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# Matrix isolation and ab initio study of the reactions of $(\text{CH}_3)_3\text{Al}$ with $\text{CH}_3\text{OH}$ and $\text{H}_2\text{O}$ : spectroscopic evidence for $(\text{CH}_3)_2\text{AlOCH}_3$

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## Abstract

The matrix isolation technique has been used to investigate the initial products of the room and high temperature reaction of trimethylaluminum with methanol and its isotopomers, as well as water, in a flowing reactor system. Reaction went substantially to completion as indicated by a dramatic reduction of bands due to parent  $(\text{CH}_3)_3\text{Al}$  when dilute samples of  $\text{Ar}/\text{CH}_3\text{OH}$  were added to the flowing gas mixture, and vice versa. At least two products were formed, an initial intermediate that has been identified as  $(\text{CH}_3)_2\text{AlOCH}_3$ , and one or more oligomers of this species (i.e. dimers and/or trimers). Heating the reaction zone above  $200^\circ\text{C}$  following by matrix trapping led to complete destruction of the bands due to  $(\text{CH}_3)_2\text{AlOCH}_3$ , and an increase in the bands due to the oligomers. The production of  $\text{CH}_3\text{D}$  as was also noted with  $\text{CD}_3\text{OD}$  was employed, but not when  $\text{CD}_3\text{OH}$  was used. Ab initio calculations at the RHF/6-31G\* and B3LYP/6-31G\* levels were carried out on  $(\text{CH}_3)_2\text{AlOCH}_3$ ; these calculations support the identification of this species. Similar experiments involving  $(\text{CH}_3)_3\text{Al}$  and  $\text{H}_2\text{O}$  did not lead to any new product bands, although reaction apparently occurred in the reaction zone, as evidenced the growth of strong bands due to  $\text{CH}_4$ . © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Matrix isolation technique; Trimethylaluminum/methanol; Flowing reactor system

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## 1. Introduction

The chemical vapor deposition (CVD) of thin films containing aluminum is commonly carried out using trimethylaluminum as a precursor [1–4]. While the reactions of this material with a wide range of electron donors in solution are well known [5,6], much less is known about the gas phase reactions which are more directly relevant to CVD processes. Since  $(\text{CH}_3)_3\text{Al}$  is electron deficient and is known to form donor–acceptor

complexes with a range of bases, one might anticipate formation of such a complex as an initial intermediate in these reactions. These complexes would then react further to produce the final thin film product in a series of steps which may be either homogeneous (gas phase) and/or heterogeneous (on the substrate surface). A very recent study [7] has explored the reaction of these two precursors on alumina surfaces, and provided new insights into the reaction mechanism. At the same time, this study was not able (and did not attempt) to characterize the initial gas phase reaction steps.

The matrix isolation technique [8–10] was developed for the study of reactive chemical intermediates

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by trapping these species at cryogenic temperatures in an inert host crystal, often argon. Radicals, ions and weakly bound molecular complexes are among the species that have been formed and characterized in this manner. Recently, complexes of  $(\text{CH}_3)_3\text{Al}$  with a range of group V and VI alkyl bases were reported in argon matrices, providing insights into the process of complex formation [11]. Bases with an active hydrogen present a quite different situation, in that methane elimination may be quite facile and further reaction may occur (in addition to the possibility of formation of an initial molecular complex). This has been observed during the high temperature reaction and subsequent trapping of reaction mixtures of  $(\text{CH}_3)_3\text{Al}$  with  $\text{H}_2\text{S}$  and  $\text{CH}_3\text{SH}$  [12]. The reaction of  $(\text{CH}_3)_3\text{Al}$  with  $\text{CH}_3\text{OH}$  should be of interest in this regard, with a substantially more acidic and reactive hydrogen than that on  $\text{CH}_3\text{SH}$ . This reaction has been reported in solution, with suggestions that dimeric, trimeric or polymeric species form. The nature of the initial reaction product has not been resolved (and may be a function of the solvent and other reaction conditions), and there has been no report to date of the initial monomeric  $(\text{CH}_3)_2\text{AlOCH}_3$ . Consequently, a study was undertaken to examine the products of reaction of  $(\text{CH}_3)_3\text{Al}$  with  $\text{CH}_3\text{OH}$  and its isotopomers in a flowing reactor with trapping of the products into an argon matrix. In addition, the role of water in these reactions was explored in a parallel set of experiments.

## 2. Experimental

All of the experiments in this study were carried out on conventional matrix isolation apparatus that has been described [13,14]. Trimethylaluminum (Akzo) was introduced into the vacuum system as the vapor above the neat liquid, and used without further purification.  $\text{CH}_3\text{OH}$  (Fisher),  $^{13}\text{CH}_3\text{OH}$  (Merck),  $\text{CH}_3^{18}\text{OH}$  (Isotec),  $\text{CD}_3\text{OH}$ ,  $\text{CD}_3\text{OD}$  (both Aldrich) and  $\text{H}_2\text{O}$  were introduced into the vacuum system as the vapor above the room temperature liquid after purification by several freeze–pump–thaw cycles at 77 K. Argon was used as the matrix gas in all experiments, and was used without further purification.

Matrix samples were deposited in both the twin jet and merged jet modes. In the former, the two reagents

were each diluted in argon in separate manifolds and sprayed simultaneously on the cryogenic surface from separate nozzles. This allows for only a very brief mixing and reaction time before matrix deposition. In the merged jet experiments [14], the two gas samples were again prepared in separate manifolds. The two deposition lines were then joined with an Ultratorr tee at some distance from the cryogenic surface. The two gas samples flowed together through the joined or ‘merged’ length, allowing for increased reaction time compared to twin jet deposition but without the static equilibration that occurs with single jet deposition. The length of the merged region or reaction zone could be adjusted from as short as 10 cm to as long as 250 cm, allowing for some variation in the time available for reaction. The merged region could also be heated to as high as 400°C to induce further reaction before trapping at 14 K. Samples were deposited at a flow rate of approximately 2 mmol h<sup>-1</sup> from each manifold for a period of 20–24 h. Infrared spectra were recorded at intervals during deposition as well as at the end of the deposition period. Spectra were recorded either on a Perkin-Elmer 983 infrared spectrophotometer over the region 4000–180 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> at 1000 cm<sup>-1</sup>, or on a Mattson Cygnus FTIR over the range 4000–400 cm<sup>-1</sup>, at 1 cm<sup>-1</sup> resolution.

Ab initio calculations were conducted on the likely intermediate species in this study, using the Gaussian 94 suite of programs [15]. Both restricted Hartree–Fock and density functional calculations employing the Becke functional B3LYP were conducted to locate stable minima, determine structures and calculate vibrational spectra. Final calculations with full geometry optimization employed the 6-31G\* double zeta basis set, after initial calculations with smaller basis sets were run to approximately locate energy minima. Calculations were carried out on a Silicon Graphics Indigo 2 workstation.

## 3. Results

Prior to any codeposition experiments, blank spectra were recorded of each of the reagents in solid argon. As has been seen previously [16,17], some dimer of  $(\text{CH}_3)_3\text{Al}$  was observed at higher sample concentrations. To minimize this, quite dilute samples

Table 1  
Band positions<sup>a</sup> for (CH<sub>3</sub>)<sub>2</sub>AlOCH<sub>3</sub> isolated in solid argon

CH <sub>3</sub> OH	<sup>13</sup> CH <sub>3</sub> OH	CH <sub>3</sub> <sup>18</sup> OH	CD <sub>3</sub> OH	CD <sub>3</sub> OD	Assignment
1204	1204	1204	1203	1203	CH <sub>3</sub> rock
1002	981	972	981	981	Al–O–C stretch
696	696	696	696	696	AlC <sub>2</sub> antisym st.
643	643	640	622	622	
614	614	614	614	614	
440	440	436	433	433	
346	340	—	336	336	

<sup>a</sup>Band positions in cm<sup>−1</sup>.

of trimethylaluminum were employed (Ar/(CH<sub>3</sub>)<sub>3</sub>Al = 1000–4000) with more concentrated samples of Ar/CH<sub>3</sub>OH (typically ratios of 200:1 to 500:1 were used). The concentration of the Ar/H<sub>2</sub>O samples were not readily determined, but were in the range 100:1–500:1, based on comparison to literature spectra. The spectra of all of the blank samples were in good agreement with literature spectra [18] and with spectra previously recorded in this laboratory.

In an initial experiment, the twin jet codeposition of a sample of Ar/(CH<sub>3</sub>)<sub>3</sub>Al = 1500 with a sample of Ar/CH<sub>3</sub>OH = 200 led to no reaction. No new infrared absorptions were noted, and no apparent reduction in the intensity of the parent bands was seen. Several additional twin jet experiments were then conducted at different concentrations of the two reactants. No product bands were noted in any of these experiments.

A merged jet codeposition experiment was then conducted with a 40-cm merged or reaction zone held at room temperature, using sample concentrations Ar/(CH<sub>3</sub>)<sub>3</sub>Al = 1500 and Ar/CH<sub>3</sub>OH = 200. In this experiment, a large number of new infrared

absorptions were observed, as listed in Table 1, Table 2. Notably, virtually all of the absorptions of parent (CH<sub>3</sub>)<sub>3</sub>Al had disappeared and the parent bands of CH<sub>3</sub>OH were substantially reduced, indicating that extensive reaction had occurred. Fig. 1 shows a representative spectrum in the low energy region. While a number of the new infrared absorptions were quite near those of parent (CH<sub>3</sub>)<sub>3</sub>Al, other distinct bands of (CH<sub>3</sub>)<sub>3</sub>Al (e.g. at 742 cm<sup>−1</sup>) were entirely absent, indicating that no parent (CH<sub>3</sub>)<sub>3</sub>Al survived intact to the matrix. While CH<sub>4</sub> was present in small amounts in all experiments using (CH<sub>3</sub>)<sub>3</sub>Al, the amount of CH<sub>4</sub> was significantly increased relative to the blank experiments, indicating that this species is also produced.

An extensive series of 15–20 additional experiments were then run, employing (CH<sub>3</sub>)<sub>3</sub>Al and CH<sub>3</sub>OH as the two reactants in the merged jet mode. In this series of experiments, the sample concentrations were varied over the range indicated above. In these experiments with relatively more (CH<sub>3</sub>)<sub>3</sub>Al and less CH<sub>3</sub>OH, parent bands of CH<sub>3</sub>OH were

Table 2  
Infrared band positions<sup>a</sup> for species B<sup>b</sup> in argon matrices

CH <sub>3</sub> OH	<sup>13</sup> CH <sub>3</sub> OH	CH <sub>3</sub> <sup>18</sup> OH	CD <sub>3</sub> OH	CD <sub>3</sub> OD
1468	1467	1467	1118	1118
1198	1197	1198	1196	1196
1154	1154	1154	1153	1154
1070	1061	1055	1048	1048
705	705	705	705	705
625	625	624	615	615
574	574	574	—	—
538	538	538	533	533
450	450	449	443	443

<sup>a</sup>Band positions in cm<sup>−1</sup>.

<sup>b</sup>See text for discussion of species B.

completely absent and those of parent  $(\text{CH}_3)_3\text{Al}$  were reduced. The product bands listed in Table 1 remained throughout. The length of the reaction zone was also varied in a number of these experiments. The yield of product did not change greatly with reaction zone length. When the length was increased above 40 cm, no clear increase in product yield was seen. When the length was decreased, the yield dropped slightly but reaction was still extensive.

Many additional experiments were then conducted with the reaction zone heated above room temperature, to as high as  $350^\circ\text{C}$ , and distinctive changes were seen. Bands seen previously at  $346$ ,  $400$ ,  $614$ ,  $695$ ,  $998$ ,  $1006$  and  $1204\text{ cm}^{-1}$  decreased in intensity as the temperature increased. When the deposition line was held at  $90^\circ$ , there was a marked decrease in the intensity of these bands. At yet higher temperatures,

these bands were completely destroyed as is shown in Fig. 2. On the other hand, a number of product absorptions were essentially unaffected by the increasing temperature of the reaction zone.

To further characterize the new infrared absorbers in this system, merged jet experiments were conducted in turn codepositing samples of  $\text{Ar}/(\text{CH}_3)_3\text{Al} = 1500$  with samples of  $\text{Ar}/^{13}\text{CH}_3\text{OH}$ ,  $\text{Ar}/\text{CH}_3^{18}\text{OH}$ ,  $\text{Ar}/\text{CD}_3\text{OH}$  and  $\text{Ar}/\text{CD}_3\text{OD}$ . With each methanol isotopomer, five to 10 experiments were run at different sample concentrations and different reaction zone temperatures. In general, the results were very similar to those reported above for the normal isotopic species. In each case, very strong new product bands were observed, with nearly complete destruction of the parent absorptions. Fig. 3 compares results with  $^{12}\text{CH}_3\text{OH}$  and  $^{13}\text{CH}_3\text{OH}$  in the  $1000\text{-cm}^{-1}$  region. In

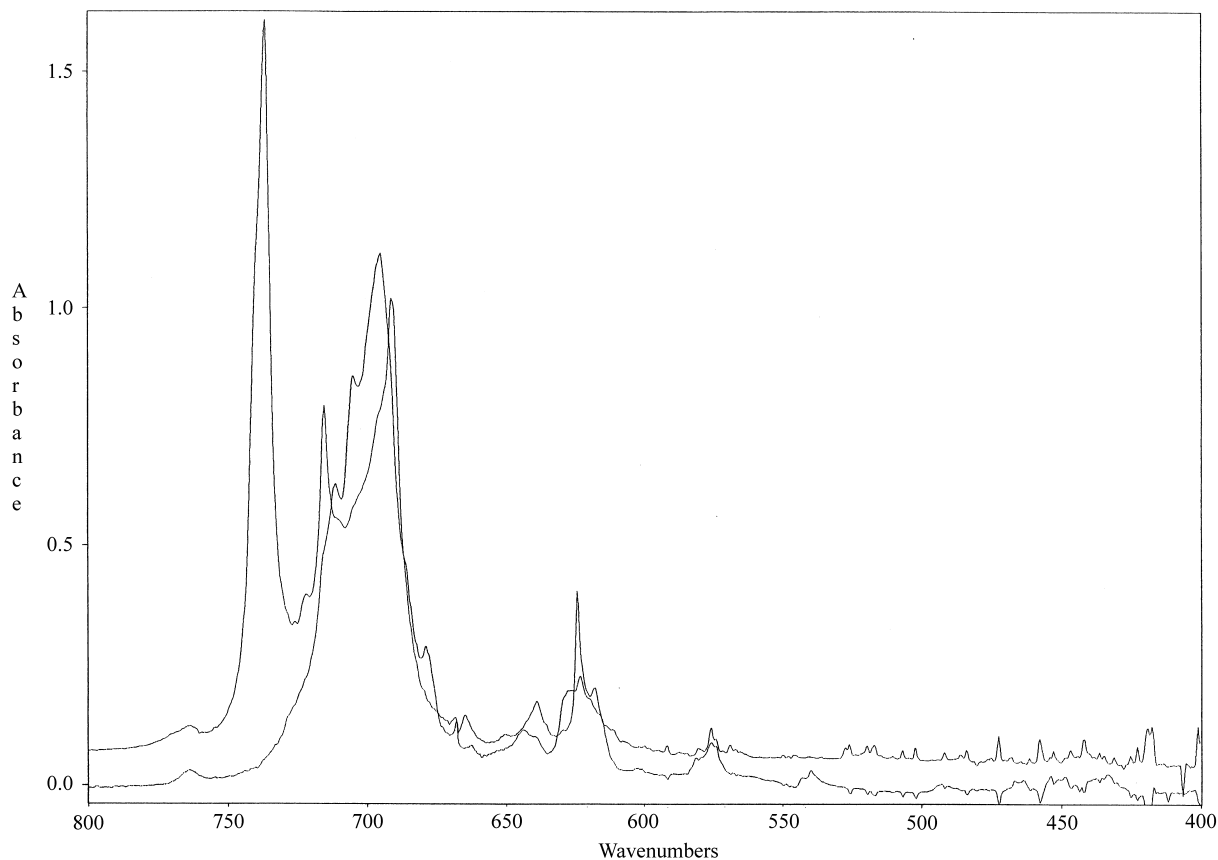


Fig. 1. Infrared spectrum taken after the merged jet codeposition of a sample of  $\text{Ar}/(\text{CH}_3)_3\text{Al} = 2000$  with a sample of  $\text{Ar}/\text{CH}_3\text{OH} = 500$ , using a room temperature reaction zone (spectrum with no absorption at  $742\text{ cm}^{-1}$ ) compared to the spectrum of a matrix formed by the deposition of a sample of  $\text{Ar}/(\text{CH}_3)_3\text{Al} = 2000$  (spectrum with an intense band at  $742\text{ cm}^{-1}$ ).

the CD<sub>3</sub>OD experiments, two clear, distinct product absorptions were noted at 1154 and 2200 cm<sup>-1</sup>, matching exactly two of the infrared absorptions of CH<sub>3</sub>D (this species, of course, has additional infrared-active modes. However, these all lie with 1–2 cm<sup>-1</sup> of modes of CH<sub>4</sub> which is present in all of these experiments). A number of these new absorptions were relatively insensitive to the isotopes that were employed, while others showed a very distinct shift as a function of isotope. In two experiments, a 50% label mixture of CH<sub>3</sub><sup>16,18</sup>OH was used. For the one mode near 1000 cm<sup>-1</sup> that was particularly isotope-sensitive, a doublet was observed with the two components matching exactly the band positions observed in the pure <sup>16</sup>O and <sup>18</sup>O experiments.

When the reaction zone was heated, a number of the new infrared absorptions were destroyed, while others were unaffected by heating, as listed in Tables 1 and 2. Monitoring band intensities as a function of reaction zone temperature permitted separation of the product bands into two distinct sets, one that was destroyed by heat and one that was unaffected by

heat. Within each set, the product bands appeared to maintain a constant intensity ratio with respect to other members of the same set, suggesting that each of the two sets can be attributed to a single new absorber.

Twin and merged jet codeposition experiments were also conducted with samples of Ar/(CH<sub>3</sub>)<sub>3</sub>Al and Ar/H<sub>2</sub>O. In the twin jet experiments, no evidence of reaction was seen. Parent bands were not decreased, and no new infrared absorptions were detected. In the merged jet experiments, using a 40-cm reaction zone held at room temperature, again no new infrared absorptions were detected. However, in these experiments a clear reduction in the intensity of the parent band absorptions was noted, along with a distinct growth in the 1303- and 3020-cm<sup>-1</sup> bands of parent CH<sub>4</sub>. Thus, it appears that reaction occurred, but that the newly produced species (other than CH<sub>4</sub>) did not survive transit through the remaining reaction zone and to the matrix. Instead, the additional product(s) are likely lost to wall collisions and deposited on the walls of the deposition line.

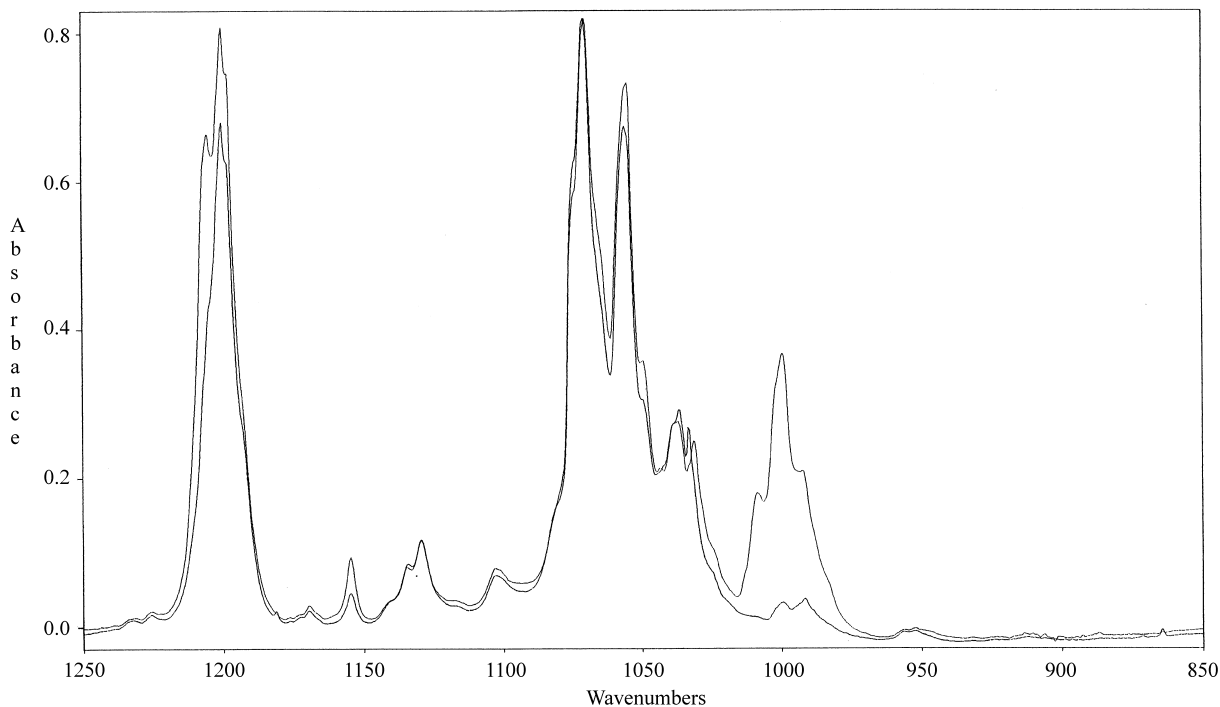


Fig. 2. Infrared spectrum taken after the merged jet codeposition of a sample of Ar/(CH<sub>3</sub>)<sub>3</sub>Al = 2000 with a sample of Ar/CH<sub>3</sub>OH = 500, using a room temperature reaction zone (upper trace), compared to a spectrum of a matrix formed from samples of the same concentration and using a reaction zone held at 250°C. Note the disappearance of bands near 1000 and 1204 cm<sup>-1</sup> (upper trace).

## 4. Discussion

### 4.1. Product identification

The merged jet codeposition of  $(\text{CH}_3)_3\text{Al}$  with  $\text{CH}_3\text{OH}$  clearly led to extensive reaction, while reaction did not occur when twin jet codeposition was employed. In the merged jet experiments, parent bands of  $(\text{CH}_3)_3\text{Al}$  were completely consumed, indicating that this reactant was fully converted to product(s). Bands of  $\text{CH}_3\text{OH}$ , the reactant in excess, were substantially reduced. At the same time, many new product bands were observed, some of which were very intense. When similar merged jet experiments were conducted with a heated deposition line, one group of product bands decreased significantly in intensity while a second group was essentially unaffected by pyrolysis. These are denoted as set A or species A (temperature sensitive) and set B or species B (temperature insensitive). Within these two sets, the product bands appeared to maintain a constant intensity ratio with respect to other members of the set

(within detection limits, since some product bands were quite intense and broad while others very quite weak). This information strongly suggests that each set corresponds to a single product species, and thus, that two products are formed when the merged jet deposition region is maintained at room temperature.

Species A is the less stable species of the two, being destroyed when the temperature of the reaction zone is raised above  $90^\circ\text{C}$ . This lack of stability might, in principle, arise from either unimolecular decomposition or bimolecular reaction. This instability suggests that it is an early intermediate in the reaction sequence, one that is converted into a more stable product (either a later intermediate or a final product) during the course of the reaction.  $(\text{CH}_3)_3\text{Al}$  is known to be a strong Lewis acid [11,19,20], forming molecular complexes with a range of weak and strong electron pair donors.  $\text{CH}_3\text{OH}$  is a moderate strength Lewis base, based on gas phase proton affinities [21] and reaction chemistry [22]. Thus, the initial product in this system might be the 1:1 molecular complex between  $(\text{CH}_3)_3\text{Al}$  and  $\text{CH}_3\text{OH}$ , analogous to those

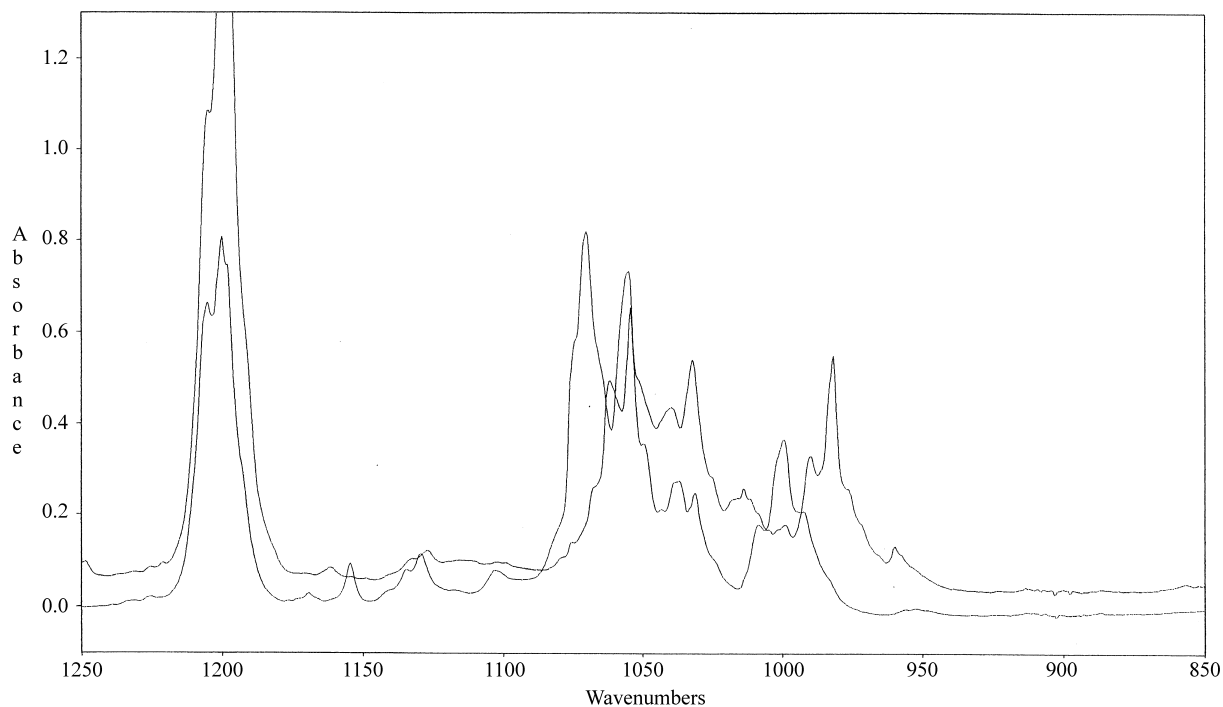


Fig. 3. Infrared spectrum taken after the merged jet codeposition of a sample of  $\text{Ar}/(\text{CH}_3)_3\text{Al} = 2000$  with a sample of  $\text{Ar}/\text{CH}_3\text{OH} = 500$ , using a room temperature reaction zone (lower trace), compared to the spectrum taken after the merged jet codeposition of a sample of  $\text{Ar}/(\text{CH}_3)_3\text{Al} = 2000$  with a sample of  $\text{Ar}/^{13}\text{CH}_3\text{OH} = 500$ , using a room temperature reaction zone (upper trace).

isolated with alkyl bases. On the other hand,  $(\text{CH}_3)_3\text{Al}$  is very reactive toward hydrogen donors, eliminating  $\text{CH}_4$ . With oxygen donors, the driving force is the strength of the Al–O bond and high thermodynamic stability of  $\text{Al}_2\text{O}_3$ . While this compound is not known, its dimer and trimer are known to form readily from the reaction of  $(\text{CH}_3)_3\text{Al}$  and  $\text{CH}_3\text{OH}$  in solution [22]. Thus, there are two likely candidates for species A, the 1:1 complex and the methane elimination product, monomeric  $(\text{CH}_3)_2\text{AlOCH}_3$ .

Several pieces of evidence point to the identification of species A as the  $\text{CH}_4$  elimination product, and not the 1:1 complex. First, the twin jet experiments demonstrate that there is a definite activation barrier to the formation of species A. Species A was not formed in the twin jet experiments, while a molecular complex would have been expected to do so, since the barrier to the formation of a complex is usually nearly zero [23]. In many chemical studies on the same equipment, molecular complex formation has been extensive during twin jet deposition. Second, a very careful search was made for the O–H stretch of a molecular complex in the spectral region near the O–H stretch of parent  $\text{CH}_3\text{OH}$ . Since extensive reaction occurred in the merged jet experiments, this region was often quite clean and devoid of interferences. Nonetheless, no product bands were observed that could be attributed to a 1:1 complex. Third,  $\text{CH}_4$  production clearly occurred during merged jet reaction (and  $\text{CH}_3\text{D}$  with  $\text{CD}_3\text{OD}$  was employed), demonstrating that some further reaction was occurring. Thus, one anticipates that  $(\text{CH}_3)_2\text{AlOCH}_3$  should be present in these matrices. These arguments together present a strong case for identification of species A as  $(\text{CH}_3)_2\text{AlOCH}_3$  and not the 1:1 complex.

It is possible that species A might be due to a larger oligomer or tertiary reaction product. However, in the experiments using a 50% mixture of  $\text{CH}_3^{16,18}\text{OH}$ , a clear 1:1 doublet was observed at the positions of the pure  $^{16}\text{O}$  and  $^{18}\text{O}$  product species, as expected for a species containing one oxygen atom. If a higher oligomer were formed (dimer or trimer), then a more complex isotopic pattern would have been expected (triplet for the dimer if the two oxygens were equivalent, as is likely, and a quartet for the trimer, if the oxygens were equivalent). In addition, solution phase studies have shown that the higher oligomers are likely to be much more stable than the monomer;

the instability of species A also points toward the monomer species. Thus, all of the evidence points toward identification of species A as the  $\text{CH}_4$  elimination product from the initial reactants, namely  $(\text{CH}_3)_2\text{AlOCH}_3$ .

Species B is thermally stable to as high as  $350^\circ\text{C}$ , and was formed in high yield in all of the merged jet experiments. Several species might be envisioned as candidates for species B, including the dimer of  $(\text{CH}_3)_2\text{AlOCH}_3$ , and the dimethoxy derivative  $\text{CH}_3\text{Al}(\text{OCH}_3)_2$  arising from the reaction of species A with a second molecule of  $\text{CH}_3\text{OH}$ . While species A was destroyed by heating above  $90^\circ\text{C}$ , this molecule should be relatively strongly bound with respect to unimolecular decomposition. Rather, its instability is more likely with respect to further reaction with other reaction partners in the flowing gas mixture. The two likely candidates for species B are both derived from a sequential reaction of monomeric  $(\text{CH}_3)_2\text{AlOCH}_3$ , either with another monomer unit to form the dimer or with a second molecule of  $\text{CH}_3\text{OH}$  to form  $\text{CH}_3\text{Al}(\text{OCH}_3)_2$ . In fact, it is difficult to spectroscopically distinguish between these two choices (or the trimeric species for that matter) [24,25]. In terms of product yield, reaction with a second molecule of  $\text{CH}_3\text{OH}$  to form the dimethoxy species should show a strong dependence on  $\text{CH}_3\text{OH}$  concentration, while formation of the monomeric species should be favored at a 1:1 stoichiometric ratio. A careful review of the many merged jet experiments at different concentrations does not clearly show a strong (quadratic) dependence on  $\text{CH}_3\text{OH}$  concentrations. This may be taken as evidence in favor of dimer formation, a result which is consistent with the solution phase chemistry of this system. However, a definitive conclusion as to the identity of species B (or even the number of species contributing to set B product bands) cannot be reached as a consequence of the complexity of these systems. Nonetheless, the evidence presented above clearly supports identification of  $(\text{CH}_3)_2\text{AlOCH}_3$  as the initial intermediate that is isolated under these reaction conditions, and represents the first report of the isolation and characterization of monomeric species.

#### 4.2. Band assignments

Spectroscopically,  $(\text{CH}_3)_2\text{AlOCH}_3$  should show many similarities to parent  $(\text{CH}_3)_3\text{Al}$ , with vibrations



of the Al–O–C linkage being most distinctly different. This linkage should be characterized by a C–O stretch, an Al–O stretch and a low energy bending mode. The first should show strong  $^{13}\text{C}$  and  $^{18}\text{O}$  shifts. The band near  $1000\text{ cm}^{-1}$  shows these characteristics, with a  $20\text{-cm}^{-1}$  shift due to  $^{13}\text{C}$ , and a  $30\text{-cm}^{-1}$  shift with  $^{18}\text{O}$ . These are, in fact, very close to the shifts observed for the C–O stretch of parent  $\text{CH}_3\text{OH}$ . For parent  $\text{CH}_3\text{OH}$ , the  $-\text{CD}_3$  shift is approximately  $45\text{ cm}^{-1}$  to lower energy, while a shift  $19\text{ cm}^{-1}$  was observed for  $(\text{CH}_3)_2\text{AlOCH}_3$  when  $-\text{CD}_3$  was employed. When  $(\text{CH}_3)_2\text{AlOCH}_3$  is formed, structural changes occur which alter the nature of the vibrational coupling and the nature of the vibrational mode itself. In the present case, this stretching mode is, in effect, the antisymmetric stretch of the three heavy atoms (Al–O–C), and coupling is to the Al center, not the deuteriums. In addition, there is mixing with other modes of the same symmetry in this spectral region, so that a shift that is nearly identical to the precursor species is not likely. In fact, *ab initio* calculations (see below) predict a small *blue* shift for this mode upon substitution of  $-\text{CD}_3$  for  $-\text{CH}_3$ . Therefore, the band near  $1000\text{ cm}^{-1}$  is assigned to the C–O stretch of the Al–O–C linkage in  $(\text{CH}_3)_2\text{AlOCH}_3$ .

The  $(\text{CH}_3)_2\text{Al}$  fragment should have spectroscopic features very similar to those of parent  $(\text{CH}_3)_3\text{Al}$ . In fact, the two most intense bands of  $(\text{CH}_3)_2\text{AlOCH}_3$  lie at  $690$  and  $1204\text{ cm}^{-1}$ , very close to bands of the parent. These are assigned to the  $\text{AlC}_2$  antisymmetric stretch and the  $\text{CH}_3$  rocking modes, respectively. The remaining few bands of species A were generally weak and fell at low energy. They cannot be definitely assigned, but are undoubtedly due to deformation modes of the heavy atom skeleton. One expects many additional modes of this species. However, most of these should lie very near the bands of species B, due to their chemical similarity and as such, they could not be clearly identified.

#### 4.3. *Ab initio* calculations

Detailed RHF and density functional calculations were carried out for  $(\text{CH}_3)_2\text{AlOCH}_3$  for comparison to the band observed for species A. Initial calculations were carried out with a low level basis set, to search for one or more local energy minima. Only one was located, although other minima of similar energy may

be present as well if a very thorough search of the potential energy surface were conducted. If others exist, they are likely simple rotational isomers of the minimum that was located. This initial minimum was then used as the starting point for calculations with the 6-31G\* basis set. A similar minimum was found in these calculations, and verified by the absence of any negative frequencies in the calculated spectrum (negative frequencies would indicate a saddle point on the potential energy surface, rather than a true minimum). Table 3 lists the key structural parameters found for  $(\text{CH}_3)_2\text{AlOCH}_3$ . The bond distances and angles listed here are generally close to those anticipated for this molecule. The angles around the central Al atom indicate just a slight deviation from planarity as a result of methoxy substitution for a methyl group.

As noted above, these calculations predict an intense band near  $1100\text{ cm}^{-1}$ , somewhat above the  $1000\text{-cm}^{-1}$  band position observed here. The calculated isotopic shifts for this mode matched quite well the observed shifts, as seen in Table 4. This table lists all of the calculated bands for  $(\text{CH}_3)_2\text{AlOCH}_3$ , and all of the isotopic shifts of these bands. Where bands were observed experimentally (such as the  $1000\text{-cm}^{-1}$  band), they are listed as well with the observed isotopic shifts. The calculations also predict an intense doublet at  $694\text{--}698\text{ cm}^{-1}$ , an absorption that does not shift with isotopic substitution. This matches very well the observed band at  $696\text{ cm}^{-1}$ . In addition, the calculations predict a band near  $1228\text{ cm}^{-1}$  for the  $\text{CH}_3$  rocking mode of the  $\text{Al}(\text{CH}_3)_2$  fragment (and insensitive to isotopic labeling on the  $-\text{OCH}_3$  group); experimentally this mode was observed at  $1204\text{ cm}^{-1}$ . The calculations predict a weaker band near  $660\text{ cm}^{-1}$  with small  $^{13}\text{C}$  and  $^{18}\text{O}$  shifts, and a somewhat larger  $-\text{CD}_3$  shift ( $13\text{ cm}^{-1}$ ).

Table 3  
Key structural parameters in the calculated<sup>a</sup> structure of  $(\text{CH}_3)_2\text{AlOCH}_3$

$R(\text{Al–C})(\text{\AA})$	1.968
$R(\text{Al–O})(\text{\AA})$	1.717
$R(\text{C–H})(\text{\AA})$	1.10
$R(\text{C–O})(\text{\AA})$	1.406
$\alpha(\text{C–Al–C})(^\circ)$	124.3
$\alpha(\text{C–Al–O})(^\circ)$	120.3
$\alpha(\text{Al–O–C})(^\circ)$	133.8

<sup>a</sup>Calculations employed density functional theory using the B3LYP functional and the 6-31G\* basis set.

As can be seen in Table 4, this matches quite well the observed band at  $643\text{ cm}^{-1}$ . The remaining calculated bands were all low in intensity, and not observed in the spectrum, except for a calculated band at  $771\text{ cm}^{-1}$ . This may lie under the very intense, broad species B band at  $705\text{ cm}^{-1}$  that was present in all of the experiments. While density functional calculations with B3LYP and a small scaling factor (0.961 in this case) generally give quite good agreement with experiment, a recent benchmark study [26] found a rms standard deviation of  $38\text{ cm}^{-1}$  for a set of 50 inorganic molecules. Thus, the differences observed here (e.g.  $121\text{ cm}^{-1}$  for the C–O stretch) are larger than anticipated, but not beyond the limits of the

calculation. The isotopic shifts, on the other hand, are relative, and should be quite accurate. As seen in Table 4, they are very good for all of the bands observed experimentally.

#### 4.4. $(\text{CH}_3)_3\text{Al} + \text{H}_2\text{O}$ Reactions

Interestingly,  $(\text{CH}_3)_3\text{Al}$  did not react with  $\text{H}_2\text{O}$  in twin jet reaction, just as reaction with  $\text{CH}_3\text{OH}$  did not occur. This is somewhat surprising, given the high driving force in these systems. Apparently, the low temperature in the mixing region combined with the very short reaction time prior to matrix condensation prevents any reaction from occurring. Clearly, in the

Table 4  
Observed and calculated<sup>a</sup> band positions and shifts for  $(\text{CH}_3)_2\text{AlOCH}_3$

Mode	Band position <sup>b</sup>		<sup>13</sup> C Shift		<sup>18</sup> O Shift		–CD <sub>3</sub> Shift	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
AlC <sub>2</sub> def.	346	252	–6	–1	—	–6	–10	–8
CH <sub>3</sub> rock	440	501	0	–1	–4	–4	–7	–5
CH <sub>3</sub> rock	614	589	0	0	0	0	0	–1
CH <sub>3</sub> rock		604		0		0		–1
CH <sub>3</sub> rock	643	663	0	–3	–3	–6	–21	–13
AlC <sub>2</sub> antisym. st.	696	694	0	0	0	0	0	0
CH <sub>3</sub> rock	698	698	0	0	0	0	0	0
CH <sub>3</sub> rock/Al–O st.		771		–2		–2		–9
C–O stretch	1002	1121	–21	–14	–30	–29	+ 3	+ 33
CH <sub>3</sub> rock		1156		–9		–3		–263
CH <sub>3</sub> rock		1178		–9		–10		–279
CH <sub>3</sub> rock	1228	1204	0	0	0	0	–1	0
CH <sub>3</sub> rock		1231		0		–1		1
CH <sub>3</sub> def.		1431		0		–1		0
CH <sub>3</sub> def.		1432		0		0		0
CH <sub>3</sub> def.		1436		0		0		0
CH <sub>3</sub> def.		1439		–1		–1		0
CH <sub>3</sub> def.		1463		–6		–1		–400
CH <sub>3</sub> def.		1470		–4		–2		–401
CH <sub>3</sub> def.		1479		–5		–2		–399
CH <sub>3</sub> st.		2880		–3		0		–816
CH <sub>3</sub> st.		2911		0		0		0
CH <sub>3</sub> st.		2915		0		0		0
CH <sub>3</sub> st.		2934		–10		0		–758
CH <sub>3</sub> st.		2948		–11		–1		–761
CH <sub>3</sub> st.		2971		0		0		0
CH <sub>3</sub> st.		2973		0		0		0
CH <sub>3</sub> st.		2991		0		0		0
CH <sub>3</sub> st.		3000		0		0		0

<sup>a</sup>Calculations employed density function theory, with the B3LYP functional and the 6-31G\* basis set, scaled by the factor 0.961.

<sup>b</sup>Band positions in  $\text{cm}^{-1}$ .

merged jet deposition of  $(\text{CH}_3)_3\text{Al}$  with  $\text{H}_2\text{O}$ , reaction did occur, based on the clear increase in  $\text{CH}_4$  reaching the matrix and the loss of some parent band intensity. However, the products of this reaction (other than  $\text{CH}_4$ ) appear to have condensed on the surface of the deposition line and were not deposited into the matrix.

## 5. Conclusions

While the reaction of  $(\text{CH}_3)_3\text{Al}$  with  $\text{CH}_3\text{OH}$  in solution is well known to yield dimeric, trimeric and polymeric alkylaluminum alkoxides, the present matrix isolation study has led to the formation, isolation and characterization of the monomeric species  $(\text{CH}_3)_2\text{AlOCH}_3$  for the first time. This species was also shown to be somewhat thermally unstable, and reacts further at elevated temperatures to form additional products. These could not be definitively identified but are likely to be either the dimeric and trimeric species, and/or  $\text{CH}_3\text{Al}(\text{OCH}_3)_2$ . No products in the merged jet reaction of  $(\text{CH}_3)_3\text{Al}$  with  $\text{H}_2\text{O}$  could be isolated, although there was evidence that reaction occurred in the flowing gas reactor.

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