SUBSTITUTION AND REDOX REACTIONS INVOLVING VANADIUM OXOTRIFLUORIDE

GEORGE A. KOLTA[†], DAVID W.A. SHARP, and JOHN M. WINFIELD*

Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland

SUMMARY

   VOF_3 is soluble in acetonitrile but is slowly reduced to give a vanadyl(IV) species as one product.   It reacts rapidly with Me_3SiNEt_2 in MeCN below ambient temperature;   fluorine is replaced by $-NEt_2$ ligands but the spectroscopic and magnetic properties of the products indicate that, in addition, reduction to V^{IV} occurs to some extent.   The products are formulated as $VOF_{3-n}(NEt_2)_n$ containing small quantities of $VOF_{2-m}(NEt_2)_m(NEt_2H)$ (n = 1-3, m = 0-2).   A similar reaction occurs between VOF_3 and Me_3SiOMe but with $Me_3SiOSiMe_3$ only VO_2F is formed.

INTRODUCTION

   Although vanadium oxotrifluoride is well characterised structurally [1], and its vibrational spectrum is well documented [2], its chemistry is relatively undeveloped.   Previous studies have been limited largely to adduct formation with inorganic fluorides [3] or with organic O- and N-donor molecules [4]. These adducts have been prepared indirectly from vanadium(V) oxide and the appropriate donor, often in HF.   We now report that fluorine in VOF_3 is replaced readily by the diethylamido-group using trimethylsilyldiethylamine.   The reactions are

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[†]Permanent address: National Research Centre, Dokki, Cairo, Egypt

formally analogous to those previously reported between Me_3SiNEt_2 and niobium or tantalum pentafluorides [5], but are complicated by accompanying redox reactions. Prior to this work no dialkyl-amido-vanadium(V) compounds had been reported, however since its completion, the formation of $VO(NEt_2)_3$ in low yield from $VOCl_3$ and $LiNEt_2$ in pentane has been described [6].

RESULTS AND DISCUSSION

The first requirement for this work was a solvent suitable for VOF_3, therefore its behaviour in a number of organic solvents was examined. It reacts rapidly at ambient temperature with n-pentane, dimethyl carbonate, and nitromethane, is insoluble in hexafluorobenzene and propionitrile, but is moderately soluble in acetonitrile. A yellow solution is formed with MeCN which gives a broad ^{19}F n.m.r. signal, δ 221 p.p.m. to low field of CCl_3F, width at half height 170 Hz. At 233 K a broad, partially resolved, doublet is observed. The spectra are presumably due to ^{51}V quadrupole relaxation, noted also in the VOF_4^- anion [3b], and to ^{19}F exchange.

Removal of solvent from a freshly prepared MeCN solution results in a yellow solid, approximately $VOF_3 \cdot NCMe$. Its i.r. spectrum indicates the presence of co-ordinated MeCN, $\nu(CN)$ 2296 cm^{-1}; $\nu(CC)$ 954 cm^{-1}; $\nu(V=O)$ is at 1015 cm^{-1} compared with 1039 cm^{-1} in solid VOF_3 [2b]. In view of the di-μ-F bridged, dimeric units present in solid VOF_3 [1a] which persist in its vapour to some extent [1b], the solid adduct may be dimeric.

VOF_3 reacts slowly with MeCN at ambient temperature to form a blue species containing the $V^{IV}O$ group and HF. The reaction is characterised by a broadening and shift to higher applied field of the solvent ^1H n.m.r. signal, and by the appearance of a band at 16,200 cm^{-1} in its electronic spectrum. Fifteen days are required for complete reduction in a solution containing 5.6 x 10^{-4} mol.1^{-1} VOF_3; in the dark the reaction is even slower. The electronic spectrum of the VOF_5^{3-} anion contains a band at 15,800 cm^{-1} [7], and since F^- and MeCN occupy similar positions in the spectrochemical series, we suggest that the species formed is VOF_2 solvated by MeCN. The behaviour of VOF_3 in MeCN is similar to that of UF_6 which is reduced slowly to UF_5 [8].

Me_3SiNEt_2 reacts rapidly with VOF_3 in MeCN below ambient
temperature.   In the absence of MeCN reactions are slow and
incomplete, but otherwise appear to be similar.   Mass balances,
product analyses, and the i.r. spectra of the products
(experimental section) are consistent with the reactions

$$VOF_3 + nMe_3SiNEt_2 \longrightarrow VOF_{3-n}(NEt_2)_n + nMe_3SiF$$

$$(n = 1-3)$$
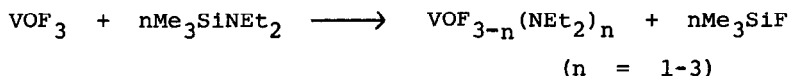
When n = 1 or 2 the vanadium containing products are brown solids
and when n = 3 a red-brown liquid is obtained, identical in
appearance to the recently described $VO(NEt_2)_3$ [6].   However
the products' i.r. spectra also contain bands at 3250, 3130
and 1610 ~ 1620 cm^{-1} attributable to N-H stretching and
deformation modes, and more importantly, their rooom temperature
magnetic moments, and low energy bands in their electronic spectra
(Table 1) indicate that some vanadium (IV) is present.   To
reconcile the experimental data, the products are formulated as
$VOF_{3-n}(NEt_2)_n$ (n = 1-3) containing small amounts of $V^{IV}OF_{2-m}$
$(NEt_2)_m(NEt_2H)$ (m = 0-2).

TABLE 1

Room temperature magnetic moments and electronic spectra of:

| | Vanadium containing products from reactions | | |
	1:1	1:2	1:3
μ_{eff} (B.M.)	1.74 [a]	1.66	1.05 [a]
	1.60		1.03
ν_{max} cm^{-1} [b]			16,300(sh) [c]
(apparent ε)			
in MeCN	19,600(31)		19,400(sh) [c]
	24,200(100)	25,000(sh)	
			28,700(470)
	32,600(120)	31,750(sh)	
		36,400(sh)	

[a] Determined from different samples.   [b] Spectra contain
intense bands >35,000 cm^{-1}.   [c] Become more pronounced on
standing for several days.

Although the magnetic moments are generally less than the spin only d^1 value commonly found in vanadyl(IV) compounds [7], they are too great to be accounted for solely by the temperature independent paramagnetism expected in vanadium(V) oxofluorides [9]. For example, μ_{eff} for VOF_3 at room temperature is 0.35 B.M. Similarly the electronic spectral bands below 20,000 cm^{-1} are too weak to be accounted for by charge transfer transitions, and they must be d-d bands.

The paramagnetism in these compounds is confirmed by the observation of e.p.r. spectra. That of the 1:1 reaction product both at ambient temperature and at 77 K is a broad signal, $\bar{g}$ 1.96. At ambient temperature the 1:3 product exhibits an eight line spectrum due to the interaction between the electronic spin and ^{51}V. The multiplet is slightly asymmetric due to second order effects; these were included in the analysis to give $\bar{g}$ 1.971 $\pm$ 0.002 and $\bar{A}$ -60 $\pm$ 2 x 10^{-4} cm^{-1}. At 77 K the spectrum is characteristic of an axially symmetric species in which $g_{\parallel}$ 1.953 $\pm$ 0.002 and $A_{\parallel}$ -127 $\pm$ 2 x 10^{-4} cm^{-1}. Values for $g_{\perp}$ and $A_{\perp}$ were obtained from $g_{\parallel}$, $A_{\parallel}$, $\bar{g}$, and $\bar{A}$, a procedure which has been shown to be valid for $V(NEt_2)_4$ [10]. The e.p.r. parameters are very similar to those of $V(NEt_2)_4$, raising the possibility that this compound might be responsible for the observed para-magnetism. However reference to the electronic spectrum of $V(NEt_2)_4$ [10, 11] indicates that this is unlikely.

The ^1H n.m.r. spectrum of the liquid 1:3 product comprises four broad peaks (A, B, C, D) at δ 2.8 ~ -2.5 p.p.m. Their chemical shifts vary slightly from sample to sample, but the peak separations remain constant at 108, 47, and 66 Hz. The peaks are too broad for accurate integration but the order of relative intensities is C > A >> D > B with A:C 1:2 and B:D 1:1.3. Spectra of MeCN solutions show four peaks but the relative intensity of B is greatly increased, indicating that it now includes the MeCN resonance. Chemical shifts reported for $VO(NEt_2)_3$ are $\delta(CH_2)$ 3.68 and $\delta(CH_3)$ 1.15 p.p.m., $\delta(CH_2)$ - $\delta(CH_3)$ 152 Hz, and the expected fine structure is observed [6]. We assign peaks A and C, separation 155 Hz, to $VO(NEt_2)_3$, and B and D to $VO(NEt_2)_2(NEt_2H)$. The $-NEt_2$ moieties in the latter compound are equivalent due to rapid H^+ exchange, and exchange

of $-NEt_2$ ligands between V^V and V^{IV} centres is responsible for the lack of fine structure in $VO(NEt_2)_3$.

The ^1H n.m.r. spectrum of the 1:1 product in MeCN shows only a broad signal δ 0 ~ 1 p.p.m. suggesting that ^1H exchange is rapid. No ^{19}F signal could be observed. Surprisingly, no e.p.r. signals could be detected from MeCN solutions of these compounds, but this may be simply a reflection of the low concentration of V^{IV} present in the solutions.

The behaviour of VOF_3 towards Me_3SiNEt_2 contrasts sharply with that of NbF_5 and TaF_5, where the sole products are $MF_4(NEt_2)$ or $MF_3(NEt_2)_2$ depending on the conditions used [5]. The behaviour observed in the present work is a reflection of the stronger oxidising ability of a 3d transition metal in its highest oxidation state compared with its 4d and 5d analogues. Reduction of VOF_3.L (L = pyridine- or picoline-N-oxides) complexes in MeCN has been noted briefly [4], and reduction of V^V occurs also in the reaction of VOF_3 with trimethyl(methoxo)- silane, both in the presence of MeCN and in its absence. VOF_3 reacts rapidly with Me_3SiOMe, 1:3 mole ratio, in MeCN below ambient temperature to give Me_3SiF and impure $VO(OMe)_3$. The product's electronic spectrum contains a weak band at 16,200 cm^{-1} indicating that V^{IV} is present. In contrast, VOF_3 and hexamethyldisiloxane reacted under similar conditions giving Me_3SiF and vanadium dioxide fluoride, which is insoluble in MeCN.

It is considered that the reactions between VOF_3 and Me_3SiNEt_2 involve an initial substitution of F- by $-NEt_2$, the extent of which depends on the reactions' stoicheiometry. However the Et_2N-V^V compounds so formed are very susceptible to reduction, presumably by loss of a $\cdot NEt_2$ radical. This is followed by hydrogen abstraction either from MeCN or from trace H_2O inevitably present. Related behaviour has been observed in the reaction of XeF_2 with Me_3SiNR_2 compounds in MeCN, although in that case, $Xe-NR_2$ compounds were not observed [12]. In contrast to the previous report [6] we find no evidence for MeCN insertion into the V-N bonds of $VO(NEt_2)_3$, although the concentration of V^{IV} increases slowly in the solution. The direct reduction of VOF_3 by MeCN is not considered to be important in this context, as it occurs too slowly.

Reduction does not occur in the reaction of VOF_3 with $Me_3SiOSiMe_3$, presumably because of the insolubility of VO_2F, and for a similar reason VOF_3 is unaffected by EtCN.

EXPERIMENTAL

All operations were carried out in a Pyrex vacuum line or in N_2 or Ar filled glove boxes equipped with gas recirculation and purification systems (Lintott). Reactions were performed in pyrex ampoules fitted with P.T.F.E. stopcocks (Rotaflo). Similar vessels, to which n.m.r. or quartz e.p.r. tubes or 10 mm Spectrosil cells were sealed, were used to prepare samples under vacuum for spectroscopic studies. Samples for i.r. spectroscopy were contained in a Pyrex cell with KBr windows, or were Nujol or Fluorube mulls or liquid films between AgCl windows. X-ray powder diffraction samples were contained in sealed Lindemann capillaries. Room temperature magnetic susceptibilities were determined by the Gouy method, samples being contained in B.7 capped tubes. Instrumentation was as follows: n.m.r., Jeol C60-HL, ^1H at 60, ^{19}F at 56.4 MHz, external referencing to Me_4Si or CCl_3F, low field shifts are positive; e.p.r., Decca X3 and Newport 11" magnet; electronic, Beckmann UV 5270; i.r., Perkin Elmer 577; X-ray, Phillips PW 1061 source, Cu Kα radiation, and powder diffraction camera; magnetic susceptibility, Stanton SM12 balance and Newport 1.5" magnet.

VOF_3 (Fluorochem) was sublimed twice before use. Trimethyl-silyl-compounds (Aldrich) were distilled under N_2, then in vacuo, and were stored over activated 4A molecular sieves. Acetonitrile (Hopkin and Williams) was refluxed successively over CaH_2, P_2O_5 (twice), and CaH_2, topping and tailing at each stage. It was then degassed and stored over activated 4A sieves in vacuo. Other organic solvents were dried by conventional procedures and were stored over activated sieves in vacuo. Vanadium analyses were by atomic absorption (Perkin Elmer 303) after sample hydrolysis in aqueous acid. Other analyses were by Malissa and Reuter, Engelskirchen, W. Germany.

Behaviour of VOF$_3$ in organic solvents

Mixtures of VOF$_3$ with n-pentane or dimethyl carbonate reacted
rapidly when warmed to ambient temperature, and brown-black
solids were formed.   VOF$_3$ and nitromethane gave a red solid,
but VOF$_3$ dissolved readily in acetonitrile to give a yellow
solution.   Removal of solvent from a solution containing 1.36 g
VOF$_3$ in MeCN (10 ml) left a yellow solid whose mass (1.72 g)
corresponded to VOF$_3$,0.8 MeCN.   Solutions of VOF$_3$ in MeCN became
green on standing at ambient temperature;   the change was
observable after 24h and the reaction's progress was conveniently
followed by monitoring the solution's electronic spectrum.
Removal of volatile material, in which SiF$_4$ was identified by
its i.r. spectrum, left a sticky blue solid whose i.r. spectrum
showed ν(V=O)   1010 cm^{-1} and co-ordinated MeCN, ν(CN) 2300 and
ν(CC) 950 cm^{-1} respectively.

Reactions between VOF$_3$ and trimethylsilyl-compounds

(i)   A mixture of VOF$_3$ (4.5 mmol), Me$_3$SiNEt$_2$ (4.5 mmol), and
MeCN (90.5 mmol) was allowed to warm slowly from 77 K to room
temperature.   As the MeCN melted the reaction mixture became
dark brown and a dark brown solution was formed at room
temperature.   Volatile material at room temperature was
identified from i.r. and n.m.r. spectroscopy as a mixture of
MeCN and Me$_3$SiF.   Found 4.10 g;   required for 4.5 mmol Me$_3$SiF
and 90.5 mmol MeCN, 4.12 g.   The residue was a dark brown solid
(Found C, 27.0; H, 5.9; F, 22.3; N, 7.8; V, 26.7.   C$_4$H$_{10}$F$_2$NOV
requires C, 26.8; H, 5.6; F, 22.3; N, 7.8; V, 28.5%) whose mass
corresponded to 4.6 mmol VOF$_2$(NEt$_2$).   The X-ray powder photograph
of the solid showed no lines attributable to VOF$_3$, and indicated
that it was not isomorphous with this compound.

(ii)   VOF$_3$ (2.9 mmol), Me$_3$SiNEt$_2$ (5.8 mmol), and MeCN
(60.0 mmol) reacted under similar conditions to give a mixture
(3.00 g) of Me$_3$SiF and MeCN (required for complete reaction
3.01 g) and a brown solid (Found C, 42.1; H, 8.7; F, 8.0; N, 12.2;
V, 23.2.   C$_8$H$_{20}$FN$_2$OV requires C, 41.7; H, 8.8; F, 8.25; N, 12.2;
V, 22.1%) whose mass corresponded to 2.8 mmol VOF(NEt$_2$)$_2$.

(iii)   VOF$_3$ (1.65 mmol), Me$_3$SiNEt$_2$ (5.3 mmol), and MeCN
(136 mmol) reacted under similar conditions to give a mixture
(6.03 g) of Me$_3$SiF and MeCN (required for complete reaction
6.03 g) and a red-brown involatile liquid (Found C, 52.0; H, 9.8;
N, 14.6; O, 5.4; V, 17.1.   C$_{12}$H$_{30}$N$_3$OV requires C, 50.9; H, 10.7;
N, 14.8; O, 5.65; V, 18.0) whose mass corresponded to 1.65 mmol
VO(NEt$_2$)$_3$.

(iv)   Reactions performed without a solvent were similar
except that unchanged VOF$_3$ was recovered even after several
hours.   Reactions in which the mole ratio VOF$_3$:Me$_3$SiNEt$_2$ was
>1:3 gave products identical to (iii) and unchanged Me$_3$SiNEt$_2$.

(v)   The reaction between VOF$_3$ (1.6 mmol) and Me$_3$SiOMe
(4.9 mmol) in MeCN (7 ml) using a procedure similar to (i) gave
Me$_3$SiF and a yellow-green solid.   The latter's i.r. spectrum
showed the presence of V=O and -OMe groups.   Its ^{1}H n.m.r.
spectrum was a broad singlet;   this and its electronic spectrum
indicated that reduction of V^V had occurred to some extent.

(vi)   VOF$_3$ (2.7 mmol) and Me$_3$SiOSiMe$_3$ (2.9 mmol) reacted
in MeCN (3.00 g) under similar conditions gave Me$_3$SiF (5.0 mmol),
unchanged MeCN and Me$_3$SiOSiMe$_3$ (3.07 g), and an insoluble, orange-
yellow solid, identified as VO$_2$F (2.6 mmol) from its analysis
(Found V 51.3. FO$_2$V requires V, 50.0%) and i.r. spectrum [13].

Infra-red spectra

Spectra obtained for the products from reactions (i) - (iii)
contained bands attributable to the internal modes of -NEt$_2$
ligands [14], and to N-H bonds.   Bands observed in the region
1050-500 cm^{-1} are shown in Table 2.   Assignments made
assuming C$_s$ or C$_{3v}$ local symmetry at vanadium resulted in an
internally consistent picture, although the effect of V^{IV} species
was ignored.   The assignment of ν_{as}(VN$_3$) in VO(NEt$_2$)$_3$ agrees
well with previous work [6].   The bands assigned to ν(V=O)
are lower than found normally, but this may be due to the presence
of the good, π-donor ligand, -NEt$_2$.

TABLE 2

I.r. spectra of products from reactions

(i) '$VOF_2(NEt_2)$'	(ii) '$VOF(NEt_2)_2$'	(iii) '$VO(NEt_2)_3$'	Tentative assignments
1005sh	1005vs	1000vs	$\nu_s(NC_2)$
985vs	970s	930s	$\nu(VO)$
	930sh		
885w	890m	890vs	NEt_2 mode
845w	840s		$\nu(VF_2)N$, $\nu(VFN_2)$
		830s	$\nu_{as}(VN_3)$
785m	775sh	787vs	NEt_2 mode
		760sh	
		740sh	
720s	725s		$\nu(VF_2N)$, $\nu(VFN_2)$
		613s	$\nu_s(VN_3)$
	605sh		
590sh	580m,br		$\nu(VF_2N)$, $\nu(VFN_2)$
505m,br	505m,br	505m,br	NEt_2 mode

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