Identification of Dimers in the Vapour of Vanadium Oxide Trifluoride

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Summary Vanadium oxide trifluoride vapour has been shown by a mass spectrometric study to contain dimers.

There has been considerable interest recently in the existence of associated groups in the vapours of inorganic fluorides.[1] The reported work has been concerned with pentafluorides, and of those investigated which have shown association in the vapour state, SbF_5, NbF_5, TaF_5, and IrF_5 have tetrameric structures in the solid state, and BiF_5 has a *trans* bridged chain structure.

In the solid state, vanadium oxide trifluoride is associated into dimer units with strong di-μ-fluoro-bridges and these dimer units are linked by weaker interactions into sheets.[2] It might therefore be expected that some dimerisation would persist in the vapour. However, a study of the i.r. spectrum at room temperature was interpreted purely on the basis of monomer units.[3] A vapour density study showed that the major species at higher temperatures is the monomer.[4]

We have examined the vapour from solid VOF_3 with a mass spectrometer (Metropolitan–Vickers MS2). The solid was held at temperatures from -23 to $+30$ °C, though most experiments were at -23 °C. The vapour passed through a glass and metal inlet tube at room temperature directly into the ion source, which has been modified to provide a crude molecular beam. Under normal conditions with 70 eV electrons the ion VOF_3^+ (mass 124) and all the possible fragment ions were observed, and also a very weak peak at mass 229, corresponding to $V_2O_2F_5^+$, the expected major ion from the dimer molecule. The intensity of this peak increases rapidly as the ionising electron energy is reduced, and reaches a maximum at *ca.* 25 eV. Since the intensity of the other main peaks in the spectrum decreases with decreasing energy, we do not think it is possible that the mass 229 peak can arise from ion-molecule reactions.

By adjusting the focus conditions for the electron beam it is possible to increase the intensity of this $V_2O_2F_5^+$ peak still further as electrons are focussed onto the molecular beam. Under optimum conditions the $V_2O_2F_5^+$ peak intensity was 3·5% of that of the VOF_3^+ peak, 1·6% of the total ion intensity. No parent ion $V_2O_2F_6^+$ peak was observed, or any other fragment, but this parallels the ionisation behaviour of the polymers of antimony pentafluoride.[1a]

Since the dimer peak is very sensitive to the electron focus conditions but the monomer parent peak is less sensitive, it seems probable that the beam contains a much higher proportion of dimers than the above figures indicate, and that the dimers fragment on collision with the hot source plates. A series of small deflections was applied to the electron beam and percentage reductions measured for the peaks at 229, 124, and the mercury background 202 peak. Assuming that the dimer species came only from the molecular beam and that the distribution of VOF_3 background monomers is uniform along the electron beam, it was estimated that the intensity of $V_2O_2F_5^+$ is *ca.* 10% of that of the VOF_3^+ ions from the beam region.

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