Thermal Decomposition of Primary and Secondary Amine Adducts of Triethylaluminium and Diethylaluminium Halides

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The stabilities of the adducts $Et_2XAl–NHMe_2$ and $Et_2XAl–NH_2Bu^t$ toward thermal elimination of ethane follow the order X = Et < Cl < Br < I. This order is correlated with i.r. and n.m.r. spectral data to show that adduct stability is principally a function of the negative charge density on the α-carbon atoms of the ethyl groups bonded to aluminium, and not a function of the nitrogen proton acidity. A discussion of the factors influencing the distribution of electron density in the Al–C bond is presented. A study of the thermal decomposition of $Et_2ClAl–NHMe_2$ shows that the reaction follows zero-order kinetics, indicating that it is predominantly surface catalysed.

ADDUCTS of organoaluminium compounds with primary or secondary amines decompose thermally to yield a saturated hydrocarbon and the corresponding aluminium amide according to equation (1). Significant differences

$$R^1{}_3Al–NHR^2{}_2 \longrightarrow R^1H + (R^1{}_2AlNR^2{}_2)_{2.3} \quad (1)$$

in the decomposition temperatures of the adducts are evident from the examples given in Tables 1—3, but so far no consistent rationalization for these differences has appeared in the literature. Previous workers have observed (a) that there is an increase in the thermal stability of the adducts as the number of alkyl groups bonded to aluminium decreases,[1,2] (b) that the lower thermal stability of aromatic amine adducts, compared with those of aliphatic amines, reflects the higher acidity of the nitrogen protons in the former cases,[2] and (c) that the higher stability of $Et_3Al–NH_2Bu^t$ compared to $Et_3Al–NH_2Me$ probably indicates steric hindrance to ethane formation.[3] This paper co-ordinates the study of adduct stability and specifically considers the adducts $Et_2XAl–NHMe_2$ (X = Et, Cl,[4] Br,[5] or I[6]) and $Et_2XAl–NH_2Bu^t$ [7] (X = Et, Cl, Br, or I). A general rationalization for the observed differences in adduct stability is presented which employs i.r. and ^1H n.m.r. data to correlate minimum decomposition temperatures with the electron distribution in crucial bonds in the molecules.

The mechanism of the adduct decomposition reaction has received a single mention in the literature [3] in which it was suggested that if steric effects are real, then the reaction is not unimolecular, but may involve two or more molecules. Here we report a kinetic study of the thermal decomposition of $Et_2ClAl–NHMe_2$ which, whilst not giving further information about the molecularity of the reaction, does show that it is surface catalysed.

RESULTS AND DISCUSSION

Adduct Stability.—A more detailed explanation of the relative thermal stabilities of organoaluminium–amine adducts requires a closer look at the reaction involved. Although the thermal decomposition of triethylaluminium has been shown [8] to proceed by a radical mechanism, leading to a variety of products, the quantitative formation of alkane and amide from the adduct decomposition, and the relatively low temperatures

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[6] K. Gosling and A. L. Bhuiyan, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 329.

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involved, indicate a molecular reaction in this case. Whatever the exact mechanism, the result is the cleavage of both N–H and Al–C bonds. The compounds specifically studied in this paper are typical examples of the 1 : 1 adducts formed between trialkylaluminiums or alkylaluminium halides, and the relatively strongly basic alkylamines.[9] There was no evidence to suggest that the adducts dissociate, and all could be purified by distillation, sublimation, or recrystallization. Similarly, the lack of any significant association was demonstrated by molecular weights determined cryoscopically from benzene solutions, and n.m.r. spectra which proved to be identical for the neat liquid adducts and carbon tetrachloride solutions of various concentrations. Additional information confirming the monomeric nature of this type of adduct has come from single crystal *X*-ray data for the related compounds Me_3Al–(quinuclidine) [10] and $Me_2IAl–NMe_3$,[11] which indicate that no abnormally close interactions exist which might suggest specific monomer association. With this evidence for the independent behaviour of the adduct molecules, it is justifiable to use data from physical measurements to gain a direct insight into the condition of the bonds in the adducts which are broken during thermal decomposition. Thus, the relative acidities of the NH protons can be estimated from the stretching frequencies in the i.r. spectra of the adducts where a decrease in the frequency would indicate a more acidic proton. The observed NH i.r. stretching frequencies of the adducts are sharp bands indicating that the lower frequencies are not due to hydrogen bonding effects. Another probe is the direct observation of the relative chemical shifts of the NH signals in the n.m.r. spectra of the adducts, where a downfield shift corresponds to a less shielded, more acidic, proton. It should be noted that the n.m.r. spectra of the adducts change drastically if aromatic solvents are used due to the formation of an adduct–solvent collision complex.[6] However, pure liquid adducts or carbon tetrachloride solutions give identical spectra, and in this work all spectra were recorded from such samples.

TABLE 1

Decomposition temperatures of Lewis base adducts of organoaluminium compounds

Adduct	Approx. minimum decomp. temp. (°C) [a]	Adduct	Approx. minimum decomp. temp. (°C) [a]
$Et_3Al–NH_3$ [b]	<0	$Et_3Al–NH_2Me$ [d]	0
$Et_2ClAl–NH_3$ [b]	<65	$Et_2ClAl–NH_2Me$ [e]	>50
$EtCl_2Al–NH_3$ [b]	<125	$EtCl_2Al–NH_2Me$ [e]	127
		$Me_3Al–NH_2Me$ [f]	55
$Et_3Al–NH_2Ph$ [c]	>-78	$[Me_3Al–OH_2]$ [f,g]	$\leqslant 0$
$Et_2ClAl–NH_2Ph$ [c]	25	$[Me_3Al–SH_2]$ [f,g]	<0
$EtCl_2Al–NH_2Ph$ [c]	120	$[Me_3Al–O(H)Me]$ [f,g]	<0

[a] The temperatures quoted in the literature should not be taken to be highly accurate as regards the initial onset of decomposition, but the differences between various compounds are sufficiently large to show general trends. [b] Ref. 1. [c] Ref. 2. [d] K. Gosling, J. D. Smith, and D. H. W. Wharmby, *J. Chem. Soc.* (*A*), 1969, 1738. [e] Ref. 4. [f] Work described by G. Bahr, F.I.A.T. Review of German Science, 1939—1945, Inorganic Chemistry, Part II, p. 155. [g] Adducts not isolated.

TABLE 2

Decomposition temperatures and spectral data for the adducts $Et_2XAl–NHMe_2$

X	Decomp. temp. (°C)	δ(NH) [a]	ν(NH)/cm^{-1} [b]	$\delta(AlCH_2CH_3)$	$\delta(AlCH_2CH_3)$	$\Delta(\delta CH_3 - \delta CH_2)$	χ
Et	90	2·73	3280	1·30	0·03	1·27	1·28
Cl	100	3·95	3220	1·43	0·32 [c]	1·11	1·38
Br	120	4·13	3213	1·53	0·48 [c]	1·05	1·42
I	140	4·32	3188	1·70	0·70 [c]	1·00	1·45

[a] Neat liquid. [b] Liquid film. [c] Average of two quartets.

TABLE 3

Decomposition temperatures and spectral data for the adducts $Et_2XAl–NH_2Bu^t$

X	Decomp. temp. (°C)	δ(NH)	ν(a-NH), ν(e-NH)/cm^{-1}	$\delta(AlCH_2CH_3)$	$\delta(AlCH_2CH_3)$	$\Delta(\delta CH_3 - \delta CH_2)$	χ
Et	90	2·77 [a]	3297,[b] 3247	1·33 [a]	0·09 [a]	1·24	1·30
Cl	100	3·64 [c]	3230,[d] 3200	1·45 [c]	0·35 [c,e]	1·10	1·39
Br	120	4·07 [c]	3250,[d] 3210	1·62 [c]	0·57 [c,e]	1·05	1·42
I	~120	3·77 [c]	3224,[d] 3182	1·48 [c]	0·53 [c,e]	0·95	1·48

[a] Neat liquid. [b] Liquid film. [c] 10% CCl_4 solution. [d] Fluorolube mull. [e] Average of two quartets.

The Al–C bonds can be studied by observation of the relative chemical shifts of the $AlCH_2CH_3$ methylene

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[9] Ref. 3, chs. 2 and 4.

[10] C. D. Whitt, L. M. Parker, and J. L. Atwood, *J. Organometallic Chem.*, 1971, **32**, 291.

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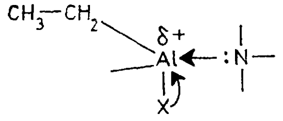
proton resonances in the n.m.r. spectra. This should be a useful measure of the relative negative charge densities at the α-carbon atoms of the ethyl groups. A downfield shift in the resonance frequency would indicate less shielded methylene protons, a lower negative charge density at the α-carbon atom, and a reduction in polarity of the Al–C bond. Similarly, an estimate of the electronegativities of the aluminium atoms in the adducts would provide useful information about the relative degrees of polarity of the Al–C bonds. Such an estimate can be obtained using the modified Dailey–Schoolery relationship,[12] $\chi = 0{\cdot}62\Delta + 2{\cdot}07$, where χ is the electronegativity of aluminium and Δ is the internal chemical shift ($\delta CH_3 - \delta CH_2$ in p.p.m.) of an ethyl group bonded to aluminium. This equation has previously [13,14] been applied successfully to ethylaluminium halides in order to estimate their relative Lewis acidities.

The adducts specifically studied here are Et_2XAl–$NHMe_2$ and Et_2XAl–NH_2Bu^t (X = Et, Cl, Br, or I) and in both series the stability with respect to thermal decomposition increases in the order Et < Cl < Br < I. The general consistency of the results (Tables 2 and 3) within these two series, suggests that the order of thermal stability can be explained satisfactorily on electronic grounds, and that any steric factors are either consistent or generally unimportant.

The following observations can be made from the data in Table 2 concerning the series Et_2XAl–$NHMe_2$. The NH stretching frequencies decrease down the series indicating that the nitrogen protons are becoming more acidic in the order Et < Cl < Br < I. Similarly, the increasing chemical shifts of the NH resonances in the n.m.r. spectra confirm this order. These results are in line with the order of increasing Lewis acidity of the diethylaluminium halides [13,14] and show that as the Lewis acidity of the aluminium atom increases, electron withdrawal from the nitrogen donor becomes more pronounced, and the nitrogen protons become more acidic. However, since the thermal stability of the adducts increases in the same order as the increasing acidic character of the nitrogen protons, it is evident that nitrogen proton acidity is not a controlling factor in adduct stability.

A direct study of the chemical shifts of the methylene protons of the ethyl groups bonded to aluminium, shows that there is a steady increase in value down the series, corresponding to a decrease in shielding in the order Et > Cl > Br > I. In turn this indicates that there is a decrease in the negative charge density associated with the α-carbon atoms of the ethyl groups in the same order, and suggests that the polarity of the $\overset{\delta+}{Al}$–$\overset{\delta-}{C}$ bond decreases down the series. Similarly, the calculated electronegativity values for the aluminium atoms increase in the order Et < Cl < Br < I, again suggesting that the polarity of the Al–C bond decreases down the series. It is apparent from Table 2 that this decrease in the Al–C bond polarity corresponds to an increase in the thermal stability of the adducts which suggests that it is the Al–C bond polarity, rather than the nitrogen proton acidity, which is the controlling factor in adduct stability. Thus the more stable adducts are those in which the α-carbon atoms of the ethyl groups carry a relatively small negative charge, and conversely, the less stable adducts are those in which the α-carbon atoms carry a well developed negative charge.

In order to explain the decreasing polarity of the Al–C bond in the series Et > Cl > Br > I, it is necessary to consider the individual electronic effects operating in the system (A). Upon replacing an ethyl group by a chlorine atom, the aluminium becomes a stronger Lewis acid through inductive electron withdrawal. In turn this leads to the following effects. (a) The nitrogen atom is encouraged to release more electron density to aluminium as shown by the increased acidity of the nitrogen proton by both i.r. and n.m.r. spectra. (b) Cl–Al, p_π–d_π Back-bonding is invoked to offset the inductive withdrawal of electron density. This is a reasonable postulate since the aluminium d orbitals would be expected to become lower in energy if the positive charge on aluminium increased. Evidence for this type of interaction comes from structural data acquired from single crystal X-ray studies or vapour phase electron diffraction work, and shows that the Al–Cl bond is significantly shorter than would be predicted from the sum of the appropriate covalent radii, 2·25 Å.[15] Thus in $(MeAlCl_2)_2$ [16] and $(AlCl_3)_2$,[17] the terminal Al–Cl bond lengths are 2·05 and 2·06 Å, respectively. Such back-bonding effects are reduced, but not eliminated, when a more efficient electron donor is bonded to aluminium as shown by the longer Al–Cl bond length found in Cl_3Al–NMe_3 (2·12 Å),[18] and $Na[AlCl_4]$ (2·13 Å).[19] (c) The α-carbon atoms of the ethyl group lose electron density to the aluminium atom, as shown by the increased chemical shift of the methylene protons in the n.m.r. spectrum. The overall result of these electron density shifts is to reduce the polarity of the Al–C bond and thus to reduce the negative charge on the



(A)

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[16] G. Allegra, G. Perego, and A. Immirzi, *Makromol. Chem.*, 1963, **61**, 69.

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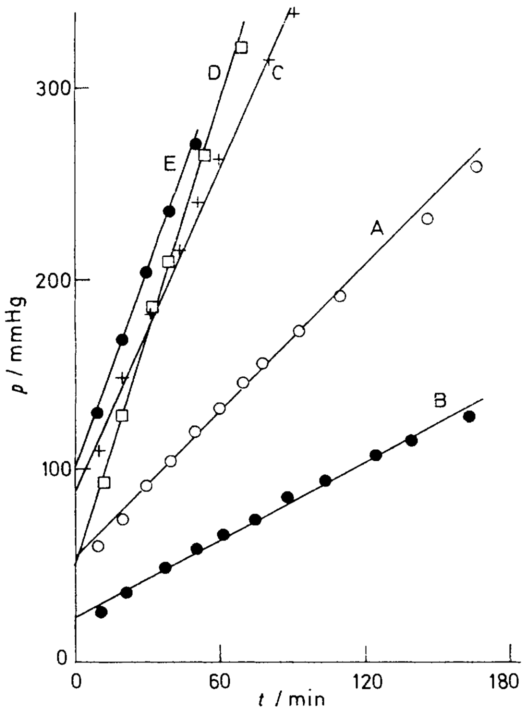
[19] N. C. Baenziger, *Acta Cryst.*, 1951, **4**, 216.

α-carbon atom of the ethyl group. In the series $Et_2XAl–NHMe_2$ (X = Cl, Br, and I) the decreasing ability of the halogen to back-bond to aluminium is shown by the smaller degree of bond shortening indicated from structural data. The Al–Br bond length given by the sum of the covalent radii is 2·40 Å, whereas in $(AlBr_3)_2$ [17] and $(Me_3SiOAlBr_2)_2$ [20] the terminal Al–Br bonds are 2·21 and 2·24 Å, respectively. By the same token, it is apparent that π back-bonding is virtually absent in the Al–I bond as shown by the terminal bond lengths in $(AlI_3)_2$ (2·53 Å) [17] and $Me_2IAl–NMe_3$ (2·58 Å),[11] which are close to the value of 2·59 Å predicted from the sum of the accepted covalent radii. This decrease in the back-bonding activity is apparent in the adducts under discussion in that the aluminium atom demands more electron density from the nitrogen donor, as shown by a further increase in the acidity of the nitrogen protons from the chloro- to iodo-substituted compounds. At the same time, the α-carbon atoms of the ethyl groups lose more electron density to the aluminium atom, as shown by a further downfield shift of the methylene proton resonance in the n.m.r. spectra. The overall result is to reduce the negative charge density on the α-carbon atom, thereby stabilizing the adduct toward thermal decomposition.

Table 3 shows i.r. and n.m.r. data for the series $Et_2XAl–NH_2Bu^t$. Again, the thermal stability increases generally in the order Et < Cl < Br < I. The n.m.r. data confirm the increasing acidity of the nitrogen protons and the decreasing negative charge density on the α-carbon atom of the ethyl groups in going from ethyl, to chloro-, to bromo-substituted adducts. Although it is possible to attribute the higher stability of $Et_3Al–NH_2Bu^t$, compared to $Et_3Al–NH_2Me$, to the greater donor ability of t-butylamine, there is insufficient evidence to rule out the steric hindrance to ethane elimination suggested by Mole and Jeffery.[3] The break in the trend in the measured spectral data for the iodo-compound, $Et_2IAl–NH_2Bu^t$, is apparently real and could be due to steric effects, in this the most crowded adduct, which prevent full donor interaction by the amine. However, it is interesting that the empirically calculated electronegativity for the aluminium atom follows the expected order.

In general, it is possible to account for the relative stabilities of various adducts of organoaluminium compounds with donors containing acidic protons in all cases where steric factors do not interfere. In this manner, relatively weak donors tend to reduce the negative charge density on the α-carbon atom of an organic group attached to aluminium, to only a small extent, thus leading to the low stability of adducts of H_2O, H_2S, ROH, RSH, and weakly basic amines. On the other hand, strong donors such as the more strongly basic amines reduce the negative charge density on the α-carbon atoms significantly, resulting in appreciably more stable adducts. Furthermore, the replacement of an organic group bonded to aluminium by a more electronegative atom again reduces the negative charge on a remaining α-carbon atom, thus stabilizing the adduct, but those atoms that are capable of effective π back-bonding to aluminium will generally not produce such a marked increase in stability.

From Table 1 it can be seen that the ethylaluminium compound, $Et_3Al–NH_2Me$, is appreciably less stable to alkane elimination than the corresponding methyl compound, $Me_3Al–NH_2Me$. The replacement of an electron-donating methyl group by a hydrogen atom results in a significantly lower negative charge density on the remaining carbon and, consistent with the arguments used so far, leads to the higher stability of the methylaluminium compounds.



Zero-order kinetic plots of the thermal decomposition of $Et_2ClAl–NHMe_2$: A Pyrex tube; B smaller sample than in A, in Pyrex tube; C crushed Pyrex capillary in Pyrex tube; D polypropylene tube; E Teflon covered stirring bar in Pyrex tube

Kinetics of the Thermal Decomposition of $Et_2ClAl–NHMe_2$.—In an attempt to understand the mechanism of thermal decomposition of the adducts discussed in the first part of this paper, a kinetic study of the decomposition of $Et_2ClAl–NHMe_2$ was undertaken. Since the reaction [equation (2)] occurs with the formation of ethane, the reaction was followed by observing

$$2Et_2ClAl–NHMe_2 \longrightarrow (EtClAlNMe_2)_2 + 2EtH \quad (2)$$

the pressure change in a closed system at constant temperature. Pressure–time data were obtained for various reaction conditions to at least 75% completion and plotted assuming first-, second-, and zero-order kinetics. Whereas the first- and second-order plots

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[20] M. Bonamico and G. Dessy, *J. Chem. Soc.* (*A*), 1967, 1786.

give distinctly curved lines, the zero-order plots (Figure) are straight suggesting that the decomposition of the adducts is surface catalysed. Line A represents the data for a pure sample in contact with a Pyrex tube. A decrease in sample size in the same tube led to a slower reaction (line B) corresponding to a decrease in the surface area in contact with the sample. Increasing the available surface significantly, through the addition of crushed Pyrex tubing, gave an appreciably faster reaction (line C) as would be anticipated for a surface-catalysed reaction. In order to determine whether sites on the Pyrex glass surface were specifically assisting the reaction, the glass reaction tube was replaced by one of similar dimensions machined from polypropylene. An increased reaction rate was observed (line D) indicating that the glass surface was not specific and also that the roughly machined polypropylene surface provided an increased surface area for the reaction. A similarly fast reaction was also observed (line E) when a Teflon covered magnetic stirring bar was added to the glass system.

The only conclusions that can be drawn from this study are that the decomposition is a molecular reaction which takes place predominantly at a solid surface and appears to be independent of the type of surface. It is notable that although the decomposition of triethylaluminium proceeds largely by a radical mechanism, it is also surface catalysed.[6] No deduction can be made at this time regarding the molecularity of the adduct decomposition reaction.

EXPERIMENTAL

Oxygen and moisture were excluded from all reactions by the usual techniques. I.r. spectra were recorded on a Beckman IR 12 spectrometer from liquid films or Nujol and Fluorolube mulls between CsBr plates, and n.m.r. spectra with a Varian T-60 instrument. Chemical shifts are reported relative to tetramethylsilane as external standard.

Preparation of Adducts.—$Et_3Al-NHMe_2$. Dimethylamine (28·4 mmol) was measured in the vacuum line and condensed on to a solution of triethylaluminium (3·24 g, 28·4 mmol) in dry n-hexane (15 ml) at −196°. The mixture was warmed slowly to room temperature and the solvent removed under vacuum. Triethylaluminium–dimethylamine distilled at 32—35° and 10^{-3} mmHg without decomposition as long as the bath temperature was kept below 75°, δ (60 MHz; neat) 2·77 (s, NCH_3), 2·73 (s, NH), 1·30 (t, $AlCH_2CH_3$), and 0·03 (q, $AlCH_2CH_3$, J 8·0 Hz).

The NCH_3 and NH resonance in the n.m.r. spectrum of neat $Et_3Al-NHMe_2$ appear as singlets separated by *ca.* 2·4 Hz. The assignments are supported unequivocally by integration. However, in the spectrum of a benzene solution, the NCH_3 resonance splits into a doublet and the NH resonance is broadened considerably, both being shifted upfield. The extent of the upfield shift and the magnitude of the coupling constant, $J(HN,CH_3)$, are dependent upon concentration. This observation is in contrast to the spectra of the neat compounds $Et_2XAl-NHMe_2$, where the NCH_3 resonance appears as the expected doublet and the NH resonance either as a broad peak or a discernible septet, with coupling constants, $J(HN,CH_3)$, decreasing in the series X = I, 6·04; Br, 6·00; Cl, 4·00 Hz. In benzene solutions, the spectra of these compounds show an upfield shift of all resonances which is most marked for the NH peak, and the observed coupling constants, $J(HN,CH_3)$, decrease to zero at high dilution. This behaviour has been explained [6] by the formation of collision complexes between the nitrogen protons and the aromatic solvent, which leads to the apparent magnetic equivalence of the NH and NCH_3 protons.

The lack of observable coupling at 60 MHz between the NH and NCH_3 protons in neat $Et_3Al-NHMe_2$ could be attributed to rapid nitrogen proton exchange. However, this seems unlikely since it was shown earlier that the nitrogen proton in this compound is the least acidic of the series $Et_2XAl-NHMe_2$ (X = Et, Cl, Br, or I), and yet all the halogen substituted compounds exhibit coupling between the NH and NCH_3 protons signifying a lack of exchange. More reasonable explanations may be (1) the deformation of the H–N–C angle in individual adduct molecules is sufficient to prevent effective coupling, or (2) intermolecular interactions lead to the apparent magnetic equivalence of these protons. The observation of coupling in the spectrum of a benzene solution would then be due either to (a) the modification of the H–N–C angle upon solvation, which then permits coupling, or (b) the breaking up of intermolecular interactions, and solvation of the monomers, which makes the NH and NCH_3 protons inequivalent and thus susceptible to coupling.

The i.r. spectrum of the neat liquid showed the following principal absorptions: 3280m, 3010m, 2902m, 2935s, 2905s, 2865vs, 2790m, 2715w, 1468m, 1407m, 1370w, 1265w, 1232w, 1215w, 1186m, 1117m, 1058vw, 1041w, 1018s, 982s, 947m, 893s, 820vw, 760vw, 637s, 498w, and 452w cm^{-1}.

$Et_2ClAl-NHMe_2$. This was prepared as previously described [4] and purified by distillation at 72° and 10^{-3} mmHg, δ (60 MHz; neat) 3·96br (NH), 2·93 (d, NCH_3, J 4·0 Hz), 1·43 (t, $AlCH_2CH_3$), and 0·33 and 0·31 (both) q, $AlCH_2CH_3$, J 8·0 Hz, $\nu_{max.}$ (neat) 3220m, 3110w, 3010w, 2990m, 2942s, 2905s, 2863vs, 2790m, 2730w, 2440vs, 1465s, 1452sh-m, 1436w, 1407m, 1372w, 1271m, 1221m, 1195m, 1112m, 1040m, 1019s, 988m, 951m, 918w, 889s, 815vw, 767w, 650vs, 625s, 596w, 550m, 480m, 420w, and 450m cm^{-1}.

$Et_2BrAl-NHMe_2$,[5] $Et_2IAl-NHMe_2$,[6] *and* $Et_2XAl-NH_2Bu^t$,[7] (X = Et, Cl, Br, *or* I). These were prepared as described in previous papers which also included all ^1H n.m.r. and i.r. data.

Thermal Decomposition of $Et_2ClAl-NHMe_2$.—The kinetic studies were carried out using a tensimeter similar in concept to that illustrated by Shriver.[21] A glass index on the inside of the sample limb of the manometer permitted the mercury level to be adjusted to the same point each time, ensuring that pressure readings were taken at constant volume. A Fischer and Porter Teflon and O ring seal joined the sample tube (Pyrex or polypropylene) to the tensimeter. Sample tubes were loaded with *ca.* 1 mmol of freshly distilled $Et_2ClAl-NHMe_2$ in the dry-box, capped, then taken to the tensimeter and attached under a flow of nitrogen. The tensimeter was evacuated and the mercury raised to contain the sample. A vigorously stirred oil-bath, maintained at 109·8 ± 0·1°, was raised to immerse

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[21] D. F. Shriver, 'The Manipulation of Air-sensitive Compounds,' McGraw-Hill, New York, 1969 p. 60.

the tensimeter completely, and as soon as the temperature was constant, pressure readings were taken at timed intervals until the reaction was at least 75% complete. Pressure–time data are given in Supplementary Publication SUP No. 21070 (6 pp.) * and are reported graphically in the Figure.

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* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Dalton*, 1973, Index issue. Items less than 10 pp. are supplied as full-size copies.