A Molecular Beam–Mass Spectrometric Study of Binary Pentafluorides

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Summary A molecular beam–mass spectrometer has been constructed and used to show that VF_5 and CrF_5 have monomeric vapours and the NbF_5, TaF_5, IrF_5, and SbF_5 are associated in the vapour phase.

KNOWLEDGE of the extent to which inorganic pentafluorides and related molecules exist in the vapour phase as discrete monomeric molecules or as associated groups such as are known in the solid state is, in addition to its intrinsic interest, prerequisite to the interpretation of other physical measurements made on these species.[1–7] Trace ion peaks ascribable to $(SbF_5)_2$ have been detected in the mass spectrum of SbF_5.[8] However, the reactivity and low volatility of many pentafluorides complicate their study using mass spectrometers with conventional sample inlets and ion sources. Therefore a mass spectrometer with a molecular beam source was constructed to examine pentafluorides and related molecules.

The molecular beam–mass spectrometer† consists of a differentially pumped molecular beam source chamber with interchangeable sources for use at, above, or below room temperature, and a chamber containing a quadrupole mass analyser. A molecular beam effuses from one of the controlled temperature sources and is collimated by a slit separating the analyser and source chambers. The beam is focussed through an open Pierce-type ionizer so as to contact neither the walls nor the filaments, thus avoiding contributions to the mass spectra from decomposition products.

It is important to rule out ion-molecule reactions as a possible mechanism for producing the higher molecular weight ion fragments. Experimentally, ions are withdrawn perpendicular to the plane of the molecular beam to minimize ion-molecule reactions. For a typical beam flux at the ionizer of 10^{14} molecules cm^{-2} s^{-1}, an average path of 0·2 cm for primary ions through the neutral beam, and an assumed reaction cross-section of 10^{-14} cm^2, the ratio of secondary ions to primary ions entering the quadrupole would be 10^{-5}. Even with this large hypothetical cross-section, the fraction of ion fragments with mass approximately twice that of the parent molecule formed in this way is small. Higher order products would be undetectable. To verify this prediction experimentally, a beam of CD_4 was analysed following electron bombardment. The absence of CD_5^+ which is formed from CD_4^+ with a large cross-section[9] confirms that ion peaks of pentafluoride oligomers when observed do not result from secondary processes.

The ion transmission of the quadrupole mass filter decreases with increasing mass, and the decrease is dependent upon the resolution. In general, the ion masses were identified at high resolution, and peak intensities were obtained using somewhat lower resolution, *i.e.* higher ion transmission. The relative intensities quoted later have been corrected for ion transmission by calibration with high molecular weight fluorocarbons whose mass spectra have been determined with magnetic sector mass spectrometers which do not discriminate against high mass ions.[10] This empirical calibration gives excellent agreement with changes in transmission with changing resolution at constant mass measured by Brubaker,[11] and permits us to make semi-quantitative estimates of fragmentation patterns over a wide mass range. Bombarding electron energies were 70eV except when the effect of this parameter was under investigation.

If gas phase polymers of pentafluorides are stable, they will be most readily detected in the saturated vapour, and their relative concentration in the saturated vapour is unlikely to have a large temperature dependence. We report initial experiments using the above apparatus which have been directed at the detection of gas phase oligomers under near-saturation conditions for the representative pentafluorides VF_5, CrF_5, NbF_5, TaF_5, IrF_5, and SbF_5.

Results obtained with SbF_5 demonstrate the advantages of the combined molecular beam-mass spectrometric technique. $Sb_2F_9^+$, the principal fragment ion expected from the SbF_5 dimer, had previously been observed in a conventional mass spectrometer[8] at mass numbers 413, 415, and 417 with intensities relative to SbF_4^+ (mass 197) = 100 of 0·24, 0·40, and 0·13. These same ions were observed with the present apparatus and, with correction for quadrupole transmission, had intensities relative to SbF_4^+ more than 100 fold greater, at 40·2, 50·4, and 28·2, respectively. In addition, four peaks for $Sb_3F_{14}^+$ at masses 629, 631, 633, and 635 with intensities of 5·1, 8·6, 6·4, and 1·7 were observed demonstrating the presence of the trimer $(SbF_5)_3$. Estimates of higher polymers were obtained by increasing the transmission of the quadrupole at the cost of resolution.

Relative abundances of polymers for SbF_5, NbF_5, and IrF_5 are summarized in the Table. Careful examination of vapours in equilibrium with solid of VF_5 at -15 °C and CrF_5 at $\sim$50 °C using a variety of electron energies from 16 to 90 eV showed no evidence of associated species. The detection limit for dimer ions is <1 in 10^5.

The relative intensities of the fragment ions are dependent

TABLE

Relative abundance of pentafluoride polymers

Fluoride	Temp. (°C)	Monomer	Dimer	Trimer	Tetramer	Pentamer
SbF_5	25	1·0	0·5	0·09	10^{-4}	*ca.* 1×10^{-6}
NbF_5	66	1·0	1·0	0·7	*ca.* 2×10^{-6}	
TaF_5	93	1·0	0·77	0·10	$<10^{-5}$	
IrF_5	69—119	1·0	0·32	0·04	4×10^{-4}	*ca.* 1×10^{-6}

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† A detailed description of the apparatus and technique is in preparation and will be submitted to the *International Journal of Mass Spectroscopy and Ion Physics.*

not only on the transmission of the quadrupole mass filter but also upon the energy of the bombarding electrons. For example, 70 V electron impact on a trimeric species can yield a monomeric ion and a dimeric neutral, whereas such processes become less probable as electron energy decreases. Furthermore, the electron impact cross-sections will vary through a series of oligomers, being larger for the higher agglomerates. The fractions quoted are therefore not necessarily those of the neutral species. Consideration of the ion abundances under typical conditions of mass analysis tends to underestimate the higher associated clusters.

These results show that reactive fluorides can be studied mass spectrometrically using a molecular beam source. Although the quantitative abundances of the various agglomerates cannot at present be deduced with high precision, the importance of association in some binary pentafluorides is apparent. VF_5 and CrF_5 are examples of non-associating pentafluorides, whereas NbF_5, TaF_5, IrF_5, and SbF_5 all associate extensively. The existence of pentamers in SbF_5 and IrF_5 suggests that the polymers are not exclusively tetrameric rings.

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[1] T. R. Dyke, A. A. Muenter, W. Klemperer, and W. E. Falconer, *J. Chem. Phys.*, 1970, **53**, 3382 and unpublished results.

[2] J. Schröder and F. J. Grewe, *Chem. Ber.*, 1970, **103**, 1536.

[3] G. V. Romanov and V. P. Spiridonov, *Siberian Chemical Journal*, 1968, 126.

[4] S. Blanchard, *J. Chem. Phys.*, 1965, **62**, 919.

[5] H. Selig, J. H. Holloway, J. Tyson, and H. H. Claassen, *J. Chem. Phys.*, 1970, **53**, 2559.

[6] H. Selig, A. Reis, and E. L. Gasner, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2087.

[7] I. R. Beattie, K. M. S. Livingstone, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc.* (*A*), 1969, 958.

[8] A. Müller, H. W. Roesky, and D. Böhler, *Z. Chem.*, 1967, **7**, 469.

[9] E. W. McDaniel, V. Cermak, A. Dalgarno, E. E. Ferguson, and L. Friedman, "Ion-Molecule Reactions", Wiley-Interscience, New York 1970.

[10] F. W. Karasek, *Research and Development*, November 1970, p. 55.

[11] W. M. Brubaker, *Adv. Mass Spectrometry*, 1968, **4**, 293.