

Solvent Effects on the Infrared Intensity of the V=O Stretching Vibration in Vanadyl Acetylacetonate

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The intensity of the infrared absorption of the V=O stretching vibration of vanadyl(IV) acetylacetonate has been measured in chloroform, carbon tetrachloride, tetrahydrofuran, ethanol, and pyridine. From these data and those of some vanadyl complexes in aqueous solution, it is suggested that coordination of ligands to the VO²⁺ group can occur in two ways, either with or without a change in the double bond character of the V=O bond.

Vanadyl complexes and especially vanadyl acetylacetonate have been intensely studied during the last decade.^{1,2} The fact that the central group of the complexes can be regarded as a two-atomic molecule ion, only slightly disturbed in its properties by the effects of the ligands, makes the VO²⁺ complexes extremely interesting from the point of view of molecular spectroscopy. This has been strongly emphasized and utilized by Selbin.¹⁻⁴

Most of the investigations of this kind have, however, centered around the effect on the frequency of the V=O stretching absorption brought about by different ligands.⁴ Specifically, it is well known³ that VO(acac)₂ dissolved in different solvent exhibits a broad range of values of $\nu(V=O)$. These changes have been discussed almost entirely in terms of the coordination of a solvent molecule at the sixth position of the VO(acac)₂ complex. Recently, however, Guzy *et al.*⁵ have raised some doubt about the absolute prevalence of this type of solvation. They argue from ESR measurements that the solvation of not only the sixth position but also that of the vanadyl oxygen atom must be of great importance. Because of this difference of opinion it was considered valuable to approach the problem by another method, IR *intensity* measurements.

In an earlier paper⁶ it has been shown that the $\nu(V=O)$ intensity is not drastically changed when complexes of the type VO(NCS)_n(OH)₂_{5-n(a-n)+} are formed from VO(OH)₂₅²⁺ although a shift of frequency up to 25 cm⁻¹ was observed. We are thus interested in learning two things from the present investigation: how is the intensity changed by substituting the five water

oxygen atoms by the four oxygen atoms belonging to the acetylacetonate ligands? Is the solvent effect on the intensity similar to that on the frequency of $\text{VO}(\text{acac})_2$?

EXPERIMENTAL

$\text{VO}(\text{acac})_2$ was prepared according to the method of Bryant and Fernelius.⁷ The following solvents of analytical grade were used without any further purification: carbon tetrachloride, tetrahydrofuran (THF), pyridine and ethanol. Chloroform was freed from ethanol by passing it through a column of aluminium oxide.

The infrared spectra were recorded with a Perkin Elmer 521, using calibrated sodium chloride cells. All solutions were stable for a long time except for the ethanolic ones. For the latter, spectroscopic readings were made immediately after dissolution to avoid the effect of the oxidative reaction (*cf.* Ref. 8).

The absolute intensity of the absorption band, A , was calculated from Ramsay's expression⁹

$$A = \pi/2 \times 2.303 \epsilon \Delta\nu_{1/2}$$

As the spectral slit width was about 1.5 cm^{-1} and most of the bands had a half-width of 10 cm^{-1} or more, no corrections were made on the intensities for the final slit width effect. The only case where such a correction is of some significance may be the tetrahydrofuran one; the reported value of A is thus possibly somewhat too large.

Spectra were recorded in the range $1100 - 900 \text{ cm}^{-1}$. The following cell thicknesses were used: CHCl_3 , 0.1 and 0.2 mm; CCl_4 , 0.2 and 0.5 mm; THF 0.05 and 0.1 mm; pyridine 0.1 mm; and ethanol 0.05 and 0.1 mm.

RESULTS

The results of the measurements are given in Table 1. A plot of the quantity $(\log T_0/T \Delta\nu_{1/2})/d$ versus $C_{\text{VO}(\text{acac})_2}$ is given (for the THF case) in Fig. 1. This was the way by which the quantity $\epsilon \Delta\nu_{1/2}$ was determined and the spread of the points is representative for the other cases. No systematic influence from any of the parameters involved can be observed.

It then emerges that the value of the absolute intensity is almost the same for carbon tetrachloride and chloroform as it is for pyridine, but significantly lower for ethanol and tetrahydrofuran. These results are given graphically in Fig. 2a.

One other point of interest came forward from the measurements. It was found on close inspection of the spectra that for all solvents but CCl_4 and

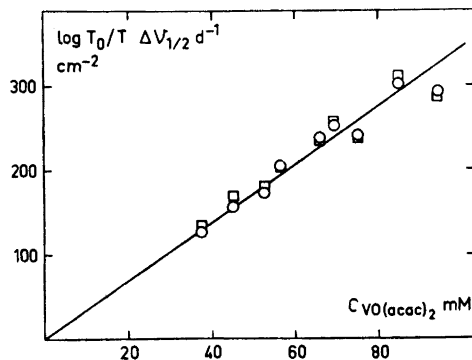


Fig. 1. $\log T_0/T \Delta\nu_{1/2} d^{-1}$ plotted against the concentration of vanadylacetylacetonate in tetrahydrofuran. O, $d = 0.113$ mm and \square , $d = 0.062$ mm.

Table 1. Presentation of the spectral data for $\nu(\text{V}=\text{O})$ of vanadyl acetylacetonate.

Solvent	ν cm^{-1}	ϵ $\text{M}^{-1} \text{cm}^{-1}$	$\Delta\nu_{1/2}$ cm^{-1}	$\epsilon \times \Delta\nu_{1/2}^2$ $\text{M}^{-1} \text{cm}^{-2}$	$A \times 10^{-4}$ $\text{M}^{-1} \text{cm}^{-2}$	$A(1+R)$ $\text{M}^{-1} \text{cm}^{-2}$
Chloroform	1001	442 ± 16	16.2 ± 0.3	7170 ± 200	2.59 ± 0.07	
Carbon tetra- chloride	1011	600 ± 60	11 ± 1	6470 ± 550	2.33 ± 0.2	
Tetrahydrofuran	991	595 ± 35	5.8 ± 0.2	3470 ± 190	1.25 ± 0.07	1.43
Ethanol	966	210 ± 20	11.0 ± 0.7	2300 ± 350	0.83 ± 0.13	0.95
Pyridine	958	732 ± 11	9.4 ± 0.1	6900 ± 100	2.49 ± 0.03	3.3

CHCl_3 a satellite band appeared with a frequency about 15 cm^{-1} higher than that of the main $\text{V}=\text{O}$ band. In order to represent this effect some pertinent spectra are recorded in Fig. 3, *viz.* for the solvents CHCl_3 , pyridine, THF, and ethanol. The satellite bands are indicated by an arrow in the figure, and by italics in Table 2. As indicated in Table 2, the 1027 and 935 cm^{-1} bands (for CHCl_3 , analogously for the other solvents) correspond to vibrations within the acetylacetonate ligand.¹⁰

The other band(s) will then be related to the $\text{V}=\text{O}$ group, more or less directly. Due to the relatively strong absorption of THF in both ends of the spectral range investigated, the ligand vibrations could be detected only with

Table 2. Assignment of the observed bands.

Solvent	ν (cm^{-1})	Assignment	$\frac{R}{A_{\text{sat}}/A_{\text{main}}}$
Chloroform	1027	$\rho_r(\text{CH}_3)$	
	1001	$\nu(\text{V}=\text{O})$	
	945(sh)	$\nu(\text{C}\cdots\text{C}) + \nu(\text{C}\cdots\text{O})$	
	935		
Carbon tetrachloride	1031	$\rho_r(\text{CH}_3)$	
	1011	$\nu(\text{V}=\text{O})$	
	950(w)	$\nu(\text{C}\cdots\text{C}) + \nu(\text{C}\cdots\text{O})$	
	940		
Tetrahydrofuran	1027(?)	$\rho_r(\text{CH}_3)$	0.14 ± 0.01
	1007		
	991	$\nu(\text{V}=\text{O})$	
Ethanol	984		0.14 ± 0.02
	966	$\nu(\text{V}=\text{O})$	
	932	$\nu(\text{C}\cdots\text{C}) + \nu(\text{C}\cdots\text{O})$	
Pyridine	1044(?)		0.32 ± 0.02
	1017	$\rho_r(\text{CH}_3)$	
	985		
	970		
	958	$\nu(\text{V}=\text{O})$	
	930	$\nu(\text{C}\cdots\text{C}) + \nu(\text{C}\cdots\text{O})$	

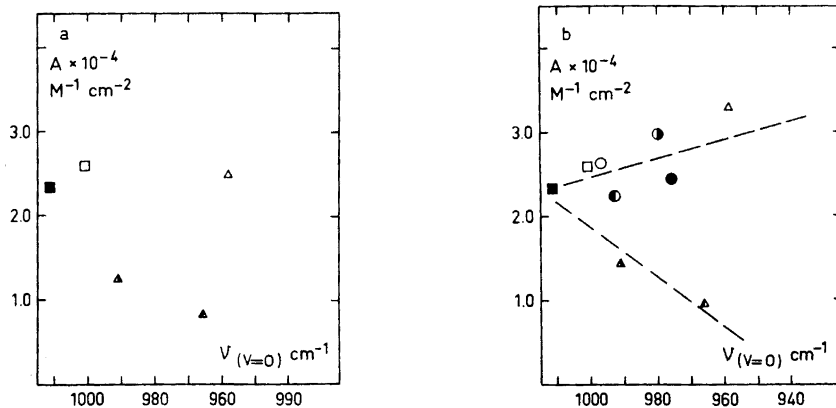


Fig. 2. *a.* Values of the integrated absorption of the $\text{V}=\text{O}$ band of $\text{VO}(\text{acac})_2$ determined in this investigation plotted against the $\text{V}=\text{O}$ frequency. *b.* Values of the integrated absorption of the $\text{V}=\text{O}$ band of some complexes. The $\text{VO}(\text{acac})_2$ values given are corrected with the factor $(1+R)$. The other points refer to the investigation⁶ in aqueous solution. The lines are drawn to emphasize the trends, not more. \blacksquare , $\text{VO}(\text{acac})_2$ in CCl_4 ; \square , $\text{VO}(\text{acac})_2$ in CHCl_3 ; \triangle , $\text{VO}(\text{acac})_2$ in pyridine; \blacktriangle , $\text{VO}(\text{acac})_2$ in tetrahydrofuran; Δ , $\text{VO}(\text{acac})_2$ in ethanol; \circ , $\text{VO}(\text{OH}_2)_5^{2+}$ in water; \bullet , $\text{VO}(\text{OH}_2)_4\text{NCS}^+$ in water; \bullet , $\text{VO}(\text{OH}_2)_3(\text{NCS})_2$ in water; \bullet , $\text{VO}(\text{OH}_2)_2(\text{NCS})_3$ in water.

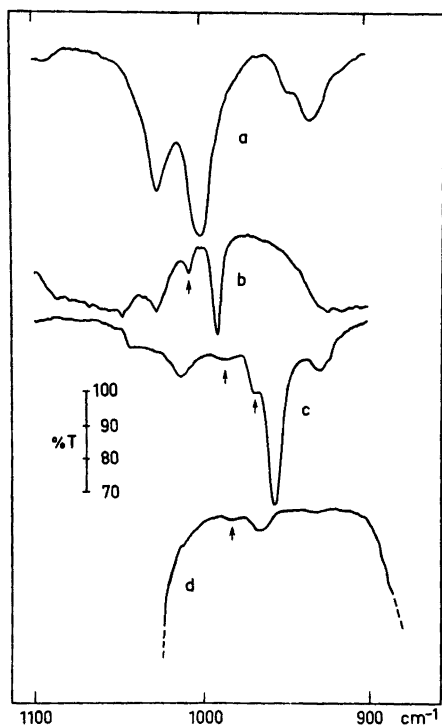


Fig. 3. Some representative spectra. The "satellites" are marked by an arrow. *a.* chloroform, $c=49 \text{ mM}$, $d=0.2 \text{ mm}$. *b.* tetrahydrofuran, $c=57 \text{ mM}$, $d=0.05 \text{ mm}$. *c.* pyridine, $c=38 \text{ mM}$, $d=0.2 \text{ mm}$. *d.* ethanol, $c=25 \text{ mM}$, $d=0.05 \text{ mm}$.

difficulty in this case. Also for pyridine, there is a considerable absorption in the 1100–1000 cm^{-1} range so this part of the recorded spectrum should be regarded with caution. (Only 0.1 mm cells were used for this solvent.) Possibly, though, there is a slight indication of a weak band at 985 cm^{-1} , *i.e.*, at about twice the distance from the V=O band compared to the “satellite” at 970 cm^{-1} .

The ratio R of the band area of the satellite to that of the main band $R = A_{\text{sat}}/A_{\text{main}}$ has been calculated and is presented in Table 2. It follows that this ratio is of the same order for THF and ethanol but twice as large for pyridine.

DISCUSSION

Fig. 2a shows that there is a very poor correlation between intensity and frequency. One can then conclude that more than one factor influences the V=O intensity.

Before discussing this in detail we must assign the origin of the “satellite”. This does not seem to appear for the non-coordinating solvents CHCl_3 and CCl_4 but for all those solvents that have at least some coordination power. Therefore we should like to suggest that the satellites appear as a combination vibration of the V=O stretching mode and a torsional or precessional mode of the V–L bond, L being the group coordinated in the sixth position. (Hence there is a possibility of a second satellite for the strongly interacting pyridine system, although with very little intensity.)

If this is so, or even if the satellite is connected to the V=O stretching mode in *any* way only, the intensity of the satellite is probably borrowed from that of the V=O stretching mode, and consequently we must add the intensity of the satellite to that of the main band in order to have a meaningful measure of the total intensity. This operation is represented in Fig. 2b.

It can be seen that there is a group of solvents that causes a downwards slope of the correlation line between A and (decreasing) ν and another one causing a rising line. It was then tempting to see how the data from the earlier work⁶ could fit into this scheme. These points have also been introduced in Fig. 2b although they do not correspond to the acetylacetonate complex. It is apparent that the data from the aqueous solutions conform reasonably well with the rising trend. Some deviations must be tolerated because of the indirect way of determination of the coefficients of absorption of the thiocyanato complexes and because of the differences in solvent dielectrical properties.

We are then faced with the problem of inferring the cause of these two different trends in the A versus ν plot. As pointed out before,⁶ one should expect from Badger's rule that a decrease in ν should correspond to an increase in the V=O bond distance and thus, as the double bond character diminishes, give rise to an increase in the polarity of the bond and hence in the infrared intensity of the stretching vibration band. (This is illustrated in Fig. 7 of Ref. 6.) So it appears that the upper line of Fig. 2b should be the expected one. But in such a case, how do we have the other trend, the lower line?

At one stage of this investigation it was thought, before making the THF measurements, that hydrogen bonding to the vanadyl oxygen atom (as suggested by Gazy *et al.*⁵) should decrease the charge on that atom without

notably changing the bond characteristics of the V=O bond and thus not change the force constant and the frequency. However, it now seems that hydrogen bonding, if it is really present, does not influence the $\nu(\text{V}=\text{O})$ intensity very much. Otherwise one would expect the measurements performed in aqueous solution to conform with the lower line, not with the upper one. This argument presupposes that all the hydrogen bonding capacity of water is not used up by the 3 M NaCl. Furthermore, of course, it is difficult to envisage tetrahydrofuran as hydrogen bonding.

Actually, it is known,¹¹ that dioxan, and thus most probably also tetrahydrofuran, is coordinated (in the solid state) at the sixth coordination position of $\text{VO}(\text{acac})_2$.

On the other hand, the explanation cannot be sought in the coordination of an oxygen ligand as such, because then the aquo complex should also belong to the lower group.

So far, and more experimental material soon to be communicated¹² seems to strengthen this view, we have evidence of only two correlation lines with no points falling significantly out of order. This must mean that there is an *either-or* type of mechanism determining the bonding of a ligand (or several ligands) in a vanadyl complex.

It is the opinion of the present author that the two alternatives are whether the degree of hybridization of the orbitals taking part in the V=O bond is changed or not upon coordination of extra-oxo-ligands. This point has been discussed (with respect to UO_2^{2+}) by McGlynn *et al.*¹³ and also by Larsson.¹⁴ The former authors¹³ regarded the spectral effects observed as being caused by coordination processes not affecting the UO_2 bonds whereas the present author¹⁴ found evidence to the contrary.

Now, looking at the VO^{2+} problem, we can merge these two theses into a synthetic compromise. This means that those coordination effects, described here as corresponding to the upper correlation line, should be those that cause a change in the bonding characteristics of the V=O bond, *i.e.* its degree of double bonding. Those solvents or ligands that cause an adherence to the lower correlation line, however, should be thought of as contributing no change to the bond order of the V=O bond. Rather, by using other vanadium orbitals than those used by the vanadium atom in forming the V=O bond, these ligands reduce by an electron donation mechanism the effective charge on the vanadium atom and thus cause a decrease of the polarity of the V=O bond. This will imply a less electrostatic interaction between the vanadium atom and the vanadyl oxygen atom, *i.e.* a decrease of the force constant even if the double bond character is not changed. Consequently, the vibration frequency of the V=O group will decrease. Obviously a frequency decrease follows also from the mere effect of masses³ even if the force constant is not changed at all. At the same time the dipole moment, μ , and hence, most probably, the dipole moment derivative, $d\mu/dr$, will decrease. Thus we have for this type of interaction a concerted decrease of both frequency and intensity of the $\nu(\text{V}=\text{O})$ band.

It must be fully understood that this interpretation is only a very tentative one and that further investigations that will be carried out may overthrow the *either-or* character of the present observations and deductions.

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