

Mass Spectral Study of the Vapour of Aluminium 2,2',2''-Nitrilotriethoxide

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Abstract

The mass spectrum of aluminium 2,2',2''-nitrilotriethoxide is consistent with a dimeric structure for the compound in the gas phase.

Introduction

Volatile oligomers of aluminium alkoxides may generate useful reference ions for the higher mass regions of electron-impact, chemical-ionization, field-ionization or field-desorption mass spectra, where ions of perfluorinated hydrocarbons may be weak or absent.¹ Further, it appears from the mass spectral studies of aluminium alkoxides¹⁻⁶ that the spectra obtained by a direct-insertion probe may reflect the molecular complexity of the alkoxide in the solid phase. For example, the different mass spectra obtained for freshly distilled and 'aged' aluminium isopropoxide^{1,2,4,5} provide direct evidence for the different degrees of association previously postulated⁷ for the condensed phases in the two cases. Also, the detection of ions representative of species up to the heptamer indicates the presence of such oligomers in the bulk sample.¹ Octamers are possible, according to Bradley's hypothesis,⁷ in which all the aluminium atoms have attained maximum covalency, but these have not been reported so far in the mass spectra of aluminium alkoxides.

Aluminium nitrilotriisopropoxide has been synthesized previously and reported to be volatile, though it was not characterized further.⁸

Aluminium 2,2',2''-nitrilotriethoxide has been synthesized previously by Hein and Albert⁹ and by Mehrotra and Mehrotra¹⁰ who determined the molecular association in benzene solution to be eight and six, respectively. We have now obtained the mass spectrum using a direct-insertion probe (Fig. 1). Elementary compositions

¹ Daasch, L. W., and Fales, H. M., *Org. Mass. Spectrom.*, 1969, 2, 1043.

² Fieggen, W., Gerding, H., and Nibbering, N. M. M., *Recl Trav. Chim. Pays-Bas*, 1968, 87, 377.

³ Chambers, D. B., Coates, G. E., Glockling, F., and Weston, M., *J. Chem. Soc. A*, 1969, 1712.

⁴ Brown, L. M., and Mazdiyasi, K. S., *Anal. Chem.*, 1969, 41, 1243.

⁵ Oliver, J. G., and Worrall, I. J., *J. Chem. Soc. A*, 1970, 845.

⁶ Oliver, J. G., and Worrall, I. J., *J. Chem. Soc. A*, 1970, 2347.

⁷ Bradley, D. C., *Prog. Inorg. Chem.*, 1960, 2, 303.

⁸ Frye, C. L., Vogel, G. E., and Hall, J. A., *J. Am. Chem. Soc.*, 1961, 83, 996.

⁹ Hein, Fr., and Albert, P. W., *Z. Anorg. Allg. Chem.*, 1952, 269, 67.

¹⁰ Mehrotra, R. C., and Mehrotra, R. K., *J. Indian Chem. Soc.*, 1962, 39, 677.

of selected ions are reported in Table 1. No ions indicative of oligomers other than the dimer are evident, and the dominance of Al_2 ions testifies to the strength of the

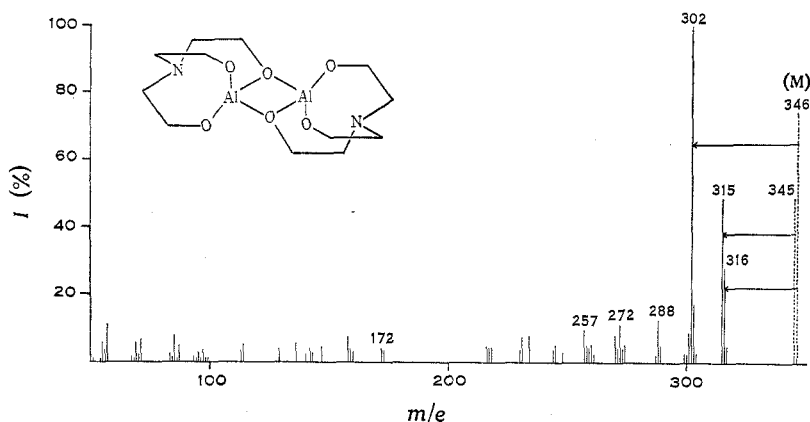
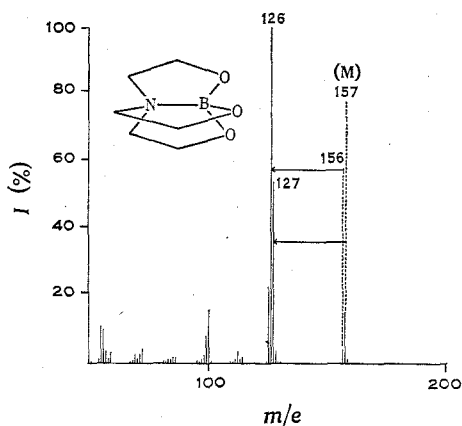


Fig. 1. 70-eV mass spectrum of aluminium 2,2',2''-nitrilotriethoxide.

Table 1. Elementary compositions of selected ions in the mass spectrum of aluminium 2,2',2''-nitrilotriethoxide

Measured m/e	Composition	Measured m/e	Composition
345·1175	$\text{C}_{12}\text{H}_{23}\text{Al}_2\text{N}_2\text{O}_6$	273·0945	$\text{C}_{11}\text{H}_{18}\text{AlO}_6$
316·1143	$\text{C}_{11}\text{H}_{22}\text{Al}_2\text{N}_2\text{O}_5$	272·0885	$\text{C}_9\text{H}_{18}\text{Al}_2\text{N}_2\text{O}_4$
315·1068	$\text{C}_{11}\text{H}_{21}\text{Al}_2\text{N}_2\text{O}_5$	271·0813	$\text{C}_9\text{H}_{17}\text{Al}_2\text{N}_2\text{O}_4$
302·0991	$\text{C}_{10}\text{H}_{20}\text{Al}_2\text{N}_2\text{O}_5$	270·0739	$\text{C}_9\text{H}_{16}\text{Al}_2\text{N}_2\text{O}_4$
289·0999	$\text{C}_{10}\text{H}_{18}\text{AlN}_2\text{O}_6$	257·0669	$\text{C}_8\text{H}_{15}\text{Al}_2\text{N}_2\text{O}_4$
288·0926	$\text{C}_{10}\text{H}_{17}\text{AlN}_2\text{O}_6$	173·0205	$\text{C}_4\text{H}_9\text{Al}_2\text{NO}_3$
287·0778	$\text{C}_9\text{H}_{17}\text{Al}_2\text{N}_2\text{O}_5$	172·0132	$\text{C}_4\text{H}_8\text{Al}_2\text{NO}_3$
274·0792	$\text{C}_9\text{H}_{18}\text{Al}_2\text{NO}_5$		

Fig. 2. 70-eV mass spectrum of boron 2,2',2''-nitrilotriethoxide.



alkoxy bridge upon electron-impact. The mass spectrum of monomeric boron 2,2',2''-nitrilotriethoxide^{11,12} is reported for comparison (Fig. 2). Loss of the

¹¹ Brown, H. C., and Fletcher, E. A., *J. Am. Chem. Soc.*, 1951, **73**, 2808.

¹² Taira, Z., and Osaki, K., *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 509.

elements of acetaldehyde from the molecular ion is the major process for the aluminium complex but is of negligible importance for the boron complex.

The mass spectral data are consistent with a dimeric structure for the aluminium complex in the vapour phase, but we have no direct evidence to suggest whether or not transannular nitrogen-aluminium bonds are formed in the compound. Monomeric triptych structures¹¹ with nitrogen-metal bonds appear to be the rule with so-called 'atranes'.¹³ Furthermore, while aluminium usually attains a covalency of four or six in its complexes, pentavalent aluminium is not unknown.¹⁴ Also, it is evident that the oligomers of aluminium 2,2',2''-nitrilotriethoxide, other than the dimer, are not sufficiently volatile or stable for mass spectral analysis.

Experimental

Mass spectra were determined on an AEI MS902 spectrometer at 70 eV and 8 kV accelerating voltage. Metastable transitions in the first field-free region were analysed by scanning the accelerating voltage. High-resolution mass spectra were obtained using a Raytheon 706 computer for on-line data acquisition and processing.

Aluminium 2,2',2''-nitrilotriethoxide was prepared by allowing a solution of aluminium isobutoxide (0.62 g) and 2,2',2''-nitrilotriethanol (0.37 g) in dry benzene (10 ml) to stand overnight at room temperature. Benzene (6 ml) was then slowly distilled off and the remaining solution was left to stand, whereupon white crystals gradually formed. Samples for mass spectrometry and for microanalysis were obtained by subliming the product at 270°/1.3 Pa (Found: C, 41.5; H, 7.2; N, 8.2. Calc. for $C_6H_{12}AlNO_3$: C, 41.6; H, 7.1; N, 8.1%).

Boron 2,2',2''-nitrilotriethoxide was prepared by the method of Brown and Fletcher.¹¹

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¹³ Voronkov, M. G., *Pure Appl. Chem.*, 1966, **13**, 25.

¹⁴ Kushi, Y., and Fernando, Q., *J. Am. Chem. Soc.*, 1970, **92**, 91.