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Formation and Exchange Reaction of the Vanadium(V) Dimer $[V_2O_2(O\text{-}i\text{-}C_3H_7)_7]^-$

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It has been known for some time that self-association occurs in compounds of type VOX_3 and $[VOX_4]^-$, where X is typically Cl^- or an alkoxide ion, especially in the solid state and in non-polar solvents [1, 2]. However, the solution structure of these complexes is not well understood [2]. Also, isopropoxy complexes have thus far been reported to be monomeric [3], presumably due to steric repulsions.

We have therefore studied the reaction of $VOCl_3$ with potassium isopropoxide, under strictly anhydrous conditions. Toluene was selected as the solvent to minimise the possibility of its coordination [2]. We first showed that ^1H NMR does not discriminate adequately between the various species formed, and then proceeded by using ^{51}V NMR at 105.2 MHz under standard conditions [4].

The displacement of Cl by isopropoxide (OiPr) proceeds stoichiometrically as far as $VO(OiPr)_3$. The ^{51}V chemical shifts are listed in Table I and do not differ from those previously reported [3] by more than an amount attributable to the change of solvent. We found no evidence for the presence of species such as $[VO(OiPr)Cl_3]^-$, although minor components could possibly be hidden by exchange processes. The resonance of $VO(OiPr)_3$ was notably the narrowest after $VOCl_3$, probably because of its higher symmetry. However, further reactions were observed upon addition of more KOiPr. At 228 K, where chemical exchange is reduced, a new resonance forms at −570 ppm, and is almost uniquely present when a large excess of KOiPr has been added. We identify this species as $[VO(OiPr)_4]^-$. The 60 ppm increase of δ_V upon anation is consistent with the known shift of +50 ppm in this solvent for $[VOCl_4]^-$.

TABLE I. ^{51}V Chemical Shifts of Isopropoxy Vanadium(V) Species

Species	Solvent	δ_V[a]	Further details
$VO(OiPr)Cl_2$	toluene $CHCl_3$	−310 −307	20 °C (ref. 3)
$VO(OiPr)_2Cl$	toluene $CHCl_3$	−507 −503	20 °C (ref. 3)
$VO(OiPr)_3$	toluene benzene	−630 −641	20 °C, WHH = 80 Hz (ref. 3)
$[VO(OiPr)_4]^-$	toluene	−570	20 °C, K^+ salt
$[V_2O_2(OiPr)_7]^-$	toluene	−401	−45 °C, K^+ salt

[a] Capillary $VOCl_3$ = 0.

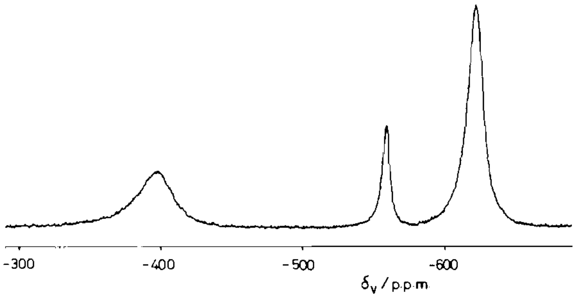

Fig. 1. ^{51}V NMR spectrum at −45 °C in toluene of an equilibrated mixture of (from left to right) $[(iPrO)_3VO(OiPr)VO(OiPr)_3]^-$, $[VO(OiPr)_4]^-$ and $VO(OiPr)_3$.

More surprisingly, a second, still broader resonance appears at −401 ppm (Fig. 1) and reaches maximum relative concentration when the concentrations of $VO(OiPr)_3$ and $[VO(OiPr)_4]^-$ are equal. The proportion of this new species varies with concentration in a manner consistent with the reaction

$$VO(OiPr)_3 + [VO(OiPr)_4]^- \rightleftharpoons [V_2O_2OiPr)_7]^-$$

$$K = 1040 \pm 130\ dm^3\ mol^{-1} \qquad (1)$$

But is the dimeric species bridged by $[O]^{2-}$ or by $[OiPr]^-$? Our studies of a different oxo-bridged dimer, $V_2O_3(NO_3)_4$, suggest that such bridging does not have a large effect on the ^{51}V chemical shift [4]. Also, vanadium(V) is usually reluctant to lose its final coordinated oxygen. Instead, the data and especially the unusually high chemical shift of −401 ppm points to a bridging isopropoxide, probably single in view of the symmetry apparent from the NMR data. Vanadium shifts are usually increased, according to a recent theory [5], when at least one bond to V is lengthened (beyond *ca.* 1.7 Å), because this lowers the $\sigma^* \leftarrow \sigma$ transition energy of the bond. This analysis is supported by our observation that the pale yellow solution darkens noticeably when dimer is present. Thus we propose a bridging isopropoxide, symmetrical at least on the NMR timescale, with substantially lengthened V–O distances.

When the temperature is raised, the proportion of this dimer decreases. (A crude calculation gave ΔH_f = −13 kJ mol^{-1} for reaction (1) above). But in addition, the resonances arising from the dimer and from $VO(OiPr)_3$ broaden and eventually merge, whereas that from $[VO(OiPr)_4]^-$ narrows as expected for a non-exchanging species. It follows that equation (1) cannot represent the actual kinetic process involved. Instead, by analogy with our earlier observations on

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vanadates [6] and thiovanadates [5], we propose an exchange reaction

$$V^*O(OiPr)_3 + [(iPrO)_3VO(OiPr)VO(OiPr)_3]^- \rightleftharpoons VO(OiPr)_3 + [(iPrO)_3V^*O(OiPr)VO(OiPr)_3]^-$$

The corresponding reaction involving $[VO(OiPr)_4]^-$ is substantially less likely, because of anion–anion repulsions, and therefore the peak at −570 ppm is not observed to broaden.

It is surprising that an isopropoxide anion should succeed in bridging two $VO(OiPr)_3$ moieties, whereas Cl^- apparently does not. The explanation of this may be related to that of recently substantiated observations [7, 8] that vanadium-containing polyanions protonate at bridging oxygen sites.

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