Temperature and Solvent Dependence of Vanadium-51 Chemical Shifts and Line Widths of Vanadyl-triisopropylate

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Line widths $\Delta\nu_{1/2}$ of ^{51}V n.m.r. signals of vanadyl-triisopropylate VO(OPr^i)$_3$ dissolved in tetrahydrofurane range from 10 to 610 Hz, increasing with decreasing temperature according to a theoretically proposed $T^{-1/2}\exp(E/RT)$ law, indicating that the molecular correlation time τ_c is the main factor influencing line widths in this system. With lowering of temperature, ^{51}V-shielding decreases (the temperature gradient of the chemical shift δ_V is about -0.5 ppm/K over a temperature range of 300—180 K), suggesting a loss of molecular symmetry due to solvation and association processes. In pentane, methylcyclohexane and diethylether, the δ_V/T and $\Delta\nu_{1/2}/T$ correlations exhibit two inconsistencies at approximately 190 and 240 K which are attributed to the formation of clusters, and of oligomers $\{VO(OPr^i)_3\}_n$, respectively. The latter gives rise to a satellite line with an upfield shift relative to the monomeric species. Exchange interactions are discussed as a second factor affecting line widths.

Introduction

Nuclear magnetic resonance studies of transition metal nuclei in organometallic and coordination compounds have recently attracted increasing interest. We contributed to these investigations by discussing correlations between n.m.r. parameters such as chemical shift or nuclear-spin-spin coupling constants and electronic interactions in the metal-ligand bonding sphere of carbonylvanadium compounds [1, 2], carbonyl-cyclopentadienyl complexes [2, 3] and vanadylesters and -halides [4]. Analytical inferences of ^{51}V n.m.r. studies were related to pH-dependent shift values of iso- and heteropolyvanadates [5]. Few data, however, were reported on line widths of n.m.r. signals of quadrupolar nuclei in solution, although analysis of line widths can impart easily accessible information both on solvent-solute interaction and on intra-electronic effects resulting in variations of the field gradient tensor at the nucleus. Line widths of carbonylmanganese [6] and octahedral cobalt complexes [7] were correlated with the σ-donor and π-acceptor ability of the ligands and with the local symmetry of the coordination compound. The data are discussed conversely, however, and presented in a rather descriptive and qualitative manner. Following a recent consideration of line width data of Mn(CO)$_5$L compounds (L = trialkyl- or triaryl-tin), based on a more quantitative evaluation [8], and a surveying report on solvent data of bromine and chlorine compounds [9], we present here first results about the temperature and solvent dependence of n.m.r. line widths of vanadyl-triiso-propylate and the implications for molecular correlation. Further, the temperature dependence of the chemical shift of VO(OPr^i)$_3$ in several solvents is discussed. Data on the temperature dependence of nuclear shielding in transition metal complexes are scarce [10], and except for some early reports on ^{59}Co-complexes [11] there are, to our knowledge, no data available for quadrupolar metal nuclei.

Results

Figures 1a and 1b represent typical ^{51}V-n.m.r. spectra of VO(OPr^i)$_3$ at low temperatures. The temperature dependence of the chemical shift and line width are shown in Figs. 2a—2b and 3a—3b respectively. The following significant trends will be considered:

(a) Generally, the signals broaden with decreasing temperature. Except for THF, no smoothe curves are obtained, though. For n-pentane as a solvent, there is a pointed maximum (cf. Figure 3b).

(b) Chemical shifts (and ^{51}V-nuclear shielding) decrease with decreasing temperature (Figure 2). Again, with the exception of THF, there are irregularities which about parallel those in the $\Delta\nu_{1/2}/T$ graphs.

(c) Almost independent of the solvent, a satellite emerges from the main signal at about 240—220 K. Simultaneously, a retardation in chemical shift and line width is observed. This accounts for one of the disconsistencies.

Figs. 1a and 1b. Calculated (solid line) and experimental (Δ) ^{51}V n.m.r. spectra of VO(OPr^i)$_3$ in 0.86 M THF (Fig. 1a) and 1.72 M Et$_2$O (Fig. 1b). The satellite is due to {VO(OPr^i)$_3$}$_n$, where n possibly $= 2$.

Figs. 2a—2b. Graphical presentation of the temperature dependence of ^{51}V-chemical shift values of VO(OPr^i)$_3$. Experimental values.

(d) A second disconsistency, which is less contoured in methylcyclohexane appears at about 190 K.

(e) The resonance for the satellite is to high field of the main signal. The separation of the two lines increases with decreasing temperature.

(f) The ratio of areas of satellite and main line depends on solvent and temperature. The solvent dependence is illustrated in Fig. 1a and 1b, representing two extreme positions. For most solvents, the satellite exhibits a maximum intensity at approximately 220 K. Selected results are tabulated in Table 1.
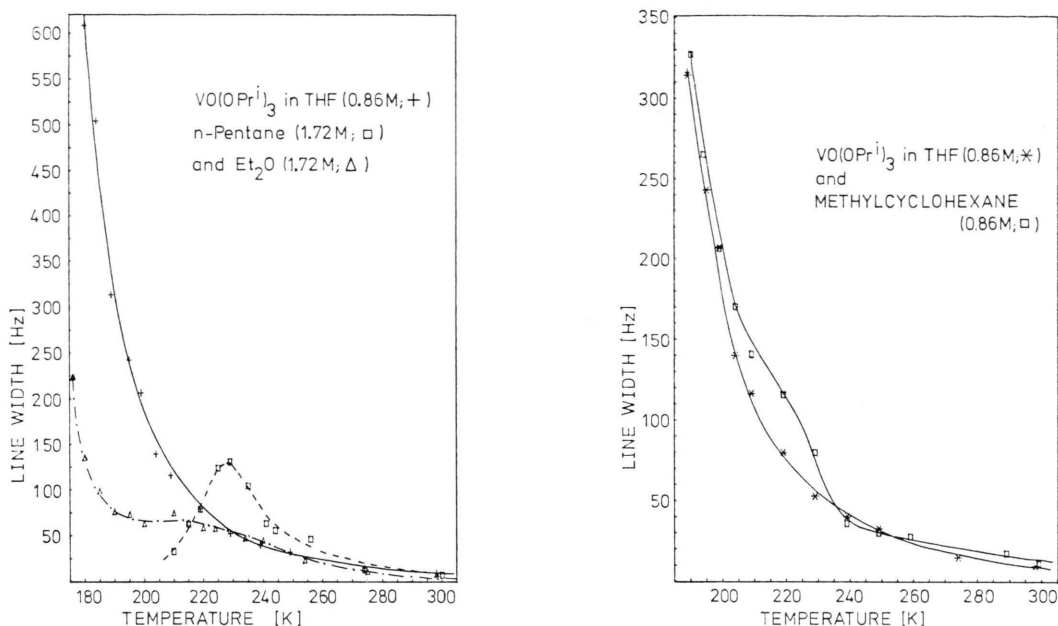
Figs. 3a—3b. Graphical presentation of the temperature dependence of the line widths (half-widths) of ^{51}V n.m.r. signals of VO(OPr^i)$_3$. The data were obtained from a Lorentzian type best-fitting procedure from experimental spectra. No unambiguous treatment could be carried out for pentane solutions below 210 K.

Table 1. Selected ^{51}V n.m.r. data for VO(OPr^i)$_3$ at low temperatures[a].

Solvent	Temperature	Main line		Satellite		Shift difference	Ratio of areas
	[K]	δ_V [ppm]	$\Delta\nu_{1/2}$ [Hz]	δ_V [ppm]	$\Delta\nu_{1/2}$ [Hz]	[Hz]	
Et$_2$O (1.72 M)	234	− 609.7	47.9	− 618.7	127.5	214	0.072
Et$_2$O (1.72 M)	220	− 608.4	58.9	− 620.9	93.3	295	0.391
Et$_2$O (1.72 M)	210	− 603.1	75.1	− 617.6	108.8	343	0.584
Et$_2$O (1.72 M)	200	− 596.2	63.4	− 614.9	82.0	443	0.438
Et$_2$O (1.72 M)	190	− 592.5	76.5	− 611.2	91.9	442	0.322
Et$_2$O (1.72 M)	180	− 587.2	135.7	− 611.8	143.6	582	0.191
Et$_2$O (0.46 M)	210	− 600.3	39.0	− 617.3	51.4	401	0.107
THF (0.86 M)	209	− 580.7	116.3	− 593.5	125.2	303	0.075
Methylcyclohexane (0.86 M)	209	− 580.8	140.5	− 606.4	278.0	606	0.141
n-Pentane (1.72 M)	210	− 586.7	32.1	− 610.3	132.8	558	0.111

[a] Line width and chemical shift (upfield a VOCl$_3$ standard) obtained from a Lorentzian type fit on experimental resonance signals (23.66 MHz spectrum).

Theory

Line Widths

Line widths $\Delta\nu_{1/2}$ of n.m.r. signals of nuclei which possess a nuclear electric quadrupole moment are considered to result almost exclusively from quadrupole relaxation mechanisms [8]. For the extreme narrowing case ($\omega_0 \tau_c \ll 1$) the relation predicted by theory is

$$\Delta\nu_{1/2} = \frac{3\pi}{10} \frac{(2I+3)}{I^2(2I-1)} \left(\frac{e^2 q_{zz} Q}{\hbar}\right)^2 \left(1 + \frac{\eta^2}{3}\right) \tau_c . \tag{1}$$

τ_c is the molecular correlation time, q_{zz} the zz-component of the field gradient tensor. η describes the symmetry of the field gradient tensor, and Q is the nuclear quadrupole moment.

With decreasing temperature, the resonance signals of dissolved substances usually broaden. This temperature dependence of the line width parallels the temperature dependence of τ_c; variations of q_{zz} and η with temperature can be neglected [9]. Two models may be employed for the evaluation of the temperature dependence of τ_c:

(i) The hydrodynamic model describes the relaxing molecule in terms of a solid body embedded in a fluid continuum. Thus, the correlation time is obtained from the Debye-Stokes-Einstein equation

$$\tau_c = 4\pi a^3 \xi / 3kT \qquad (2)$$

where a is the radius of the solute molecules and ξ is the viscosity. Documented by earlier investigations, the correlation with emperical values is, however, less than satisfactory [12] except for large solute molecules in solvents of low molecular mass.

(ii) In O'Reilly's quasilattice model [13], relaxation is carried out by jump reorientation into empty sites of a hypothetic lattice. The correlation time is then evaluated according to [14]

$$\tau_c = \tfrac{1}{6}(2\pi m/kT)^{1/2}\, v_f \exp(E/RT) \qquad (3)$$

with E being the activation energy and v_f the "free volume" [14]. Provided the only factor influencing τ_c is the temperature, variations of line widths of n.m.r. signals with temperature are described by

$$\Delta v_{1/2} \propto T^{-1/2} \exp(E/RT). \qquad (4)$$

Chemical Shift

Since nuclear shielding of nuclei other than protons is mainly determined by the paramagnetic term of the overall shielding (the diamagnetic contribution is subjected only to minor changes), variations of the shielding of metal nuclei in coordination compounds with temperature should be imparted by variations of the paramagnetic term. In fact, the temperature gradient dv/dT of the resonance frequency v can be described according to [11]

$$dv/dT = -\tfrac{1}{2}\gamma\, B_0 A\,(1/\Delta E)^2\, d\Delta E/dT. \qquad (5)$$

In this equation, B_0 is the external magnetic field, A contains the $\langle r^{-3}\rangle$-values and the matrix elements for relevant transitions, and ΔE is the ligand field parameter. According to the above equation, paramagnetic shielding increases with increasing temperature. Decreasing ΔE with increasing temperature was explained by improved occupation of vibronic levels [11]. The relation was verified for octahedral [59]Co^{3+}-complexes [11], [103]Rh-compounds (temperature gradient 0.25 ppm/K), planar [195]Pt-complexes (0.25—0.5 ppm/K) [10], and carbonyl-vanadium complexes (0.25 ppm/K) [15]. We will see, vanadyltriisopropylate shows a different behaviour.

Discussion

To explain the various trends (a)—(f), we will employ the following criteria:

1. Formation and collapse of dimeric (or oligomeric) structures (Equation (6)). Formation of a new species gives rise to a distinct

$$2\,\{V\}\underset{(\leftarrow)}{\overset{\rightarrow}{}}\{V\}_2;\quad n\,\{V\}\underset{(\leftarrow)}{\overset{\rightarrow}{}}\{V\}_n \qquad (6)$$
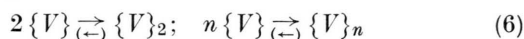
resonance line with a shift different from that of the monomer. Also, the field gradient is subjected to changes as a new species is formed.

2. Solvation, the coordination of solvent molecules in the second coordination sphere of the solute (Eq. (7)), should

$$\{V\} + n\,\{\text{solvent}\}\underset{(\leftarrow)}{\overset{\rightarrow}{}}\{V\}\cdot n\,\{\text{solvent}\} \qquad (7)$$
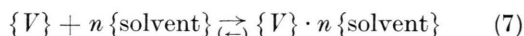
but slightly effect the chemical shift. Solvation will, however, influence line widths via the correlation time, and if solvation is anisotropic, also via the field gradient. Solvation effects are supposed to parallel solvent properties usually associated with polarity; further, they should compete with molecular association of the solute molecules (Eq. (8)):

$$\{V\} + n\,\{V\}\underset{(\leftarrow)}{\overset{\rightarrow}{}}\{V\}\cdot n\,\{V\}. \qquad (8)$$
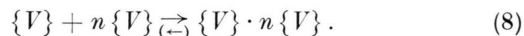
We presume that the net effect of loose association is the same as that of solvation. At sufficiently low temperatures, defined and stable solvated species and/or congealed clusters may arise.

3. Interchange effects between (i) monomers and dimers (oligomers) down to moderately low temperatures and (ii) within the solvated or associated systems will cause a dynamic line broadening. The exchangeability between different forms will increasingly be suppressed with decreasing temperature as viscosity increases, and hindered by the formation of oligomers and defined solvated species or clusters.

4. Viscosity, correlated with solvent bulkiness and solvent polarity is a main factor influencing line widths via the molecular correlation time, as discussed in the theoretical section.

Following this scheme and the concept outlined above in the theoretical section, a discussion of the graphs (Fig. 1—3) leads to the following conclusions concerning the intermolecular interactions in our systems:

Based on cryoscopic measurements, Lachowicz and Thiele [16] noted that vanadyl esters VO(OR)₃ tend to form dimers in solution. Provided the groups R are not too bulky and the solutions are sufficiently concentrated, dimerization rates are up to 30% (room temperature). No significant dimerization was found for VO(OPr^i)₃ solutions. We may, however, assume that, in neat VO(OPr^i)₃, dimers or oligomers are the predominant species. These defined structures will almost completely collapse when a solvent is added to VO(OPr^i)₃, as may be derived from the downfield solvent shift of VO(OPr^i)₃ in various solvents, ranging from 6.8 ppm (n-pentane) to 11.6 ppm (THF) relative to a neat sample (− 631.0 ppm). Although this effect is more marked with polar solvents, the solvent shift apparently cannot be solely accounted for by solvation. We actually contribute this down-field shift upon addition of a solvent to the formation of monomeric species. A second order contribution should then arise from solvation and/or association.

As we noted, there is a general decrease of chemical shift (and nuclear shielding) with decreasing temperature, contradicting theoretical prediction and experimental results on various complexes [10, 11, 15]. A possible explanation for this adverse trend in vanadyl esters is the continuous formation of either stable solvated species with a defined number of solvent molecules closely packed around solute molecules (Eq. (7)) or formation of clusters (Equation (8)). Deshielding may then be imparted by inductive electron withdrawal or, more likely, by a decrease in local symmetry, giving rise to a greater number of electron transitions relevant for the paramagnetic term of the shielding constant.

In principal, line widths increase with decreasing temperature. Only where THF is used as a solvent the increase of viscosity (and hence influence via the correlation time) dominates over the whole range of temperature. This is illustrated in Fig. 4, where $\Delta v_{1/2}$ is plotted against $T^{-1/2} \exp(1/T)$. From the curve, the activation energy for the rotation barrier is calculated to 14.7 kJ.

The smoothe $\Delta v_{1/2}/T$ (and δ_V/T) correlation for the THF/VO(OPr^i)₃ is likely caused by strong solvation, overpowering other effects. The other extreme is encountered with n-pentane, for which line widths run through a maximum at about 230 K (Figure 3 b). Up to this temperature, line widths increase as expected. At about the same tempera-
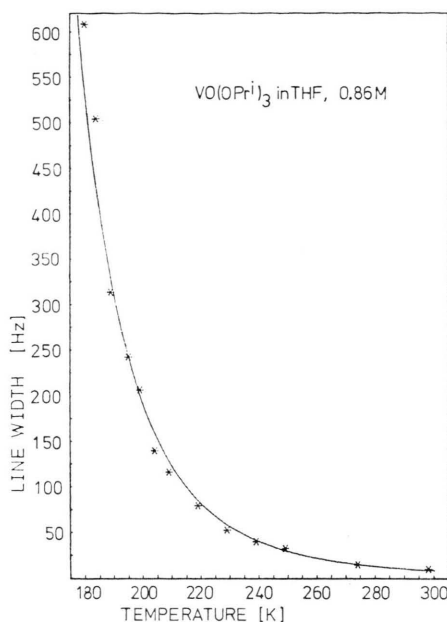

Fig. 4. Plot of line width versus temperature for VO(OPr^i)₃ in 0.86 M THF solution, calculated according to the relation $\Delta v_{1/2} = T^{-1/2} A \exp(B/T)$; $A = 0.39404$, $B = 1767.55704$, $R^2 = 0.99389$. * = experimental values.

ture, there is a deviation in the δ_V/T correlation in that the chemical shift increases over a narrow temperature range. Similar effects, less pointed however, are observed with methylcyclohexane and diethylether. Where the pentane solutions exhibit a maximum, these solvents show but a bulge of the curve.

The irregularity at approximately 240−230 K is accompanied by the appearance of a satellite line (Fig. 1) with varying intensity relative to the main signal (Fig. 4 and Table 1). While the satellite shows a similar down-field shift with decreasing temperature, it is shifted at a lower rate and hence seems to wander off the main line. After going through a maximum intensity, the satellite signal rapidly broadens and finally is beyond detection. As we pointed out above, the formation of a new species (a dimer {VO(OPr^i)₃}₂ or an oligomer {VO(OPr^i)₃}$_n$) at low temperatures will result in distinct alterations in the electronic system in the coordination sphere of vanadium, thus giving rise to a second resonance. The formation of definite oligomers will temporarily disturb solvation or association of monomers, producing a delay of down-field shift of the main signal, and, through increased mobility of remaining monomers, a

simultaneous delay in line broadening. Down to temperatures of about 240 K, exchange processes between monomers and dimers (Eq. (6)) will contribute to the line broadening. No such contribution is then to be expected below 240 K. If the satellite is due to oligomeric structures, its formation should be prevented upon addition of a compound incorporating strong ligating properties. In fact, no satellite signal was observed when tetramethyletylenediamine was added to the solution. A sample containing $Me_2NCH_2CH_2NMe_2$ in a 0.86 methylcyclohexane solution of $VO(OPr^i)_3$ had a single signal at -543 ppm (line width $\Delta\nu_{1/2} = 185$ Hz; 221 K), apparently due to a pseudo-octahedral complex $VO(OPr^i)_3(Me_2NCH_2CH_2NMe_2)$.

Further lowering of the temperature will reduce exchange interactions within molecular associations (solvent-solute and solute-solute). This is reflected in a temporary slow-down of line broadening down to approximately 190 K, counteracting the otherwise dominating influence by increasing viscosity. At about this temperature, an increase in chemical shift is observed (Fig. 2), which may well account for a more rigid arrangement of solute molecules, giving rise to slightly enhanced shielding similar to that responsible for the high-field shift of the satellite representing the oligomeric species or to the shielding in neat $VO(OPr^i)_3$. The second inconsistency is thus explained by the formation of congealed clusters. No such effect is then to be expected in THF, where cluster formation is overpowered by strong solvation, nor in methylcyclohexane which, due to steric factors, hinders the formation of defined clusters.

Experimental

Vanadyl-triisopropylate was obtained from Dynamit-Nobel and used without further purification. Since $VO(OPr^i)_3$ is sensitive to moisture, samples, dissolved in absolute solvents, were filled under nitrogen and measurements were carried out in sealed vials. ^{51}V n.m.r. spectra were run on a Bruker WH 90 PFT spectrometer equipped with a multikern unit and a temperature regulating device. Samples were measured in rotating 10 mm n.m.r. vials relative to a $VOCl_3$–$CDCl_3$ (2:1) standard. External lock was $CDCl_3$. Temperature measurements were carried out with an accuracy of ± 1 K. Absolute error of the chemical shift measurements was less than 1 ppm, for the line widths between 3 and 10 Hz, depending on the width. Line widths are recorded as half-widths. Digitalized n.m.r. spectra were fitted on a linear combination of Gaussian and Lorentzian type functions, employing a Fortran IV program. Exact half-widths and shift data were thus obtained for main line and satellite. Absorption curves turned out to be exclusively of thr Lorentzian type, as expected for n.m.r. signals in liquids.

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