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MECHANISM OF THERMOLYSIS OF TETRAMETHYLAMMONIUM µ-CHLOROBIS(TRIETHYLALUMINATE)

JOHN E. BOZIK, DAVID L. BEACH * and JAMES J. HARRISON *

Gulf Research and Development Company, P.O. Drawer 2038, Pittsburgh, PA 15230 (U.S.A.)

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Summary

The thermolysis of tetramethylammonium μ-chlorobis(triethylaluminate) has been investigated. In addition to the previously reported products, $[Me_4N]$-$[Cl{-}AlEt_3]$ and $(AlEt_3)_2$, $Me_3N \cdot AlEt_3$ is formed simultaneously in lesser amounts. A mechanism for the observed thermolysis reactions is presented which predicts formation of methyl chloride as a transient species which undergoes further reaction with $(AlEt_3)_2$ to ultimately produce methane and ethylene. The experimentally observed methane/ethylene ratio supports the proposed mechanism.

Introduction

Lewis base adducts of electron-deficient main group organometallic compounds constitute a broad, well-known group of complexes. An interesting, sub-class of this group is defined by the reaction products of alkylaluminum compounds with alkali metal halides, originally reported by Ziegler in 1960 [1], equations (1) and (2):

$$MX + 1/2(R_3Al)_2 \rightarrow M(R_3Al{-}X) \qquad (1)$$

$$M(R_3Al{-}X) + 1/2(R_3Al)_2 \rightarrow M(R_3Al{-}X{-}AlR_3) \qquad (2)$$

The unusual nature of these complexes is exemplified by the reaction products obtained from excess trimethylaluminum and triethylaluminum with potassium fluoride. The crystal structure determinations of the complexes isolated show colinear Al—F—Al bonds (bond angle 180°) with Al—F bond lengths of 1.782 Å for the trimethylaluminum complex [2] and 1.820 Å for the triethylaluminum complex [3]. These data have been interpreted in terms of π-bonding between filled fluorine $2p_y$ and $2p_z$ orbitals and vacant aluminum

3d orbitals [3]. Further interest in these complexes arises from their ability to "trap" aromatic molecules, forming liquid clathrates [4].

Recent reports have discussed the reactions of trimethylaluminum with a variety of alkali and pseudoalkali metal halides and pseudohalides [4—15]. The chemistry of these adducts has been described, including thermal behavior [12, 15,16] and the reversibility of equation (2) [11,13,14].

During the course of our investigations into reactions of alkylaluminum compounds with pseudoalkali metal halides, we discovered an unexpected thermal reaction of tetramethylammonium μ-chlorobis(triethylaluminate). We report herein the results of these investigations along with mechanistic information concerning the thermal disproportionation/decomposition of this Lewis acid-base complex.

Results and discussion

Triethylaluminum (TEA) reacts with tetramethylammonium chloride in equimolar amounts to yield the 1/1 complex (I), shown in equation (3).

$$1/2(\mathrm{Et_3Al})_2 + \mathrm{Me_4NCl} \rightarrow \underset{\text{(I)}}{(\mathrm{Me_4N})(\mathrm{Cl{-}AlEt_3})} \tag{3}$$

In the presence of an excess of TEA, the 1/1 complex forms a 2/1 TEA complex (II), equation (4).

$$\mathrm{I} + 1/2(\mathrm{Et_3Al})_2 \rightarrow \underset{\text{(II)}}{(\mathrm{Me_4N})(\mathrm{Et_3Al{-}Cl{-}AlEt_3})} \tag{4}$$

We have found that the latter reaction is thermally reversible but does not cleanly yield the starting reactants. Thermal degradation of II, yielding a thermally stable trimethylamine TEA adduct (III), equation (5), occurs simultaneously with the reverse of equation (4). It is not possible to avoid formation of III by using lower disproportionation temperatures.

$$\underset{\text{(II)}}{(\mathrm{Me_4N})(\mathrm{Et_3Al{-}Cl{-}AlEt_3})} \xrightarrow{\Delta} \underset{\text{(III)}}{\mathrm{Me_3N \cdot AlEt_3}} \tag{5}$$

These results indicate that the thermal behavior of II is not as simple as previously thought and represent the first example of formation of a neutral amine-trialkylaluminum adduct from an ionic tetraalkylammonium halide-trialkylaluminum complex. The behavior of II complements that reported for an analogous complex, $[\mathrm{N(CH_3)_4}]\,[\mathrm{Al(CH_3)_3I}]$, which yields on thermolysis at 280°C the amine-dialkylaluminum halide adduct $(\mathrm{CH_3})_3\mathrm{N} \cdot \mathrm{Al(CH_3)_2I}$ [12].

Thermolysis of II

Thermolysis of II was initially effected at a pressure of 20—30 mmHg. The temperature was gradually increased to 200°C and TEA and other volatiles distilled into a receiver. These were analyzed for Al, Cl, and N and, by ^{1}H NMR spectroscopy. At 90% recovery of the theoretical quantity of TEA (calculated as $\mathrm{AlEt_3}$ monomer), integration of appropriate resonances in the NMR spectrum indicated the presence of 21 mol % III. Elemental analyses for Al and N indicated the presence of 20 mol % III, in good agreement with the NMR results. These analyses are reported in Table 1 and serve as an indication of the practicality of using NMR spectroscopy as a routine analytical tool in our investigations.

In the solution ^{1}H NMR spectrum of III the magnetically equivalent methyl groups give rise to a singlet at $\delta = 2.02$ ppm. This resonance allows integrations of relative amounts of III and TEA in spite of the fact that the more complex multiplet signals from the aluminum ethyl groups have overlapping chemical shifts. Moreover, it is possible to qualitatively observe the presence of III in the presence of TEA by noting that the quartet from the methylene group in triethylaluminum appears upfield from tetramethylsilane ($\delta = -0.07$ ppm). Quantitative analysis was achieved by integrations of the $N-CH_3$ signal and $Al-CH_2$ signal. Pertinent ^{1}H NMR data are reported in Table 2.

The presence of III was confirmed by an independent synthesis of this adduct from trimethylamine and TEA. The ^{1}H NMR spectrum of this material was identical to that present in the TEA distillate from the previously described experiment. The boiling point of III was determined to be 71°C at 2 mmHg; pure TEA boils at 70°C at 2 mmHg [17]. These data are consistent with our previous observations that under the conditions used for thermolysis of II, free TEA and III codistill.

Hydrolysis and subsequent elemental analysis of the residue from thermolysis of II showed it to be deficient in nitrogen from that expected for I. This is wholly consistent with the presence of ca. 20% III in the distillate (Table 1).

Similar experiments on the thermal behavior of II were conducted by gradually heating the complex under higher vacuum. The primary purposes of these experiments were: (a) to determine if a lower pressure in the system would yield a greater amount of TEA relative to III at lower temperature; (b) to col-

TABLE 1

RESULTS OF ANALYSIS OF COMPOUNDS FROM THERMOLYSIS OF II AT 20 mmHg

Distillate

Weight %			Mole %		^{1}H NMR Analysis Mole %	
Al [a]	N [b]	Cl [c]	TEA	Adduct III	TEA	Adduct III
0.177	0.016	0.0017	80.0	20.0	79.0	21.0

Residue

	Weight %		
	Al	N	Cl
Found	0.12	0.047	0.14
Calculated for I	0.12	0.066	0.17

[a] Atomic absorption spectroscopy. [b] Kjeldahl determination. [c] Determined gravimetrically by titration with $AgNO_3$.

TABLE 2

^{1}H NMR DATA FOR THE COMPLEXES I AND II AND THE ADDUCT III [a]

Compounds	δ (ppm)	Multiplicity [b]	Assignment [c]
$[\mathrm{NMe_4}]^+[\mathrm{Et_3Al{-}Cl{-}AlEt_3}]^-$	0.05	quartet	$-\mathrm{CH_2}-$
	1.32	triplet	$-\mathrm{CH_3}$ (Al)
	2.17	singlet	$-\mathrm{CH_3}$ (N)
$[\mathrm{NMe_4}]^+[\mathrm{Et_3Al{-}Cl}]^-$	0.12	quartet	$-\mathrm{CH_2}-$
	1.35	triplet	$-\mathrm{CH_3}$ (Al)
	2.28	singlet	$-\mathrm{CH_3}$ (N)
$(\mathrm{AlEt_3})_2$	0.32	quartet	$-\mathrm{CH_2}-$
	1.08	triplet	$-\mathrm{CH_3}$
$\mathrm{Me_3N{:}AlEt_3}$	-0.07	quartet	$-\mathrm{CH_2}-$
	1.18	triplet	$-\mathrm{CH_3}$ (Al)
	2.02	singlet	$-\mathrm{CH_3}$ (N)

[a] Recorded in benzene-d_6 with tetramethylsilane as internal standard. [b] Additional fine structure was observed for all alkylaluminum resonances [23,24]. In all cases $J \approx 8$ Hz. [c] Based on chemical shifts, multiplicities, and relative intensities.

lect the distillate in several fractions to determine if III was formed simultaneously with free TEA, or only at higher, prolonged pot temperatures; and (c) to check the reproducibility of the final III to TEA ratio observed. The ^{1}H NMR spectra of the first and fourth fractions obtained from thermolysis at 2 mmHg indicated the presence of III in both samples, suggesting that it is formed concurrently with TEA, even at low conversions. (The first fraction represented approximately 20% conversion based on the theoretical amount of TEA).

Use of an even higher vacuum, 0.4 mmHg, in the thermolysis of II and subsequent fractional collection and ^{1}H NMR analysis of the distillate confirmed previous results. The data suggest that under conditions of higher vacuum using the minimum temperature necessary to effect TEA recovery via distillation, III is formed even at low conversions. These results are summarized in Table 3. A comparison of the analytical techniques utilized for these analyses is also reported (Table 4) and further confirms the utility of NMR analysis.

We anticipated that $\mathrm{Et_2AlCl}$ or $\mathrm{EtAlCl_2}$ would be found in the distillate if formed as end products under our thermolysis conditions. However, analysis of the "overhead" materials indicated the absence of chloride, eliminating these

TABLE 3

RESULTS OF ^{1}H NMR ANALYSIS OF DISTILLATE FROM THERMOLYSIS OF $[\mathrm{NMe_4}]^+[\mathrm{Et_3AlClAlEt_3}]^-$ COMPLEX AT 0.4 mmHg

Fraction	Temperature (°C)	Total conversion (%) [a]	TEA (mol%)	Adduct III (mol%)
1	131—174	25	94.7	5.3
2	174—186	50	80.3	19.7
3	186—199	75	78.2	21.8
4	199—218	95	88.9	11.1

[a] Approximate.

TABLE 4

COMPARISON OF ANALYTICAL METHODS USED FOR DISTILLATE FROM THERMOLYSIS OF $[NMe_4]^+[Et_3AlClAlEt_3]^-$ COMPLEX AT 0.4 mm Hg

Fraction	Proton NMR		Atomic absorption (aluminum)	
	Mol % TEA	Mol % III	Mol % TEA	Mol % III
1	94.7	5.3	92.9	7.1
2	80.3	19.7	80.0	20.0
3	78.2	21.8	75.0	25.0
4	88.9	11.1	87.5	12.5

alkylaluminum halides from consideration as possible thermolysis end byproducts.

Thermolysis experiments were additionally performed in evacuated glass bombs in order to analyze total gases evolved. The composition of the thermolysis gases from II as a function of temperature from 130—190°C are reported in Table 5. The most striking aspect of these data is the relatively large amount of methane which is observed. Methane is reportedly produced in only trace amounts during pyrolysis of TEA [18] and this is substantiated by our work (Table 6). The C-2, C-4, and C-6 species present in the thermolysis gases from II are also observed during thermolysis of TEA (Table 6). The C-4 and C-6 species result from dimerization and trimerization, respectively, of liberated ethylene. Other organic species, e.g. methyl or ethyl chloride, were not detected.

The data obtained at 130°C (Table 5) appear anomalous when compared to data at the higher temperatures. Specifically, the relative mole percent of methane is low, while the quantity of ethane is unexpectedly high. We attribute this result to the low total conversion; since the absolute quantities of gases at this stage in the thermolysis are small, normalization to relative mole percentages yields numbers which may be misleading.

Physical properties of III

The trimethylamine-triethylaluminum adduct is a colorless liquid, highly

TABLE 5

DATA FROM VACUUM THERMOLYSIS OF $[NMe_4]^+[Et_3AlClAlEt_3]^-$

Component (mol %)	Temperature (°C)						
	130	140	150	160	170	180	190
Methane	11.3	32.4	47.9	46.6	52.9	55.8	68.1
Ethylene	6.4	14.5	14.8	14.1	14.2	14.2	8.9
Ethane	73.5	13.8	10.3	9.1	6.4	5.4	5.2
Propylene	0	0.7	1.2	0.8	0.8	0.8	0.5
Propane	0	0	0	trace	trace	trace	trace
1-Butene	6.1	35.7	24.0	27.7	24.1	21.6	12.3
Other C-4	2.7	1.1	0.6	0.4	0.2	0.5	2.1
Total C-5	0	0.1	0.1	0.1	0.1	0.1	0.2
Total C-6	0	1.7	1.1	1.2	1.3	1.6	2.7

TABLE 6

DATA FROM VACUUM THERMOLYSIS OF TRIETHYLALUMINUM

Component	Temperature (°C)						
(mol %)	130	140	150	160	170	180	190
Methane	0	0.6	0.5	0.3	0.3	0.2	0.1
Ethylene	10.8	11.9	15.4	16.8	9.2	9.6	3.5
Ethane	61.3	54.4	49.8	46.5	52.5	45.8	48.7
Propylene	trace	0.7	0.9	0.8	0.4	0.4	0.1
Propane	trace	0.1	0.2	0.1	0.1	0.1	0.1
1-Butene	14.2	23.4	25.7	24.4	15.7	17.3	22.2
Other C-4	13.1	7.8	5.7	7.6	16.2	19.4	17.1
Total C-5	0.4	0.1	0.1	0.3	0.3	0.4	0.6
Total C-6	0.4	0.9	1.6	3.2	5.2	6.8	7.5

soluble in hydrocarbon solvents. Its boiling point was determined as 71°C (2 mmHg) and it is totally miscible with TEA at all concentrations. Separation of III and TEA via fractional distillation was not attempted, because of the very small (ca. 1°) difference in boiling points.

The adduct exhibits relatively high chemical and thermal stabilities and is unreactive toward methyl chloride in the presence of excess TEA, even at elevated temperatures (110°C). It is, therefore, not possible to regenerate either 1/1 or 2/1 tetramethylammonium-TEA complexes from III and CH_3Cl under one atmosphere CH_3Cl.

The thermal stability of the adduct is sufficiently high that temperatures necessary to free the complexed TEA decompose the TEA itself.

Comments on thermolysis mechanism

The production of III simultaneously with the thermal disproportionation reaction of II is the first example of formation of a neutral nonhalide containing amine-alkylaluminum adduct from the thermolysis reaction(s) of a 2/1 TEA-MX complex. The methane observed in the thermolysis gases may arise from CH_3Cl which is produced initially with III.

$$\underset{(II)}{(Me_4N)(Et_3Al{-}Cl{-}AlEt_3)} \rightarrow \underset{(I)}{(Me_4N)(AlEt_3Cl)} + 1/2(Et_3Al)_2$$

$$\longrightarrow \underset{(III)}{Me_3N \cdot AlEt_3} + CH_3Cl$$

Sampling of gases during the thermolysis reaction and analysis by gas chromatography and mass spectrometry showed the absence of CH_3Cl, CH_3CH_2Cl, HCl, and Cl_2. This is not surprising, since alkylaluminums are known to react with HX to form AlX_3 and alkanes, with halogens to produce alkylaluminum halides and alkyl halides, and with alkyl halides to produce alkanes or olefins (through dehydrohalogenation) [19]. Analyses of the gases evolved during thermolysis of II lend support to a mechanism which predicts formation of CH_3Cl. This species, however, would not be detected directly because of subsequent reaction according to equations (6) through (8).

$$CH_3Cl + Et_3Al \xrightarrow{k_1} CH_4 + C_2H_4 + Et_2AlCl \qquad (6)$$

TABLE 7

"EXCESS" [a] ETHYLENE FROM THERMOLYSIS OF $[NMe_4]^+[Et_3AlClAlEt_3]^-$ (II)

	Temperature (°C)			
	150	160	170	180
Total ethylene derived olefins from TEA thermolysis (mol %) [c]	83.0	90.4	88.6	103.4
Ethylene/ethane ratio from TEA thermolysis [d]	1.67	1.94	1.69	2.26
Ethylene predicted from TEA during thermolysis of II (mol %) [e]	17.2	17.7	10.8	12.2
"Excess" ethylene (mol %) [f]	50.1	56.2	55.9	51.0
Methane observed in thermolysis of II (mol %) [g]	47.4	46.3	52.6	55.6

[a] Based on mechanism discussed in text. [b] The 130°C and 140°C points have been omitted because of the inherent inaccuracy in numbers based on very low thermolysis conversions. The 190°C data have also been omitted because unreliable conclusions result from an additional decomposition pathway at this temperature, i.e. TEA decomposition to metallic aluminum and hydrogen [18]. [c] Σ[(Mol % ethylene) + (Mol % C-4 × 2) + (Mol % C-6 × 3)]. [d] Total ethylene-products/ethane (from Table 6). [e] Ethane (from Table 5) × (ethylene/ethane ratio). [f] Total ethylene-derived olefins (c) (Table 5) — ethylene predicted. [g] Methane (Table 5) — methane (Table 6), assuming one mol of ethylene is produced per mol of methane (discussion of mechanism in text).

$$CH_3Cl + Et_2AlCl \xrightarrow{k_2} CH_4 + C_2H_4 + EtAlCl_2 \qquad (7)$$

$$CH_3Cl + EtAlCl_2 \xrightarrow{k_3} CH_4 + C_2H_4 + AlCl_3 \qquad (8)$$

with $k_3 > k_2 > k_1$, based on relative rates of reaction of $RAlCl_2 > R_2AlCl > R_3Al$ with alkyl halides [20]. This explains the absence of Et_2AlCl and $EtAlCl_2$ in our reaction mixture as well. (We have not attempted to identify $AlCl_3$.)

The decomposition of II may proceed through nucleophilic attack of chloride ion on an N—CH_3 group to produce methyl chloride, trimethylamine, and TEA. We have made no attempt to determine whether attack of chloride involves free Cl^-, $(Et_3Al—Cl)^-$, or $(Et_3Al—Cl—AlEt_3)^-$. However, the presence of free Cl^- in a solution of TEA is highly unlikely and given the expected increased nucleophilicity of $(Et_3Al—Cl)^-$ over $(Et_3Al—Cl—AlEt_3)^-$, we favor attack by the 1/1 TEA—Cl anion. The resulting trimethylamine formed rapidly reacts with TEA to form the observed adduct.

This mechanistic model predicts that one mole of ethylene will be produced with each mole of methane. This prediction has been verified experimentally by determining the amount of total ethylene * produced in excess of that derived from TEA decomposition. From Table 7 we see that pure TEA produces an ethylene/ethane ratio of 1.67 to 2.26 at temperatures of 150° to 180°C. The "excess" ethylene produced during the thermolysis of II can be estimated to a first approximation by subtracting the contribution TEA has on the total ethylene produced.

$$\text{"Excess" ethylene} = \text{ethylene observed} - \text{ethane observed} \times \frac{\text{ethylene}}{\text{ethane}}$$

We are aware that the ethylene/ethane ratio may not be constant with time

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* See footnote *c* in Table 7.

[18]. However, our data for each temperature were obtained by sampling the reaction which had been held at that temperature for one hour. Methane production from pyrolysis of TEA, although small ($\leqslant$0.6 mol %), was also subtracted from the methane observed in the pyrolysis of II. We find that within experimental error, in the temperature range 150—180° C, one mole of ethylene is produced per mole of methane * in support of our proposed mechanism.

Experimental

Equipment and reagents

All crucial manipulations of alkylaluminum species were performed in a Vacuum Atmospheres glove box containing a purified nitrogen atmosphere, where oxygen and water levels were continuously monitored and maintained at <2 ppm and <1 ppm, respectively. Those experiments which involved manipulations sufficiently complex or difficult to preclude the use of the glove box, were performed using a Schlenk line and argon purified by passage through a drying agent and oxygen scavenger of hydrogen-reduced BASF R3-11 catalyst. Preparation of samples for critical NMR experiments was accomplished on a vacuum line and NMR tubes immersed in liquid nitrogen and sealed off with a torch. All solvents were purified by distillation from lithium aluminum hydride or sodium benzophenone ketyl under purified argon. In the case of vacuum line manipulations using deuterated solvents, they were purified by repeated freeze-pump-thaw cycles and subsequent trap-to-trap distillation.

In the initial stages of our work with tetramethylammonium chloride complexes of TEA, we were concerned that commercially obtained samples of tetramethylammonium chloride might contain trapped trimethylamine. Therefore, appropriate precautions were taken and control experiments performed to ensure that the TMA · TEA adduct was formed directly from thermal decomposition of the 2/1 complex, and not as a result of the reaction between TEA and free trimethylamine. The tetramethylammonium salt was routinely dried for at least 16 h in a vacuum oven at 125° C and then repeatedly degassed by applying vacuums of $<10^{-3}$ mmHg, backpressuring with purified nitrogen (<1 ppm H_2O, <2 ppm O_2) each time. The purified tetramethylammonium chloride was stored in a Vacuum Atmospheres glove box until needed.

Analyses of gases from vacuum thermolysis experiments were made with a Varian 3700 gas chromatograph utilizing a 14 ft × 1/8 in SS column packed with 60/80 mesh Chromosorb 102. Column temperature was programmed from 60—180° C at 10° C min^{-1}. Integration of peaks was performed automatically via interfacing with a Perkin-Elmer PEP-II Digital Integrator. Areas under curves were then divided by the relative response value for each compound based on molecular weight and detector response giving a true response value. These values were normalized to yield the relative mole percent of each component [21] (Tables 5 and 6).

Additional analyses of these gas samples by mass spectrometry did not reveal the presence of alkyl chlorides, HCl, or Cl_2.

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* The coproduction of small quantities of either HCl or Cl_2 cannot be rigorously excluded with our data.

NMR spectra were recorded on a Varian T-60 instrument using tetramethylsilane as internal standard.

Chemical analyses of all alkylaluminum-containing materials, unless otherwise indicated, were performed by hydrolyzing one cm^3 samples with 0.5 *N* H_2SO_4, and analyzing for Al, N, and Cl, by atomic absorption spectroscopy (Perkin-Elmer 403 instrument), Kjeldahl method, and titration with $AgNO_3$, respectively.

Syntheses

Preparations of tetramethylammonium chloride-TEA complexes were performed inside the glove box and samples examined by ^1H NMR spectroscopy. They routinely showed the absence of II, based on chemical shift measurements obtained from authentic materials (Table 2). NMR spectra of samples of III either pure or in the presence of TEA, I or II indicated that III could be easily detected if present.

Synthesis of tetramethylammonium μ-chlorobis(triethylaluminate). Triethylaluminum (11.40 g, 100 mmol) was added in 1 cm^3 portions to $Me_4N^+Cl^-$ (10.95 g, 100 mmol) at room temperature. During the course of the addition, the temperature rose to 48° C, then slowly dropped to room temperature. The mixture was stirred for 2 h until a clear, semi-solid mass was formed. Additional Et_3Al (11.40 g, 100 mmol) was added giving $(NMe_4)(Et_3Al{-}Cl{-}AlEt_3)$ as a viscous liquid. Elemental analysis, (Galbraith Microanalytical Labs) found: C, 57.09; H, 12.02; N, 4.97. $C_{16}H_{42}Al_2ClN$ calcd.: C, 56.82; H, 12.53; N, 4.14%.

Synthesis of trimethylamine-triethylaluminum. Synthesis was performed by a modification of the literature procedure [22]. Trimethylamine (Air Products) was slowly bubbled through 15 cm^3 Et_3Al under an argon atmosphere for 2 h to give 18.63 g of clear, colorless liquid (b.p. 71°C at 2 mmHg).

Sealed tube vacuum thermolysis of tetramethylammonium μ-chlorobis(triethylaluminate). Approximately 5 cm^3 of the complex was placed in a heavy-walled glass reaction vessel (ca. 70 cm^3 capacity) equipped with a high vacuum stopcock and rubber septum. The tube was evacuated (10^{-3} mmHg), immersed in an oil bath, and heated from 130° to 190° C at 10° intervals. The tube was kept at each temperature for 1 h, after which a sample of the gas phase was removed using a gas-tight syringe for GC analysis. Gases obtained in this way are expected to also contain lesser amounts of TEA and III in the vapour phase. The TEA pyrolyzes in the injection port of the GC (400° C) to give mostly ethane and ethylene, while III dissociates to TEA and TMA, giving normal TEA decomposition products. We have observed that these pyrolyses contribute only a small fraction of the total gases produced at 130°—180° C.

Thermolysis of tetramethylammonium μ-chlorobis(triethylaluminate). A typical procedure is described. The title complex (33.8 g, 100 mmol) was vacuum-distilled at 0.4 mmHg and fractions collected at pot temperatures of 169—171° C (3.5 cm^3), 171—186° C (3.5 cm^3), 186—195° C (3.6 cm^3), and 195—218° C (3.0 cm^3).

References

1 K. Ziegler, R. Koster, H. Lehmkuhl and K. Reinert, Ann., 629 (1960) 33.
2 J.L. Atwood and W.R. Newberry, III, J. Organometal. Chem., 66 (1974) 15.
3 G. Allegra and G. Perego, Acta Cryst., 16 (1963) 185.
4 J.L. Atwood and J.D. Atwood, Adv. Chem. Ser., 150 (1976) 112.
5 J.L. Atwood, K.D. Crissinger and R.D. Rogers, J. Organometal. Chem., 155 (1978) 1.
6 J.L. Atwood, W.E. Hunter and K.D. Crissinger, J. Organometal. Chem., 127 (1977) 403.
7 J.L. Atwood and W.R. Newberry, III, J. Organometal. Chem., 87 (1975) 1.
8 J.L. Atwood and W.R. Newberry, III, J. Organometal. Chem., 65 (1974) 145.
9 J.L. Atwood and R.E. Cannon, J. Organometal. Chem., 47 (1973) 321.
10 J.L. Atwood and W.R. Newberry, III, J. Organometal. Chem., 42 (1972) C77.
11 F. Weller and K. Dehnicke, J. Organometal. Chem., 36 (1972) 23.
12 J.L. Atwood and P.A. Milton, J. Organometal. Chem., 36 (1972) C1.
13 F. Weller and K. Dehnicke, J. Organometal. Chem., 35 (1972) 237.
14 F. Weller, I.L. Wilson and K. Dehnicke, J. Organometal. Chem., 30 (1971) C1.
15 S.K. Seale and J.L. Atwood, J. Organometal. Chem., 73 (1974) 27.
16 J.L. Atwood and D.C. Hrncir, J. Organometal. Chem., 61 (1973) 43.
17 T. Mole and E.A. Jeffery, Organoaluminum Compounds, Elsevier, Amsterdam, 1972, p. 93.
18 W.L. Smith and T. Wartik, J. Inorg. Nucl. Chem., 29 (1967) 629.
19 T. Mole and E.A. Jeffery, Organoaluminum Compounds, Elsevier, Amsterdam, 1972, p. 349.
20 S. Pasynkiewicz and W. Kuran, J. Organometal. Chem., 16 (1969) 43.
21 W.A. Dietz, J. Gas Chromatogr., 5 (1967) 68.
22 F.M. Peters, B. Bartocha and A.J. Bilbo, Can. J. Chem., 41 (1963) 1051.
23 O. Yamamoto, Bull. Chem. Soc. Jap., 36 (1963) 1463.
24 O. Yamamoto, Bull. Chem. Soc. Jap., 37 (1964) 1125.