Contrasts in the Hydrolysis of $VOCl_3$ and $VO(NO_3)_3$: A Multinuclear Magnetic Resonance Study†

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Controlled hydrolysis of $VO(NO_3)_3$ in CH_3CN or CH_3NO_2 first gives the dimer $V_2O_3(NO_3)_4$, then a complex mixture of polymeric species. In contrast, the hydrolysis of $VOCl_3$ in CH_3CN gives $[VO_2Cl_2]^-$, together with some $[VOCl_4]^-$. The ion $[VO_2Cl_2]^-$ has also been prepared independently, and then converted into $[VO_2Cl(NO_3)]^-$ and $[VO_2(NO_3)_2]^-$. Species have been characterised by ^{51}V, ^{17}O, ^{15}N, and ^{14}N n.m.r. spectroscopy, and by stoicheiometry. The ^{51}V and ^{17}O chemical shifts are consistent with the anticipated bonding.

Although the aqueous chemistry of vanadium(V) has been extensively studied,[1] notably by ^{51}V n.m.r. spectroscopy,[2] very little has been reported until recently concerning species existing under highly acidic conditions. The ion $[VO_2(OH_2)_n]^+$ is the only species observed in aqueous acid, although Begun and co-workers [3] have presented evidence for dimeric species in very concentrated aqueous H_2SO_4 and $HClO_4$. They proposed a structure based on either $[V_2O_3]^{4+}$ or $[V_2O_4]^{2+}$, and preferred the former. A qualitative ^{51}V n.m.r. study has also been made[4] of the alcoholysis products of $VOCl_3$.

The present study uses not only $VOCl_3$ in various solvents, but also $VO(NO_3)_3$, which can be prepared as a pure liquid[5] in anhydrous form. Controlled hydrolysis of these reactive compounds is a plausible route to novel vanadium(V) species, some of which can be prepared independently to assist characterisation. The reactions investigated here are outlined in the Scheme.

Experimental

N.m.r. spectra were obtained in the Fourier-transform mode on either a Bruker WM250 instrument operating at 65.79 MHz (^{51}V) and 18.07 MHz (^{14}N) or a Bruker WH400 operating at 105.12 MHz (^{51}V), 54.24 MHz (^{17}O), 40.56 MHz (^{15}N), and 28.91 MHz (^{14}N). Vanadium, oxygen, and nitrogen shifts were referred to external $VOCl_3$, water, and the nitrate resonance of 5 mol dm^{-3} NH_4NO_3 in 2 mol dm^{-3} HNO_3 respectively. The ^{51}V shifts were reproducible to within 2 p.p.m., ^{17}O shifts to 5 p.p.m., and nitrogen shifts to 1 p.p.m. The ^{51}V n.m.r. spectra required *ca.* 1 000 transients at *ca.* 10 per second, ^{17}O spectra needed 4 000—16 000 transients, ^{14}N spectra 40—400 transients, and ^{15}N spectra 100—1 000 transients. At 54.22 MHz it was impossible to stimulate the nitrate and vanadyl oxygens of $VO(NO_3)_3$ equally and simultaneously and so the ^{17}O n.m.r. spectra of the two different types of oxygen were observed separately.

Infrared spectra between 4 000 and 400 cm^{-1} were recorded in a solution cell with silver chloride windows using a Perkin-Elmer 577 spectrometer.

The compound $VO(NO_3)_3$ was prepared by reaction of V_2O_5 with N_2O_5[5] and isolated *in vacuo* (10^{-2} Torr) at 60 °C; 5% ^{15}N-enriched $VO(NO_3)_3$ was prepared from enriched N_2O_5. The enriched N_2O_5 was prepared by dehydration of 100% HNO_3 with P_4O_{10}. The enriched 100% HNO_3 had previously been prepared by vacuum distillation (10^{-2} Torr) of a mixture of 5% ^{15}N-enriched KNO_3 (Amersham International) and 98% H_2SO_4. The salt NEt_4Cl (Fluka) was dehydrated *in vacuo* (10^{-4} Torr) at 60 °C until it sublimed. Vanadyl trichloride (Aldrich) and 20 atom % ^{17}O-enriched water (Amersham International) were used as supplied. Acetonitrile was dried over molecular sieves (type 4A), refluxed with CaH_2, and fractionated before use. Nitromethane and dichloromethane were dried over molecular sieves (type 4A) and fractionated before use.

Quantitative hydrolysis experiments were carried out by adding known weights of a solution of known water content to a solution containing a known amount of VOX_3 ($X = NO_3$ or Cl). Quantitative experiments involving $AgNO_3$ were carried out by taking known weights of $AgNO_3$ and $[NBu_4][VO_2Cl_2]$, dissolving them separately (in either MeCN or CH_2Cl_2), and then mixing the two solutions.

The previously unreported tetrabutylammonium salt of dichlorodioxovanadate(V), $[NBu_4][VO_2Cl_2]$, was obtained by a method analogous to the literature preparation[6] of $[MPh_4][VO_2Cl_2]$ (M = As or P) (Found: C, 48.4; H, 9.2; N, 3.5. $C_{16}H_{36}Cl_2NO_2V$ requires C, 48.5; H, 9.2; N, 3.5%). The salts $[AsPh_4][VO_2Cl_2]$ and $[AsPh_4][VO_2F_2]$ were prepared by literature methods.[6] Solutions of $[VOCl_4]^-$ were generated by the addition of NEt_4Cl to solutions of $VOCl_3$ in MeCN.[7]

Results and Discussion

The Table summarises the species obtained, together with their chemical shifts where measurable. Many of these shifts represent the first reported example of their chemical kind. Some ^{17}O shifts for the hydrolysis products may be obscured by the resonance at δ *ca.* 450 due to HNO_3; unfortunately, this cannot be avoided by addition of $H_2{}^{17}O$, because of chemical exchange. Separate ^{15}N resonances for HNO_3 and $V_2O_3(NO_3)_4$ were observed only at −20 °C, which indicates a fairly rapid exchange of the nitrato-ligands with HNO_3. In contrast, no such exchange was observed with $VO(NO_3)_3$.

Nitrato-species.—The results of the initial hydrolysis are shown in Figures 1 and 2. Integration of the resonances, together with the measured stoicheiometry, are entirely and solely consistent with the reaction (1) proceeding to up to

$$2VO(NO_3)_3 + H_2O \xrightarrow{\text{MeCN or MeNO}_2} V_2O_3(NO_3)_4 + 2HNO_3 \quad (1)$$

ca. 60% removal of $VO(NO_3)_3$ in $MeNO_3$. Beyond, this, further species appear, in exchange with each other. These cannot at present be readily identified except to note that the

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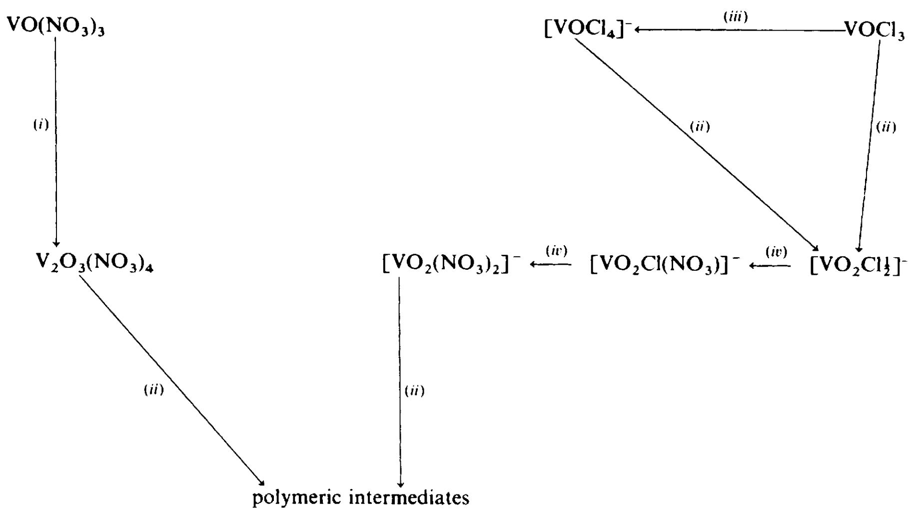
† *Non-S.I. unit employed:* Torr ≈ 134 Pa.



Scheme. (*i*) Water (0.5 mol); (*ii*) water; (*iii*) Cl⁻; (*iv*) $AgNO_3$

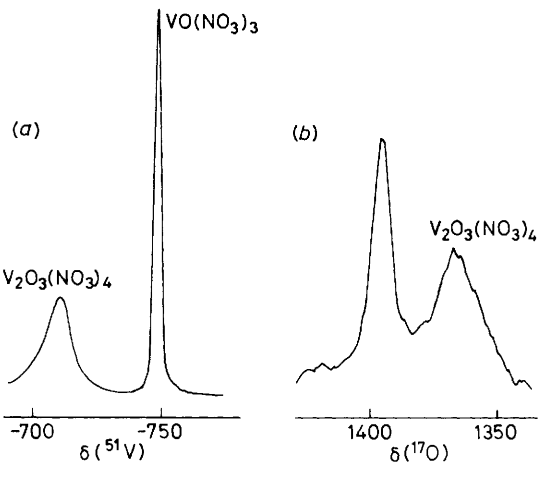


Figure 1. N.m.r. spectra at 294 K of the $VO(NO_3)_3$–water (mole ratio 1 : 0.3) system in $MeNO_2$: (*a*) ^{51}V and (*b*) ^{17}O

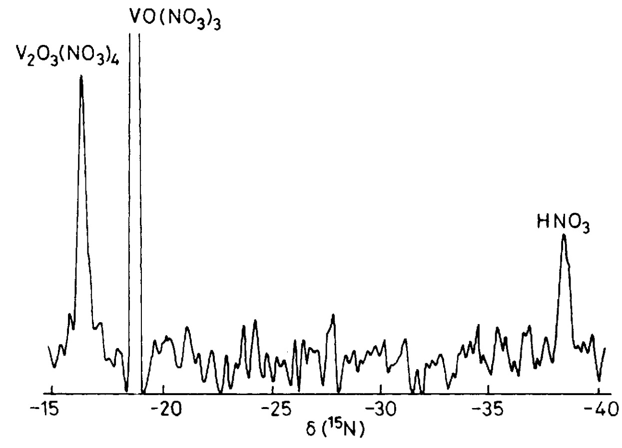


Figure 2. Nitrogen-15 n.m.r. spectrum, at 250 K, of the $VO(NO_3)_3$–water (mole ratio 1 : 0.07) system in $MeNO_2$

dependence of their formation upon concentration suggests that they are polymeric. Here we concur with Begun and co-workers[3] in their conclusions regarding sulphuric acid media. However, our unequivocal observation of $\delta_V = -710$ for $V_2O_3(NO_3)_4$, together with other more extensively hydrolysed products at higher δ_V, tilts the balance of the argument strongly towards an underlying $[V_2O_4]^{2+}$ formulation for the species observed by Begun and co-workers[3] at $\delta_V = -640$ in 13 mol dm^{-3} H_2SO_4

On the basis of i.r. spectra we propose that $V_2O_3(NO_3)_4$ is an oxygen-bridged species, even though the spectra are complicated by many bands due to $VO(NO_3)_3$, HNO_3, and acetonitrile or nitromethane. In the latter solvent, bands attributed only to $V_2O_3(NO_3)_4$ were observed at 852 and 960 cm^{-1} (a shoulder), and are tentatively assigned to ν(O–V–O) and ν(V–O–V) respectively.[3] The appearance of this latter band indicates that the V–O–V bridge is not linear. Similar bands, together with those of co-ordinated nitrate, were observed in more extensively hydrolysed solutions containing only polymeric species. The chemical shift of $[VO_2(NO_3)_2]^-$ (−543) is very similar to that of VO_2^+ (aq) ($\delta_V = -546$),[8] perhaps suggesting that here the nitrate moieties are not strongly co-ordinated. There is also a significant dependence of chemical shift upon solvent with most of the nitrato-species, entirely consistent with the known ability of acetonitrile to enter the first co-ordination sphere in $VO(NO_3)_3$.[9]

Chloro-species.—Vanadyl trichloride in acetonitrile gives a single peak at $\delta_V = -117$, ascribed elsewhere[10] to $VOCl_3(NCCH_3)_2$. Gradual addition of water at room temperature shifts this resonance progressively towards a limiting value of −365, identical to that found for $[VO_2Cl_2]^-$ prepared independently (see Experimental section) and dissolved in acetonitrile. Both solutions also showed i.r. absorptions at 965 [$\nu_{asym}(VO_2)$], 957 [$\nu_{sym}(VO_2)$], and 452 cm^{-1} [ν(V–Cl)]. The ion $[VOCl_4]^-$, the ^{51}V shift of which has recently been reported,[7] gave the same hydrolysis product. However, in this case exchange was slower, with separate resonances for $[VOCl_4]^-$ and $[VO_2Cl_2]^-$ observable in all stages of hydrolysis. Thus, no evidence exists in the chloro-system for polymeric or even dimeric species other than the formation of a darkly coloured precipitate on hydrolysis of $VOCl_3$ solutions of high concentration. Oxygen-17 chemical shift values were obtained (see Table), for the first time, by using 20% $H_2{}^{17}O$ in the hydrolysis. The values for $[VO_2Cl_2]^-$ and $[VO_2F_2]^-$ are of especial interest because ^{17}O n.m.r.

Table. Chemical shifts of species described, together with those of some related species

Species	$\delta(^{51}V)$	$\delta(^{17}O)$	$\delta(^{15}N)$	$\delta(^{14}N)$	Ref.
$VO(NO_3)_3$	−745[a]	1 399,[a] 449[a]		−16.8[a]	*b*
	−746[c]	1 398[c]	−18.0[c]	−20.0[c]	*b*
	−749[d]	1 395[d]	−18.9[d]	−18.1[d]	*b*
$V_2O_3(NO_3)_4$	−724[c]	1 384[c]	−11.0[c]		*b*
	−710[d]	1 365[d]	−16.7[d]		*b*
$[VO_2(NO_3)_2]^-$	−543[c,e]			−10.8[c]	*b*
$[VO_2Cl(NO_3)]^-$	−472[c,e]			−13.6[e]	*b*
$[VO_2Cl_2]^-$	−365[c,e]	1 182			*b*, 7
$VOCl_3$	0,[a] −117[c]	1 327[a]			*b*
$[VOCl_4]^-$	42.5[c]	1 272[c]			*b*, 7
VOF_3	−793[c]				*b*
$[VO_2F_2]^-$	−593[c]	1 109[c]			*b*, 7
$VO_2^+(aq)$	−546	*f*			8
Polymeric nitrato-species	*ca.* −700 to −610[c]	*ca.* 1 320[c]		*f*	*b*
HNO_3		444[c,d]	−38.4[d]	−40.0[d]	*b*

[a] Pure liquid. [b] This work. [c] In acetonitrile. [d] In nitromethane. [e] In dichloromethane. [f] Not observed, probably due to exchange with solvent.

measurements on aqueous VO_2^+ have not been reported, presumably because of rapid oxygen exchange with solvent.

Addition of solid $AgNO_3$ to a solution of $M[VO_2Cl_2]$ ($M = AsPh_4^+$ of NBu_4^+) in MeCN or CH_2Cl_2 ($\delta_V = -543$) caused immediate precipitation of AgCl. New ^{51}V peaks appear at δ −472 and −543. The latter peak alone remained when the mole ratio $AgNO_3$: $M[VO_2Cl_2]$ exceeded 2.0:1. The use of very small amounts of $AgNO_3$ resulted in the formation of the resonances at δ_V −472 without that at δ_V −543. We assign the resonances at δ_V −472 to $M[VO_2Cl(NO_3)]$ and that at δ_V −543 to $M[VO_2(NO_3)_2]$ as noted above. Integrations of the resonances in the ^{14}N spectra when $M = NBu_4^+$ were fully consistent with the production of $[VO_2Cl(NO_3)]^-$ and $[VO_2(NO_3)_2]^-$. Both $[VO_2Cl(NO_3)]^-$ and $[VO_2(NO_3)_2]^-$ give rise to ^{14}N resonances in positions characteristic of covalent nitrate[11] (see Table).

Chemical Shifts.—The ^{51}V shift of $VO(NO_3)_3$ is close to that for VOF_3, probably because either ligand forms only a weakly covalent bond with V, and so has little effect on its temperature-independent paramagnetism (t.i.p.). Addition of a second oxo-ligand does contribute to t.i.p. at the vanadium centre, thus increasing δ_V. At the same time, the oxygens compete to some extent for the empty *d* orbitals on vanadium, despite the probability that they minimise such competition by adopting a *cis* configuration. This lowers δ_O. According to a simple correlation,[2] $\delta_O \approx 1\,400$ corresponds to a V–O bond order of 2.0, dropping to 1.8 for $[VO_2Cl_2]^-$ ($\delta_O = 1\,182$) and 1.7 for $[VO_2F_2]^-$ ($\delta_O = 1\,109$). Vibrational spectroscopy suggests a bond order of 1.9 for the latter two ions.[6] All these values are higher than the value of 1.5 suggested by a simple valence formalism with the negative charge solely on oxygen, but lower than that (2.0) with all the charge on the halogen. They are also a little higher than found in the corresponding diperoxo-complexes.[12]

The replacement of NO_3^- by Cl^- has only a small effect on δ_O, in a direction implying some $Cl \rightarrow V$ charge transfer. However, it increases δ_V markedly, in approximate proportion to the number of bound chlorines, providing evidence of the much greater charge transfer in low-lying excited states.

Conclusions

The very different hydrolysis reactions of $VO(NO_3)_3$ and $VOCl_3$ demand explanation. Both these apparently four-co-ordinate compounds are unusual in that vanadium(V) is normally five- or six-co-ordinate under acidic conditions: $VO(NO_3)_3$ in fact has three bidentate nitrato-ligands,[13] and $VOCl_3$ shows its co-ordination unsaturation by readily forming $[VOCl_4]^-$ and $VOCl_3(NCCH_3)_2$. Each V in $V_2O_3(NO_3)_4$ will have one terminal and one bridging O ligand, probably arranged mutually *cis* as argued above. Its remaining four co-ordination positions could then be occupied by two bidentate nitrates, one of which could become monodentate upon further polymerisation. The dimeric molecule is novel even for nitrato-complexes, for these are normally monomeric [*e.g.*, $Ti(NO_3)_4$[14] and $VO(NO_3)_3$[13]] or extensively polymerised [*e.g.*, $Cu(NO_3)_2$[15]]. The only known nitrato-oligomer is tetrameric, $Be_4O(NO_3)_6$.[16]

Chloride, in contrast, cannot chelate. Also, most chloro-complexes reported here carry negative charge, which will further inhibit polymerisation. It remains to be seen, however, whether polymeric chloro-complexes of vanadium(V) can be made when these two restraints are minimised.

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