# The Reaction of Vanadium Pentafluoride with Phosphorus Oxytrifluoride and with Trifluoroacetic Acid

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# SUMMARY

Vanadium pentafluoride reacts via an oxygen exchange reaction with phosphorous oxytrifluoride to give  $VOF_3$  and  $PF_5$ . The latter forms a weak 1:1 adduct.  $VF_5$  reacts with trifluoroacetic acid to form trifluoroacetyl fluoride and  $VOF_3$ . Both reactions are indicative of the strength of the V=O bond and its influence on the course of the reactions of  $VF_5$  with oxygen containing materials.

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# INTRODUCTION

Many adducts of  $POCl_3$  and  $POBr_3$  are known and all involve co-ordination through the oxygen lone pair. In contrast, there are very few known adducts of  $POF_3$  where bond formation can occur in three ways - a) through the oxygen atom, b) through an F<sup>-</sup> transfer, or c) by means of a fluorine bridge. It appears that  $AsF_5$  forms a fairly weak 1:1 adduct via the oxygen atom of  $POF_3$  and so does  $BF_3$ but here the adduct is even more thermally unstable 1,2. However the 1:1 adduct with  $SbF_5$  is a white, non-volatile solid at room temperature; presumably this very strong Lewis Acid is forming an ionic product 1. We have shown that  $VF_5$  is a remarkably weak F<sup>-</sup> acceptor and that it acts as a weak base in  $SbF_5$ <sup>3</sup>. There also seems to be very little interaction with  $AsF_5$ . Consequently, in the reaction of  $VF_5$  with  $POF_3$  we expected formation of a simple adduct via the oxygen atom.

### RESULTS

When  $\text{POF}_3$  was condensed onto excess  $\text{VF}_5$  and warmed to  $-20^{\circ}\text{C}$ , the two immiscible materials reacted slowly; upon warming to  $+20^{\circ}\text{C}$  all the  $\text{POF}_3$  reacted to give a clear, amber coloured, viscous solution. If  $\text{POF}_3$  was used in excess, then at  $-23^{\circ}\text{C}$  an apple green solution was formed from which a green precipitate appeared. When warmed to  $0^{\circ}\text{C}$ , this precipitate dissolved and a sky blue solid was precipitated from the green solution accompanied by the evolution of a colourless gas. No further apparent reaction occurred at  $+20^{\circ}$ C. Because of the complexity of this reaction we used a variety of VF<sub>5</sub>: POF<sub>3</sub> mole ratios in our n.m.r. study of the reaction.

The room temperature spectrum of the amber coloured solution containing a large excess of VF<sub>5</sub> shows a broad peak A  $(\delta = -463 \text{ p.p.m.}; W_{\frac{1}{2}} 600 \text{ Hz})$  and a sharp doublet D  $(\delta = +73 \text{ p.p.m.};$ J = 940 Hz) which also contains some partially resolved fine structure. Upon cooling A vanishes as did the fine structure. Peak A is assigned to free VF<sub>5</sub>  $(\delta = -473 \text{ p.p.m.})^3$ . The chemical shift and coupling constant of D correspond closely to those of PF<sub>5</sub>  $(\delta = +70.5 \text{ p.p.m.}, \text{ J}(\text{P-F}) = 938 \text{ Hz}^4)$ . The origin of the partially resolved fine structure is discussed later on in the text. There is no sign of a peak due to POF<sub>3</sub>  $(\delta = 93.6 \text{ p.p.m.}, \text{ J}(\text{P-F}) = 1060 \text{ Hz}^5)$ ; evidently an oxygen exchange reaction, VF<sub>5</sub> + POF<sub>3</sub> + PF<sub>5</sub> + VOF<sub>3</sub> having occurred. A weak broad resonance at approximately,  $\delta = -350 \text{ p.p.m.}$ , is most likely to be due to the VOF<sub>3</sub> formed in the reaction.

As the concentration of VF<sub>5</sub> is decreased (to a mole ratio 1.05) so the intensity of A diminishes and three new resonances B, C and E appear in addition to the PF<sub>5</sub> signal. On cooling to  $-15^{\circ}$ C, the broad low field peak B ( $\delta$  = -278 p.p.m.) and the broad doublet, E ( $\delta$  = 88.7 p.p.m., J(P-F) = 1045 Hz) collapse and C sharpens to a distorted septet.

At even higher  $POF_3$  concentrations (mole ratio 0.90) no peak due to  $VF_5$  is observed. Peaks B, C and E are more intense and a signal (F) due to  $POF_3$  now appears ( $\delta = 94$  p.p.m., J(P-F) = 1060 Hz). At this concentration and at  $-15^{\circ}C$  the resolution of C is greatly improved. It is a distorted doublet of septets and is further distorted by the broad underlying doublet of E.

The septets are very similar to a second order A<sub>4</sub>BX splitting pattern (A =  $F_{eq}$ , B =  $F_{ax}$ , X = P). The only ligands present in the system which could form adducts with PF5 are VOF, and POF,. The <sup>19</sup>F n.m.r. spectrum of an equimolar mixture of PF5 and POF3 showed negligible interaction over a wide temperature range and so we conclude that B and C are the signals due to a F<sub>2</sub>VO.PF<sub>5</sub> adduct. We obtained quite good agreement between the experimental spectrum C and a computed spectrum with  $J(F_{ax}-F_{eq})/(\delta_{F_{ax}}-\delta_{F_{eq}}) = 0.6$  giving  $J(P-F_{ax}) = J(P-F_{eq}) =$ 938 Hz;  $J(F_{ax}-F_{eg}) = 80$  Hz,  $\delta(F_{eg}) = 72.7$  p.p.m. and  $\delta(F_{ax}) =$ 74.8 p.p.m. Confirmation of this assignment comes from the fact that the disappearance of B and C on cooling below -25°C coincides with the precipitation of the sky-blue solid from the solution. The size of J(P-F) of the broad doublet E indicates that it is probably due to a four-coordinate phosphorus atom but it is obviously not free POF, and neither can it be due to  $VF_5.OPF_3$  since E is observed even when no free VF<sub>5</sub> is present.

The visible observations and  $^{19}$ F n.m.r. data can be summarized by the following sequence of reactions. On mixing at low temperature, VF<sub>5</sub> and POF<sub>3</sub> form a slightly soluble green adduct VF<sub>5</sub>.OPF<sub>3</sub>. Above -15<sup>o</sup>C, this adduct decomposes to give PF<sub>5</sub> and pale yellow VOF<sub>3</sub>. These latter subsequently react to form the sky blue, insoluble, 1:1 adduct which appears to be significantly dissociated at 20<sup>o</sup>C. The PF<sub>5</sub> adducts with Me<sub>2</sub>O and Me<sub>3</sub>N have J(P-F) in the region 770 to 850 Hz<sup>6</sup> which are somewhat smaller than in this work. However as both of these ligands are good donors there should be significant changes in the hybridisation of phosphorus on coordination. The consequent change in s-electron density will thus be reflected in the size of J e.g., PF<sub>5</sub>, J(P-F) = 930 Hz;  $PF_6^-$ , J(P-F) = 715 Hz. With very weak donors and hence less change in hybridisation J(P-F) should stay quite large. The very weak donor,  $SbF_6^-$ , forms a 1:1 adduct with  $PF_5$ ,  $J(P-F_{ax}) = 940$  Hz and  $J(P-F_{eq}) = 913$  Hz)<sup>7</sup>. Thus the value of J(P-F) found for  $F_5P.OVF_3$  indicates that  $VOF_3$  is a weak donor as is to be expected. There is in fact considerable evidence that  $VOF_3$  is a good  $F^-$  acceptor <sup>8,9</sup>.

The reaction of VF<sub>5</sub> with POF<sub>3</sub> illustrates the strong driving force to form the V=O bond and the big difference in behaviour between it and SbF<sub>5</sub>. The ability of the latter to form anions, polyanions and bridged species is well documented. We decided to see if this difference in behaviour is also exhibited in the reaction with  $CF_3CO_2H$ . Harris and Milne <sup>10</sup> have shown by <sup>19</sup>F n.m.r. that simple 1:1 and bridged 2:1 adducts exist in solutions of SbF<sub>5</sub> in  $CF_3CO_2H$ .

Vanadium pentafluoride was condensed onto excess trifluoroacetic acid at  $-196^{\circ}$ C and then allowed to warm up slowly. At  $-45^{\circ}$ C reaction occurred during which a colourless gas was evolved and an off-white solid precipitated from a pale green solution. Reaction was complete at  $0^{\circ}$ C, although the precipitate became increasingly yellow upon standing at room temperature for several hours. The <sup>19</sup>F n.m.r. spectrum revealed a solvent peak ( $\delta$  +76.5 p.p.m.) with a high field shoulder B ( $\delta$  = 77.6 p.p.m.) and a broad low field peak C ( $\delta$  = -90 p.p.m., W<sub>1</sub> 1000 Hz). Also present was a sharp singlet at 163.4 p.p.m. due to SiF<sub>4</sub> and a pair of peaks at +74.8 p.p.m. and -14.1 p.p.m. which we assign to CF<sub>3</sub>COF ( $\delta$  CF<sub>3</sub>COF = 75.2 p.p.m.,  $\delta$  CF<sub>3</sub>COF = 14.1 p.p.m. <sup>10</sup>. No signal was detected for VF<sub>5</sub>.

On standing overnight both B and C decreased considerably in intensity. Peak C occurs at a relatively high field; one which is characteristic of vanadium oxyfluoro species <sup>8</sup>. The disappearance of B and C upon standing suggests that both of these signals originate from the same species, perhaps  $[VF_4(OH)$  $(CF_3COO)]^-$ . On standing this could decompose to give VOF<sub>3</sub> and which would thus correspond to the observed yellow precipitate. The SiF<sub>4</sub> would then be produced from the HF, thus liberated viz:

> $VF_5 + CF_3CO_2H \rightarrow VOF_3 + HF + CF_3COF$  $VF_4(OH)(CF_3CO_2)H \rightarrow VOF_3 + CF_3CO_2H + HF$

Trifluoroacetyl fluoride has also been formed in the  ${\rm HBF}_4/{\rm CF}_3{\rm CO}_2{\rm H}$  system  $^{10}.$ 

### EXPERIMENTAL

 $POF_3$  was prepared from  $CaF_2$  and  $P_2O_5$  by a modification of the method of Tarbutton et al.<sup>11</sup>. Its purity was checked by n.m.r. and by i.r. spectroscopy. Trifluoroacetic acid was purified by distillation and was stored over molecular serves.  $VF_5$  was purified and handled as previously described <sup>3</sup>. N.m.r. spectra were recorded on a Varian HA60 IL spectrometer at 56.4 MHz; all chemical shifts are reported with reference to external CCl<sub>3</sub>F (downfield:negative).

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We thank Mrs. Christine Greenwood for assistance with the n.m.r. spectra. We also gratefully acknowledge financial assistance from the National Research Council of Canada and from the University of Victoria.

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