong Al and O atoms. The Al–O bond length is 2.092 Å, which is close to the Al–O distance when TMA bonding with an –OH ligand on the silicon surface [24]. Another reason for making this compound more stable is that the two reactants holds together by an OH···C hydrogen bond. In fact, the binding energy is the sum of two contributions, and it amounts to −15.1 kcal/mol.

Decomposition of the $(CH_3)_3Al{:}OH_2$ adduct may produce CH_4 and a stable molecule, $(CH_3)_2AlOH$. The $\mathbf{TS_{1b}}$ is formed by one of the two H atoms of water interacting with one of the CH_3 ligands in this process. The values of two O–Al–C and HOAl angles decrease by large amounts (17–45°) and the Al–O bond length decreases from 2.092 to 1.909 Å, while Al–C bond length increases from 1.984 to 2.156 Å. The transition vector is dominated by the migration of hydrogen, which is 1.181 Å away from the O atom and 1.5 Å in its interaction with the C atom. The energy barrier via $\mathbf{TS_{1b}}$ is calculated at ~15 kcal/mol above the complex. Formation of