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setup. This result indicates almost all the reaction product, TEGa:NH_3, is in a condensed phase. The difference in the volatilities of TMGa:NH_3 and TEGa:NH_3 is important. At room temperature, TMGa:NH_3 is more volatile than TEGa:NH_3. In MOCVD of GaN with a cold-wall reactor, using TMGa is beneficial because more Ga carrying species would reach the reaction zone. If TEGa were selected, most of TEGa would condense as TEGa:NH_3 before reaching the reaction zone. Adducts resulting from predeposition reactions during MOCVD of compound semiconductors probably would have higher vapor pressures when metalorganics with small alkyl groups (methyl instead of ethyl) are utilized. Thus, in considering the growth efficiency, the metallorganics with small alkyl groups would be favored as the presursors. For example, in MOCVD of GaAs using TMGa and AsH_3, the reported growth efficiencies vary from 1.8×10^3 to 1.5×10^4 μm/mol of TMGa. When TEGa was used, the growth efficiency was on the order of 10^2 μm/mol of TEGa.[26] In MOCVD of InP using TMIn and PH_3, a typical value of the growth efficiency was 6.9×10^3 μm/mol of TMIn. When TEIn was used, the growth efficiency dropped to a range of 4.5×10^2–3.8×10^3 μm/mol of TEIn.[26]

To eliminate the condensation of predeposition adduct in the MOCVD process, one possible solution is to use a hot-wall reactor instead of a cold-wall reactor. For example, wall temperatures set at about 150 °C would reduce the predeposition reaction and increase the vapor pressure of any adduct formed. Certainly, the optimal temperature will have to be determined experimentally. It must be much lower than the growth temperature in order to prevent premature deposition on the reactor walls.

From the aspect of limiting predeposition reactions, NF_3 is a good alternative nitrogen source since no evidence was obtained that predeposition reactions occurred between NF_3 and TMGa or TEGa. However, fluorine has a higher chemical activity than nitrogen; thus, fluorine-containing byproducts may be formed in addition to the growth of the nitride semiconductor. For example, in MOCVD of AlN with TMAl and NF_3 as the source materials, aluminum trifluoride (AlF_3) has been detected in the AlN films.[27]

Conclusions

The room-temperature predeposition reaction between the Ga source (TMGa or TEGa) and NH_3 is complete in less than 0.2 s following mixing. The resulting adduct TMGa:NH_3 had a vapor pressure of 0.92 Torr, while the vapor pressure of TEGa:NH_3 was lower. With FTIR spectroscopy, absorption spectra of gaseous TMGa:NH_3 and TEGa:NH_3 were observed, and the assignments of vibrational frequencies were given. Since no chemical bond was destroyed when adducts were formed, the correspondences between the adduct spectrum and the single-component spectra were evident. When TMGa or TEGa was mixed with NH_3 at 150 °C, chemical equilibrium was reached between the gaseous adduct (TMGa:NH_3 or TEGa:NH_3) and the reactants. By assuming a reversible bimolecular reaction, a forward rate constant of 5.89×10^{-3} $\text{Torr}^{-1}\ \text{s}^{-1}$ was measured for the predeposition reaction between TMGa and NH_3. For TEGa + NH_3 system, the forward rate constant at 150 °C is 3.12×10^{-3} $\text{Torr}^{-1}\ \text{s}^{-1}$. With NF_3 as the nitrogen source, no evidence of adduct formation was observed with TMGa or TEGa at either room temperature or 150 °C. Therefore, NF_3 could be used as an alternative source of nitrogen in order to limit predeposition reactions.

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Registry No. TMGa, 1445-79-0; TEGa, 1115-99-7; GaN, 25617-97-4.

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Ligand Exchange in Adducts of Ethylaluminum Hydrides

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The compounds $EtAlH_2{\cdot}NMe_3$ and $Et_2AlH{\cdot}NMe_3$ have been shown by ^1H NMR spectroscopy to be fluxional mixtures of all species $Et_xAlH_{3-x}{\cdot}NMe_3$ (x = 0–3) in aromatic solvents. The pure liquids have also been shown to be mixtures by their volatilization behavior, and the tendency for $EtAlH_2{\cdot}NMe_3$ to separate at low temperatures into a solid plus a liquid, each of which has a different composition. This has potentially dire consequences for the usefulness of both of these compounds as precursors for the MOCVD of aluminum-containing layers.

Introduction

Metalloorganic chemical vapor deposition (MOCVD) is a technique whereby thin films of certain substances may be deposited on substrate materials by the chemical reaction of volatile metalloorganic precursors which are transported to the substrate via the vapor phase.[1] It has become an increasingly important process for a variety of applications, including the fabrication of microelectronic

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[1] Manasevit, H. M. *Appl. Phys. Lett.* **1968**, *12*, 156.

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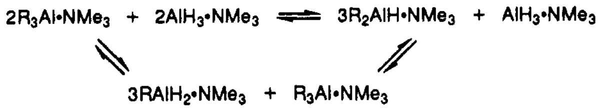
Scheme I



devices, e.g., those involving III–V materials.[2]

The metalloorganic precursors used to incorporate the group III components in the MOCVD of III–V materials have been almost invariably the trialkyls R_3M, where R = Me, Et and M = Al, Ga, or In.[2] However, there have been recent reports of the promise shown by the hydrido compounds such as $AlH_3{\cdot}(NMe_3)_n$ (n = 1 or 2) or $GaH_3{\cdot}NMe_3$ for the growth of Al- and Ga-containing III–V materials by MOCVD, thus giving deposits that contain significantly reduced carbon and oxygen relative to the trialkyls.[3] Indeed, $AlH_3{\cdot}NMe_3$ was initially used for the low-temperature deposition of aluminum metal over 20 years ago,[4] and more recently both this and related amine adducts of AlH_3 have been used to this end by MOCVD[5–9] or focused ion beam stimulated deposition.[10]

In addition to the adducts of the simple alane, AlH_3, the use of $R_2AlH{\cdot}NMe_3$ (R = Me, Et) has also been reported for the successful growth of $Al_zGa_{1-z}As$ over a wide range of z.[11,12] However, there has been some debate as regards whether $MeAlH_2{\cdot}NMe_3$ and $Me_2AlH{\cdot}NMe_3$ are single entities or are fluxional mixtures containing all possible species in the series $R_xAlH_{3-x}{\cdot}NMe_3$, where x is an integer in the range 0–3. Peters et al. interpreted the two signals due to the Me–Al protons in the ^1H NMR of each compound as due to partial association in solution: the presence of both monomers and dimers.[13] Conversely, Storr et al. observed three signals (one of which was rather smaller than the other two) which were identical for both $MeAlH_2{\cdot}NMe_3$ and $Me_2AlH{\cdot}NMe_3$, only the relative intensities being different in the two cases. From this it was concluded that in solution these compounds were actually mixtures of $Me_xAlH_{3-x}{\cdot}NMe_3$, where x is 0–3: the exchange of ligands between metals was so facile that all four species could be formed, and furthermore, because the free energies of formation of the compounds were likely to be so similar, then all four were present in appreciable amounts at equilibrium. A similar conclusion was drawn for the analogous gallium compounds.[14] This exchange may be illustrated by Scheme I.

However, Beachley et al. subsequently reasserted the Peters hypothesis that the observed spectra were the result of association rather than fluxionality, on the following evidence: the relative intensities of the NMR signals were concentration dependent; the compounds showed a tendency to associate in alkane solution as indicated by molecular weight determination by depression of vapor pressure; the gas-phase infrared spectrum showed no Al–H vibration at 1792 cm^{-1}, characteristic of $AlH_3{\cdot}NMe_3$; and furthermore, that reaction of $Me_2AlH{\cdot}NMe_3$ with $NHMe_2$ gave Me_2AlNMe_2 as the only Al-containing elimination product, whereas the fluxional mixture proposed by Storr et al. could give a mixture of amido products.[15]

The compounds $EtAlH_2{\cdot}NMe_3$ and $Et_2AlH{\cdot}NMe_3$ have also been reported in the literature,[16,17] although these do not appear to have occasioned a similar controversy to their methyl analogues. However, some reports of the use of $Et_2AlH{\cdot}NMe_3$ in MOCVD indicate the possibility of exchange, at least in benzene solution.[11,12]

It is of paramount importance that a source for MOCVD should give a reliable dosimetry of the desired vapors from its receptacle, otherwise the rate of deposition would fluctuate and accurate control of the composition of ternary and quaternary materials would be impossible. This requires that the vapor pressure of the source is dependent only upon its temperature and that its efficiency of entrainment by the carrier gas does not change perceptibly with time and/or usage. The latter requirement is normally satisfied for organometallic compounds which are liquid at the temperature at which they are used. However, if a compound were not actually a single species but a fluxional mixture, then entrainment of the vapors with a carrier gas—the normal manner by which precursor vapor is introduced into the MOCVD reactor—would give preferential vaporization of the more volatile components in that mixture. As the overall composition of the resulting vapor need not be the same as that in the liquid (indeed it would be very unlikely to be so) then the composition of the liquid would change as the sample evaporated. Concomitant with this would be a change in vapor pressure.

This effect has already been noted in the case of Me_2EtIn, which upon vaporization at around ambient temperature gave preferential loss of methyl- relative to ethyl-containing species: the initial volatiles from simple distillation of this liquid were found to be a "wet" solid: Me_3In contaminated with traces of ethyl-containing material.[18] This is not a matter of thermal instability wherein the compound is decomposing back to Me_3In plus Et_3In over a period of time: at ambient temperatures all species in the series $Me_xEt_{3-x}In$ (x = 0–3) are present in their equilibrium concentrations and are very rapidly interchanging by a ligand-exchange mechanism; the only constraint is that the initial overall stoichiometry of methyl:ethyl is 2:1 as this was defined in the synthetic routes. Because the initial stoichiometry of methyl:ethyl in the vapor was different from that in the liquid (a reflection of the greater volatility of the methyl-rich species over the ethyl-rich ones), the ratio in the liquid will inevitably change as the material is entrained away in the carrier gas. This will lead to changes in the concentrations of all the species $Me_xEt_{3-x}In$ present in the liquid as the system tries to compensate the preferential loss of methyl-rich compounds and bring the mixture back to equilibrium. This compositional change will be accompanied by a change in the vapor pressure. Of course, with a total sample of precursor which is large relative to the amount entrained away in each MOCVD growth experiment the change in

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Table I. ^{1}H NMR Data on $EtAlH_2 \bullet NMe_3$ and $Et_2AlH \bullet NMe_3$

compound	temp, °C	δ(Al–H)[a]	δ(Al–CH_2)[b]	δ(CH_2–CH_3)[c]	δ(N–CH_3)
$EtAlH_2 \cdot NMe_3$[d] (in C_6D_6)	24	4.80	0.18, 0.12	1.44[e]	1.88[f]
$Et_2AlH \cdot NMe_3$[g] (in C_6D_6)	30	3.93	0.18, 0.12, 0.08	1.41	1.91[f]
$Et_2AlH \cdot NMe_3$[g] (in $C_6D_5CD_3$)	60	3.73	−0.06[h]	1.21	1.95[f]
	30	3.73	0.06, 0.01, −0.03	1.25	1.88[f]
	−93	3.83	0.06, 0.01, −0.03	1.34, 1.33, 1.28	1.84,[a] 1.79,[a] 1.76,[f] 1.73[f]

[a] Broad singlet. [b] Quartet(s), $J \approx 8$ Hz. [c] Triplet(s) $J \approx 8$ Hz. [d] Spectrum obtained at 200 MHz. [e] Shoulder at 1.41 ppm. [f] Sharp singlet. [g] Spectra obtained at 400 MHz. [h] Slightly broadened quartet.

composition of the liquid may be so gradual that the resulting change in partial pressure of indium-containing species is almost imperceptible, becoming apparent only after substantial depletion of the sample has occurred.

The case in which several different compounds coexist in a liquid must be contrasted with that in which a single compound exists in more than one oligomeric form, i.e., monomers, dimers, trimers, etc., are present. (The explanation given by Beachley et al. for the observed ^{1}H NMR spectrum of $MeAlH_2 \cdot NMe_3$ and $Me_2AlH \cdot NMe_3$.[15]) Although there would again be preferential loss of the less associated (and hence more volatile) species, the vapor phase would always contain the same ratio of substituents on the metal as found in the liquid, and so no compositional change would accompany vaporization: the system would rapidly and continuously compensate the departure from equilibrium due to loss of the more volatile species simply by dissociating higher oligomers; therefore, the vapor pressure would be independent of the extent of depletion of the source.

In view of the controversy in the literature concerning the $Me_xAlH_{3-x} \cdot NMe_3$ compounds, we felt that it was vital to investigate whether the analogous ethyl compounds are fluxional mixtures, as this could seriously limit their usefulness for the MOCVD of aluminum-containing layers.

Results and Discussion

The compounds $EtAlH_2 \cdot NMe_3$ and $Et_2AlH \cdot NMe_3$ were prepared by literature routes: by heating together $Et_3Al \cdot NMe_3$ and $AlH_3 \cdot NMe_3$ in 1:2 or 2:1 molar ratios respectively;[13] alternatively, $Et_2AlH \cdot NMe_3$ was prepared by addition of NMe_3 to Et_2AlH.[12] The compounds were characterized by ^{1}H NMR spectroscopy. Both compounds were colorless liquids at ambient temperatures and very sensitive to air and moisture. Although neither has been reported to be pyrophoric, exposure of $EtAlH_2 \cdot NMe_3$ (about 5 g) to air initially gave little reaction until after a 5-min induction period when the compound spontaneously inflamed with the liberation of sufficient heat to flame polish the shards of its former borosilicate glass ampoule.

The ^{1}H NMR data on both compounds are presented in Table I. The spectrum of $EtAlH_2 \cdot NMe_3$ in d_6-benzene was consistent with that found in the literature except that the greater resolution of our spectrometer showed the signal from the CH_2 moiety of the Et–Al to be two distinct sets of quartets at 0.18 and 0.12 ppm, as opposed to the undefined "splitting" reported previously;[13] these signals are shown in Figure 1a. The triplet at 1.44 ppm due to the CH_3 of the Et–Al was also accompanied by a shoulder at 1.41 ppm. Also present were a single very broad peak due to the Al–H and a singlet due to the N–Me groups. The relative integration of these signals was consistent with the predicted overall stoichiometry of 1:2:3 for the Et–Al:Al–H:N–Me (corrected for the differences in proton counts for each substituent). These data indicate that a number of species are present in solution but do not distinguish per se between association and ligand fluxionality: the two ethyl signals may be due to the presence of monomers plus dimers or to $EtAlH_2 \cdot NMe_3$ plus $Et_2AlH \cdot NMe_3$ (the third ethyl-containing species, $Et_3Al \cdot NMe_3$, may be present in concentrations too low to be observed).

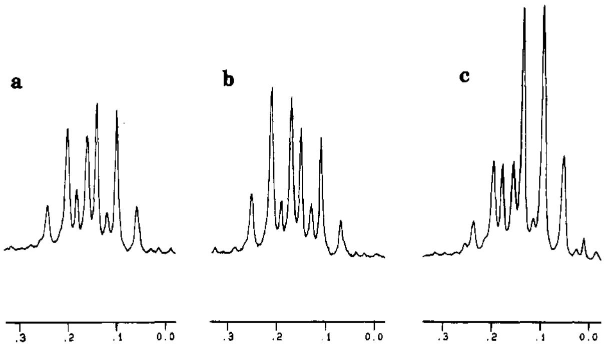

Figure 1. Al–CH_2 signals from the ^{1}H NMR of the fractions of $EtAlH_2 \cdot NMe_3$ (obtained at 200 MHz): (a) initial product; (b) solid fraction; (c) liquid fraction.

Although $EtAlH_2 \cdot NMe_3$ was a homogeneous liquid at ambient temperatures, upon cooling to −18 °C it separated into a white crystalline solid and a colorless liquid; this was reversed by allowing to warm to ambient temperature and was completely repeatable. This behavior was not described in any earlier literature, although the melting point of $Et_2AlH \cdot NMe_3$ was reported to be −28 °C.[13,16] The solid and liquid were separated by decantation and the separate fractions analyzed by ^{1}H NMR. The spectra were both similar to that of the original sample except that the overall ratios Et–Al:Al–H:N–Me had changed, and the relative intensities of the two signals at 0.18 and 0.12 ppm had altered, as is shown in Figure 1b,c. In fact the overall stoichiometry of the solid and liquid corresponded to $Et_{0.7}AlH_{2.3} \cdot NMe_3$ and $Et_{1.4}AlH_{1.6} \cdot NMe_3$, respectively. As can be seen from Figure 1, relative to the original sample the signal at 0.18 ppm is enhanced in the solid, while that at 0.12 ppm is enhanced in the liquid. This is a clear indication that pure $EtAlH_2 \cdot NMe_3$ is a fluxional mixture at ambient temperature: if the phase separation were due merely to the presence of species with different degrees of association, then the overall ratio of ligands in the different fractions would be identical; in fact, all three NMR spectra would be identical. The observed spectra for the different fractions enables the assignment of the signals at 0.18 and 0.12 ppm to the species $EtAlH_2 \cdot NMe_3$ and $Et_2AlH \cdot NMe_3$, respectively.

The ^{1}H NMR spectrum of $Et_2AlH \cdot NMe_3$ at 30 °C in d_6-benzene (see Table I) was broadly consistent with that reported in the literature[11,13] and largely similar to that of $EtAlH_2 \cdot NMe_3$. The overall ratio of Et–Al:Al–H:N–Me was precisely 2:1:3 in the initial product, as expected. From Table I it can be seen that there were three distinct quartets due to the CH_2 moiety of the ethyl groups at 0.18, 0.12, and 0.08 ppm, the first two of which are identical to those found in the spectrum of $EtAlH_2 \cdot NMe_3$ and the last corresponding to $Et_3Al \cdot NMe_3$. This similarity may be explained by both compounds being fluxional mixtures of $Et_xAl_{3-x} \cdot NMe_3$ in solution: they would then give identical signals, albeit with different intensities; the extra signal

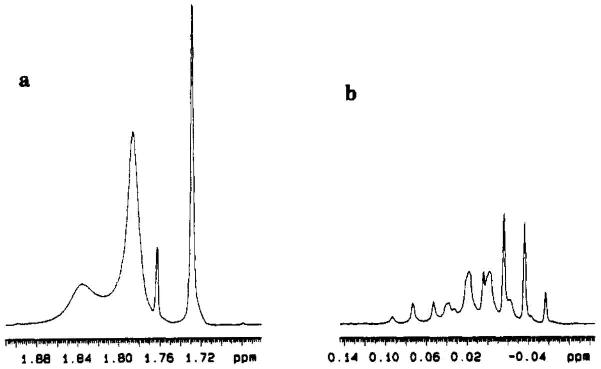

Figure 2. Selected signals from the ^1H NMR of $Et_2AlH{\cdot}NMe_3$ at −93 °C (obtained at 400 MHz): (a) N–Me; (b) Al–CH_2.

in the spectrum of $Et_2AlH{\cdot}NMe_3$ at 0.08 ppm may not be observable in that of $EtAlH_2{\cdot}NMe_3$ because the $Et_3Al{\cdot}NMe_3$ may be present in too low abundance (since the overall ratio of Et–Al:Al–H is lower in this compound).

A similar spectrum was obtained for $Et_2AlH{\cdot}NMe_3$ in d_8-toluene (see Table I) as in d_6-benzene except that the chemical shifts were slightly different, as expected. Upon warming to 60 °C, the ethyl signals coalesced to give a sharp triplet plus a slightly broadened quartet; the original spectrum was obtained upon allowing to cool to 30 °C. Upon cooling from 30 to −93 °C, the signals due to the CH_2 of the Et–Al groups remained essentially unchanged, the CH_3 of the Et–Al split into three distinct triplets, the Al–H became slightly less broad, but most significantly, the N–Me groups, which gave a very sharp singlet at ambient temperature, split into four singlets, of which the two most downfield were broad. The signals for the N–Me and Al–CH_2 groups at −93 °C are shown in Figure 2. If the complexity of the NMR spectrum at ambient temperature were simply due to association phenomena, then the same number of N–Me as Et–Al signals would be expected (assuming that no additional inequivalence of groups which could be distinguished by NMR would result from the oligomerization). The most consistent explanation of these observations is the presence of four species in solution, three of which contain Et–Al groups: $Et_xAlH_{3-x}{\cdot}NMe_3$ where $x = 0$–3. All species may be distinguished at −93 °C, but at 60 °C the rate of exchange is rapid with respect to the time scale of the NMR transitions, and only averaged signals are obtained.

The ^1H NMR evidence for fluxionality is limited by the fact that the spectra have been obtained in solutions in which the exchange may be more facile than in the pure liquid. Therefore, it was decided to study the vaporization properties of the pure liquids for both compounds in order to obtain conclusive evidence as to whether the compounds show fluxionality in this phase and consequently give variable dosimetry if used as MOCVD precursors. A sample of $EtAlH_2{\cdot}NMe_3$ (36 g) was distilled in vacuo into a receiver flask at −196 °C. It was noted that a considerable amount of material (around 5 g) vaporized readily at 20 °C/0.05 Torr, which upon allowing to warm to ambient temperature proved to be a mixture of a crystalline solid and a colorless liquid. The main fraction was found to distill at a bath temperature of 50 °C at 0.05 Torr, but a residue (5–10 g) of liquid did not distill until the bath temperature was raised to 80 °C at similar pressure. This may be explained by the preferential vaporization of $AlH_3{\cdot}NMe_3$ (the crystalline solid) relative to the less volatile ethyl-containing species.

A similar effect was observed during the distillation of $Et_2AlH{\cdot}NMe_3$: the initial fraction was obtained at 49–51 °C (bath temperature 73–76 °C) at 0.7–1.0 Torr and contained an overall ratio of Et–Al:N–Me of 1:1.9 instead of the 1:1.5 required by the formulation; the second fraction (49% w/w of the original sample) distilled at 55–57 °C in the range 0.3–0.5 Torr and was shown by ^1H NMR to be essentially pure $Et_3Al{\cdot}NMe_3$ with only a trace signal for the Al–H. It was noticed that with these fractions, which were of intermediate composition, integration of the Al–H was difficult because it was so broad; therefore the relative integrations are quoted here only with respect to the sharp (and, therefore, easily integrated) signals due to the Et–Al and the N–Me.

Table II. Distillate and Residue Compositions from Successive Partial Vaporization of $Et_2AlH{\bullet}NMe_3$[a]

sample temp, °C	evaporation time, h	amt of distillate[b]	Et-Al/N-Me in distillate[c]	Et-Al/N-Me in residue[c]
0	1	0.12	0.39	0.68
0	1	0.11	0.38	0.65
0	2	0.18	0.39	0.73
24	3	1.19	0.49	0.89

[a] Nitrogen gas was passed at 2.5 dm^3/h over the sample and the distillate condensed in a trap held at −78 °C; total pressure in the system was 2.5 Torr. [b] In gram, from an initial sample of 4.2 g. [c] Determined from ^1H NMR (400 MHz); required ratio 0.67 according to the formulation $Et_2AlH{\cdot}NMe_3$.

It might be argued that the relatively high temperatures of distillation enhanced the ligand exchange and that at lower temperatures the compound would distill as a single compound. Therefore, a sample of $Et_2AlH{\cdot}NMe_3$ (4.2 g) was held at 0 °C and a flow of nitrogen (2.5 dm^3/h) was passed over it such that the total pressure in the system was 2.5 Torr. The resulting distillate and the residue were analyzed by ^1H NMR after 1, 2, and 4 h of evaporation (by the end of which a total of 0.41 g had distilled). The residue was then allowed to warm to 24 °C, the entrainment continued, and after 3 h a further 1.19 g of distillate was obtained. The ratio of the Et–Al signal to that of the N–Me in these fractions are presented in Table II (corrected for the difference in proton counts for each substituent). It is clear that the composition of the distillate obtained at 0 °C and up to 10% sample depletion is constant within the accuracy of the NMR integration (5–10%) and corresponds to a ratio of Et–Al:N–Me of approximately 0.4:1. However, that of the residue over the same period was about 0.7:1. Obviously, for distillation of $Et_2AlH{\cdot}NMe_3$, were it a bona fide compound, the ratio in both would be 0.67:1. This clearly shows that preferential evaporation is occurring. From further distillation of the resulting residue at 24 °C (the temperature around which the compound has been used as an MOCVD source) this effect can be seen even more clearly: the distillate (29% w/w of the original sample) contained a ratio of Et–Al:N–Me of around 0.5:1 whereas that in the residue was around 0.9:1. The early fractions were richer in Al–H than the initial sample (low Et–Al:N–Me ratio), so any later fraction would necessarily contain relatively more Et–Al.

Experimental Section

As all compounds were very sensitive to oxygen and moisture, all operations were performed under an atmosphere of purified argon or nitrogen using Schlenk-style apparatus and a glovebox. The ^1H NMR spectra were obtained in d_6-benzene or d_8-toluene using Bruker AC200 FT or a Varian Unity-400 spectrometers; signals are quoted as δ ppm relative to Me_4Si. Data on the ^1H NMR are presented in Table I.

The $AlH_3{\cdot}NMe_3$[19] and $Et_3Al{\cdot}NMe_3$[13] were prepared by minor modifications of literature routes; heating these two compounds together in 2:1 or 1:2 molar ratio gave $EtAlH_2{\cdot}NMe_3$ and

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(19) Ruff, J. K.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 2141.

$Et_2AlH{\cdot}NMe_3$ respectively, as outlined in the literature.[13] Alternatively, $Et_2AlH{\cdot}NMe_3$ was prepared by addition of NMe_3 to Et_2AlH, as described in the literature;[12] the routes gave products with identical ^1H NMR spectra.

Conclusions

The ^1H NMR data show strong evidence that both $EtAlH_2{\cdot}NMe_3$ and $Et_2AlH{\cdot}NMe_3$ are mixtures of all the species $Et_xAlH_{3-x}{\cdot}NMe_3$ in solutions of benzene or toluene.

The tendency for $EtAlH_2{\cdot}NMe_3$ to separate at −18 °C into a solid and a liquid which show different ratios of substituents on the metal is strongly suggestive that a fluxional mixture of species is also found for this compound in the pure liquid, and the vaporization behavior of both compounds further supports this hypothesis. For $Et_2AlH{\cdot}NMe_3$ the evaporation studies were performed under conditions similar to those in which the compound would be used in an MOCVD experiment: there was clear evidence that the composition of the vapor was different from that of the liquid, and after substantial exhaustion of the sample it was also clear that the compositions of both vapor and liquid were changing throughout the distillation. There was also evidence that the volatility of the compound progressively decreased during distillation.

In conclusion, although these compounds can be used as precursors for the MOCVD of aluminum-containing layers (this should be possible with virtually any mixture of aluminum alkyls and/or hydrides), there are very strong indications that the sources will not be well-behaved: the partial pressure of aluminum species they deliver into the reactor will be dependent upon their degree of exhaustion.

Registry No. $EtAlH_2{\cdot}NMe_3$, 19582-10-6; $Et_2AlH{\cdot}NMe_3$, 12079-02-6; $Et_3Al{\cdot}NMe_3$, 15318-08-8; $AlH_3{\cdot}NMe_3$, 16842-00-5.

Reactivity of Chromium Oxide in Aqueous Solutions. 1. Oxidative Dissolution

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Chromium(III) oxide, α-Cr_2O_3, is dissolved in aqueous media in the presence of Ce^{4+}, MnO_4^-, BrO_3^-, and $S_2O_8^-/Ag^+$ species in a process preceded by the formation of surface Cr–O–X complexes. The last cited reactant causes oxidation of Cr(III) by Ag^{2+} attack on the surface complex, whereas the other three additives promote dissolution by the formation of Cr(VI) through an internal redox process within the surface complex. Langmuir-type conditional constants for the formation of the surface complexes are presented and discussed, together with the rate constants that describe their evolution to dissolved Cr(VI). The analogy between these heterogeneous oxidations of α-Cr_2O_3 and oxidations of dissolved $Cr(H_2O)_6^{3+}$ is discussed.

Introduction

The general subject of metal oxide dissolution mechanisms poses interesting questions about the underlying chemistry. In particular, the relationship between the chemical interactions at the surface of a metal oxide with the known aqueous chemistry of the same metal ion has been the subject of several recent studies.[1-4]

Segall[5] et al. have proposed a classification of the dissolution reactions of metal oxides on the basis of the type of chemical bonding and electronic properties in the solid. According to this scheme, the most resistant to dissolution in aqueous media are covalent oxides, such as SiO_2, ZrO_2, etc. This classification of metal oxides in "ionic", "semiconductor", and "insulating covalent" is of course mainly operative, in the sense that it accounts for broad types of dissolution mechanisms. It is well-known that the true ionicity of metal oxides is still elusive,[6] and the distinction of semiconductors and covalent oxides is simply made on the basis of an arbitrary value of the bandgap.[7] Chromium(III) oxide is in itself a good example of a solid that can be described as either ionic or covalent: the ionicity from XPS data is calculated to be 2.6, whereas the use of a more sophisticated model leads to the value of 0.15.[6] Furthermore, it is possible to impart semiconducting properties to α-Cr_2O_3 by adequate thermal treatment in oxidizing or reducing atmospheres. In the classification of Segall et al., however, α-Cr_2O_3 falls clearly in the covalent class;[7] its thermodynamic solubility is high both in acids and in bases,[8] but the dissolution rates are higher in the basic media.[9] Indeed, the covalent Cr–O–Cr

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