ELSEVIER

Journal of Organometallic Chemistry 572 (1999) 169–175

Journal of Organo metallic Chemistry

Matrix isolation investigation of the reaction of $(CH_3)_3Al$ with O_2

Bruce S. Ault *

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172, USA

Received 29 April 1998; received in revised form 7 August 1998

Abstract

The matrix isolation technique has been employed to isolate and characterize the initial intermediate in the reaction of $(CH_3)_3Al$ with O_2. Using a flow gas reactor system immediately prior to matrix deposition, evidence of reaction was noted only when a constricted nozzle was employed. Under these conditions, four product bands that can be assigned to a single product species were formed. Oxygen isotopic labeling and comparison with literature spectra identified the product species as monomeric $(CH_3)_2AlOCH_3$. Experimental and theoretical evidence are also presented to support the conclusion that $(CH_3)_3AlOO$ is not the initial product of this reaction. Heating the deposition line to as high as 350°C destroyed the initial bands and led to the formation of one or more secondary species. These could not be conclusively identified; the well-known dimer $[(CH_3)_2AlOCH_3]_2$ is the most likely candidate. The fact that the reaction only occurred with a constricted nozzle suggests that O_2 is reacting with the trimethylaluminum dimer, across the four-membered ring to form two molecules of $(CH_3)_2AlOCH_3$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Aluminum; Alkyls; Matrix isolation; Oxygen

1. Introduction

The strength of the Al–O bond provides a strong driving force for the oxidation of organoaluminum compounds, including $(CH_3)_3Al$. This oxidation is often rapid, and in the case of $O_2/(CH_3)_3Al$ mixtures, the reaction can be explosive. At the same time, a number of groups have reported the synthesis of stable transition metal complexes with diatomic molecules as ligands (e.g. O_2, H_2). Lokshin [1] recently reported the spectra of several weakly bound molecular complexes of N_2, O_2 and H_2 with organometallic compounds and observed evidence for both monodentate and bidentate interactions. On the other hand, Alexandrov and co-workers [2] reported the formation of a reaction product of O_2 with $(CH_3)_3Ga$ at low temperatures and concluded that this product was in fact, the O_2 insertion product or peroxide, $(CH_3)_2GaOOCH_3$. They also carried out semi-empirical calculations in support of their assignment. These results suggest that there are multiple possibilities for the interaction of O_2 with simple organometallic compounds.

The matrix isolation technique [3–5] was developed for the study of reactive chemical intermediates 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 $(CH_3)_3Al$ with a range of Group V and VI alkyl bases were reported in argon matrices, providing insights into the process of complex formation [6]. While the research of Lokshin et al. and Alexandrov et al. used low temperatures to stabilize their reported intermediates, matrix isolation provides an additional stabilizing factor by isolating the product species in a complete inert cage of rare gas atoms at 14 K. Therefore, in view of the interest in the interaction of O_2 with $(CH_3)_3Al$, and the possible intermediates in this system, a matrix isolation study was undertaken to isolate and characterize the initial intermediate arising from this pair of reactants.

---

* Tel.: + 1-513-556-9200; fax: + 1-513-556-9239.

PII: S0022-328X(98)00915-2

2. Experimental

All of the experiments in this study were carried out on conventional matrix isolation apparatus that has been described [7,8]. Trimethylaluminum (Akzo) was introduced into the vacuum system as the vapor above the neat liquid, and used without further purification. O_2 (Matheson), $^{18}O_2$ (99% ^{18}O, Isotec) and $^{16,18}O_2$ (51% ^{18}O, Cambridge Isotope Laboratories) were introduced into the vacuum system from lecture bottles, and were used without further purification. 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, 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 with 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 ca. 2 mmol h^{-1} from each manifold for a period of 20–24 h. IR 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 Spectrum 2000 or a Mattson Cygnus FTIR, both over the region 4000–400 cm^{-1}.

3. Results

Prior to any co-deposition experiments, blank spectra were recorded of each of the reagents in solid argon. As has been seen previously [9,10], dimers of $(CH_3)_3Al$ were observed at higher sample concentrations. To minimize this, quite dilute samples of trimethylaluminum were employed ($Ar/(CH_3)_3Al = 1000–4000$) with more concentrated samples of Ar/O_2 (typically ratios of 100/1 to 200/1 were used). Traces of CH_4 were observed in all experiments employing $(CH_3)_3Al$. However, the quantities were very small and did not interfere with the reaction of interest. No impurities were observed in the O_2 blank experiments. One blank was run of a pure O_2 matrix; in the resulting spectrum, the weakly activated O–O stretching mode [11] was observed at 1548 cm^{-1}.

3.1. $(CH_3)_3Al + O_2$

In an initial experiment, a sample of $Ar/(CH_3)_3Al = 2000$ was co-deposited with a sample of $Ar/O_2 = 50$ in the twin jet mode. The spectrum of the resulting matrix showed no changes from the spectrum of the blank spectra of the two reagents. Consequently, all further experiments in this study were conducted in the merged jet mode. When a sample of $Ar/(CH_3)_3Al = 2000$ was co-deposited with a sample of $Ar/O_2 = 50$ in the merged jet mode, the resulting spectrum was quite similar to the blank spectra. The only clear difference between the spectrum of this matrix and that of a blank experiment of $Ar/(CH_3)_3Al = 2000$ was a weak band at 1002 cm^{-1}. As the concentration of the Ar/O_2 experiments was increased stepwise in a series of experiments up to $Ar/O_2 = 50$, the band at 1002 cm^{-1} grew in intensity. In addition, new features were observed at 643 and 1204 cm^{-1}, as well as a distinct decrease in the intensity of the $(CH_3)_3Al$ band at 742 cm^{-1}. When the Ar/O_2 concentration was very high (50/1), this band was reduced to nearly zero intensity, and a new product feature was noted near 695 cm^{-1} as can been seen in Fig. 1. All of these features and observations were reproducible, using the same experimental geometry and deposition nozzle, over a series of 20 or more experiments employing a range of concentrations for both the Ar/O_2 and $Ar/(CH_3)_3Al$ samples.

An additional experiment was run in which a sample of $Ar/(CH_3)_3Al = 2000$ was co-deposited with pure O_2 in a merged jet experiment using the same deposition system. The resulting spectrum was very similar to that obtained with concentrated $Ar/O_2 + Ar/(CH_3)_3Al$ experiments, namely moderately intense bands at 643, 695, 1002 and 1204 cm^{-1} (hereafter referred to as set A), along with the disappearance of the band at 742 cm^{-1} due to $(CH_3)_3Al$. An experiment was then run in which a sample of $O_2/(CH_3)_3Al = 2000$ was prepared. However, this sample reacted audibly within seconds in the stainless steel vacuum manifold prior to the start of matrix deposition. Subsequent deposition of the gaseous mixture led to strong absorptions due to H_2O and CO_2 in the IR spectrum of this matrix.

The merged region or reaction zone of the deposition system was then heated in a series of experiments, to as high as 350°C. When samples of $Ar/O_2 = 50$ and $Ar/(CH_3)_3Al = 2000$ were passed through this region together, additional changes in the spectrum were noted at temperatures above 200°C. The set A bands decreased and then were destroyed at higher temperatures, as shown in Fig. 2. New bands appeared in the spectrum, particularly near 705, 1070 and 1198 cm^{-1}, along with several broad, weak bands (hereafter re-

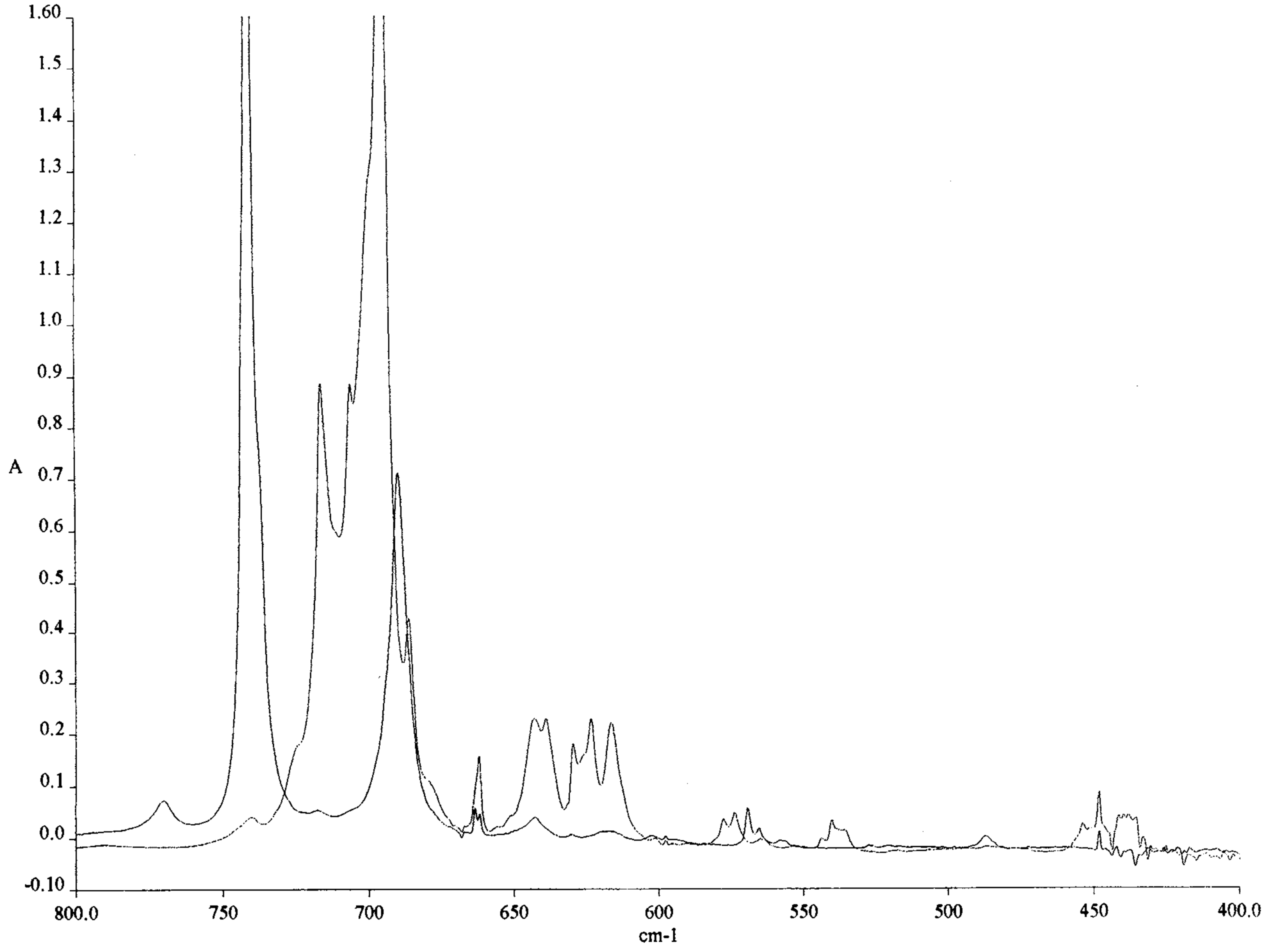

Fig. 1. IR spectrum of a matrix prepared by the merged jet co-deposition of a sample of Ar/$(CH_3)_3Al$ = 2000 with a sample of Ar/O_2 = 50 through a small orifice (upper trace—essentially no absorption at 742 cm^{-1}) compared with the spectrum of a matrix prepared by the merged jet co-deposition of a sample of Ar/$(CH_3)_3Al$ = 1000 + Ar (strong absorption at 742 cm^{-1}).

ferred to as set B). Here too, a number of experiments were run over a range of sample concentrations and the results were reproducible using the same deposition system.

The nozzle of the deposition system was changed to a larger diameter tube, and further merged jet experiments were conducted. Under these conditions, the set A bands were observed only very weakly regardless of the concentrations of the two reagents. The flow rate of argon was then measured through the two nozzles to provide an estimate of the nozzle size. The flow rate through the original nozzle was ca. 10% of the flow rate through the new nozzle, under identical conditions of pressure and temperature, indicating a very constricted flow rate through the original nozzle. Additional experiments were conducted on a different matrix isolation system in the same lab. Here the nozzle diameter was similar to the second, larger nozzle. In a series of experiments over the same range of Ar/O_2 and Ar/$(CH_3)_3Al$ samples as described above, only a very slight reaction was seen (very weak appearance of the 1002 cm^{-1} band and no measurable decrease in bands of $(CH_3)_3Al$). Finally, a set of experiments using the original nozzle probed the effects of changing the length of the reaction zone and the material of the reaction zone (stainless steel, heavily conditioned copper or new copper). No variations were noted as a result of these changes.

3.2. $(CH_3)_3Al + {}^{18}O_2$, ${}^{16,18}O_2$

Samples of Ar/$(CH_3)_3Al$ = 2000 were co-deposited in several experiments with samples of Ar/${}^{18}O_2$ = 50 (99% enrichment), using merged jet deposition and the original nozzle. Similar results were obtained to those using normal isotopic O_2. A reduction in the intensity of bands due to $(CH_3)_3Al$ was seen, and new product bands grew in at 640, 695, 970 and 1204 cm^{-1}, as shown in Fig. 3. Only the band at 1002 cm^{-1} showed a strong dependence on oxygen isotope (a trace of the band at 1002 cm^{-1} remained in this experiment due to residual ${}^{16}O_2$). The band at 643 cm^{-1} showed a relatively small 3 cm^{-1} red shift, while the bands at 695 and 1204 cm^{-1} did not shift with ${}^{18}O$ substitution.

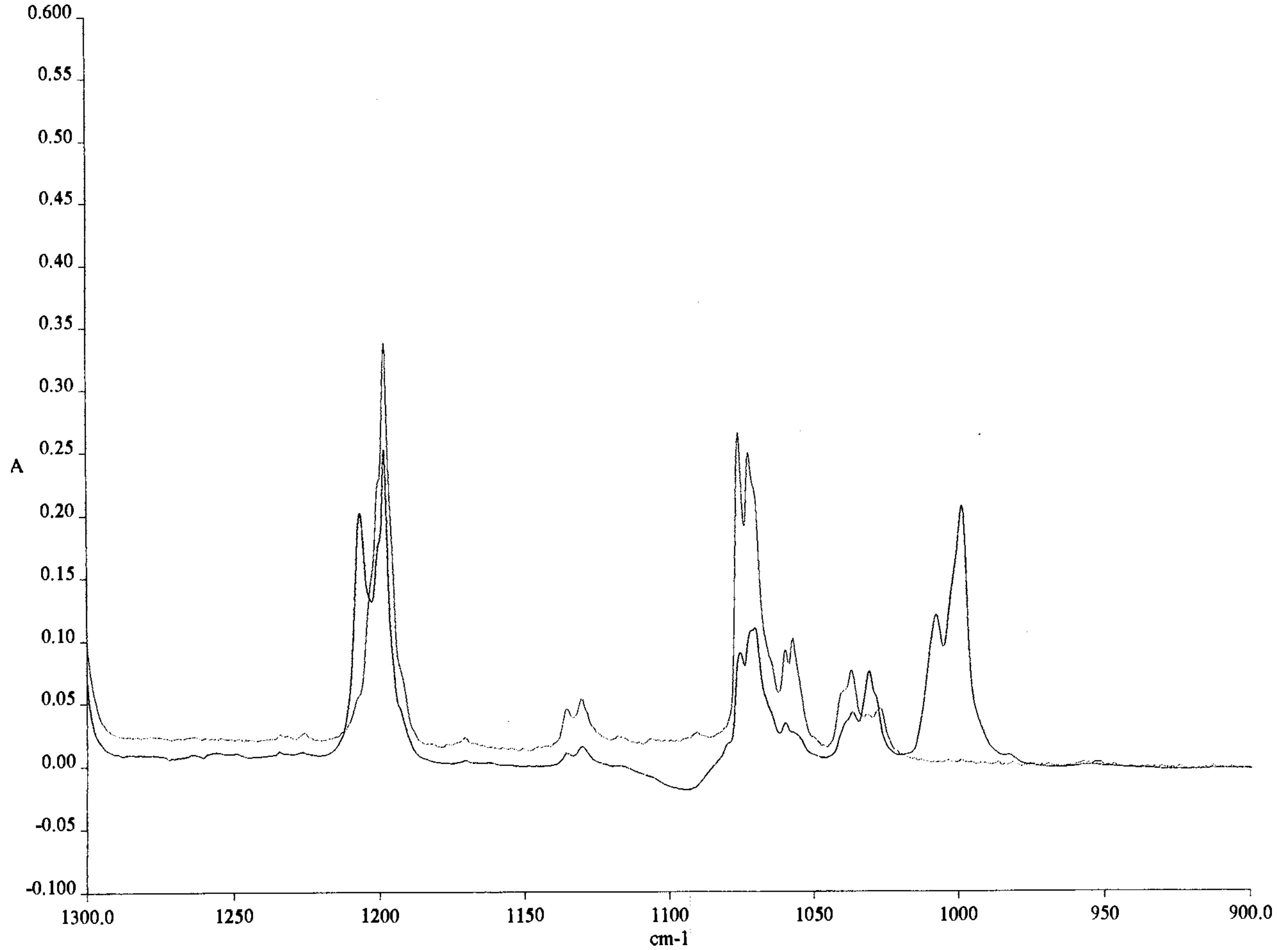

Fig. 2. IR spectrum of a matrix prepared by the merged jet co-deposition of a sample of Ar/$(CH_3)_3Al$ = 2000 with a sample of Ar/O_2 = 100 through a small orifice (darker trace, with band at 1002 cm^{-1}) compared with the spectrum of a matrix prepared from similar samples, but with the merged region heated to 300°C (lighter trace, no absorption at 1002 cm^{-1}).

Heating the reaction zone to 300°C in a subsequent experiment led to the destruction of these bands, and the growth of set B bands. Experiments were then conducted with a 50/50 mixture of $^{16}O_2$ and $^{18}O_2$ (i.e. Ar/$^{16}O_2$/$^{18}O_2$ = 100/1/1). In this experiment, product bands were noted at 643, 695, 970, 1002 and 1204 cm^{-1}; the bands at 970 and 1002 cm^{-1} were nearly identical in intensity. Finally, two experiments were conducted in which samples of Ar/$(CH_3)_3Al$ = 2000 were co-deposited with samples of Ar/$^{16}O_2$/$^{16}O^{18}O$/$^{18}O_2$ = 200/1/2/1. In this experiment, product bands were noted at 640, 643, 695, 970, 1002 and 1204 cm^{-1}. Overall, the results were nearly identical to those obtained with a sample of Ar/$^{16}O_2$/$^{18}O_2$ = 100/1/1.

4. Discussion

4.1. Product identification

Under certain deposition conditions, particularly the nozzle diameter, the merged jet co-deposition of $(CH_3)_3Ar$ and O_2 into argon matrices led to a set of new absorptions, set A, above. Under other conditions, particularly with larger nozzle diameters, only very weak new absorptions were seen. Based on the experimental observations and comparisons with the literature, the absorber responsible for the set A bands will be identified. Then, the mechanism of formation will be discussed, including the role of deposition geometry and nozzle diameter.

It is clear that O_2 is essential for product formation (in addition to $(CH_3)_3Al$), since ^{18}O labeling led to a 32 cm^{-1} shift of the 1002 cm^{-1} product band (see Fig. 3) and a 3 cm^{-1} shift of the 643 cm^{-1} product band. The other bands in set A did not shift, yet can be associated with the same absorber based on product band intensities in many experiments over a wide range of concentrations. The experiments involving mixtures of $^{16}O_2$ and $^{18}O_2$, and $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$ demonstrate clearly that the absorber responsible for the set A bands contains a *single* oxygen atom. No additional features were observed in the 'scrambled' experiment containing the mixed $^{16}O^{18}O$ species, as would have been expected

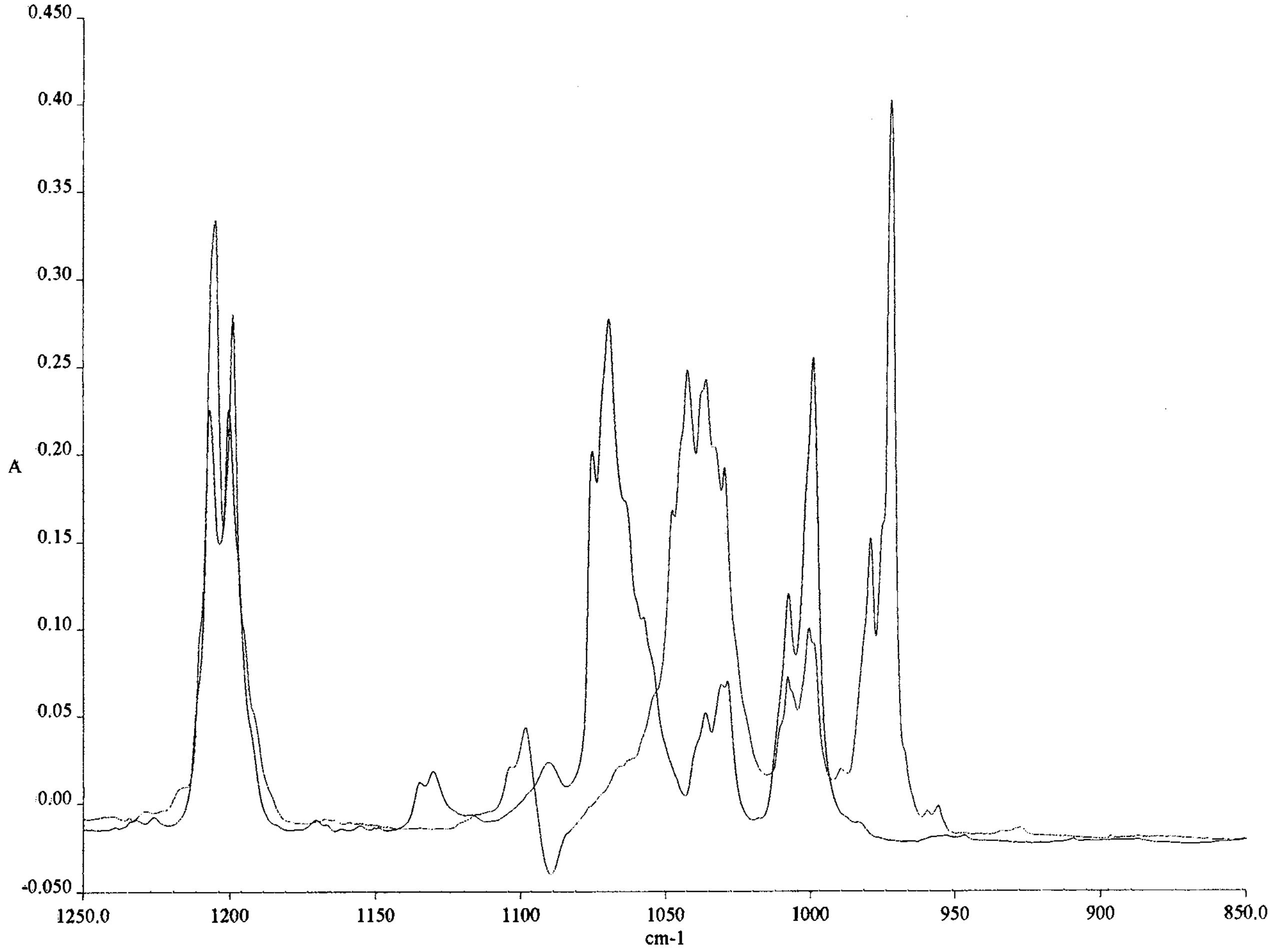

Fig. 3. IR spectrum of a matrix prepared from the merged jet co-deposition of a sample of $Ar/(CH_3)_3Al = 2000$ with a sample of $Ar/^{16}O_2 = 50$ through a small orifice (trace with stronger absorption at 1002 cm^{-1}) compared with the spectrum of a matrix prepared by the merged jet co-deposition of a sample of $Ar/(CH_3)_3Al = 2000$ with a sample of $Ar/^{18}O_2 = 50$ through the same orifice (weak absorption at 1002 cm^{-1} due to residual $^{16}O_2$, strong absorption at 972 cm^{-1}).

for a product containing two or more oxygen atoms. The pyrolysis experiments indicate that the product is thermally unstable, either with respect to unimolecular decomposition or with respect to bimolecular reaction. At the same time, it is clear that the destruction of this species at elevated temperatures does not regenerate the parents (specifically, the bands of $(CH_3)_3Al$ do not grow back when the deposition line temperature is increased).

The above observations, while giving some clues as to the identity of species A, are insufficient to completely identify this species. Fortunately, a recent study [12] in this laboratory of the reaction of $(CH_3)_3Al$ with CH_3OH led to precisely the same initial product bands, namely set A. These were at exactly the same band positions with the same relative intensities. They showed the same ^{18}O shifts and were also destroyed by increasing the temperature of the reaction zone. In this study, these experimental observations were augmented by ^{13}C, –OD and $-CD_3$ isotopic labeling, as well as by high level ab initio calculations. Based on all the data, this study [12] conclusively identified species A as monomeric $(CH_3)_2AlOCH_3$. Table 1 lists the band positions observed in this study and in [12] for monomeric $(CH_3)_2AlOCH_3$, and compares these with the values determined by an ab initio calculation. While the dimer and higher oligomers of $(CH_3)_2AlOCH_3$ are well-known, this represented the first observation of the monomeric species. Its thermal instability supported the transient nature of this species, with respect to either dimerization or to further reaction. One must conclude that this same product, monomeric $(CH_3)_2AlOCH_3$, is formed and isolated (under some conditions) in the reaction of $(CH_3)_3Al$ with O_2. The species responsible for the set B bands at elevated temperatures was not conclusively identified in the $(CH_3)_3Al + CH_3OH$ study. The most likely candidate is the very stable dimeric species $[(CH_3)_2AlOCH_3]_2$. Insufficient evidence was available to reach a firm identification, and the same situation occurs here as well.

4.2. Mechanism of product formation

Formation of $(CH_3)_2AlOCH_3$, a single oxygen atom species, from $(CH_3)_3Al$ and O_2 is remarkable, since the O–O bond is very strong. Thus, the direct reaction:

$$(CH_3)_3Al + O_2 \rightarrow (CH_3)_2AlOCH_3 + O$$

is highly endothermic and unlikely. Rather, it is likely that the O_2 reaction occurs with the dimer of $(CH_3)_3Al$, $[(CH_3)_3Al]_2$. This species is always present to a small extent in gas phase samples of trimethylaluminum, and at a level that increases quadratically with partial pressure. The dimer contains a structure consisting of a four-membered Al–C–Al–C ring, so that O_2 reaction across the ring can lead to product formation:

$$[(CH_3)_3Al]_2 + O_2 \rightarrow 2(CH_3)_2AlOCH_3$$

In these experiments, efforts were made to work at low concentrations of $(CH_3)_3Al$ to minimize dimer formation. However, the original nozzle contained a very small orifice, leading to low, turbulent flow and a bottleneck region. In this region, the pressure increases relative to the laminar flow region, and the concentration of the dimer would be expected to increase. The experiments conducted with larger diameter nozzles (and very minimal dimer concentration) did not lead to significant product formation, while the original, small diameter nozzle (with a high dimer concentration) consistently did. Unfortunately, the nozzle diameters are not accurately known, nor are the pressures in the flow regions, so that an accurate calculation of collisions in this region cannot be carried out. Nonetheless, this is a plausible mechanism for the formation of the observed reaction product, and a mechanism that takes into account the observations with different deposition systems/nozzles.

Table 1
Observed and calculated bands[a] of selected vibrations of $(CH_3)_2AlOCH_3$

Shift	^{16}O		^{18}O	
Mode	Exp.	Calc.[b]	Exp.	Calc.
AlC_2 def.	346[c]	252[c]	–	−6
CH_3 rock	440	501	−4	−4
CH_3 rock	614	589	0	0
CH_3 rock		604	–	0
CH_3 rock	643	663	−3	−6
AlC_2 antisym. st.	696	694	0	0
CH_3 rock	698	698	0	0
CH_3 rock/Al–O st.		771	–	−2
C–O stretch	1002	1121	−30	−29
CH_3 rock		1156	–	−3
CH_3 rock		1178	–	−10
CH_3 rock	1228	1204	0	0
CH_3 rock		1231	–	−1

[a] From [12].

[b] Calculations employed density functional theory, with the B3LYP functional and the 6-31G* basis set, scaled by the factor 0.961.

[c] Band positions in cm^{-1}.

Table 2
Key structural parameters[a] for $(CH_3)_3AlOO$

	Å
R(O–O)	1.253
R(Al–O)	1.926
R(Al–C_1)	2.094
R(Al–C_2)	1.964
R(Al–C_3)	1.975
R(C–H)	1.099
α(Al–O–O)	123.3°

[a] Calculated using density functional theory, with the B3LYP functional and the 6-31G* basis set.

In all of the experiments conducted in this study, no evidence was observed for either a co-ordination complex between O_2 and $(CH_3)_3Al$ $[(CH_3)_3AlOO]$ or the insertion product to form the peroxide species $[(CH_3)_2AlOOCH_3]$. Both of these species contain two oxygen atoms, and would show very distinctive oxygen isotopic substitution patterns, different than those observed here. As noted above, the isotopic pattern observed here and shown in Fig. 3 clearly requires that the absorbing species contain exactly *one* oxygen atom. Further, there is no realistic mechanism by which these products would form in the $(CH_3)_3Al + CH_3OH$ experiments, yet the same product was observed in that study. This does not definitively rule out the existence of these species, but rather they were not formed in detectable amounts in the current experiments.

To further explore this possibility, ab initio calculations were undertaken to investigate the structure, spectrum and energetics of $(CH_3)_3AlOO$. Using density functional theory with the B3LYP functional and the 6-31G* basis set, the species did optimize to a stable structure (local minimum). The key geometric parameters are given in Table 2. The vibrational spectrum of this species was then calculated at the same level of theory; key spectral features are presented in Table 3. As can be seen, the most intense band predicted in the spectrum is the O–O stretch at 1324 cm^{-1}, far above the most intense product band at 1000 cm^{-1}. Moreover, this mode should appear as a quartet of bands in the scrambled isotope experiment, whereas a doublet was actually observed. Finally, the energetics of the reaction:

$$(CH_3)_3Al + O_2 \rightarrow (CH_3)_3AlOO$$

were evaluated. The calculation indicated that this reaction is exothermic by about 15 kcal mol^{-1}. However, no attempt was made to evaluate the energetics of the barrier to reaction. Finally, if the initial reaction between $(CH_3)_3Al$ and O_2 were this direct addition reac-

Table 3
Calculated key vibrational modes and intensities for $(CH_3)_3AlOO$[a]

Mode	Position[b]	Intensity[c]
Torsion	407	10.4
AlC_3 sym. st.	442	3.6
CH_3 rock	555	7.8
CH_3 rock	579	11.0
CH_3 rock	590	3.8
CH_3 rock	595	6.6
AlC_3 asym. st.	647	16.8
AlC_3 asym. st.	680	34.4
CH_3 rock	689	58.7
CH_3 rock	723	137.3
CH_3 rock	1062	161.1
CH_3 rock	1173	12.5
CH_3 rock	1197	10.1
O–O st.	1324	177.3

[a] Calculations employed density functional theory, with the B3LYP functional and the 6-31G* basis set, scaled by the factor 0.961.

[b] Band positions in cm^{-1}.

[c] Intensities in km mol^{-1}.

tion, then the unusual dependence on orifice diameter should not have been a factor, yet it clearly was. Overall, the evidence strongly indicates that $(CH_3)_3AlOO$ cannot be identified as species A.

It is remarkable that a flowing sample of Ar/$(CH_3)_3Al$ did not react more completely when combined with a flow of pure O_2; only the set A bands were observed. In comparison, mixing $(CH_3)_3Al$ and O_2 in a static container led to very rapid, exothermic reaction and the production of CO_2 and H_2O. This may suggest that the reaction is initiated between O_2 and the dimer of trimethylaluminum, not the monomer, or that the static reaction is in some way mediated by the surface of the container.

Acknowledgements

The National Science Foundation is gratefully acknowledged for support of this research through grant 93-22622.

References

[1] B.V. Lokshin, I.I. Greenwald, J. Mol. Struct. 222 (1990) 11.

[2] Yu.A. Alexandrov, N.N. Vyshinskii, V.N. Kokorev, V.A. Alferov, N.V. Chikinova, G.I. Makin, J. Organomet. Chem. 332 (1987) 259.

[3] S. Craddock, A. Hinchliffe, Matrix Isolation, Cambridge University Press, New York, 1975.

[4] H.E. Hallam, Vibrational Spectroscopy of Trapped Species, Wiley, New York, 1973.

[5] L. Andrews, Annu. Rev. Phys. Chem. 22 (1971) 109.

[6] J.L. Laboy, B.S. Ault, J. Mol. Struct. 300 (1993) 351.

[7] B.S. Ault, J. Am. Chem. Soc. 100 (1978) 2426.

[8] J.D. Carpenter, B.S. Ault, J. Phys. Chem. 95 (1991) 3502.

[9] S. Kvisle, E. Rytter, Spectrochim. Acta 40A (1984) 939.

[10] S. Kvisle, E. Rytter, J. Mol. Struct. 117 (1984) 51.

[11] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A, 5th edn, Wiley Interscience, New York, 1997.

[12] B.S. Ault, J.L. Laboy, J. Mol. Struct., in press.