An Optical Absorption Study of the Reaction of Bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV) with Pyridine

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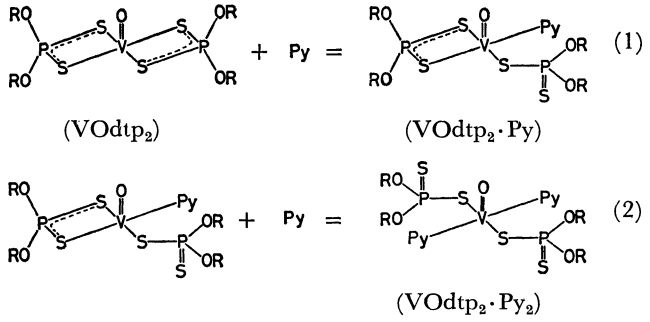
The interaction of bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV), $VOdtp_2$, with pyridine has been studied in toluene by means of the optical absorptions. It has been found that the visible absorption band characteristic of $VOdtp_2$ was shifted toward longer wavelengths upon the formation of the complex species identified as $VOdtp_2 \cdot Py$ and $VOdtp_2 \cdot Py_2$. The equilibrium constants and enthalpy and entropy changes for the formation of $VOdtp_2 \cdot Py$ were determined from the spectral characteristics, measured as a function of the solvent composition and the temperature. The results obtained were then discussed in comparison with those for the base addition of other oxovanadium complexes.

In the foregoing paper,[1] ESR evidence was presented that bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV), $VOdtp_2$, reacts with pyridine to form both mono- and dipyridine complexes. Pyridine bases were found to coordinate the vanadium nucleus, as is shown by the following scheme:



Since such a coordination scheme affords a marked contrast to that generally accepted for the base addition of oxovanadium(IV) complexes,[2] it seems worthwhile to investigate Reactions (1) and (2) in more detail. In the present work, an optical absorption method was used to investigate the equilibria involved and to obtain their thermodynamic data; the results will be reported here.

Experimental

Materials. Bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV), $VOdtp_2$, was prepared as has been described previously.[1] The pyridine and toluene were obtained from Wako Junyaku Kogyo Co. and were used after distillation from calcium hydride and potassium hydroxide respectively.

Measurements. Since the complex species in solutions were unstable to air, all the measurements were carried out on sample solutions carefully prepared in an atmosphere of nitrogen or *in vacuo*. The optical absorption spectra were measured with a Hitachi spectrophotometer (Model EPS-3T), using 10-mm quartz cells fitted with vacuum stopcocks or a nitrogen-bubbling device. The spectrophotometer was equipped with a temperature-regulated cell holder, and a constant temperature was maintained by circulating water through the cell holder. The temperatures were regulated by circulating through the cell holder water that had been cooled or warmed to the desired temperature. The temperatures were measured by means of a copper-constantan thermocouple directly inserted into the toluene placed in the reference cell. The ESR spectra were recorded with a JEOL spectrometer (Model P-10), as has been described previously.[1]

Results

Visible Absorption Spectra of Complex Species in Solutions. The optical absorption spectra of toluene solutions containing $VOdtp_2$ and pyridine in various mole ratios, as well as those of toluene and pyridine solutions of $VOdtp_2$, were measured at 18 °C. Some typical visible absorption spectra thus obtained are illustrated in Fig. 1. It is apparent from Fig. 1 that the spectrum A, obtainable without pyridine bases, shifts to B and C successively upon an increase in the pyridine content, thus affording three types of visible spectra.

In light of the ESR spectra of these solutions,[3] the visible spectra mentioned above can readily be

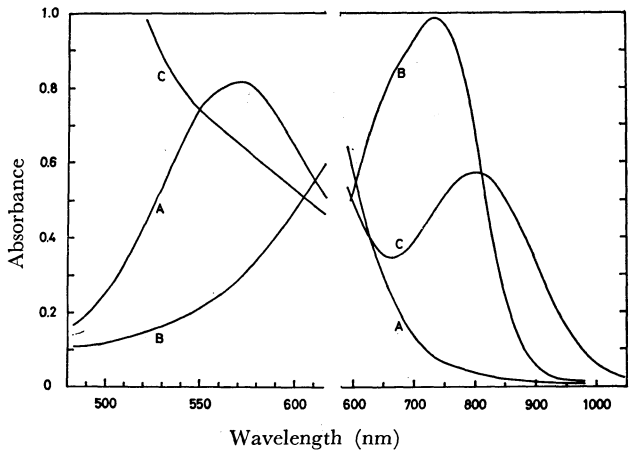


Fig. 1. Visible absorption spectra of toluene-pyridine solutions of $VOdtp_2$ at 18°C.
(A) $VOdtp_2$ in toluene, $[VOdtp_2]_0=0.015$ M;
(B) $VOdtp_2$-pyridine in toluene, $[VOdtp_2]_0=0.015$ M, $[Py]_0=0.091$ M;
(C) $VOdtp_2$ in pyridine, $[VOdtp_2]_0=0.012$ M.

1) M. Sato, Y. Fujita, and T. Kwan, This Bulletin, **46**, 3007 (1973).

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

3) Corresponding to the three types of visible absorption spectra, ESR spectra characterized with 24, 16, and 8 resonance lines were observed. The interpretation of these ESR spectra has already been reported in the foregoing paper, together with the proposed structures of the complex species.

interpreted as due to the complex species, $VOdtp_2$, $VOdtp_2 \cdot Py$, and $VOdtp_2 \cdot Py_2$, in the respective solutions. The absorption maxima and molar extinction coefficients determined for these complex species were given by:

(A) $VOdtp_2$; λ_{max} 570 nm, $\varepsilon_{A(max)}$ 53 $M^{-1}cm^{-1}$.

(B) $VOdtp_2 \cdot Py$; λ_{max} 735 nm, $\varepsilon_{B(max)}$ 71 $M^{-1}cm^{-1}$.

(C) $VOdtp_2 \cdot Py_2$; λ_{max} 800 nm, $\varepsilon_{C(max)}$ 47 $M^{-1}cm^{-1}$.

where the values of $\varepsilon_{A(max)}$ and $\varepsilon_{C(max)}$ were derived directly from Fig. 1, while that of $\varepsilon_{B(max)}$ was obtained by the procedure to be described below.

The band at 570 nm observed for $VOdtp_2$ seems to originate from a d–d transition;[4] this band is considered to shift to lower energies to produce a new band at 735 nm or 800 nm when one or two of the equatorial sulfur ligands are displaced by pyridine bases.

The Equilibrium Constant of Reaction (1). Job's method of continuous variations and the mole-ratio method[5] were applied to the $VOdtp_2$-pyridine system at 18 °C, first to confirm the stoichiometry of Reactions (1) and (2) and then to evaluate their equilibrium constants. It was found, however, that Reaction (2) did not proceed at all under the conditions employed in these experiments.

As can be seen from the results of the continuous variation method (Fig. 2), the absorbance at 735 nm reached its maximum at 50 mole% pyridine, indicating that one mole of $VOdtp_2$ reacts with one mole of pyridine, consistent with the stoichiometry of Reaction (1). On the other hand, the mole-ratio method showed

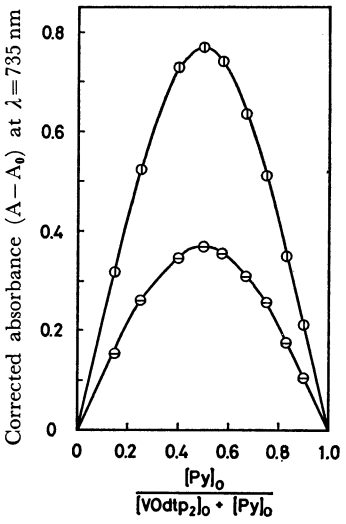


Fig. 2. Continuous variation method as applied to the $VOdtp_2$-pyridine system by visible absorption measurements at 18 °C.
⊕: $[VOdtp_2]_0+[Py]_0=0.041$ M (const.);
⊖: $[VOdtp_2]_0+[Py]_0=0.023$ M (const.).

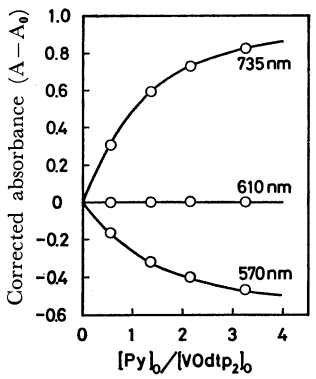


Fig. 3. Mole-ratio method as applied to the $VOdtp_2$-pyridine system by visible absorption measurements at 18 °C.
$[VOdtp_2]_0=0.015$ M (const.).

the presence of two absorbing species, $VOdtp_2$ and $VOdtp_2 \cdot Py$, in solutions, as can be seen from Fig. 3, where an isosbestic point at 610 nm is shown with the increasing and decreasing absorbances at 735 and 570 nm. These results are in accordance with the previous ESR information[1] that $VOdtp_2 \cdot Py$ is rather stable in toluene and is present in equilibrium with $VOdtp_2$ and pyridine over a wide concentration range, while $VOdtp_2 \cdot Py_2$ is formed only when $VOdtp_2 \cdot Py$ interacts with a large excess of pyridine bases.

The equilibrium constant, $K=[VOdtp_2 \cdot Py]/[VOdtp_2][Py]$, of Reaction (1) was then evaluated from the data shown in Figs. 2 and 3 after the procedure by Lang.[5,6] On the basis of the presence of two absorbing species, $VOdtp_2$ and $VOdtp_2 \cdot Py$, in solutions, the measured absorbance, A, at the chosen wavelength is given by:

$$A = \varepsilon_A[VOdtp_2] + \varepsilon_B[VOdtp_2 \cdot Py]$$
$$= \varepsilon_A[VOdtp_2]_0 + (\varepsilon_B - \varepsilon_A)[VOdtp_2 \cdot Py] \quad (3)$$

We then obtain the following expression for the equilibrium constant:

$$K = \frac{[VOdtp_2 \cdot Py]}{([VOdtp_2]_0 - [VOdtp_2 \cdot Py])([Py]_0 - [VOdtp_2 \cdot Py])}$$
$$= \frac{\dfrac{A-A_0}{\varepsilon_B-\varepsilon_A}}{\left([VOdtp_2]_0 - \dfrac{A-A_0}{\varepsilon_B-\varepsilon_A}\right)\left([Py]_0 - \dfrac{A-A_0}{\varepsilon_B-\varepsilon_A}\right)} \quad (4)$$

where ε_A and ε_B are the molar extinction coefficients at the chosen wavelength for $VOtdp_2$ and $VOdtp_2 \cdot Py$ respectively, where A_0 is the absorbance of $VOdtp_2$ at the wavelength in the absence of pyridine ($A_0=\varepsilon_A[VOdtp_2]_0$), and where $[VOdtp_2]_0$ and $[Py]_0$ are the initial concentrations of the two species.

To estimate the two unknowns, K and ε_B, the equation was rewritten as:

$$\frac{[VOdtp_2]_0[Py]_0}{A-A_0} = \left\{[VOdtp_2]_0 + [Py]_0 - \frac{A-A_0}{\varepsilon_B-\varepsilon_A}\right\} \cdot \frac{1}{\varepsilon_B-\varepsilon_A} + \frac{1}{K} \cdot \frac{1}{\varepsilon_B-\varepsilon_A} \quad (5)$$

4) R. G. Cavell, E. D. Day, W. Byers, and P. M. Watkins, *Inorg. Chem.*, **11**, 1591 (1972).

5) H. Hosoya, "Jikken Kagaku Koza," Vol. 11, ed. by The Chemical Society of Japan (1965), p. 523.

6) R. P. Lang, *J. Amer. Chem. Soc.*, **84**, 1185 (1962).

$[VOdtp_2]_0[Py]_0/(A-A_0)$ was plotted against $\{[VOdtp_2]_0+[Py]_0-(A-A_0)/(\varepsilon_B-\varepsilon_A)\}$ by using a tentative value[7] of ε_B and also by employing the absorbance data at $\lambda=735$ nm shown in Figs. 2 and 3. The plot yielded a straight line with a slope of $1/(\varepsilon_B-\varepsilon_A)$ and an intercept of $1/K(\varepsilon_B-\varepsilon_A)$, from which a new value of ε_B was determined along with that of K. This procedure was repeated until a consistent set of values for both ε_B and K was obtained from two successive plots. The final plot is presented in Fig. 4, with the following consistent values: $K_{(18°C)}=1.2\times10^2\ M^{-1}$, $\varepsilon_{B(\lambda=735nm)}=71\ M^{-1}\,cm^{-1}$. The uncertainties in the values estimated from the deviations in the linearity of the plots are about $\pm0.3\times10^2\ M^{-1}$ and $\pm5\ M^{-1}\,cm^{-1}$ for K and ε_B respectively.

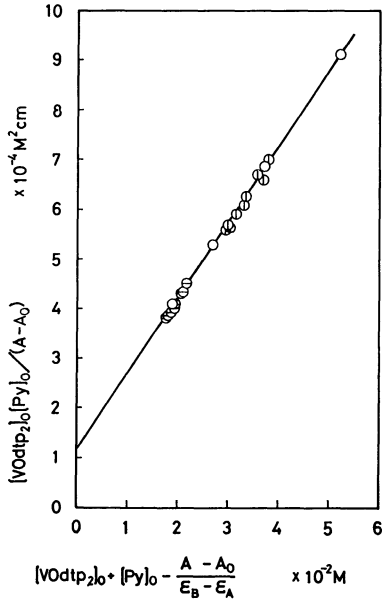


Fig. 4. Lang's plots of the $VOdtp_2$-pyridine system ($\lambda=735$ nm).
⊕⊖: Absorbance data from Fig. 2;
○: Absorbance data from Fig. 3.

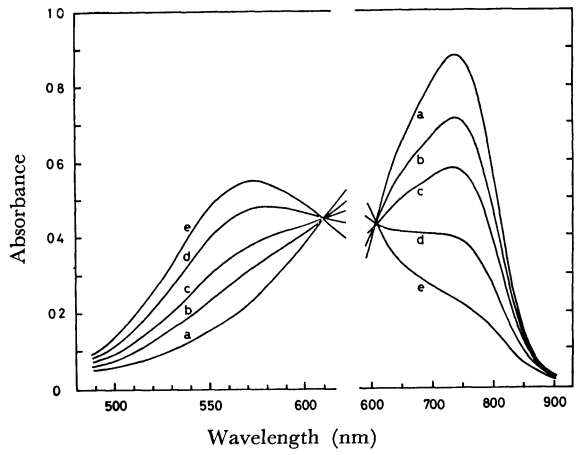


Fig. 5. Effect of temperature on visible absorption spectra.
$[VOdtp_2]_0=0.015$ M, $[Py]_0=0.035$ M.
a) 10 °C, b) 24 °C, c) 34 °C, d) 51 °C, e) 73 °C.

7) A tentative value of ε_B was advantageously determined by using data from two solutions and by solving Eq. (5) simultaneously for ε_B and K.

Temperature Dependence of the Equilibrium Constant. Figure 5 shows a typical set of visible spectra observed at different temperatures. It can be seen that the spectra show a sharp isosbestic point at 610 nm, with two absorption peaks at 570 and 735 nm. The presence of the isosbestic point again indicates that the equilibrium relation (1) is valid even at higher temperatures without any side reaction. Such an equilibrium relation between $VOdtp_2$ and $VOdtp_2\cdot Py$ was clearly evidenced also by the ESR spectra observed at different temperatures, as is shown in Fig. 6.

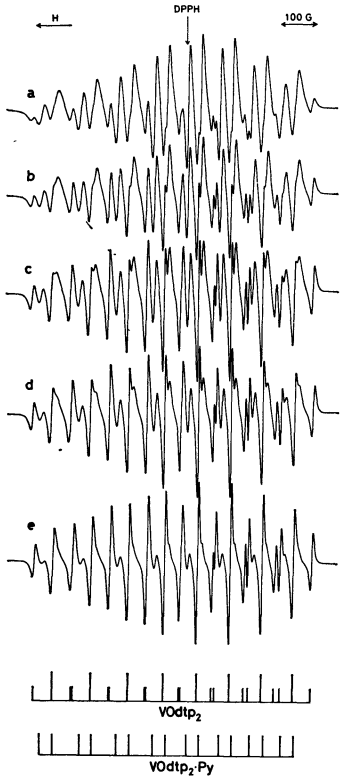


Fig. 6. Effect of temperature on ESR spectra.
$[VOdtp_2]_0=0.015$ M, $[Py]_0=0.035$ M.
a) 18 °C, b) 31 °C, c) 45 °C, d) 56 °C, e) 84 °C.
(The stick diagrams at the bottom of Figure indicate the 24 and 16 resonance lines expected from the complex species, $VOdtp_2$ and $VOdtp_2\cdot Py$.)

The equilibrium constant at each temperature was calculated using Eq. (4) on the assumption that molar extinction coefficients of $VOdtp_2$ and $VOdtp_2\cdot Py$ were constant over the entire temperature range. The resulting K values were found to be:

$K=160$ (10 °C), 65 (24 °C), 35 (34 °C), 15 (51 °C), $5.5\ M^{-1}$ (73 °C).

A plot of $\ln K$ *vs.* $1/T$ yielded a good straight line, and the following standard enthalpy and entropy changes for Reaction (1) were derived from the slope and intercept:

$$\Delta H^\circ = -10.5\ \text{kcal/mol},$$
$$\Delta S^\circ = -27.0\ \text{e.u.}$$

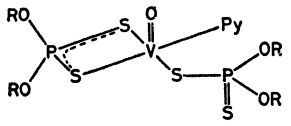
These values may be compared to those ($\Delta H^\circ=-12$ kcal/mol, $\Delta S^\circ=-30$ e.u.) obtained from an

analysis of the ESR spectra shown in Fig. 6. In view of the uncertainties in the values from the ESR spectra, both results seem to be compatible within the limit of experimental errors.

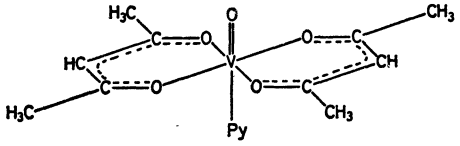
Discussion

It has generally been accepted[2] that square pyramidal oxovanadium(IV) complexes have a tendency to add a sixth ligand to the open coordination site *trans* to the apical oxygen atom when they are allowed to react with a variety of bases in solutions. For example, the formation of base adducts of bis(acetylacetonato)oxovanadium(IV), $VO(acac)_2$, has long been studied extensively by many workers,[8] and the thermodynamical data for the equilibria of the base addition to the sixth coordination site have already been repoted.[9,10]

However, our ESR and optical absorption studies have shown that the base addition reaction of $VOdtp_2$ is not a simple process in which the pyridine base adds to the open coordination site. The reaction has been found to be a rather complicated process involving the displacement of the equatorial sulfur ligand and leading to the formation of the complex species, $VOdtp_2 \cdot Py$, depicted as:



This type of base addition affords a marked contrast to the corresponding base adduct of $VO(acac)_2 \cdot Py$:



It is, however, not completely clear why there exists such a structural difference between $VOdtp_2 \cdot Py$ and $VO(acac)_2 \cdot Py$. For the moment, we can only say that the difference seems to result in part from the different natures of the equatorial ligands.

From this point of view, it is interesting to compare the thermodynamical data determined for the equilibrium of the $VOdtp_2$-pyridine system with those reported previously for the $VO(acac)_2$–pyridine system ($K_{(25°C)} = 58\ M^{-1}$, $\Delta H° = -7.4$ kcal/mol, $\Delta S° = -16.6$ e.u.).[10] A close similarity in the K values at 25 °C is noticeable, although there are some differences in the $\Delta S°$ and $\Delta H°$ values. The difference in the $\Delta S°$ values may be taken to reflect the different steric and solvation effects between the two systems. The $\Delta H°$ values may indicate that the vanadium-nitrogen coordination in $VOdtp_2 \cdot Py$ is much stronger than that in $VO(acac)_2 \cdot Py$, since the $\Delta H°$ for the $VOdtp_2$-pyridine system is attributable mainly to the differences in the bond energies of the vanadium-sulfur bond broken and the vanadium-nitrogen bond formed, while the $\Delta H°$ for the $VO(acac)_2$–pyridine system results mainly from the bond energy of the vanadium nitrogen bond formed. Such a notion is in accordance with the view that oxovanadium complexes coordinate a sixth axial ligand much more weakly than the equatorial ligands.

Since, in properties and structure, $VOdtp_2$ closely resembles bis(dithiocarbamato)oxovanadium(IV), $VOdtc_2$, rather than $VO(acac)_2$, it is important for us to note the recent spectroscopic studies of the interaction of $VOdtc_2$ with pyridine. McCormick[11] found that visible absorption bands associated with the d–d transitions of $VOdtc_2$ were shifted about 5000 cm^{-1} to lower energies when $VOdtc_2$ was dissolved in pyridine. He interpreted this red shift in terms of the addition of pyridine to the open coordination site and was able to isolate $VOdtc_2 \cdot Py$ as a solid.

However, the magnitude of the red shift observed for $VOdtc_2 \cdot Py$ is much closer to that (about 4000 cm^{-1}) for $VOdt_2p \cdot Py$ than to that (about 2000 cm^{-1}) for $VO(acac)_2 \cdot Py$.[10,11] Moreover, the ESR spectra of the $VOdtc_2$-pyridine system have provided no conclusive information about the structure of the complex species formed.[13]

From these points of view, we consider that at least two possibilities should be discussed equally for the base addition of $VOdtc_2$. The first possibility is, of course, that $VOdtc_2$ reacts with pyridine similarly to $VO(acac)_2$, while the second is that it reacts similarly to $VOdtp_2$. In order to distinguish these two possibilities, we have also made an ESR examination of the $VOdtc_2$-pyridine system. However, our ESR results have again provided no conclusive information as to which of the two possibilities is more probable. For the moment, it can only be said that further work, such as structural analysis by X-ray, will be required to confirm the structure of $VOdtc_2 \cdot Py$ and to decide between the above possibilities.

This work was supported in part by a grant of the Ministry of Education, to which the authors' grateful acknowledgements are made.

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9) R. T. Claunch, T. W. Martin, and M. M. Jones, *J. Amer. Chem. Soc.*, **83**, 1073 (1961).

10) R. L. Carlin and F. A. Walker, *ibid.*, **87**, 2128 (1965).

11) B. J. McCormick, *Inorg. Chem.*, **7**, 1965 (1968); *Can. J. Chem.*, **47**, 4283 (1969).

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

13) G. Vigee and J. Selbin, *ibid.*, **31**, 3187 (1969); B. J. McCormick and E. M. Bellott, Jr., *Inorg. Chem.*, **9**, 1779 (1970); F. E. Dickson, C. J. Kuncsh, E. L. McGinnis, and L. Petrakis, *Anal. Chem.*, **44**, 978 (1972).