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Laser-powered homogeneous pyrolysis of trimethylaluminium: trapping of the dimethylaluminium radical

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Abstract

The laser powered homogeneous pyrolysis of trimethylaluminium has been investigated using a continuous wave CO_2 laser with SF_6 photosensitisation. Under certain circumstances, the $(CH_3)_2Al$ intermediate generated can be trapped with the SF_6 as $(CH_3)_2AlF$, or with CCl_4 as $(CH_3)_2AlCl$. Under these conditions, spectroscopic and vapour pressure evidence suggest that the preferred degree of association of the fluoride is lower than that in the tetramer formed in condensed phases at lower temperatures.

Introduction

During the past decade there has been a marked renewal of interest in the mechanisms of pyrolysis of the simple alkyls of Group III and IV metals [1]. This activity is a direct result of the recognised potential of such compounds as precursors for the deposition of metals and semi-conductor materials via metal organic chemical vapour deposition (MOCVD) and metal organic molecular beam epitaxy (MOMBE) [2]. In particular, the trimethyls and triethyls of aluminium [3], gallium [4], and indium [5] have been widely used as sources of these metals in a range of applications. However, despite an extensive accumulation of data of an empirical nature, there is still considerable uncertainty about the details of the fundamental processes in such pyrolyses; as an example, activation energies as widely different as 158.6 kJ mol^{-1} [6] and 38 kJ mol^{-1} [7] for the pyrolysis of trimethylaluminium have recently been published. This almost certainly reflects the difficulty in disentangling homogeneous and heterogeneous contributions to the overall process, especially in the latter work [7]. It is clear that there is a need for more fundamental work in this area in order to facilitate a rational approach to the design of novel precursors and technologies for MOCVD and MOMBE applications.

We have recently initiated an extensive programme of study of these reactions using the technique of laser powered homogeneous pyrolysis (LPHP). This technique has a number of practical advantages of direct relevance to the study of MOCVD processes, as described in detail below. During our investigations of the LPHP of trimethylaluminium $(CH_3)_3Al$, we have observed trapping of the presumed dimethylaluminium intermediate with the SF_6 photosensitiser in the form of dimethylaluminium fluoride, $(CH_3)_2AlF$, and with CCl_4 as dimethylaluminium chloride, $(CH_3)_2AlCl$. We believe that these observations represent the first direct confirmation of the central rôle of this intermediate in the homogeneous pyrolysis of $(CH_3)_3Al$: the observations also underline the utility of the LPHP technique in the investigation of reactions leading to deposition. Interestingly, in this relatively high temperature gas phase process the $(CH_3)_2AlF$ is apparently produced in a dimeric or trimeric form, rather than as the tetramer produced in the conventional lower temperature reaction. This observation has a precedent in the corresponding gallium system [8].

Experimental

The apparatus is relatively simple, following that of earlier descriptions [9,10]. A mixture of precursor gas(es), in this case $(CH_3)_3Al$ either alone or with CCl_4, and photo-sensitiser (SF_6) at pressures of a few torr is contained in a 100 cm^3 Pyrex cell. SF_6 is particularly suitable as a photosensitiser, combining the ideal requirements of strong IR absorption, very fast intra- and inter-molecular energy transfer, and (in general) chemical inertness and thermal stability. In addition, its low thermal conductivity permits the generation of large temperature gradients. The cell is fitted with ZnSe windows. This material is considerably superior to the alternative NaCl, not only because of its greater IR transmission and superior mechanical strength, but also because it is not hygroscopic, even traces of adsorbed water can drastically alter the course of reactions of compounds such as $(CH_3)_3Al$. Infrared power (up to 50 W, but normally in the range 5–15 W) is supplied by a free-running Edinburgh Instruments PL4 CO_2 gas laser, and power levels are monitored with a coherent radiation power meter. It proved unnecessary to focus the laser radiation: indeed, focusing considerably reduces the reproducibility of quantitative measurements. As shown in other work [9,11], this arrangement generates a static, spatially inhomogeneous temperature profile in which the cell walls and windows remain cool, with maximum temperatures of 400–500 K near the centre of the cell. In work to be published elsewhere, we have measured this temperature distribution by monitoring the high resolution IR spectrum of an added trace of the unreactive CO by use of a tunable lead salt diode laser spectrometer [12]. Although detailed knowledge of this profile is needed for the extraction of quantitative parameters, in the present work the input laser power was used simply as an approximate guide to temperature. The progress of the reaction was monitored in the absence of laser radiation by Fourier transform infrared (FTIR) spectroscopy. In addition, the cell was fitted with an isolatable cold trap for collection and further manipulation of reaction products.

The advantages of this technique over conventional pyrolysis for the study of reactions leading to deposition are considerable. The most significant of these is the fact that the cell walls remain at room temperature, resulting in complete elimination of wall-initiated reaction. In kinetic and mechanistic studies of deposition reactions this is of great value, since many such processes under conventional pyrolysis are highly autocatalytic (a recent example is provided by the reaction between $(CH_3)_4Sn$ and O_2, which was shown to be catalysed by the SnO_2 deposited [13]), and thus the elimination of heterogeneous contributions can be very difficult. In qualitative studies, this feature also largely eliminates the wall loss of reactive intermediates, since they are generated only at the centre of the cell. A further possible benefit of direct relevance to MOCVD is that delicate substrates for deposition are not exposed to extreme conditions. A second feature is the excellent spatial and temporal control of the pyrolysis; as is indicated by the high resolution IR spectra of the SF_6 or the reacting gas, thermal equilibrium is achieved within a few tenths of a second on both initiation and termination of laser radiation [14]. Finally, the use of very small quantities (a few μmol) in this static and highly localised arrangement permits the study of scarce reagents, particularly of the isotopically labelled forms widely used in mechanistic studies.

Trimethylaluminium and CCl_4 (Aldrich) were purified by three or four freeze-pump-thaw cycles; SF_6 (British Oxygen) was used without further purification. Greaseless joints were used throughout, and the pyrolysis cell and collection tube were conditioned by exposure to $(CH_3)_3Al$ before each experiment (this eliminates residual adsorbed H_2O and O_2, with which $(CH_3)_3Al$ reacts very readily). Infrared spectra were recorded using a Digilab FTS40 FT-IR spectrometer at a maximum resolution of 1 cm^{-1}, and NMR spectra were obtained using a Bruker AM300 Fourier Transform spectrometer. Cryoscopic studies, and Raman spectroscopy, were conducted with apparatus constructed in the Department of Chemistry, University of Leicester.

Observations

Figure 1 shows the changes observed in the FTIR spectrum of a mixture of 2 torr of $(CH_3)_3Al$ with 10 torr of SF_6 on irradiation with 8 W of IR laser power for a period of a few minutes. Under these conditions, the SF_6 is known to be thermally stable, so that at least the initial steps in any observed reaction are attributable to breakdown of the $(CH_3)_3Al$. In addition to the appearance of features readily assignable to CH_4 (sharp Q-branches at 1306 and 3020 cm^{-1}), there are considerable changes in the region associated with the skeletal vibrations of the $(CH_3)_3Al$ dimer; in particular, a new band at 740 cm^{-1}, attributable to $(CH_3)_2AlF$, appears. The formation of this species is moderately sensitive to conditions. At lower laser power (i.e. temperature), only CH_4 and a yellowish deposit are observed; the latter is presumably the carbon-containing Al observed in conventional pyrolysis. At higher power the $(CH_3)_2AlF$ product itself is pyrolysed, albeit more slowly than the $(CH_3)_3Al$. Addition of a small amount of hydrogen increases the yield of CH_4, as observed by Suzuki et al. [7], and largely suppresses the formation of $(CH_3)_2AlF$ under all conditions. This latter observation is of considerable relevance in MOCVD applications, since H_2 is often used as a carrier gas; a detailed kinetic and mechanistic study of this system will be published elsewhere [15]. In order to clarify the changes in this region (which is partly overlapped by very strong SF_6 absorptions), the products of the pyrolysis were rapidly condensed at 77 K, followed by pumping at 196 K (at which temperature both CH_4 and SF_6 are removed) and re-expansion into the cell at room temperature. This yielded the spectrum illustrated

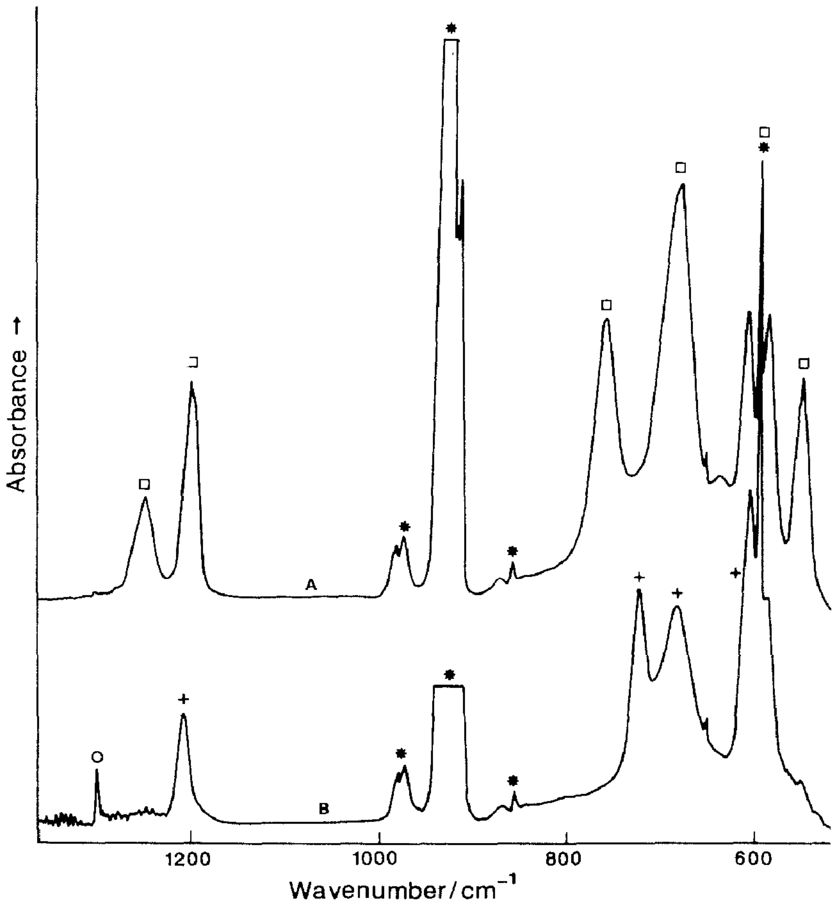

Fig. 1. FTIR spectra showing LPHP of $SF_6+(CH_3)_3Al$ mixtures. 10 torr SF_6+2 torr $(CH_3)_3Al$ subjected to 8 W IR laser power for 5 min; A: before irradiation, B: after irradiation. ★, SF_6; □, $(CH_3)_3Al$; ○, CH_4; +, $(CH_3)_2AlF$. The sharp feature near 650 cm^{-1} in this and other spectra is an artefact.

in Fig. 2 and 3, which also shows those of the liquid product (see below) and $(CH_3)_3Al$ for comparison.

For further spectroscopic and other studies, the products of about 20 experiments were accumulated in the cold trap, and purified as described above. The product proved to be a highly viscous colourless liquid, as observed by earlier workers [16], and was examined by a variety of techniques. The FTIR (see Fig. 3) and Raman spectra of the liquid are listed in Table 1, together with those from ref. 16 and the FTIR spectrum of the vapour. The ^1H NMR spectrum in $CDCl_3$ revealed a single broad feature at a chemical shift of -0.637 ppm; cooling to the freezing point of the solvent produced no change in this spectrum, but addition of a small amount ($<5\%$) of $(CH_3)_3Al$ produced a 1/2/1 pattern with a splitting of 4.50 Hz. The ^{19}F NMR spectrum consisted of a single broad feature at -144.9 ppm (referred to $CFCl_3$); when CF_3CH_2OH was used as an external standard, the $^1H/^{19}F$ ratio was estimated to be 6.5 ($\pm 10\%$). Cryoscopic measurements using carefully dried CCl_4 as a solvent yielded a relative molecular mass of 324, with an accuracy of $\pm 5\%$. No useful mass spectrum could be obtained, as is often the case for organoaluminium

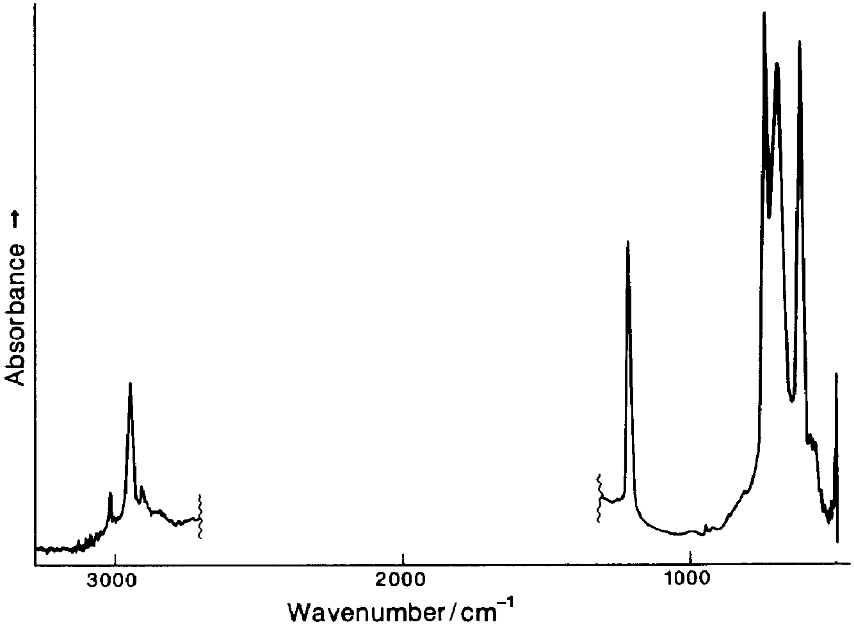

Fig. 2. FTIR spectrum of $(CH_3)_2AlF$ vapour produced in the LPHP process. The region between 1300 and 2500 cm^{-1} has been removed; this region contains only features due to CO_2 and H_2O in the background. Traces of CH_4 (3020 cm^{-1}) and SF_6 (950 cm^{-1}) remain.

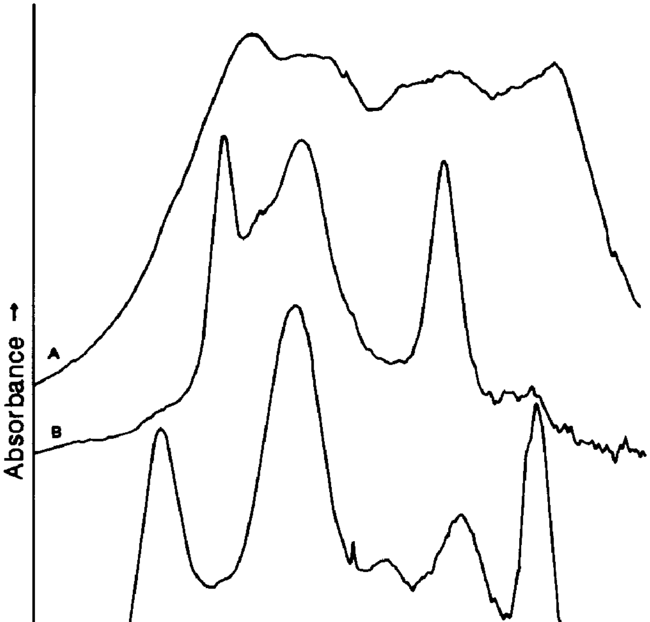

Fig. 3. FTIR spectra of $(CH_3)_2AlF$ in the region 500–850 cm^{-1}. The region of the skeletal vibrations of $(CH_3)_2AlF$ liquid (A), $(CH_3)_2AlF$ vapour (B), and $(CH_3)_3Al$ vapour (C); note the absence of a band near 560 cm^{-1} in B.

Table 1

IR and Raman vibrational spectra (cm^{-1}) and assignments for $\{(CH_3)_2AlF\}_n$

IR (liquid)	Raman (liquid)	IR [16]	Raman [16]	IR (vapour)	Assignment
2943(s)	2950(w)	2946(s)	2948(w)	2949(s)	$\nu_{as}(CH_3)$
2901(m)	2908(s)	2905(m)	2904(s)	2906(w)	$\nu_{sym}(CH_3)$
2861(w)	2840(w)	2855(w)	2845(w)	–	
1435(w)	1434(w)	1430(w)	1433(w)	–	$\delta_{as}(CH_3)$
1210(s)	1220(m)	1214(s)	1213(s)	1216(s)	$\delta_{sym}(CH_3)$
988(m)	–	988(w)	980(w)	–	
718(vs)	720(w)	726(vs)	717(m)	740(vs)	$\nu_{as}(AlC_2)$
685(s)	–	689(s)	–	689(s)	
636(m)	–	638(m)	–	617(s)	$\nu_{as}(AlF_2)$
608(m)	–	614(m)	–	–	$\nu_{sym}(AlF_2)$
551(s)	603(vs)	560(s)	599(vs)	–	$\nu_{sym}(AlC_2)$
–	370(m)	–	370(m)	–	

compounds. Elemental analysis of the modest amount of sample available yielded C, 27% (expected 31.6%), and H, 7% (expected 7.9%); insufficient sample was available for measurements of Al and F content, and the C and H measurements are likewise imprecise. Finally, the vapour pressure of the product at room temperature, as measured with the limited equipment available, was found to be very low ($\ll 1$ torr); this measurement is inconsistent with the observation of the FTIR spectrum of the vapour, as discussed below.

In order to provide further clarification of the reaction channels available to organoaluminium intermediates, trapping of the $(CH_3)_2Al$ radical with other species was investigated. By analogy with the fluoride formed as described above, it might be anticipated that the corresponding chloride would be formed in the presence of a suitable trap. Such a trap must be carefully chosen; the tendency of $(CH_3)_3Al$ to form adducts with almost any electron donor is very well established, and the formation of such adducts would obscure the course of reaction. For this reason, CCl_4 was selected; this is of interest in its own right, since free radicals have been implicated in the explosive reaction of $(CH_3)_3Al$ with CCl_4 [17]. This latter species was found to be thermally stable under the conditions of our experiments (laser power of 5 W), and there is no evidence of adduct formation from the IR spectrum of $(CH_3)_3Al/CCl_4$ mixtures. With a $(CH_3)_3Al/CCl_4$ ratio of 1/1, the spectra of Fig. 4 were obtained. The changes are readily assignable to almost quantitative conversion of $(CH_3)_3Al + CCl_4$ into $(CH_3)_2AlCl$ and CH_4. In this case, the FTIR and Raman spectra of the $(CH_3)_2AlCl$ product (isolated in the manner described above for $(CH_3)_2AlF$ are in complete agreement with those reported by Hoffmann [18]. The ^1H NMR spectrum of the isolated product showed a single broad peak at -0.276 ppm (cf. -0.32 ppm measured by Hoffmann [19]), with traces assignable to the dichlorinated product $(CH_3)AlCl_2$ and to $(CH_3)_2AlF$. Irradiation at higher powers, or for extended periods, led to conversion of the $(CH_3)_2AlCl$ into CH_4 and a solid, presumably C-containing $AlCl_3$. In this case, addition of H_2 had little effect on the course of reaction, indicating that the reaction of the $(CH_3)_2Al$ radical with CCl_4 must be faster than any reaction with H_2. The $(CH_3)_2AlCl$ product was also

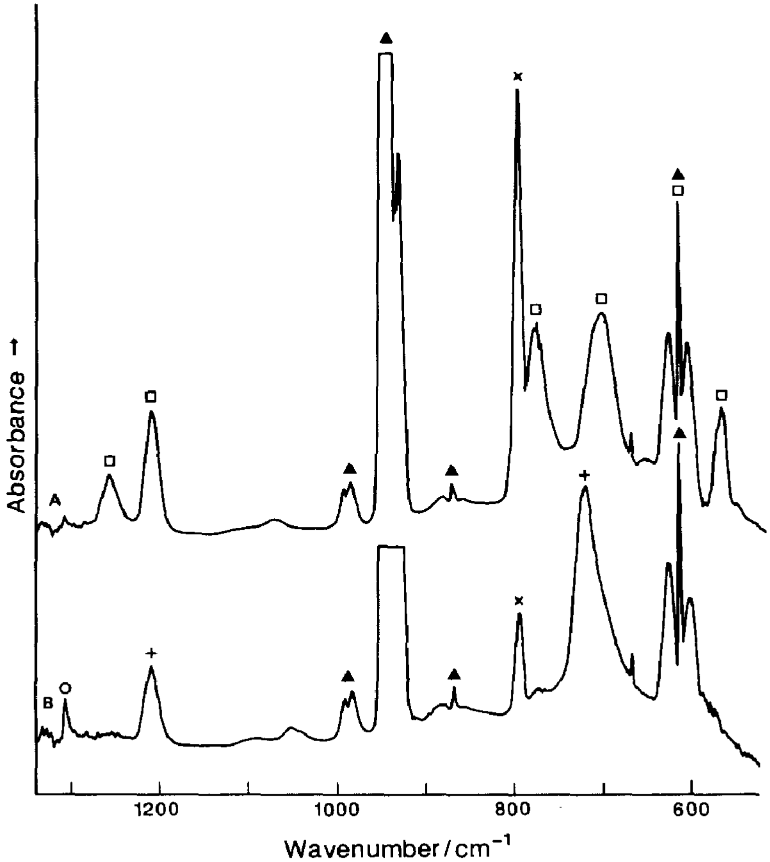

Fig. 4. FTIR spectra showing LPHP of $SF_6+CCl_4+(CH_3)_3Al$ mixtures. 10 torr SF_6 + 2 torr CCl_4 + 2 torr $(CH_3)_3Al$ subjected to 5 W IR laser power for 3.5 min; A; before irradiation, B: after irradiation. ▲, SF_6; □, $(CH_3)_3Al$; ○, CH_4; ×, CCl_4; +, $(CH_3)_2AlCl$.

observed in the presence of other chlorides, such as $CHCl_3$, although other unidentified products were also found.

Finally, extensive kinetic measurements were carried out on all three systems ($(CH_3)_3Al+SF_6$, $(CH_3)_3Al+SF_6+CCl_4$, and $(CH_3)_3Al+SF_6+H_2$ or D_2). The results of these measurements will be reported elsewhere [15], but they do have a considerable bearing on the elucidation of the mechanism of the reaction, as described below.

Discussion

The spectroscopic observations clearly identify the condensate of the product formed in the $(CH_3)_3Al+SF_6$ system as $(CH_3)_2AlF$. As Table 1 shows, the IR and Raman spectra of the liquid are in very close agreement with those of Weidlein and Krieg [16]. The ^1H NMR spectrum is consistent with that of other $(CH_3)_2AlX$ compounds [20]; the observation of a splitting of 4.65 Hz (arising from the two equivalent bridging ^{19}F nuclei) in the presence of $(CH_3)_3Al$ was noted in passing earlier by Schmidbauer et al. in a report on the NMR spectra of the corresponding Ga systems [21]. The ^{19}F shift is comparable to that of -160 ± 1 ppm reported for $(C_2H_5)_2AlF$ [22]. The cryoscopic measurements confirm the degree of association as tetrameric (expected RMM = 304). The vapour pressure of the liquid is consistent with earlier reports, which would indicate a value of < 0.1 torr at room temperature [16,23]. However, this value would render the IR spectrum of the vapour almost completely undetectable; on the other hand, a comparison of the relative intensities of the terminal $\delta_{sym}(CH_3)$ vibrations of $(CH_3)_3Al$ (1208 cm^{-1}) and $(CH_3)_2AlF$ (1216 cm^{-1}), which are securely assigned and can reasonably be assumed to be of comparable strengths, indicates that the vapour pressure of the $(CH_3)_2AlF$ as formed initially in the vapour phase is at least 5 torr. Furthermore, there are some differences between the liquid and vapour phase spectra which are rather larger than can be accounted for by intermolecular interactions. In particular, the liquid phase peak at 551 cm^{-1}, which is assigned to the $\nu_{sym}(AlC_2)$ by Weidlein and Krieg [16], is absent in the vapour phase spectrum. This vibration is likely to be shifted by less than 20 cm^{-1} by intermolecular interactions if the corresponding asymmetric stretching frequencies at 726 cm^{-1} (liquid) and 740 cm^{-1} (vapour) are used as a guide. Its absence in the vapour phase spectrum must therefore be attributed to a considerably reduced oscillator strength in the form present in the vapour. It is of interest to compare the intensities of these vibrations in other $\{(CH_3)_2AlX\}_n$ species of well-established degrees of association. In the tetrameric $\{(CH_3)_2AlCN\}_4$, this vibration appears at 586 cm^{-1}, and is very strong [24], whereas in the trimeric $\{(CH_3)_2AlOCH_3\}_3$, it appears at 570 cm^{-1} and is weak [25].

We therefore conclude that the major product of the LPHP of the $SF_6 + (CH_3)_3Al$ system is $(CH_3)_2AlF$ vapour, probably in a trimeric (or possibly dimeric) form, and that it reverts to the tetrameric form on condensation over a period of a few hours at lower temperatures. There is certainly no evidence of any further chemical reaction in the system either on condensation or in the liquid over this period from the NMR spectra, and isomeric changes are also ruled out by the close similarity of the major portion of the IR spectra. The formation of the trimer in the LPHP process can be ascribed to the increased significance of the entropy contribution in determining the preferred form at higher temperature, since the enthalpies of formation of the two oligomers are likely to be very similar. This observation has a precendent in the corresponding Ga system, in which the trimer formed at room temperature is converted into the tetramer over a period of 2–3 weeks when stored at 5–15 °C [8].

In the $SF_6 + (CH_3)_3Al + CCl_4$ system, the major product is clearly identified as $(CH_3)_2AlCl$. The rate of formation is slightly greater than that of $(CH_3)_2AlF$ (but see below), implying a somewhat lower activation energy for the abstraction reaction, as expected. In the liquid phase, the reaction of $(CH_3)_3Al$ and CCl_4 is well-known to be potentially explosive [17]; our results strongly support the contention that free radicals are involved, although we have observed no evidence of chain reaction in the gas phase.

These observations may be rationalised in the reaction scheme below:

$$(CH_3)_3Al \rightarrow (CH_3)_2Al + CH_3 \quad (1)$$

$$CH_3 + (CH_3)_3Al \rightarrow CH_4 + (CH_3)_2AlCH_2 \quad (2)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \quad (3)$$

$$(CH_3)_2Al + SF_6 \rightarrow (CH_3)_2AlF + SF_5 \quad (4)$$

$$(CH_3)_3Al + CCl_4 \rightarrow (CH_3)_2AlCl + CCl_3 \quad (5)$$

$$(CH_3)_2Al \rightarrow (CH_3)Al + CH_3 \quad (6)$$

At the temperatures used in this study SF_6 and CCl_4 are thermally stable, and cannot therefore initiate reaction. Further, at the temperature of the reaction, the $(CH_3)_3Al$ is largely in the form of monomer; this is confirmed by the observation of the FTIR spectrum in the presence of laser radiation in a cell fitted with additional windows for perpendicular viewing. Measurement of the rates of pyrolysis of $(CH_3)_3Al$ alone by other workers yield results comparable to those observed in our system [6,7]; thus $(CH_3)_3Al$-initiated reactions must play a significant part (at least) in the overall process. Furthermore, under identical conditions, the rate of disappearance of $(CH_3)_3Al$ is virtually identical in the presence of SF_6 alone, in the $SF_6 + CCl_4$ system, and in the presence of added H_2 or D_2, despite the fact that very different products are observed in the three systems. This observation strongly suggests that the initial (and rate-determining) step involves $(CH_3)_3Al$ alone. This is in keeping with precedent; there is little evidence for direct bimolecular reactions involving SF_6 and stable species, but considerable evidence for abstraction of fluorine from SF_6 by free radicals, especially those centred on metalloids. Thus metal atoms yield fluorides, and silyl radicals produce silyl fluorides [26]. Further evidence against a bimolecular initiation step is provided by the failure to observe $(CH_3)_2AlF$ at low temperatures; this must arise from a considerable activation energy associated with the F-abstraction step (eq. 4).

Methyl radicals have been observed directly in the pyrolysis of $(CH_3)_3Al$ by Sqire et al. [27]. Thus there are considerable indications that the initial step in the reaction is loss of a methyl radical from $(CH_3)_3Al$ (eq. 1). The subsequent fate of the methyl radicals is not clear, but probably involves abstraction of hydrogen from $(CH_3)_3Al$ to yield the observed CH_4 (eq. 2), or recombination to yield ethane (eq. 3). In our experiments, no ethane is observed, ruling out eq. 3 as a major loss process. There are two likely paths open to the $(CH_3)_2Al$ radical: abstraction from SF_6 (eq. 4) or CCl_4 (eq. 5), or loss of a further methyl group (eq. 6). Presumably the latter (or some similar process, such as direct elimination of CH_4) results in the eventual deposition of the carbon-containing Al observed in this and other studies [7].

We believe this to be the first convincing verification of the reaction 1 as the initial step in the homogeneous pyrolysis of $(CH_3)_3Al$ (as opposed, for example, to direct β-elimination of CH_4 with formation of a π-bonded Al=C species), and of the central rôle played by the $(CH_3)_2Al$ radical. The observations suggest that the $(CH_3)_2Al$ is the predominant short-lived aluminium species in this system. This has been found to be the case in the pyrolysis of other Group III trimethyls, and suggests that loss of a second methyl group has a higher activation energy. Furthermore, as shown elsewhere, measurement of the rate of appearance of the trapped species can provide a straightforward determination of the kinetic parameters of this initiation step [15]. The results of this work confirm that the technique of LPHP can provide mechanistic information not easily accessible using other methods. Finally, the results presented here also have synthetic implications; the small scale apparatus described above can easily be adapted to a preparative scale, as has been demonstrated by Bristow et al. [10], and this may provide a convenient route to novel $(CH_3)_2AlX$ compounds.

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