February, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (2), 401—405 (1977) 401

Spectral Studies on the Interaction between Oxovanadium(IV) β-Diketonates and Organic Solvents

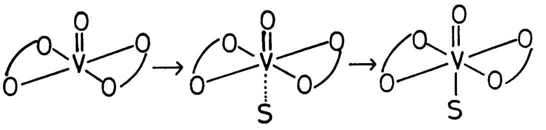
Natumi Adachi, Yutaka Fukuda, and Kozo Sone

Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112

(Received August 14, 1976)

The effect of temperature on the visible absorption spectra of oxovanadium(IV) β-diketonates [VO (β-dik)$_2$] (β-dik=aca, bza, tfa, and dpm*) were studied in organic solvents. The results together with the spectral and thermogravimetric data of the pyridine and dioxane adducts of these chelates lead to the conclusion that the ease of taking up a solvent molecule to form a six-coordinate solvated chelate in solution increases in the order: VO(tfa)$_2$> VO(bza)$_2$≈VO(aca)$_2$>VO(dpm)$_2$. Various proofs for the existence of a polymeric structure of VO(tfa)$_2$, which was formerly indicated on the basis of its IR spectrum, were found.

The visible absorption spectrum of oxovanadium(IV) acetylacetonate (VO (aca)$_2$) in an organic solvent changes remarkably with solvent.[1-3] This is explained on the assumption that the square pyramidal five-coordinated structure of the original chelate is more or less transformed into an octahedral six-coordinated one by the coordination of a solvent molecure, and that the spectral change observed is the reflection of the degree of this structual change.



Increase in DN of the solvent (S) →
Increase in $\Delta_{\mathrm{I,II}}$ →

According to Selbin *et al.*,[1-3] the difference between the wave numbers of the two visible bands of this chelate ($\Delta_{\mathrm{I,II}}$) serves as a good measure of the degree of this change; when the coordination ability of the solvent (which may be expressed by the donor number (DN) of Gutman)[4] is very low (*e.g.*, in 1,2-dichloroethane or nitromethane) and the chelate nearly retains its original structure in solution, $\Delta_{\mathrm{I,II}}$ is in the vicinity of 1—2 kK, but it increases with the DN of the solvent used, reaching 4—5 kK in DMSO and pyridine. It was also pointed out that there is a fairly good linear relationship between $\Delta_{\mathrm{I,II}}$ and DN.[4]

Although these relations, which we shall call the Selbin-Gutmann rule, were well established in the case of VO(aca)$_2$, published data on other β-diketonates of VO^{2+} seem to be rather scanty. We have tried to confirm the applicability of this rule to three such chelates.

Experimental

Preparations. VO(aca)$_2$ and VO(tfa)$_2$ were prepared by the method of Rowe and Jones,[5] and VO(bza)$_2$ and VO(dpm)$_2$ by that of Selbin *et al.*[6] Their identity was confirmed by means of their IR spectra which agreed well with the data published.

VO(aca)$_2$py and VO(tfa)$_2$py: VO(aca)$_2$ or VO(tfa)$_2$ was dissolved in pyridine and the mixture was evaporated at low temperature (*ca.* 77 K) under reduced pressure. The concentrated solution was then allowed to stand at 0 °C. After 12 h, green microcrystals of the pyridine adduct separated out in the case of VO(aca)$_2$, but it took about a month to get similar crystals of VO(tfa)$_2$py. They were filtered and dried in a vacuum.

VO(bza)$_2$py: VO(bza)$_2$ was dissolved in pyridine and the mixture was refluxed for 2 h, and then allowed to stand at room temp for 12 h. The solution was then evaporated under reduced pressure at 70 °C. The brown microcrystals which separated out were filtered and dried in a vacuum.

VO(aca)$_2$diox, and VO(tfa)$_2$diox: These adducts were prepared as in the case of VO(bza)$_2$py, using dioxane insted of pyridine.

The results of elementary analyses are given in Table 1.

Solvents and Reagents. All the solvents and reagents used were of "Extra Pure" or "Spectro" Grade.

Measurements. The IR spectra between 400 cm^{-1} and 4000 cm^{-1} were determined with Nujol mulls between caesium bromide plates using a JASCO IR-G spectrophotometer. The electronic spectra of the solutions were recorded with a Shimadzu D-40R Spectrophotometer, using 50, 10, and 5 mm quartz cells, and Dewar-equipped cells described by Iwasaki *et al.*[7] The reflectance spectra of solid samples between 300 and 700 nm were recorded with the same spectrophotometer and those between 700 and 800 nm were recorded with a Hitachi EPS-3T spectrophotometer, using reflectance attachments and MgO discs as reference. Thermogravimetric analyses of the adducts were carried out with a Shinku Riko TGD-3000 Differential Thermal Microbalance with a heating rate of 5 °C/min in a nitrogen stream (flow rate: 50 ml/min), using *ca.* 30 mg of the sample in each measurement.

Table 1. Elementary analyses of the adducts

Adduct	Found (Calcd) % C	N	H
VO(aca)$_2$py	52.32(51.74)	4.07(4.19)	5.57(5.49)
VO(bza)$_2$py	62.77(62.56)	3.07(3.15)	4.76(5.23)
VO(tfa)$_2$py	39.21(39.84)	2.85(3.09)	3.22(2.90)
VO(aca)$_2$diox[a]	42.48(47.60)		5.59(6.28)
VO(tfa)$_2$diox[a]	33.59(36.45)		3.36(3.50)

a) These adducts slowly decompose on standing, losing dioxane, and revert to the parent complexes, making agreement with calculation less satisfactory. The values for carbon were deduced from the data of the thermogravimetric analyses.

---

* Abbreviations; β-dik=a β-diketonate ion, aca=acetylacetonate ion, bza=benzoylacetonate ion, tfa=trifluoroacetylacetonate ion, dpm=dipivaloylmethanate ion, py=pyridine, and diox=dioxane. kK=10^3 cm^{-1}.

Results and Discussion

Thermochromism of VO(β-dik)$_2$ in Organic Solvents. When the four chelates VO(aca)$_2$, VO(bza)$_2$, VO(tfa)$_2$, and VO(dpm)$_2$ are dissolved in various solvents at room temperature, and the observed values of $\Delta_{\mathrm{I,II}}$ are plotted against DN of the solvents (Fig. 1), the Selbin-Gutmann relation holds quite well in the case of VO(aca)$_2$ and VO(bza)$_2$, but apparently not for the other two chelates.** For the sake of clarification, the influence of temperature on the spectra (thermochromism) was studied. The results for VO(aca)$_2$ are summarized in Fig. 2. A similar figure is obtained for VO(bza)$_2$. The $\Delta_{\mathrm{I,II}}$ values increase with DN at each observed temperature, but decrease more or less distinctly with increasing temperature, showing that the bonding of solvent molecule at the bottom of the pyramid is gradually loosened and the complex becomes more "five-coordinated" on heating. In the course of these spectral changes no distinct isosbestic point was observed,*** so it seems that they are due not to the shift of the simple solvation equilibrium of

$$\mathrm{VO(aca)_2 + S = VO(aca)_2{\cdot}S}$$

type, but to the gradual structure change of the dissolved species.

Figure 3 shows the results for VO(dpm)$_2$. The curves go down with the rise of temperature, but only the curves for pyridine and DMF, *i.e.*, those for solvents with especially high DN, lie high above, while those for chloroform, nitromethane and acetonitrile lie close to each other near the abscissa. This suggests that the chelate is less easily solvated in solution, and the solvents with lower DN are not bound effectively by it, so that there is only little spectral difference between their solutions. This reluctance for solvation is probably the result of the electron-donating effect of C(CH$_3$)$_3$ groups in dpm, which strengthens the V–O bonds in the chelate rings and reduces the positive charge of vanadium and the steric effect caused by the same groups.

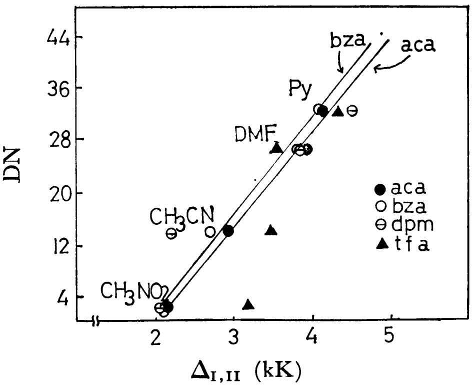


Fig. 1. The relation between DN and $\Delta_{\mathrm{I,II}}$ at room temperature; concentration: 1×10^{-2} mol/l.

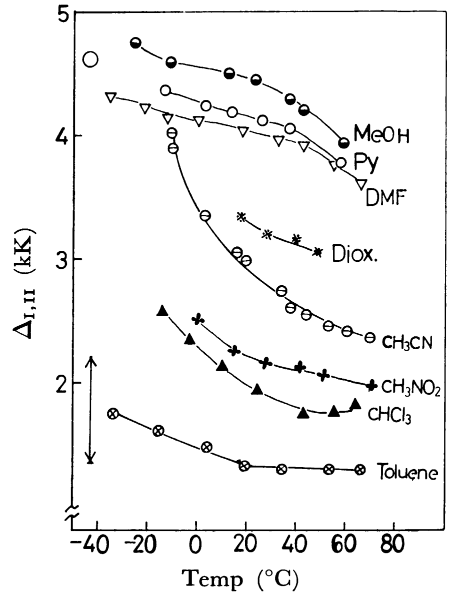


Fig. 2. Thermochromism of VO(aca)$_2$ in some organic solvents; cell thickness: 5 mm, concentration: 1×10^{-2} mol/l.

↔ and ○ on the ordinate axis correspond, respectively, to the $\Delta_{\mathrm{I,II}}$ values of the chelate and its pyridine adduct in solid state.

Figure 4 shows the results for VO(tfa)$_2$. Since all the curves flock closely together, the scale for $\Delta_{\mathrm{I,II}}$ is expanded twice in comparison with that shown in Figs. 2 and 3. We see that pyridine, DMF, methanol, and acetonitrile form octahedral solvates nearly equally well. Nitromethane also does so at lower temperature, but the solvation becomes remarkably weaker at higher temperature. Thus it is clear that this chelate, in contrast to VO(dpm)$_2$, is more easily solvated, probably owing to the electron-withdrawing effect of tfa which weakens the V–O bonds in the chelate rings.

It seems strange that even in chloroform, which is a very poor donor, a six-coordinated complex species seems to be formed with VO(tfa)$_2$. However, the $\Delta_{\mathrm{I,II}}$ of VO(tfa)$_2$ in chloroform was found to be notably dependent on its concentration, changing from *ca.* 3.4 to 2.9 in going from 1×10^{-1} to 4×10^{-3} M. This leads one to suppose that there is a monomer-polymer equilibrium (1) in this solution, and the

$$n\ \mathrm{VO(tfa)_2} \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} [\mathrm{VO(tfa)_2}]_n \qquad (1)$$

Monomer Polymer with O=V←O=V bonds
5-coordinated 6-coordinated

** Alcoholic solutions poses some problems. The $\Delta_{\mathrm{I,II}}$-values of VO(aca)$_2$ and VO(bza)$_2$ in methanol are much higher than expected from the DN scale. However, as stated by Gutman concerning values in aqueous solution, this may be explained by the formation of the hydrogen bond (V=O···H–OR), in addition to the coordinate bond to vanadium (O=V···OHR), by the solvent. The values of $\Delta_{\mathrm{I,II}}$ in other alcohols at room temperature are nearly the same as that in methanol. On the other hand, all the chelates studied are not stable in alcoholic solutions against oxidation, becoming brownish within several hours. In the case of VO(dpm)$_2$, this color change begins within several minutes, making it impossible to measure the spectra.

*** An apparent isosbestic point was found to appear in acetonitrile and nitromethane at lower temperature. Moreover, a drastic reversible color change from blue to pink took place when VO(aca)$_2$ was dissolved in acetonitrile or nitromethane and frozen in liquid nitrogen, but this was not observed with the other chelates. The nature of these phenomena is not clear.

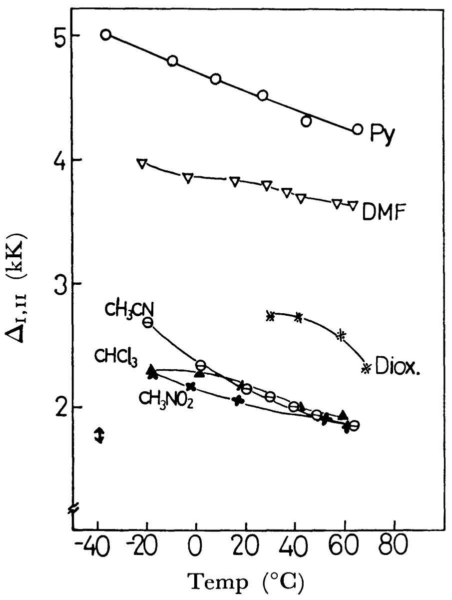


Fig. 3. Thermochromism of $VO(dpm)_2$; the conditions are the same as in the case of $VO(aca)_2$.

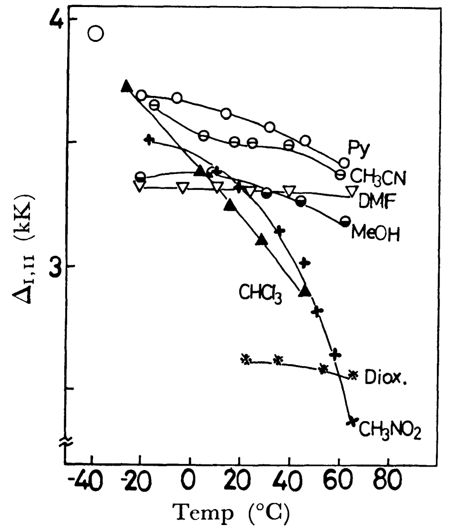


Fig. 4. Thermochromism of $VO(tfa)_2$; the conditions are the same as in the case of $VO(aca)_2$.

observed changes of $\Delta_{I,II}$ with temperature and concentration are, in fact, due to the shifts of this equilibrium.† This view is also supported by the view of Al-Niami *et al.*[13] who observed that the infrared spectrum of $VO(tfa)_2$ indicates its polymeric structure, with the molecules forming chains of O=V←O=V←O=V. Thus it seems possible that a similar kind of association occurs in a non-coordinating solvent like chloroform, to various degrees, according to the temperature and concentration.

In most cases, Band I (*i.e.*, that of the red side) shifts toward blue and Band II toward red with increasing temperature, the first shift being much larger. In terms of the Ballhausen-Gray[8] MO scheme with the assumption that Band I is $^2B_2$-^2E and Band II is $^2B_2$-$^1B_1$,[11,13,15] Band I is due to the excitation of an electron from a nonbonding orbital (b_2) to a π-antibonding one (e_π^*), and its blue shift means the corresponding stabilization of e_π, *i. e.*, that the π-bond formation between the vanadium d_{xz} and d_{yz} and oxygen p_x and p_y orbitals in the V=O group is enhanced with the rise of temperature and in non-coordinating solvents. On the other hand, Band II is due to the excitation of the same electron to a σ-antibonding orbital (b_1^*), its red shift indicating the corresponding instabilization of b_1, leading to the weakening of V-aca coordinate bonds. These relations are all compatible with the view that the complex changes gradually from an octahedral structure to a tetragonal pyramidal one upon heating and with a decrease in solvent polarity.

Comparison of the Thermochromism Data with Some Properties of Solid Adducts. In order to see the difference in the ease of solvation among the chelates, their pyridine, dioxane and DMF adducts were prepared, and a comparison was made between some of their properties and the data of thermochromism. Adducts of the compositions $VO(aca)_2py$, $[VO(aca)_2]_2$-diox, $VO(\beta\text{-dik})_2\cdot$4-methylpyridine *N*-oxide have been reported.[12–14] We have prepared the monopyridine adducts of $VO(aca)_2$, $VO(bza)_2$, and $VO(tfa)_2$ and monodioxane adducts of $VO(aca)_2$, $VO(tfa)_2$, the pyridine adduct of $VO(dpm)_2$, the dioxane adduct of $VO(bza)_2$, and DMF adducts being obtained only paste-like samples. The method of preparation for $VO(aca)_2py$ (*cf.* Experimental) seemed to be better than that given in literature, since a product which was analytically quite pure could be obtained with nearly theoretical yield.

It was pointed out formerly that all the parent chelates show a V=O streching band between 950 and 1000 cm^{-1} in their IR spectra, except for $VO(tfa)_2$ which shows the same band at 925 cm^{-1} owing to its polymeric six-coordinated structure.[6,13] From the data given in Table 2, we see that, on adduct formation, the ν value of this band for $VO(aca)_2$ and $VO(bza)_2$ decreases, but that for $VO(tfa)_2$ increases, approaching from each side. This indicates that the polymeric structure of $VO(tfa)_2$ is destroyed by adduct formation, and the strength of the V–O bond in the resulting adduct becomes nearly the same as that in other adducts. The dioxane in the adducts seems to be held more loosely than pyridine, since the ν values of the dioxane adducts lie between those of the parent chelates and those of the pyridine adducts. The thermal instability of the dioxane adducts (Table 1, footnote) supports this view.

The solid reflectance spectra of the parent chelates and adducts are also of interest. The $\Delta_{I,II}$ of VO-$(aca)_2$, $VO(bza)_2$, and $VO(dpm)_2$ are 1.5—2,[6] and in the neighborhood of the values for their chloroform solutions at room temperature. As expected, the $\Delta_{I,II}$ values of the adducts are much higher, Band I shifting to red and Band II to blue. However, the $\Delta_{I,II}$ of $VO(tfa)_2$ is 4.44 and even larger than that for its pyridine adduct (3.9, with Band I shifting to blue). The fact that $VO(tfa)_2$ is six-coordinate in its solid

---

† No such strong dependence of $\Delta_{I,II}$ on concentration was observed with other solvents.

Table 2. V=O and V-O stretching frequencies (cm^{-1}) and ν_{max} and $\Delta_{I,II}$ from solid reflectance spectra (kK)

Complex	V=O$^{b)}$	V-O$^{a,b)}$	ν_{I}^{c}	ν_{II}^{c}	ν_{III}^{c}	$\Delta_{I,II}$
VO(aca)$_2$	992	602	14.59	16.12—16.80 bf	25.00 sh	1.53—2.21
VO(aca)$_2$·py	962	590	12.84	17.36	25.32 sh	4.52
VO(aca$_2$·diox	980	598	13.51	16.52—18.98 bf	24.39	3.01—5.47
VO(bza)$_2$	994	565	14.52	15.74—16·26 bf	27.77 sh	1.22—1.74
VO(bza)$_2$·py	948	550	12.90	17.70	21.14	4.8
VO(bza)$_2$·diox	(975)	(555)				
VO(tfa)$_2$	925	592	13.03	17.47	23.80 sh	4.44
VO(tfa)$_2$·py	958	588	13.39	17.27	22.72	3.88
VO(tfa)$_2$·diox	987	592	13.64	16.20—18.80 bf	22.65	2.56—5.16
VO(dpm)$_2$	1000	648	14.83	16.50	22.00	1.67
VO(dpm)$_2$·py	(961)	(632)				

a) β-diketonate oxygen. b) Values in parentheses are those obtained with paste-like samples. c) bf: broad or flat, sh: shoulder.

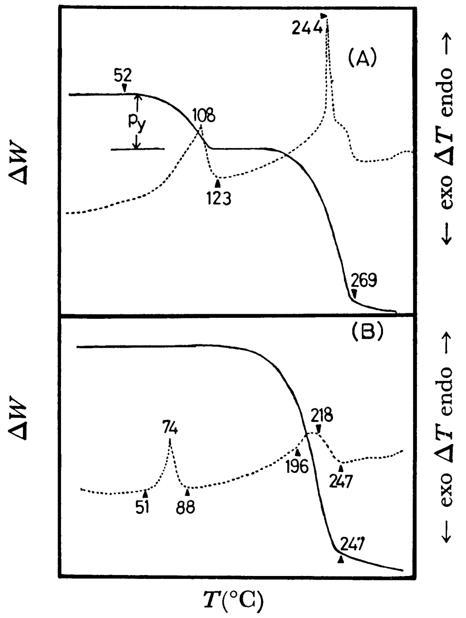


Fig. 5. The TG(——)-DTA(----) curves. A) VO(aca)$_2$·py, B) VO(tfa)$_2$·py.

owing to polymerization is evident.

The $\Delta_{I,II}$ values in the solid spectra of the adducts are indicated on the ordinate axis in Figs. 2 and 4. We see that, in each case, this value corresponds approximately to the low-temperature limit of the curve for the corresponding solution, supporting the idea that the chelate in solution tends to be more 6-coordinate with the fall of temperature.

The pyridine adducts were also studied thermogravimetrically. VO(aca)$_2$py liberates pyridine at 53—120 °C, and the remaining parent chelate sublimes at a higher temperature (>159 °C). A similar result was obtained with VO(bza)$_2$py. On the other hand, VO(tfa)$_2$py melts at 74 °C without evolution of pyridine, and begins to evaporate only at 196 °C, showing that pyridine is more firmly held in this adduct than in the other two (Fig. 5). The curve for VO(aca)$_2$ is similar to that of VO(aca)$_2$py after evolution of pyridine, that of VO(tfa)$_2$ differing a great deal. Evaporation takes place at a much higher temperature (>256 °C), and a strong endothermic peak appears at 209 °C, suggesting that the intermolecular O=V←O=V bonds must be broken, or essentially weakened, in advance of evaporation.

From the results it can be concluded that the ease of solvation among the chelates studied increases in the order: VO(tfa)$_2$>VO(bza)$_2$≈VO(aca)$_2$>VO(dpm)$_2$, and the Selbin-Gutman rule on the relation between $\Delta_{I,II}$ and DN ceases to hold at one or the other end of this series, *i. e.* when the chelate is too apt, or too reluctant, to be solvated and become six-coordinate. The data also offer various new proofs for the polymeric nature of solid VO(tfa)$_2$, which was formerly indicated on the basis of its infrared spectrum by Al-Niami *et al.*

The authors wish to express their sincere thanks to Dr. Kenzo Nagase, Tohoku University, for carring out thermogravimetric measurements, and to Prof. Yukio Kondo, St. Paul's University, for use of the Hitachi EPS-3T spectrophotometer.

References

1) J. Selbin, *Chem. Rev.*, **65**. 153 (1965).

2) J. Selbin and T. R. Ortoland, *J. Inorg. Nucl. Chem.*, **26**, 37 (1964).

3) J. Selbin, H. R. Manning, and G. Cessac, *J. Inorg. Nucl. Chem.*, **25**, 1253 (1963).

4) V. Gutman, "Coordination Chemistry in Non-Aqueous Solution," Springer, Wien (1963).

5) R. Rowe and M. M. Jones, *Inorg. Synth.*, **5**, 115, (1957).

6) J. Selbin, G. Maus, and P. L. Jonson, *J. Inorg. Nucl. Chem.*, **29**, 1735 (1967).

7) N. Iwasaki, K. Sone, and Y. Fukuda, *Z. Anorg. Allg. Chem.*, **412**, 170 (1975).

8) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **2**, 1315 (1963).

9) J. Selbin, T. R. Ortolano, and F. J. Smith, *Inorg. Chem.*, **2**, 1315 (1963).

10) G. Basu, W. A. Yeranous, and R. L. Belford, *Inorg. Chem.*, **3**, 929 (1964).

11) M. H. Valek, W. A. Yeranous, G. Basu, P. K. Hornand, and R. L. Belford, *J. Mol. Spectrosc.*, **37**, 228 (1971).

12) M. R. Caira, J. M. Haigh, and L. R. Nassimbeni, *J. Inorg. Nucl. Chem.*, **34**, 3171 (1972).

13) N. S. Al-Niami, A. R. Al-Karaghouli, S. M. Aliwiand, and M. G. Jolhoom, *J. Inorg. Nucl. Chem.*, **36**, 283 (1974).

14) K. Dichmann, G. Hamer, S. C. Nyburg, and W. F. Reynolds, *Chem. Commun.*, **1970**, 1295.

15) R. L. Farmerand and F. L. Urbach, *Inorg. Chem.*, **13**, 587 (1974).

16) J. Selbin, L. H. Holmes, and S. P. Mcglynn, *J. Inorg. Nucl. Chem.*, **25**, 1539 (1963).

17) R. Larsson, *Acta Chem. Scand.*, **26**, 549 (1972).