Journal of Fluorine Chemistry, 14 (1979) 485–494
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Received: July 1, 1979

AN N.M.R. STUDY OF THE SOLUTION CHEMISTRY OF VANADIUM PENTAFLUORIDE

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SUMMARY

^{19}F n.m.r. spectroscopy has been used to investigate the solution chemistry of vanadium pentafluoride in a wide range of solvents. It is shown that VF_5 is a remarkably weak F^- acceptor even in the VF_5/AgF/HF system, and that it acts as a weak base in SbF_5 to give a fluxional mixed polymer.

INTRODUCTION

Although a number of papers have been published on the chemistry of vanadium pentafluoride there is still not much known about its detailed chemistry. This is due, in the most part, to its extreme reactivity both as an oxidising and as a fluorinating agent. In this respect it varies greatly from the other two group VA pentafluorides which exhibit an ability to form a wide variety of adducts with organic ligands and with no tendency to oxidise or fluorinate them. In addition, although niobium and tantalum pentafluoride are ready acceptors

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of F^- there is little published evidence of the ability of VF_5 to accept F^- in solution. Indeed little is known about the solution chemistry of VF_5 as spectroscopic methods have only been rarely applied to it. In this paper we describe the interaction of vanadium pentafluoride with a variety of potential solvents and the results of ^{19}F n.m.r. studies on such solutions.

RESULTS AND DISCUSSION

Solutions of VF_5 in inert solvents

The structure of VF_5 in the solid state is known to consist of polymeric octahedral units linked via *cis* fluorine bridges [1]. From a study of the vibrational spectra of both the vapour and liquid phase Claasen and Selig [2] concluded that the polymeric nature persists into the liquid phase This is borne out by the viscous nature of liquid VF_5. If VF_5 could be dissolved in inert, i.e. non-co-ordinating solvents, then it should be possible to get information about the structure in the liquid phase by ^{19}F n.m.r. as has been done for SbF_5 [3,4]. Such a study has been reported by Brownstein and Latremouille [5] using SOF_2Cl as a solvent. At -135°C the ^{19}F n.m.r. spectrum consists of three lines with intensity ratios of 2:2:1 and is interpreted as arising from chains, either linear or cyclic, of *cis*-bridged VF_6 units. Unfortunately no fine structure was resolvable. We have examined the ^{19}F n.m.r. spectrum of VF_5 in a number of inert solvents in the hope of getting more information.

Vanadium pentafluoride is slightly soluble in C_4F_8, C_7F_{13} and SF_6 showing that there is some interaction between the solute and the solvents but in each case the

^{19}F n.m.r. spectrum showed only one broad band in addition to the solvent peak. Low temperature studies were not possible because of the low solubility at -10° and below. The chemical shift of the VF_5 signal in the three solvents was -473.5, -476 and -472 compared with that of neat VF_5 of -474.0 p.p.m. from external CCl_3F. $W_{\frac{1}{2}}$ at 25° was in each case $\sim$ 300 Hz.

Canterford and O'Donnell [6] have reported that VF_5 does not react with either Cl_2 or Br_2 even after being heated to 125° for two days. We discovered that VF_5 dissolved readily in Cl_2 to form a mobile cherry red coloured liquid. VF_5 could be crystallised from such solutions at about -50° and the ^{19}F n.m.r. gave only a single line at -468.6 p.p.m. ($W_{\frac{1}{2}}$ 250 Hz at 25°). This data indicates little interaction between the two liquids but does not explain the deep colour. However, the solutions were found to be slightly paramagnetic and so the e.p.r. spectrum was obtained. It consisted of a well resolved six line resonance at room temperature overlying a much broader resonance (g = 1.9984). Olah and Comisarow [7] have reported e.p.r. spectra for Cl_2 dissolved in highly acidic media but their interpretation has been challenged [8,9,10] and it is now believed that the species they observed were probably Cl_2O^+, $ClOF^+$, $COClF^+$ and ClO_2F^+. In our ^{19}F n.m.r. spectra there was a very small peak due to SiF_4 and we conclude that the presence of the paramagnetic species may be due to a small trace of HCl in the very carefully dried Cl_2 viz:

$$HCl + VF_5 \rightarrow HF + VF_4Cl$$

$$HF + SiO_2 \rightarrow SiF_4 + H_2O$$

$$H_2O + Cl_2 + VF_5 \rightarrow ClOF^+ + \text{etc.}$$

Vanadium pentafluoride dissolved in bromine to give a mobile brown solution from which lustrous blue-black crystalline plates were formed upon standing in sealed glass tubes for a period of several weeks. The ^{19}F n.m.r. spectra again showed only a broad resonance which sharpened on cooling to -60° ($\delta = \sim 500$ p.p.m. $W_{\frac{1}{2}}$ at -20° = 1500 Hz). These solutions were also paramagnetic and this may account for the line broadness. The e.p.r. spectrum of a Br_2/VF_5 solution showed a broad seven line resonance superimposed on a narrower four line spectrum. Apparently no e.s.r. spectra can be obtained for solutions of the paramagnetic Br_2^+ cation over a temperature range from about 25° to -100° presumably because of strong spin-orbit coupling in the $^2\pi_{3/2g}$ state. This ion also had no effect on the narrow line width of the counter ion (SO_3F^-)[10] in contrast to the effect of the paramagnetic I_2^+ ion in similar systems. The e.p.r. spectra of our solutions must therefore be due to some species similar to that observed in the Cl_2/VF_5 system, perhaps also with a contribution from vanadium (IV) species.

Solutions in Anhydrous Hydrogen Fluoride

Antimony pentafluoride readily dissolves in anhydrous HF to give a variety of antimony fluoro anions depending on concentration [11] i.e. SbF_6^-, $Sb_2F_{11}^-$, $Sb_3F_{16}^-$. It is also well established that both niobium and tantalum form a variety of fluoro anions in HF [12] but all of them monomeric. It is of interest to see how VF_5 behaves in such systems for the preparation of stable hexafluorovanadates and the increased conductivity of liquid VF_5 when KF is added have been cited as evidence for self-ionisation in VF_5 [13]. A Raman study by Selig and Frlec [14] of the VF_5/HF system concluded that no ionisation occurred, and this was corroborated by measurements of electrical conductivity. Even in the KF/HF/VF_5 system no clear conclusions could be arrived at concerning the formation of VF_6^-.

We have found that VF_5 is moderately soluble in HF at 20° to give a colourless solution. ^{19}F n.m.r. spectra of dilute VF_5 solutions showed, at room temperature, only one signal at +26 p.p.m. ($W_{\frac{1}{2}}$ 500 Hz) and which, on cooling, moved upfield rapidly, the chemical shift approaching that of pure HF (202 p.p.m.). The ^{19}F n.m.r. spectra of VF_5 saturated with HF at 10°C showed a broad peak (A) at -462 p.p.m. ($W_{\frac{1}{2}}$ 1800 Hz) and a narrow peak (B) at +9.8 p.p.m. Upon cooling A disappeared and B moved upfield to 93 p.p.m. as VF_5 crystallised out. We conclude that the signals we observe are of VF_5 and HF. The fact that no resonance due to the VF_6^- ion is observed confirms the Raman study [14] and reinforces the view that VF_5 is a surprisingly weak fluoride acceptor and is in contrast to NbF_5 which gives rise to NbF_6^- even in aqueous HF [12].

In an effort to force the formation of VF_6^- we dissolved the very soluble AgF in VF_5/HF to give a solution approximately 0.8 molar in AgF and 2.7 molar in VF_5. The room temperature ^{19}F n.m.r. spectrum revealed two signals, A at -474 p.p.m. ($W_{\frac{1}{2}}$, 1100 Hz) and B at +123 p.p.m. ($W_{\frac{1}{2}}$, ∿ 10,000 Hz). Upon cooling, A became less intense and disappeared at about -10° whilst B became even broader and less intense below -30°C. Peak A is assigned to VF_5 and shows virtually no interaction either with solvent or F^-. B is assigned to the exchange between F^- and HF which would be expected to be very rapid. Again no separate signal was seen for VF_6^- although B could be due to exchange between F^-/HF and VF_6^-.

Solutions in Halogen Fluorides

The halogen fluorides are only weakly basic and should dissolve in the somewhat acidic VF_5. ClF_3, BrF_3 and BrF_5 all dissolved VF_5 to give pale, mobile solutions. The ^{19}F n.m.r. spectra of such solutions exhibited one signal at room temperature and even at -108^{o} the ClF_3 system showed only a broad peak at -280 p.p.m. and a sharper singlet whose shift approached the mean shift of the equatorial and axial fluorines of ClF_3. It is probable that some fluoride transfer is taking place. This would account for the lack of resolution, even at the lowest temperatures of the spectrum of the halogen fluorides for it is well established that a trace of a Lewis acid produces rapid fluorine exchange in these compounds, thus reducing the spectra to singlets [15,16,17]. The ^{51}V n.m.r. spectra also gave broad featureless resonances indicating that VF_6^- is not formed in any appreciable amount ($W_{\frac{1}{2}}$ 800 Hz at 27^{o}; 5000 Hz at $0^{o}C$).

Solutions in SbF_5 and AsF_5.

Antimony pentafluoride is a very strong acid and it has been shown recently that it can remove, or at least partially remove, fluoride ion from niobium and tantalum pentafluorides [18,19]. In view of the reluctance of VF_5 to form VF_6^- it seemed likely that SbF_5 would be a strong enough acid so as to cause VF_5 to act as a base.

We found that the two liquids are miscible in all proportions giving solutions that are very much more mobile than either of the pure pentahalides. Solutions of various concentrations were prepared and the ^{19}F n.m.r. data is given in Table 1.

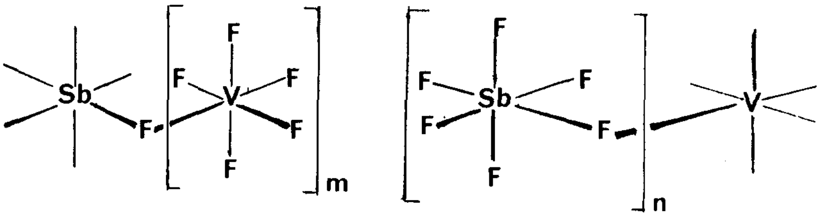
TABLE 1. ^{19}F n.m.r. data for VF_5/SbF_5 Solutions

Mol Ratio VF_5/SbF_5	Temperature (^oC)	Chemical Shift (p.p.m.) A	B	C	D	I_V/I_{Sb} [b]
1.07	27	-606		+113		0.72
0.67	-20	-685		+112		0.36
0.55	27	-688 [a]		+112		0.40
0.55	-10	-688 [a]	+92.5	+111	+133	0.36
0.40	-60	-603	+93.2	+110	+132	0.08
0.18	-49	-603	+92.3	+110	+133	0.13

[a] $W_{\frac{1}{2}}$ = 120 Hz; solution dark blue and paramagnetic.

[b] I_V = area under A (F on V); I_{Sb} = area under B, C and D (F on Sb)

The solutions were generally almost colourless when prepared but on standing in glass became increasingly blue in colour. Solutions of NbF_5 in SbF_5 have also been noted to exhibit a similar tendency [18]. In approximately equimolar solutions two sharp singlets A and C were observed. At lower VF_5 concentrations (0.55 and 0.40 Mole ratio) two minor additional highfield peaks, B and D, occur at low temperatures. However in the most dilute solutions all four peaks are observable at room temperatures. The ratio of intensities of B:C:D approached 1:2:2 with dilution and became increasingly similar to the spectrum of SbF_5 in which chains of *cis* bridged SbF_6 octahedra give three peaks of intensity 1:2:2. Peak A is assigned to F on V and peaks B, C and D to F on Sb. The intensity measurements indicate extensive transfer of fluorine from vanadium to antimony and is confirmed by the sustantial shift of the F on V resonance downfield from that of pure VF_5 (130 p.p.m. The intensity ratio of the equimolar solution was ∿ 2:3 strongly suggesting fluoride transfer to form $VF_4^+ SbF_6^-$. However, similar ionic systems generally give spectra with broad lines as a consequence of rapid intermolecular fluoride exchange, e.g. Et_4NSbF_6/SbF_5 system [20]. We conclude, from the similarity in the spectra and the trends in chemical shift, that the state of VF_5 in SbF_5 is very similar to that of NbF_5 (and TaF_5) in SbF_5 [18] i.e., fluxional polymers of the type:



VF_5 was found to be only slightly soluble in AsF_5 the other strong Lewis acid used. No n.m.r. evidence was obtained for any significant interaction. It would thus appear that VF_5 has little tendency to form VF_6^- and that in very strong acidic media it acts as a weak base. We therefore suggest that VF_5 is a weaker acid than either Nb or TaF_5 and that its main reactions will be as an oxidising and fluorinating agent.

EXPERIMENTAL

Vanadium pentafluoride (Ozark-Mahoning) was handled in a greaseless, rigorously dried, pyrex vacuum line using break-seal techniques and p.t.f.e. valves where appropriate. It was purified by distillation from dry NaF several times. All reactions and subsequent n.m.r. measurements on VF_5 were done in sealed systems.

A similar line, constructed of silica, was used to handle the halogen fluorides BrF_3, BrF_5 and ClF_3 (Ozark-Mahoning). These were purified by distillation. Hydrogen fluoride (Matheson) was handled using a monel and Kel-F vacuum line. It was purified by absorbing onto NaF, pumping at 120° to remove water, and then by regenerating the HF at 300° by decomposing the $NaHF_2$. N.m.r. samples were distilled into Kel-F n.m.r. tubes which were then sealed off. The halogens were purified by double distillation from P_2O_5 and then MgO to remove H_2O and HBr respectively. SbF_5 was purified in a double distillation apparatus at atmospheric pressure and under N_2; it was subsequently distilled on the vacuum line. Anhydrous AgF was prepared as previously described [21].

N.m.r. spectra were recorded on a Varian HA 60 IL spectrometer, ^{19}F at 56.4 MHz and ^{51}V at 10.3 MHz. All chemical shifts are reported with reference to external CCl_3F (downfield:negative). E.s.r. spectra were obtained on a Varian E6-S spectrometer.

We thank Mrs. Christine Greenwood for assistance in obtaining the n.m.r. spectra. We also thank the National Research Council of Canada and the University of Victoria for financial support.

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