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ESR Studies on Bis(*O,O′*-diethyldithiophosphato) Oxovanadium [IV] in Ether Solutions

MITSUO SATO, TAKASHI KATSU, YUZABURO FUJITA, and TAKAO KWAN

Faculty of Pharmaceutical Sciences, The University of Tokyo[1]

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ESR studies have been made on bis(*O,O′*-diethyldithiophosphato) oxovanadium[IV], $VOdtp_2$, in ethyl ether, isopropyl ether, *n*-butyl ether, and tetrahydrofuran solutions. It has been found that at lower temperatures $VOdtp_2$ reacts with each of the ethers to form an adduct, $VOdtp_2\cdot(R_2O)$, with structure characterized by the coordination of ether molecule to the equatorial position. The equilibrium constant for the $VOdtp_2\cdot(R_2O)$ formation has also been evaluated; it increased with increasing basicity of the ether (tetrahydrofuran>ethyl ether>isopropyl ether—*n*-butyl ether).

We have recently reported the results of electron spin resonance (ESR) and optical absorption studies on the adduct formation of bis(*O,O′*-diethyldithiophosphato) oxovanadium [IV], $VOdtp_2$, with pyridine bases.[2,3] As a continuation and extension of the work, the ESR spectra of ether solutions of $VOdtp_2$ were now investigated, with special interest being taken in the interaction of $VOdtp_2$ with such weak bases as ethers. As a result, we found an ESR evidence that $VOdtp_2$ reacts with ethers to form adducts, $VOdtp_2\cdot(R_2O)$, at lower temperatures. The $VOdtp_2\cdot(R_2O)$ adducts showed spectral characteristics quite similar to those of the $VOdtp_2\cdot$Py adducts. The results will briefly be reported in this paper.

Experimental

$VOdtp_2$ was prepared as described previously.[2] The ethers employed in this work were ethyl ether, isopropyl ether, *n*-butyl ether, and tetrahydrofuran. These were commercial reagents of G.R. grade (Tokyo Kasei Kogyo Co.), and were purified by distillation after drying over sodium or calcium chloride. $VOdtp_2$ was dissolved in the ethers *in vacuo* in a concentration range of 1×10^{-3}—1×10^{-2}M, and each of the solutions was subjected to ESR measurements at various temperatures. The spectra at room temperature (about 28°) and at liquid nitrogen temperature (−196°) were recorded with a JEOL spectrometer, Model PE-1X (100 KHz field modulation), while the spectra at intermediate temperatures were obtained with a P-10 type spectrometer (JEOL, X-band, 100 KHz field modulation) equipped with a temperature controlling device (JEOL-UCT-2X). Other experimental details were similar to those of the previous report.[2]

Result and Discussion

ESR Spectra at Room Temperature

In Fig. 1 is shown a typical ESR spectrum recorded at room temperature for an ethyl ether solution of $VOdtp_2$. Essentially identical spectra were obtained in other ether solutions, although the apparent linewidth was different from one solvent to the other.[4]

As can be seen from Fig. 1, the spectrum consists of the eight hyperfine (*hf*) lines characteristic to the vanadium nucleus ($I=7/2$) each of which further splits into three

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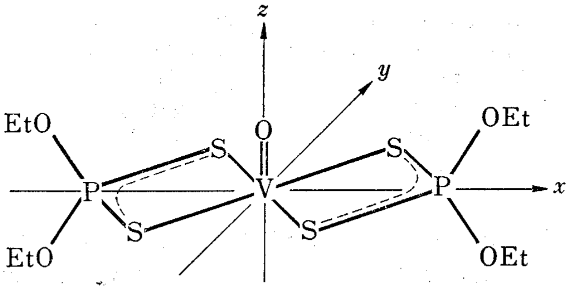
[1] Location: *Hongo 7-3-1, Bunkyo-ku, Tokyo.*

[2] M. Sato, Y. Fujita, and T. Kwan, *Bull. Chem. Soc. Japan*, **46**, 3007 (1973).

[3] M. Sato and T. Kwan, *Bull. Chem. Soc. Japan*, **46**, 3745 (1973).

[4] The order of increasing linewidth was found to be ethyl ether<tetrahydrofuran<isopropyl ether<*n*-butyl ether. This is the order of increasing viscosity of the ether, indicating that the major contribution to the linewidth arises from anisotropic *g* and *hf* interactions (R.W. Wilson and D. Kivelson *J. Chem. Phys.*, **44**, 154, 4440 (1966)).

components with the intensity ratio of 1: 2: 1 as the result of the superhyperfine (*shf*) interaction with the two equivalent phosphorus nuclei ($I=1/2$). ESR parameters obtained (Table I) are in close agreement with those previously reported for VOdtp$_2$ in toluene,[2] indicating that the coordination structure of VOdtp$_2$ in both ether and toluene solutions is identical. Thus, it follows that VOdtp$_2$ in ether solutions also has the following square pyramidal coordination with symmetry of C_{2v}:



I: VOdtp$_2$

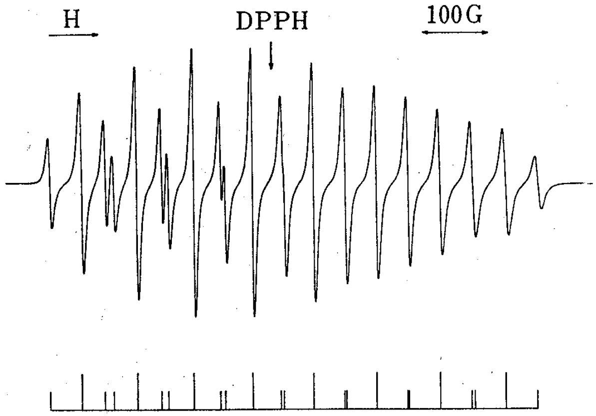


Fig. 1. ESR Spectrum Obtained from the Ethyl Ether Solution of VOdtp$_2$ at Room Temperature (28°)

The line-positions of the 24-resonance lines expected from I are indicated in the stick diagram at the bottom, although fewer than the 24 expected lines are resolved because of line overlappings.

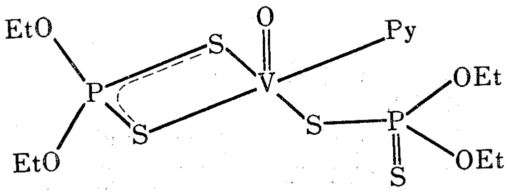
Here, it is important to note that a single unpaired electron is located in an A_1 molecular orbital mainly consisting of the vanadium $3d_{x^2-y^2}$ orbital, and that this orbital possesses the correct symmetry so as to interact directly with the two phosphorus nuclei yielding an anomalously large *shf* splitting ($a^P=51$ gauss).

ESR Spectra at Liquid Nitrogen Temperature

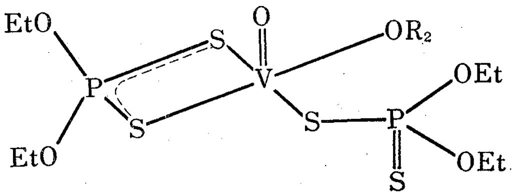
Upon freezing at liquid nitrogen temperature, each of the ether solutions changed its color from purple to bluish green, suggesting that some significant change in the coordination of I took place. Such frozen solutions gave almost identical ESR spectra at −196° irrespective of the kind of the ethers employed.

A typical ESR spectrum obtained from the ethyl ether solution is illustrated in Fig. 2. It can be seen from Fig. 2 that the spectrum is composed of two distinct sets of 16 resonance lines that correspond to $g_{\parallel}$ and $g_{\perp}$ respectively. Such 16 resonance lines can be explained by the *shf* interaction due to one phosphorus nucleus.

We have previously shown that the adducts of VOdtp$_2$ with pyridine bases, VOdtp$_2$·Py, give rise to similar spectra characterized by such 16-resonance lines as shown in Fig. 2 and that ESR parameters of VOdtp$_2$·Py can be compatible with the following coordination structure (II′).[2] Thus, in analogy with this, it must be conceded that the spectrum shown in Fig. 2 results from the adduct of VOdtp$_2$·(R$_2$O) having a coordination structure (II).



II′: VOdtp$_2$·Py



II: VOdtp$_2$·(R$_2$O)

On the same ground as was described previously,[2] one can reasonably expect that only the phosphorus nucleus in II located in the direction of the vanadium $3d_{x^2-y^2}$ orbital lobes contributes the shf splittings, hence causing each of the vanadium *hf* lines further to split into two components with equal intensity. This expectation is, in fact, in good accordance with the observed spectrum. The ESR parameters obtained are listed in Table I. It is noted that the *shf* coupling constants for the parallel and perpendicular components are $A^{\mathrm{P}}_{\parallel} \fallingdotseq A^{\mathrm{P}}_{\perp} \fallingdotseq 34$ gauss, indicating that the phosphorus *shf* interaction is quite isotropic. Furthermore, the *g*-values and *hf* coupling constants obtained for II fit the following relations:

g-values $(\mathrm{VO})\mathrm{S}_4\!: \mathrm{I} > (\mathrm{VO})\mathrm{S}_3\mathrm{N}\!: \mathrm{II}' > (\mathrm{VO})\mathrm{S}_3\mathrm{O}\!: \mathrm{II}$
hf-values $(\mathrm{VO})\mathrm{S}_4\!: \mathrm{I} < (\mathrm{VO})\mathrm{S}_3\mathrm{N}\!: \mathrm{II}' < (\mathrm{VO})\mathrm{S}_3\mathrm{O}\!: \mathrm{II}$

These orders are also consistent with those expected from the empirical relation between the ESR parameter and the ligand environment of oxovanadium complexes.[5]

ESR Spectra at Intermediate Temperatures and Equilibria of the Adduct Formation

In view of the ESR results described above, it seems very likely that at lower temperatures VOdtp$_2$, I, reacts with ethers to form the adducts, VOdtp$_2$·(R$_2$O), II, according to the scheme:

$$\underset{\mathrm{I}}{\mathrm{VOdtp_2}} + \mathrm{R_2O} = \underset{\mathrm{II}}{\mathrm{VOdtp_2\cdot(R_2O)}} \qquad (1)$$

In consistent with this scheme, we were, in fact, able to observe an isotropic ESR spectrum which can be assigned to II from the ether solutions at intermediate temperatures.

A typical result obtained from an ethyl ether solution at −30—−70° is illustrated in Fig. 3, from which it is evident that gradual lowering of

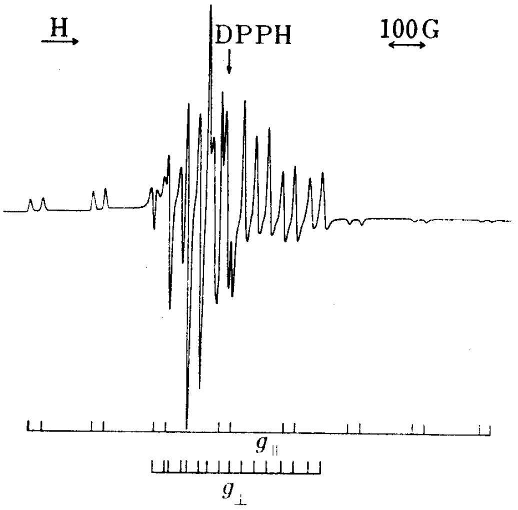


Fig. 2. ESR Spectrum Obtained from the Ethyl Ether Solution of VOdtp$_2$ at Liquid Nitrogen Temperature (−196°)

The line-positions of the two sets of the 16-resonance lines expected from II are indicated.

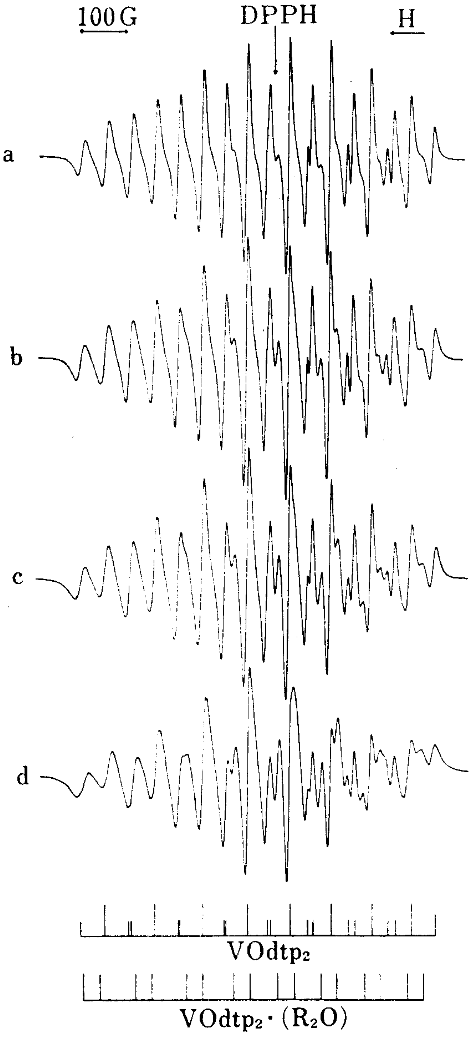


Fig. 3. ESR Spectra Obtained from the Ethyl Ether Solution of VOdtp$_2$ at Intermediate Temperatures

a: −34°, b: −51°, c: −60°, d: −70°
The stick diagrams at the bottom indicate the 24- and 16-resonance lines expected from I and II respectively.

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[5] F.E. Dickson, C.J. Kunesh, E.L. McGinnis, and L. Petrakis, *Anal. Chem.*, **44**, 978 (1972).

TABLE I. ESR Data of the Ether Solutions of $VOdtp_2$[a]

	$VOdtp_2$ in toluene[b]	$VOdtp_2$ in ethyl ether at room temp.	$VOdtp_2$ in ethyl ether at $-60°$[c]		$VOdtp_2$ in ethyl ether at $-196°$	$VOdtp_2 \cdot Py$ in toluene[b]
Isotropic values						
g_0	1.981	1.981	1.981	1.973	(1.970)[d]	1.976
a^V (gauss)	95.5	95.7	95.7	101	(102)[d]	95.5
a^P (gauss)[e]	51.0 (2P)	51.0 (2P)	51.0 (2P)	35 (1P)	(34 (1P))[d]	37.0 (1P)
Anisotropic values						
$g_\parallel$	1.967	—[f]	—[f]	—[f]	1.948	1.958
$g_\perp$	1.987	—	—	—	1.981	1.982
$A^V_\parallel$ (gauss)	168	—	—	—	180	170
$A^V_\perp$ (gauss)	59	—	—	—	63	59
$A^P_\parallel$ (gauss)[e]	52 (2P)	—	—	—	34 (1P)	37 (1P)
$A^P_\perp$ (gauss)[e]	50 (2P)	—	—	—	34 (1P)	38 (1P)
Assignments	I	I	I +	II	II	II′

a) No significant differences were found in the ESR parameters between the spectra obtained from the ethyl ether, isopropyl ether, n-butyl ether, and tetrahydrofuran solutions.
b) See ref. 1.
c) Two types of spectra were observed (see text).
d) Calculated isotropic values ($g_0=(g_\parallel+2g_\perp)/3$, $a^V=(A^V_\parallel+2A^V_\perp)/3$, $a^P=(A^P_\parallel+2A^P_\perp)/3$).
e) *shf* resolutions due to the two equivalent phosphorus nuclei (2P) and due to one phosphorus nucleus (1P).
f) Only the isotropic values are obtainable at the temperature indicated.

temperature brings about an appearance and growth of a new spectrum overlapping on the spectrum of I. The new spectrum is composed of eight hf lines each of which further splits into two components with equal intensity. This is consistent with the spectrum expected from II. In addition, the isotropic ESR parameters determined ($g_0=1.973$, $a^V=101$ gauss, $a^P=35$ gauss) are in good agreement with those calculated from the anisotropic data of II.

The equilibrium constant of Reaction (1) at each temperature

$$K = \frac{[VOdtp_2 \cdot (R_2O)]}{[R_2O][VOdtp_2]}$$

was then evaluated roughly from Fig. 3, by approximating $[VOdtp_2 \cdot (R_2O)]/[VOdtp_2]$ as the ratio of integrated intensities of the two spectra and $[R_2O]$ as $10\,\text{M}$ (constant). The K values thus obtained for ethyl ether are as follows:

$$K = 0.6\times10^{-2}\ (-34°),\quad 1.5\times10^{-2}\ (-51°),$$
$$2.7\times10^{-2}\ (-60°),\quad 7.0\times10^{-2}\,\text{M}^{-1}\ (-70°).$$

A plot of log K *vs.* $1/T$ yielded $-\Delta H=6$ Kcal/mole and $-\Delta S=36$ e.u.

The tetrahydrofuran solution gave a similar spectral change to that observed for the ethyl ether solution, although the temperature range to give such spectral change was found to be higher; the appearance of the spectrum of II was observable even at 10—20°. The equilibrium constants roughly estimated were much larger than those for ethyl ether:

$$K = 0.4\times10^{-2}\ (-5°),\quad 1.0\times10^{-2}\ (-23°),$$
$$1.9\times10^{-2}\ (-40°),\quad 5.2\times10^{-2}\,\text{M}^{-1}\ (-53°).$$

The van't Hoff plot gave a similar value for $-\Delta H$ and a slightly smaller value for $-\Delta S$.

In the cases of the isopropyl ether and n-butyl ether solutions, no appreciable appearance of the spectrum of II was observed even at $-40°$. Further decrease in temperature brought about only the resonance lines accompanied with larger linewidth and anisotropic lineshape, which made it difficult to obtain an evidence of the isotropic spectrum of II. From these observations, the K values for isopropyl ether and n-butyl ether are considered to be smaller than those for tetrahydrofuran and ethyl ether.

The p*K*a values of the ethers employed in this work have already been reported:[6)]tetrahydrofuran (−2.08), ethyl ether (−3.59), isopropyl ether (−4.30), and *n*-butyl ether (−5.40). Thus, it is quite certain from these values and the above results that the equilibrium constants for the $VOdtp_2 \cdot (R_2O)$ formation decrease in the order of decreasing basicities of the ethers. The role of the basicity of ligand for the adduct formation can also be revealed by the comparison of the results obtained here with those for $VOdtp_2 \cdot Py$ formation.[3)]

To summarize briefly, the adduct formation of $VOdtp_2$ was well demonstrated with respect to such weak bases as ethers. The reaction scheme was also found to be similar to that reported previously for the N-donor ligands such as pyridine bases.[2,3)]

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6) E.M. Arnett and C.Y. Wu, *J. Am. Chem. Soc.*, **82**, 4999 (1960); *idem*, *ibid.*, **84**, 1680, 1684 (1962).