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Electron-spin-resonance Studies of the Formation and Properties of the Trimeric Vanadyl Dibutylphosphate Complex

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The extraction of the vanadyl ion (VO^{2+}) from aqueous solutions by di-*n*-butylphosphoric acid ($(C_4H_9O)_2PO_2H$) in hexane has been studied by ESR. It has been found that monomeric and trimeric vanadyl di-*n*-butylphosphate complexes were present in the organic phase, and the equilibrium constant of the reaction involving monomeric and trimeric forms was determined. The ESR spectrum of the trimeric complex, characterized by 22 hf lines with a separation of 39 gauss, was interpreted as resulting from the magnetic exchange interaction between three vanadyl ions. A crystalline vanadyl complex was isolated from the hexane solution and found to be $(VOX_2)_3$, where X represents $(C_4H_9O)_2PO_2^-$. The properties of the complex were investigated by means of ESR, IR, and the optical absorptions. The mechanism of the extraction of VO^{2+} by $(C_4H_9O)_2PO_2H$ was discussed, and a cyclic model was proposed for the structure of $(VOX_2)_3$.

The extraction of the vanadyl ion (VO^{2+}) dissolved in aqueous solutions by di-(2-ethylhexyl)-phosphoric acid (HDEHP) in kerosene has been studied by several workers.[1,2] Accordingly, the vanadium/HDEHP ratios of the extracts ranged from 0.25 to 0.50, suggesting that at least two species of vanadyl complexes were formed. Moreover, it has been suggested[2] that polymeric vanadyl complexes are formed at lower HDEHP concentrations, while monomeric complexes are formed at higher HDEHP concentrations.

In the present study, the vanadyl complexes extracted from sulfuric acid solutions into the hexane phase by di-*n*-butylphosphoric acid (HDBP) have been investigated, with special interest being taken in the formation of polymeric species. Preliminary observations of extracts by electron spin resonance revealed that trimeric complexes rather than polymeric ones are formed. It was decided, therefore, to investigate first the conditions for the formation of the trimeric complex. Subsequently attempts were made to isolate the complex and to clarify the chemical stoichiometry and properties of the complex. The present paper will report the results of these investigations.

Experimental

Materials. HDBP (E.P. grade, Tokyo Kasei Kogyo Co.,) was used without further purification. The IR spectrum showed few impurities. Hexane (G.R. grade, Wako Junyaku Kogyo Co.,), which has previously been known to be the most effective diluent in the extraction of vanadium by HDEHP,[2] was used as the diluent after distillation. The vanadyl sulfate hydrate ($VOSO_4 \cdot nH_2O$) was obtained from Kishida Kagaku Co.; the colorimetric peroxide method indicated that the $VOSO_4$ content was 55 wt%. All the other reagents used were of a reagent grade and were commercially available.

Extraction of the Vanadyl Ion (VO^{2+}) by HDBP. The extraction of VO^{2+} from acidic aqueous solutions by HDBP in hexane was carried out in a 300 ml separating funnel, generally with equal volumes (100 ml) of the aqueous and organic phases. The two phases were mixed vigorously by shaking for about 10 min at the ambient temperature, and were then allowed to stand until the separation into two layers was complete. Little trouble was experienced with emulsions. The extractions were carried out under the following conditions:

initial HDBP concentrations as monomer in the organic phase: $C_{HX(i)} = 0.12—1.2M$

initial VO^{2+} concentrations in the aqueous phase: $C_{V(i)} = 0.02—1.5M$

final pH values in the aqueous phase: $pH_{(f)} = 0.8—5.5$

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[1] T. Rigg and J. O. Garner, *J. Inorg. Nucl. Chem.*, **29**, 2019 (1967).

[2] T. Sato and T. Takeda, *ibid.*, **32**, 3387 (1970).

The variation in the final pH values in the aqueous phase was accomplished by adding the requisite amounts of H_2SO_4 or NaOH solutions either immediately before or during the mixing. The $pH_{(f)}$ values were determined by means of a Toadempa pH-meter (Model HM-5A) after the separation.

Isolation of the Trimeric Vanadyl Complex. The hexane phase was dehydrated with anhydrous sodium sulfate, and then the solvent was evaporated under a reduced pressure. The resulting blue viscous liquid was then chromatographed over a column packed with SiO_2, using benzene as the eluent; the blue fractions thus obtained were evaporated under a sufficiently reduced pressure 10^{-4} Torr) at 60°C for about 3 hr to give again a blue, oily liquid. After 1—2 weeks' standing in a refrigerator, a light blue crystalline material was obtained (mp 43°C).[3]

Measurements of ESR, IR, and Optical Spectra. The ESR spectra were recorded at room temperature with a JEOL spectrometer, Model JES P-10 (X-band), using 100 KHz field modulation. The magnetic field was calibrated with an ESR marker, $MgO:Mn^{2+}$ powder, supplied by JEOL. Powdered DPPH was used as a reference in the determination of the *g*-values. Samples from the extracted organic phases were subjected to ESR measurements without any pretreatment, while those from isolated crystals were measured, generally *in vacuo*, after dissolving them in various organic solvents.

The IR spectra were recorded on a DS-402G grating spectrophotometer (Japan Spectroscopic Co.,) in Nujol mulls and in thin liquid films. The optical spectra were recorded on a Hitachi spectrophotometer (Model EPS-3T) in the range of 300—1200 nm.

Chemical Analyses. Vanadium was analysed by the colorimetric peroxide method.[4] Samples dissolved in hexane were back-extracted with 2N HCl, and color development was performed by the successive additions of 2N H_2SO_4, 85% phosphoric acid, and 30% hydrogen peroxide. The optical densities of the colorimetric solutions were determined at wavelength of 450 nm with a Shimadzu spectrophotometer (Model QV-50). The analyses of carbon and hydrogen were performed at the Microanalytical Center of our laboratory.

Molecular-weight Measurements and Differential Scanning Calorimetry. The molecular weights were determined in a chloroform solution at 35°C using a Hitachi Model 115 vapor-pressure osmometer calibrated with benzil. Scale readings were made 5 min after a drop of the solution had been placed on the thermistor. The concentrations of the solution were in the range of 10^{-2}—10^{3}-M. The DSC thermograms were recorded on a DSC-1B calorimeter (Perkin-Elmer) in an atmosphere of nitrogen.

Results and Discussion

ESR Spectra of Extracted Vanadyl Complexes. Hexane solutions of the extract were subjected to preliminary ESR measurements at room temperature in order to obtain some information about the states of the extracted vanadyl complexes.

Two types of spectrum were observed, depending upon the extraction conditions. As will be discussed below, one was assigned to a monomeric vanadyl species, and the other, to a trimeric one. Hereafter, the former will be denoted as the "M-spectrum", and the latter, as the "T-spectrum".

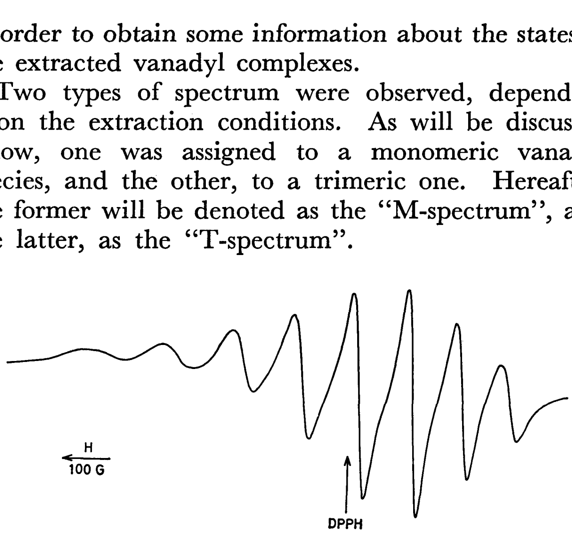

Fig. 1. ESR spectrum of the hexane phase (M-spectrum) obtained under the following extraction condition; $C_{HX(i)}=1.20M$, $C_{V(i)}=0.30M$, $pH_{(f)}=0.8$.

Assignment of M-spectrum: A typical M-spectrum obtained from the hexane solution extracted under the conditions; $C_{HX(i)}=1.20$ M, $C_{V(i)}=0.30$ M, and $pH_{(f)}=0.8$, is shown in Fig. 1. The spectrum was characterized by eight resonance lines with unequal separations and linewidths. It is quite similar to the reported spectra[5] for many monomeric vanadyl complexes in liquid solutions, and can be interpreted by an isotropic spin Hamiltonian as:

$$\mathscr{H} = g_0\beta HS_z + a\boldsymbol{I}\cdot\boldsymbol{S} \qquad (1)$$
$$S=1/2,\ I=7/2$$

where the *z* axis is defined by the direction of the external magnetic field, where g_0 is the isotropic *g* value, where *a* is the isotropic hyperfine constant due to the vanadium nucleus, and where the other symbols have their usual meanings. The solution of the above Hamiltonian up to second order of *a* leads to the resonance condition described as:[5,6]

$$h\nu = g_0\beta H + am + \frac{a^2}{2g_0\beta H}\left(\frac{63}{4}-m^2\right) \qquad (2)$$
$$m=7/2,\ 5/2,\ 3/2,\ \cdots\cdots,\ -5/2,\ -7/2$$

The M-spectrum shown in Fig. 1 was then fitted to the equation to obtain the following parameters:

$$g_0 = 1.961 \qquad a = 119\ \text{gauss}$$

These values are in good agreement with those reported for monomeric vanadyl complexes coordinated with oxygen ligands, such as $VO(H_2O)_5^{2+}$,[6,7] $VO(Ac)_2$,[8] and $VO(\text{phthalic acid})_2^{2-}$.[9]

On the other hand, it has generally been accepted that dialkylphosphoric acids ($(RO)_2PO_2H$) extract a

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[3] In some cases the crystallization did not take place even after a much longer period of standing. This was because of the contamination by a small amount of monomeric species in a blue oily liquid; the contamination was obvious from the ESR and molecular-weight measurements. It was necessary in such cases to wash the blue oily liquid after dissolving it in hexane with an appropriate amount of the 0.01N NaOH solution and then to repeat the treatment described above.

[4] E. R. Wright and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **9**, 375 (1937); A. Weissler, *ibid.*, **17**, 695 (1945).

[5] H. A. Kuska and M. T. Rogers, "Radical Ions," ed. by E. T. Kaiser and L. Kevan, Interscience Publisher (1968), p. 579.

[6] R. N. Rogers and G. E. Pake, *J. Chem. Phys.*, **33**, 1107 (1960).

[7] N. S. Garifianov and B. M. Kozyrev, *Doklady Akad. Nauk SSSR*, **98**, 929 (1954); B. M. Kozyrev, *Discuss. Faraday Soc.*, **19**, 135 (1955).

[8] H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962); I. Bernal and P. Reiger, *Inorg. Chem.*, **2**, 256 (1963).

[9] K. Wuethrich, *Helv. Chim. Acta*, **48**, 1012 (1965).

number of metal cations by this ion-exchange reaction:[10]

$$M^{n+}_{(a)} + n(HX)_{2(o)} = M(X_2H)_{n(o)} + nH^{+}_{(a)} \qquad (3)$$

in which X represents the anion $(RO)_2PO_2^-$; $(HX)_2$, the dimeric $(RO)_2PO_2H$; and (a) and (o), the aqueous and organic phases respectively. Furthermore, Sato *et al.*[2] have recently shown that the mechanism is applicable also in the case of the extraction of VO^{2+} by excess HDEHP, and they have confirmed the existence of $VO(X_2H)_2$, $X=(C_8H_{17}O)_2PO_2$, in kerosene from an analysis of the partition coefficients. Therefore, it is quite natural in our system also that the monomeric vanadyl complex $VO(X_2H)_2$, $X=(C_4H_9O)_2PO_2$, is formed in hexane *via* the reaction:

$$VO^{2+}_{(a)} + 2(HX)_{2(o)} = VO(X_2H)_{2(o)} + 2H^{+}_{(a)} \qquad (4)$$

Consequently, the M-spectrum can be interpreted as resulting from the monomeric vanadyl complex, $VO(X_2H)_2$. This assignment may be further supported by the spin Hamiltonian parameters, and also by the experimental findings to be described in the later sections.

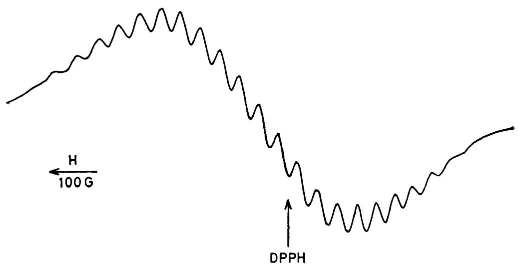

Fig. 2. ESR spectrum of the hexane phase (T-spectrum) obtained under the following extraction condition; $C_{HX(i)}=0.12$M, $C_{V(i)}=1.5$M, pH$_{(f)}=1.6$.

Assignment of T-spectrum: When the extraction was carried out under these conditions; $C_{HX(i)}=0.12$ M, $C_{V(i)}=1.5$ M, and pH$_{(f)}=1.6$, a typical T-spectrum was obtained. As is illustrated in Fig. 2, the T-spectrum has the following characteristics; (I) 22 resonance lines are found to be equally spaced with a separation almost equal to one-third of the average splitting found for the M-spectrum, (II) the resonance intensity for each line decreases with the line position almost symmetrically from the center of the spectrum to the outside. From such characteristics, it can readily be presumed that there are magnetic exchange interactions between three vanadyl ions.

In order to explain the observed T-spectrum qualitatively, we further assume that vanadium atoms of the trimer form equilateral triangular arrangements and that three vanadium ions of $S=1/2$ are exchange-coupled with an isotropic exchange Hamiltonian:

$$\mathscr{H}_{ex} = J(\boldsymbol{S}_1\cdot\boldsymbol{S}_2+\boldsymbol{S}_2\cdot\boldsymbol{S}_3+\boldsymbol{S}_3\cdot\boldsymbol{S}_1) \qquad (5)$$

where J denotes the isotropic exchange integral and where $\boldsymbol{S}_1$, $\boldsymbol{S}_2$, and $\boldsymbol{S}_3$ are the spin operators for the respective vanadium ions. Thus, the total spin Hamiltonian describing the system becomes:[11]

$$\mathscr{H} = \mathscr{H}_1 + \mathscr{H}_2 + \mathscr{H}_3 + \mathscr{H}_{ex} \qquad (6)$$

in which $\mathscr{H}_1$, $\mathscr{H}_2$, and $\mathscr{H}_3$ are each given by the form (1); it can be rewritten as:

$$\mathscr{H} = g_0\beta H(S_{1z}+S_{2z}+S_{3z}) + a(\boldsymbol{S}_1\cdot\boldsymbol{I}_1+\boldsymbol{S}_2\cdot\boldsymbol{I}_2+\boldsymbol{S}_3\cdot\boldsymbol{I}_3) + J(\boldsymbol{S}_1\cdot\boldsymbol{S}_2+\boldsymbol{S}_2\cdot\boldsymbol{S}_3+\boldsymbol{S}_3\cdot\boldsymbol{S}_1) \qquad (7)$$

The eigen values of this Hamiltonian can readily be evaluated[12,13] by solving the secular determinant of the Hamiltonian on the assumption $|J|\gg|a|$; we then obtain the following ESR transitions[14] for the quartet state and for the two doublet states which are degenerate and which lie at a distance $3/2\ |J|$ from the quartet state.

Transitions for the quartet state:

$$h\nu = g_0\beta H + a/3(m_1+m_2+m_3) \qquad (8)$$

Transitions for the two doublet states:

$$h\nu = g_0\beta H + a/3(m_1+m_2+m_3) \pm 2/3a(m_1^2+m_2^2+m_3^2-m_1m_2-m_2m_3-m_3m_1)^{1/2} \qquad (9)$$

where m_1, m_2, and m_3 are the magnetic quantum numbers for each vanadium nucleus; each takes on the value of 7/2, 5/2, 3/2, ……, −5/2, −7/2.

Thus, it can be shown for the quartet-state spectrum that the 22 hf lines have the equal separation of $a/3$ and the intensity ratio of 1:3:6:10:15:21:28:36:42:46:48:48:46:42: ……, while the predicted spectrum for the doublet states consists of two sets of irregularly-spaced hf lines, both of which are symmetric to each other with respect to the magnetic filed defined by $h\nu=g_0\beta H$.

The characterisic (I) for the observed T-spectrum is quite consistent with the above expectation for the quartet-state spectrum. Furthermore, the observed intensity distribution of hf lines (Characteristic (II)), which is difficult to measure accurately, seems to follow approximately the expected one. One can, then, reasonably state that the T-spectrum results from the quartet-state transitions. On the other hand, it is not obvious at the moment why irregularly-spaced hf lines due to the doublet-state transitions are not observable.

The parameters determined from the T-spectrum on the basis of Eq. (8) are:

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[10] C. A. Blake, Jr., C. F. Baes, Jr., K. B. Brown, C. F. Coleman, and J. C. White, *Proc. 2nd. Int. Conf. on Peaceful Uses of Atomic Energy*, **28**, 289, Geneva (1958); C. A. Blake, Jr., C. F. Baes, Jr., and K. B. Brown, *Ind. Eng. Chem.*, **50**, 1763 (1958); D. F. Peppard, G. W. Mason, W. J. Driscoll, and R. J. Sironen, *J. Inorg. Nucl. Chem.*, **7**, 276 (1958).

[11] G. F. Kokoszka and G. Gordon, *Transition Metal Chem.*, **5**, 181 (1969).

[12] A. Hudson and G. R. Luckhurst, *Mol. Phys.*, **13**, 409 (1967).

[13] A. Hasegawa, Y. Yamada, and M. Miura, This Bulletin, **42**, 846 (1969); A. Hasegawa, *J. Chem. Phys.*, **55**, 3101 (1971).

[14] The second-order correction terms with respect to a must be added to Eqs. (8) and (9). The correction terms evaluated for (8) are as follows:

$$\frac{a^2}{18g_0\beta H}\{3I(I+1)-m_1^2-m_2^2-m_3^2\} + \frac{a^2}{18g_0\beta H}(2m_S-1)(m_1+m_2+m_3)$$

where $I=7/2$ and $m_S=3/2$, 1/2, −1/2. However, these terms are much smaller than that given in Eq. (2) and do not contribute to the line positions very much. Thus, the terms are ommitted from Eq. (8), although it seems that the terms are more or less related to the linewidth because of the superposition of resonance lines differing in m_S values.

$$g_0 = 1.960 \qquad a/3 = 39 \text{ gauss}$$

These values are in good agreement with those obtained for the monomeric complex $VO(X_2H)_2$, indicating that our interpretation is valid. Moreover, the interpretation is consistent with that reported by Hasegawa *et al.*,[13] who studied the ESR of the trinuclear vanadyl pyrophosphate complex.

As will be described in the later section, a crystalline trimer was in fact isolated from the hexane solution. Thus, it can be concluded with reasonable certainty that the appearance of the T-spectrum results from a trimeric vanadyl complex.

Extraction Conditions for the Formation of the Trimeric Vanadyl Complex. In order to find how extracting conditions affect the selective formation of the trimeric or monomeric complex, the ESR measurements were further applied to hexane solutions obtained under systematically varied conditions. The results are summarized in Table 1.

TABLE 1. EXTRACTION CONDITIONS AND ESR SPECTRA OF HEXANE PHASES

Exp No	$C_{HX(i)}$ (M)	$C_{V(i)}$ (M)	$C_{HX(i)}/C_{V(i)}$	$pH_{(f)}$	Type of ESR spectra[a)]
1	0.12	0.024	5.0	1.3—1.4	M
2		0.048	2.5		M≫T
3		0.096	1.25		M>T
4		0.24	0.50		T≫M
5		0.48	0.25		T≫M
6		1.20	0.10		T
7	0.012	0.12	0.10	1.7—1.8	T
8	0.060		0.50		T≫M
9	0.15		1.25		T>M
10	0.30		2.5		M>T
11	0.60		5.0		M≫T
12	0.03	0.10	0.3	0.9—1.0	M
13	0.10		1.0		M
14	0.20		2.0		M
15	0.40		4.0		M
16	1.0		10.0		M
17	0.03	0.10	0.3	3.6—4.0	T
18	0.10		1.0		T
19	0.20		2.0		T
20	0.40		4.0		T
21	1.0		10.0		T
22	0.40	0.20	2.0	0.9	M
23				1.3	M>T
24				1.9	T
25				2.9	T
26				4.6	T
27	1.0	0.15	6.7	0.8	M
28				1.7	M>T
29				3.4	T
30				4.3	T
31				5.7	T

a) Relative intensities of the M- and T-spectra are given roughly by an inequality.

Effect of $C_{V(i)}$: Extractions were carried out with $C_{V(i)}$ values varying from 0.024 to 1.2 M, while $C_{HX(i)}$ and $pH_{(f)}$ were kept constant as follows: $C_{HX(i)}=0.12$ M, $pH_{(f)}=1.3$—1.4 (Table 1, Exp. No. 1—6).

As is shown in the last column of Table 1, the M- and T-spectra were obtained for $C_{V(i)}=0.024$ and 1.2 M respectively. However, when $C_{V(i)}$ was intermediate between the above two extreme values, superimposed spectra of the M- and T-spectra with varying relative intensities were obtained. Some of the superimposed spectra are illustrated in Fig. 3.

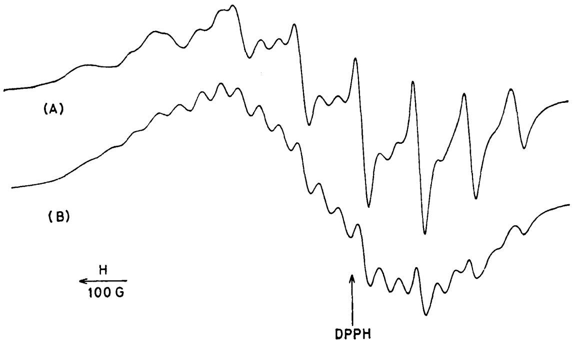

Fig. 3. ESR spectra of the hexane phases obtained under the following extraction conditions; (A) $C_{HX(i)}=0.12$M, $C_{V(i)}=0.096$M, $pH_{(f)}=1.4$; (B) $C_{HX(i)}=0.12$M, $C_{V(i)}=0.24$M, $pH_{(f)}=1.4$.

As can be seen from Table 1 (Exp. No. 1—6), an increase in $C_{V(i)}$ caused a progressive decrease in the ratio of the monomeric to the trimeric vanadyl complex; that is, $C_{V(i)}$ had a significant effect on the selective formation of the respective vanadyl complex.

Effect of $C_{HX(i)}$: As is obvious from Table 1 (Exp. No. 7—11), $C_{HX(i)}$ also had a significant effect; the increase in $C_{HX(i)}$ favored the formation of the monomeric vanadyl complex. The increase in the ratio of $C_{HX(i)}$ to $C_{V(i)}$ resulted in a greater formation of monomeric vanadyl complex, but the decrease in the ratio resulted in that of trimeric one, as is evident from Table 1 (Exp. No. 1—11).

Such effects of $C_{HX(i)}/C_{V(i)}$ were closely correlated with the pH values of the final aqueous phase ($pH_{(f)}$) and were noted only in the $pH_{(f)}$ range from 1.0 to 2.0. For example, when the $pH_{(f)}$ values were kept constant at 0.9—1.0 (Table 1, Exp. No. 12—16), only the monomeric complex was formed for any value of $C_{HX(i)}/C_{V(i)}$, while the trimeric complex was selectively formed for $pH_{(f)}$ from 3.6 to 4.0 (Table 1, Exp. No. 17—21). Therefore, it appears that the effect of $C_{HX(i)}/C_{V(i)}$ is less significant than that of $pH_{(f)}$.

Effect of $pH_{(f)}$: Extractions were further carried out with $pH_{(f)}$ values varying from 0.8 to 5.7 and with a constant $C_{HX(i)}/C_{V(i)}$ (Table 1, Exp. No. 22—31). As expected, the extracted vanadyl complex was monomeric at $pH_{(f)}$ values below 1.0. The monomeric complex was, however, replaced by the trimeric one when $pH_{(f)}$ reached 1.3—1.8, while the trimeric complex was exclusively formed at higher $pH_{(f)}$ values. It is interesting to note that the coexistence of monmeric and trimeric complexes in the extracted hexane phase is limited to a narrow range of $pH_{(f)}$, where the effect of $C_{HX(i)}/C_{V(i)}$ is significant.

Distribution Ratios for Vanadium: Although we have not measured accurately the distribution ratios for vanadium ($D_V=[V_{(o)}]/[V_{(a)}]$) as functions of $C_{HX(i)}$, $C_{V(i)}$, and $pH_{(f)}$, it has been found that D_V depends rather sensitively upon $pH_{(f)}$. D_V increased markedly with the increase in $pH_{(f)}$ from 1.0 to 2.0. It reached a maximum at $pH_{(f)}$ about 2.0, and then decreased remarkably beyond $pH_{(f)}$ 3—4, accompanied by the appearance of turbidity or a precipitate of hydrolyzed vanadyl ions in the aqueous phase. On the contrary, D_V was not markedly influenced by $C_{HX(i)}$ and $C_{V(i)}$ except in the $pH_{(f)}$ range below 2, where the increase in $C_{HX(i)}/C_{V(i)}$ brought about an increase in D_V.

Chemical Stoichiometry and Properties of Trimeric Vanadyl Complex. *Isolation and Thermal Properties*: As has already been described in the Experimental section, a light blue crystalline solid with a somewhat amorphous appearance was isolated from the hexane phase which exhibited the T-spectrum. The crystalline solid was stable to air and light. It melted at about 43°C to a blue, oily liquid, which was also stable in air but which decomposed to a dark brownish mass at higher temperatures (about 260—280°C).

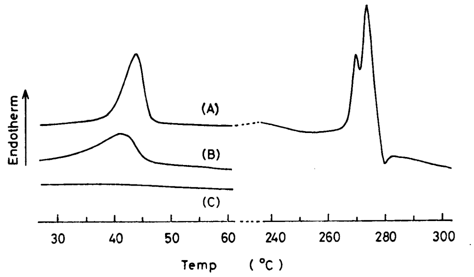

Fig. 4. DSC thermograms of trimeric vanadyl complex (sample S-II) crystallized from the oily state at the ambient temperature for different periods of time; (A) about 60 days, (B) 5 days, (C) 1 day.
(Heating rate and recorder sensitivity are 2°C/min and Range-4 for the low temperature region and 4°C/min and Range-16 for the high temperature region, respectively.)

Such thermal behavior of a crystalline sample is shown diagrammatically in the DSC thermograms (Fig. 4). The thermograms further indicated that the sample crystallizes with considerable difficulty. As is illustrated in Fig. 4, the crystallization took place very slowly when the crystalline sample was once melted to an oily liquid and then allowed to stand at the ambient temperature.

Table 2. Analytical data of the trimeric vanadyl complex

Sample[a)] No	Elementary analyses V(%)	C(%)	H(%)	Molecular Weight
S-1	10.3	39.32	7.57	1385—1435
S-2	10.2	39.58	7.51	1365—1450
S-3	10.4	39.81	7.47	1390—1465
Calcd[b)]	10.50	39.60	7.48	1456.1

a) Crystalline solids obtained from three independent preparations.
b) Calculated values for $(VOX_2)_3$

Chemical Stoichiometry: Three crystalline samples obtained from independent preparations were subjected to chemical analyses and molecular-weight measurements; the results are summarized in Table 2. No significant difference was found between the three samples, indicating that all the samples were chemically identical and of a high purity, in spite of the facts that they were obtained without further recrystallization and were somewhat different in the color and crystallinity from each other.

The chemical formulae determined from the results given in Table 2 were in close agreement with the following stoichiometry:

$$(VOX_2)_n;\ n=3$$

where n denotes the association value, and X, the di-*n*-butylphosphate anion $(C_4H_9O)_2PO_2^-$. The association value of 3 is consistent with the appearance of the T-spectrum.

Dissolved States of $(VOX_2)_3$ in Various Solvents: Although the crystalline sample of $(VOX_2)_3$ was insoluble in water and ethyleneglycol, it was highly soluble in most of the organic solvents. However, the dissolved state and stability of $(VOX_2)_3$ were found to be dependent upon the solvents.

As is summarized below, the solvents were classified roughly into two groups according to the type of ESR spectrum of the solution *in vacuo*:[15)]

1) Non-polar or weakly polar solvents (hexane, *iso*-pentane, benzene, toluene, chloroform, methylenechloride, carbon disulfide, ethylacetate, acetone, ethylether, tetrahydrofuran, *etc.*): $(VOX_2)_3$ was dissolved in these solvents to give the T-type spectra. This means that, in these solvents, $(VOX_2)_3$ is present as the trimeric state.

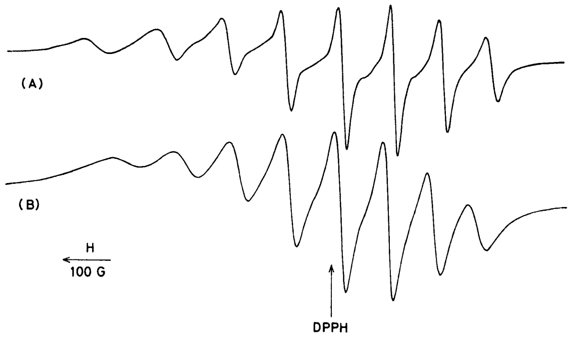

Fig. 5. ESR spectra resulting from methyl alcohol (A) and pyridine (B) solutions of $(VOX_2)_3$.

2) Polar solvents (methyl alcohol, ethyl alcohol, pyridine, picolines, *etc.*): In these solvents, the M-type spectra shown in Fig. 5 were observed with the disappearance of the T-type spectra. The ESR parameters for some of the M-type spectra were determined as follows:

$g_0=1.968$ $a=106$ gauss (for a pyridine solution)

$g_0=1.962$ $a=117$ gauss (for a methyl alcohol solution)

The results imply that $(VOX_2)_3$ reacts with these polar solvents to be converted into monomeric species. The reactions can presumably be expressed as follows:

$$(VOX_2)_3 + 6Py = 3VOX_2Py_2 \qquad (10)$$

$$\left.\begin{aligned}&(VOX_2)_3 + 6ROH = 3VOX_2(ROH)_2\\&VOX_2(ROH)_2 + 2ROH = VO(RO)_2(ROH)_2 + 2HX\end{aligned}\right\} \qquad (11)$$

where Py denotes pyridine or picolines, and ROH, methyl or ethyl alcohol. Here, the di-*n*-butylphosphate

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[15)] Although no spectral change with time was observed *in vacuo*, some of the solutions were found to show progressive spectral changes with time when the solutions were exposed to air. Work along this line is now in progress; the details will be reported in the future.

anion, X^-, in monomeric species is assumed to be coordinated as a monodentate ligand. The ESR parameters given above do not seem to be incompatible with these postulated monomeric species, because vanadyl complexes coordinated with nitrogen ligands usually give smaller hf constants than with oxygen ligands.

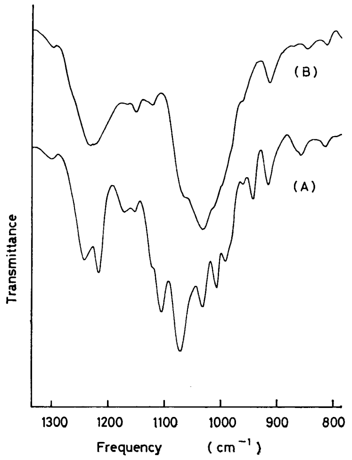

Fig. 6. Infrared spectra of $(VOX_2)_3$ as a Nujol mull (A) and of $(HX)_2$ as a thin liquid film (B).

IR Spectra: The spectrum of $(VOX_2)_3$ as a Nujol mull is given in Fig. 6, where it is compared with that of HDBP as a thin liquid film. As is shown in the literature,[16,17] the spectrum of HDBP shows the P=O stretching band at 1230 cm^{-1}, the superimposed bands due to P–O–(C), P–O–(H), and (P)–O–C stretching modes in the 1000—1070 cm^{-1} region, and three broad bands at *ca.* 2700, 2350, and 1700 cm^{-1} which are assignable to the vibrational modes of hydrogen-bonded hydroxyl groups in the HDBP dimer, $(HX)_2$.

It is seen, however, in the spectrum of $(VOX_2)_3$ that the P=O stretching band splits into two peaks at 1215 and 1240 cm^{-1}, with the complete disappearance of the hydrogen-bonded hydroxyl bands. Furthermore, the spectrum of $(VOX_2)_3$ shows a well-resolved structure in the 940—1100 cm^{-1} region with new bands at 945 and 1105 cm^{-1}, the former of which is presumed to be the V=O stretching vibration.[2,18]

Although an unambiguous assignment of each band is difficult, the above results may indicate that HDBP is coordinated to vanadium through two vacant oxygens as a result of the ionization of hydroxyl hydrogen atom, causing hence the spectral change from HDBP to $(VOX_2)_3$.

Visible Absorption Spectra: The visible absorption spectrum of the trimeric complex $(VOX_2)_3$ dissolved in hexane is presented in Fig. 7, along with that assignable to the monomeric complex $VO(X_2H)_2$. The latter spectrum was obtained from the hexane solution containing $(VOX_2)_3$ and a large excess of HDBP. The details will be described below.

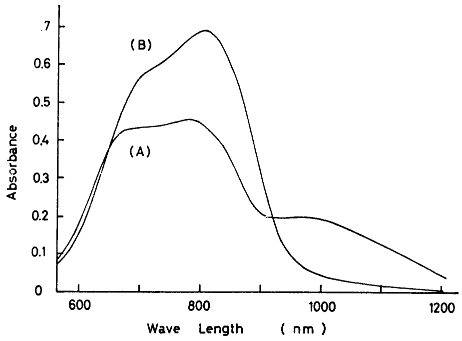

Fig. 7. Visible absorption spectra of $(VOX_2)_3$ (A) and $VO(X_2H)_2$ (B).

The following absorption maxima (with molar extinction coefficients given in parentheses) were derived from Fig. 7:

$(VOX_2)_3$	680 nm (40 $M^{-1}\cdot cm^{-1}$)
	780 nm (45 $M^{-1}\cdot cm^{-1}$)
	980 nm (19 $M^{-1}\cdot cm^{-1}$)
$VO(X_2H)_2$	700 nm (19 $M^{-1}\cdot cm^{-1}$)
	805 nm (23 $M^{-1}\cdot cm^{-1}$)

As will be shown below, $VO(X_2H)_2$ may have a local symmetry of C_{4v} with an unpaired electron in the $3d_{xy}$ orbital. Thus, according to the Ballhausen and Gray energy level scheme,[19] it seems probable that the absorption bands for $VO(X_2H)_2$ at 700 and 805 nm can be identified as $B_2(3d_{xy}) \rightarrow B_1^*(3d_{x^2-y^2})$ and $B_2(3d_{xy}) \rightarrow E_\pi^*(3d_{xz}, 3d_{yz})$ transitions respectively.

On the other hand, the situation in $(VOX_2)_3$ is more complicated, because exchange interactions among three vanadium ions exert a perturbing influence on the energy levels derived from the combination of three sets of monomeric energy levels. It is not within the scope of this paper to examine possible assignments for the visible spectra of $(VOX_2)_3$. However, it seems likely that the three absorption bands at 680, 780, and 980 nm originate from the perturbed d—d transitions, since the typical exchange energies for most of the polynuclear metal complexes thus far reported are of the order of a few hundred cm^{-1} or less.[11]

Equilibrium Reaction between $(VOX_2)_3$ and $VO(X_2H)_2$ in Hexane. In order to get information about the extraction mechanisms of $(VOX_2)_3$ and $VO(X_2H)_2$, the reaction of $(VOX_2)_3$ with HDBP in hexane was investigated at the ambient temperature (about 20°C) by both ESR and visible-absorption methods.

ESR Method: When HDBP was added, little by little, to a hexane solution of $(VOX_2)_3$, the ESR spectrum of the solution was found to show gradual changes from the T-spectrum to the M-spectrum with an increasing HDBP through such an intermediary spectrum as is given in Fig. 3. The change was reversed when $(VOX_2)_3$ was added to a HDBP solution. It was thus presumed that $(VOX_2)_3$ reacts reversibly with HDBP to form $VO(X_2H)_2$ according to:

$$(VOX_2)_3 + 3(HX)_2 = 3VO(X_2H)_2 \qquad (12)$$

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16) D. F. Peppard, J. R. Ferraro, and G. W. Mason, *J. Inorg. Nucl. Chem.*, **7**, 231 (1958).

17) D. F. Peppard and J. R. Ferraro, *ibid.*, **10**, 275 (1959); J. Kennedy and A. M. Deane, *ibid.*, **19**, 142 (1961).

18) J. Selbin, L. H. Holmes, Jr., and S. P. McGlynn, *ibid.* **25**, 1359 (1963).

19) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

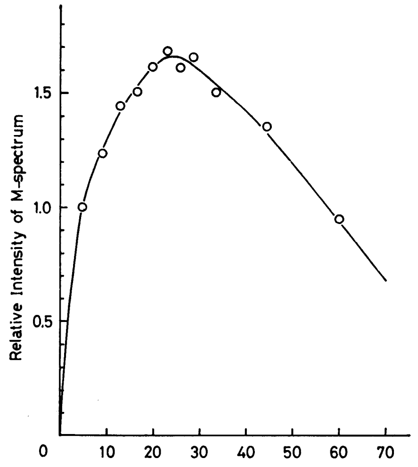

Fig. 8. Continuous variation method as applied to the $(VOX_2)_3$-$(HX)_2$ system by ESR measurements. $[(VOX_2)_3]+[(HX)_2]=2\times10^{-2}M$ (const)

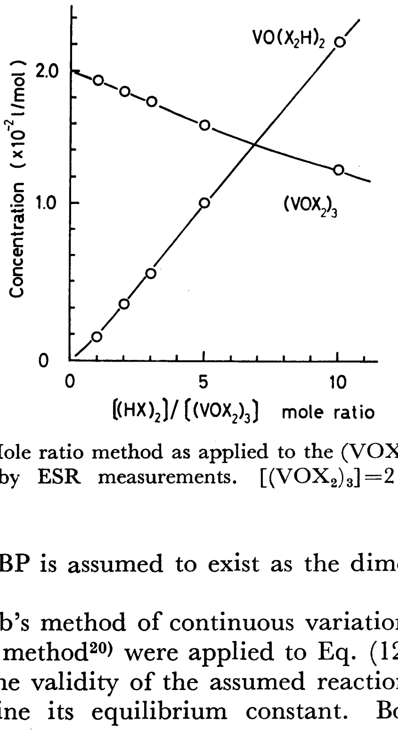

Fig. 9. Mole ratio method as applied to the $(VOX_2)_3$-$(HX)_2$ system by ESR measurements. $[(VOX_2)_3]=2\times10^{-2}M$ (const)

where HDBP is assumed to exist as the dimer, $(HX)_2$, in hexane.

Then Job's method of continuous variations and the mole-ratio method[20] were applied to Eq. (12) in order to verify the validity of the assumed reaction and also to determine its equilibrium constant. Both results are presented graphically in Figs. 8 and 9. It is apparent from Fig. 8 that the signal intensity due to the M-spectrum, which is proportional to the concentrations of $VO(X_2H)_2$ formed, reaches a maximum at about 25 mol% of $(VOX_2)_3$, indicating that one mole of $(VOX_2)_3$ reacts with three moles of $(HX)_2$ in accordance with the presumed reaction scheme. On this basis, the equilibrium constant was evaluated directly from Fig. 9, where the equilibrated concentrations of $VO(X_2H)_2$ and $(VOX_2)_3$ are plotted as functions of the mole ratio of $(HX)_2$ to $(VOX_2)_3$. The equilibrium constant thus obtained is given by:

$$K=\frac{[VO(X_2H)_2]^3}{[(VOX_2)_3][(HX)_2]^3}=(1.0\pm0.5)\times10^{-1}\ \text{l/mol}$$

The rather poor accuracy of the value seems to have arisen from the inaccurate determination of the equilibrium concentrations because of the superposition of the M- and T-spectra.

Visible Absorption Method: The continuous-variation method was applied to the visible absorption spectra of the reaction system in a manner similar to that used in the case of the ESR measurements. Unfortunately, however, the method was found to be unusable for this system because the effective variation in the absorbance with a change in the mol% of $(VOX_2)_3$ was too small.

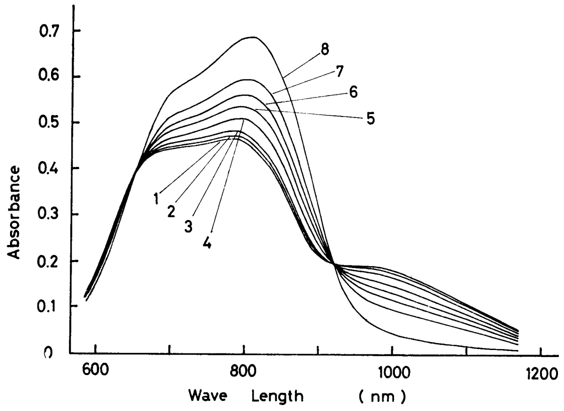

Fig. 10. Mole ratio method as applied to the $(VOX_2)_3$-$(HX)_2$ system by visible absorption measurements. $[(VOX_2)_3]=1\times10^{-2}M$ (const.); $[(HX)_2]=2\times10^{-2}M$ (1), $3\times10^{-2}M$ (2), $5\times10^{-2}M$ (3), $1\times10^{-1}M$ (4), $1.5\times10^{-1}M$ (5), $2\times10^{-1}M$ (6), $3\times10^{-1}M$ (7), $8\sim12\times10^{-1}M$ (8).

On the other hand, the mole-ratio method was found to be successful in the evaluation of the equilibrium constant. A typical set of data is illustrated in Fig. 10, where a sharp isosbestic point is observed at 920 nm; this is consistent with our hypothesis of the presence of two absorbing species, $(VOX_2)_3$ and $VO(X_2H)_2$, in solutions.

The equation used for the calculation of the equilibrium constant was:[21]

$$K=\left\{\frac{3(A-A_0)}{3\varepsilon_M-\varepsilon_T}\right\}^3\Big/\left\{[(VOX_2)_3]_0-\frac{A-A_0}{3\varepsilon_M-\varepsilon_T}\right\}\times\left\{[(HX)_2]_0-\frac{3(A-A_0)}{3\varepsilon_M-\varepsilon_T}\right\}^3$$

where ε_T and ε_M are the molar extinction coefficients at the chosen wavelengths for $(VOX_2)_3$ and $VO(X_2H)_2$ respectively; A, the measured absorption at the wavelength $(A=\varepsilon_T[(VOX_2)_3]+\varepsilon_M[VO(X_2H)_2])$; A_0, the absorption of $(VOX_2)_3$ in the absence of $(HX)_2$ $(A_0=\varepsilon_T[(VOX_2)_3]_0)$, and $[(VOX_2)_3]_0$ and $[(HX)_2]_0$, the initial concentrations of the two species.

The resulting K values were then averaged to give the following one, with a much smaller deviation than that determined by the ESR method:

$$K=(1.1\pm0.2)\times10^{-1}\ \text{l/mol}$$

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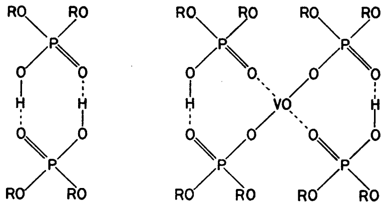
[20] A. Nakahara, "Jikken Kagaku Koza," Vol. 6, ed. by The Chemical Society of Japan, (1965), p. 184; H. Hosoya, "Jikken Kagaku Koza," Vol. 11, ed. by The Chemical Society of Japan (1965), p. 523.

[21] R. L. Carlin and F. A. Walker, *J. Amer. Chem. Soc.*, **87**, 2128 (1965).

The extinction coefficient, ε_M, used for the calculation was approximated by that obtained from the spectra of the solution containing a large excess of $(HX)_2$, ranging from 80 to 120 times the amount of $(VOX_2)_3$. Under such conditions, the absorbance of the solution showed no significant change in relation to the variation in the $(HX)_2$ concentration, suggesting that $(VOX_2)_3$ is almost completely converted into $VO(X_2H)_2$. Consequently, one can consider the approximation in ε_M fairly good.

Mechanism of the Formation of $VO(X_2H)_2$ and $(VOX_2)_3$. It is well known that dialkyl phosphoric acids show a strong tendency to form dimers[16,22-24] in non-polar solvents similar to carboxylic acids. The proposed structure[16,22-24] of the dimer is illustrated in Fig. 11 (A), where an eight-membered ring structure is formed as the result of hydrogen bonding. If one of the acidic hydrogen atoms of this dimer is removed by ionization, and if the remaining hydrogen bond is not broken, the resulting, singly-charged dimeric anion should have the possibility of a relatively stable chelation with metal ions.



(A) (B)

Fig. 11. Proposed structures of $(HX)_2$[16,22-24] and monomeric vanadyl complex $VO(X_2H)_2$[1].

From this point of view, it is well understandable that HDBP dimer extracts the vanadyl ion by the simple hydrogen ion-exchange reaction[10] given in Eq. (4), which then leads to the formation of a monomeric complex, $VO(X_2H)_2$, with the structure[1] shown in Fig. 11(B).

However, it should be noted here that the formation of $VO(X_2H)_2$ by this mechanism is strongly dependent upon the extraction conditions. As was described in the previous section, the monomeric complex $VO(X_2H)_2$ was selectively formed when the $pH_{(f)}$ was below 1. However, as the $pH_{(f)}$ increased from 1 to 2, the selective formation was suppressed by the simultaneous formation of the trimeric complex $(VOX_2)_3$; this was observed in this $pH_{(f)}$ region only when HDBP was present in excess. Furthermore, an increase in $pH_{(f)}$ values above 2 brought about the selective formation of $(VOX_2)_3$ in place of $VO(X_2H)_2$.

It is thus obvious that the simple ion-exchange mechanism is not applicable to all cases, and we are now in a position to take another mechanism into consideration in order to interpret the formation of $(VOX_2)_3$.

According to Rigg *et al.*,[1] who investigated the extraction isotherm for the vanadium-HDEHP system, a monomeric complex with the VOX_2 stoichiometry is formed at higher vanadium concentrations *via* this reaction:

$$VO^{2+}_{(a)} + VO(X_2H)_{2(o)} = 2VOX_{2(o)} + 2H^{+}_{(a)} \tag{13}$$

where the formation of polymeric species is discounted on the ground that no increase in viscosity is noticeable in the solvent extracts. On the other hand, it has been postulated more recently by Sato *et al.*[2] that the formation of polymeric species is involved under the condition of a relatively low HDEHP concentration and that all the extraction reactions in the vanadium-HDEHP system can be described by the following general equilibrium reaction:

$$nVO^{2+}_{(a)} + (n+1)(HX)_{2(o)} = (VO)_nX_{2(n+1)}H_{2(o)} + 2nH^{+}_{(a)} \tag{14}$$

where $n \geq 1$.

The latter mechanism, leading to the formation of a chain polymer of the $HX_2(VO)X_2(VO)X_2\cdots\cdots(VO)X_2(VO)X_2H$ type, is the most readily acceptable one if one remembers that Equation (14) is only an extension of the simple ion-exchange mechanism and that such a mechanism has already been accepted for the extraction of such metal ions as UO_2^{2+},[25,26] Th^{4+},[27] and Zr^{4+}.[28] In fact, the mechanism can interpret the extraction isotherm, because the $(VO)_nX_{2(n+1)}H_2$ chemical stoichiometry can be approximated to 1:2 for the vanadium-to-HDEHP mole ratio when n is large.

Unfortunately, the previous workers did not isolate the extracted vanadyl species. In view of the extraction conditions employed by the previous workers, it seems very likely that the postulated complex, VOX_2 or $(VO)_nX_{2(n+1)}H_2$, is identical with the trimeric complex, $(VOX_2)_3$, disclosed in the present work.

Equation (14) does not exclude the formation of trimeric species; according to this equation, many sorts of polymeric species, such as dimer, trimer, and tetramer, could be present. In this work we have observed no vanadyl species other than monomer and trimer. Furthermore, the chemical stoichiometry, $(VOX_2)_3$, determined for the isolated species was quite different from the formula, $(VO)_3X_8H_2$, expected from Eq. (14).

It has now become clear that Eqs. (13) and (14), proposed by previous workers, are inadequate for extractions at high $pH_{(f)}$ values and at high vanadium concentrations. Accordingly, the over-all reaction scheme under such conditions must be rewritten as follows:

$$3VO^{2+}_{(a)} + 3(HX)_{2(o)} = (VOX_2)_{3(o)} + 6H^{+}_{(o)} \tag{15}$$

At the same time, one can obtain from Eqs. (4) and (15) such additional reactions as:

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[22] D. F. Peppard, J. R. Ferraro, and G. W. Mason, *J. Inorg. Nucl. Chem.*, **4**, 371 (1957).

[23] D. Dyrssen, *Acta Chem. Scand.*, **11**, 1771 (1957).

[24] D. Dyrssen and L. D. Hay, *ibid.*, **14**, 1091 (1960).

[25] C. F. Baes, Jr., R. A. Zingaro, and C. F. Coleman, *J. Phys. Chem.*, **62**, 129 (1958).

[26] T. V. Healy and J. Kennedy, *J. Inorg. Nucl. Chem.*, **10**, 128 (1959); T, Sato. *ibid.*, **27**, 1853 (1965).

[27] T. Sato, *ibid.*, **27**, 1359 (1965).

[28] T. Sato and T. Nakamura, *ibid.*, **33**, 1081 (1971).

$$\begin{aligned}VO(X_2H)_{2(o)}+2VO^{2+}_{(a)}+(HX)_{2(o)} &= (VOX_2)_{3(o)}+4H^+_{(a)}\\ 2VO(X_2H)_{2(o)}+VO^{2+}_{(a)} &= (VOX_2)_{3(o)}+(HX)_{2(o)}+2H^+_{(a)}\end{aligned} \quad (16)$$

These equations are similar to the Eq. (13) proposed by Rigg *et al.*,[1] suggesting that the monomeric complex, $VO(X_2H)_2$, once formed *via* Eq. (4) reacts immediately with excess vanadyl ions to give the trimeric complex, $(VOX_2)_3$. It thus seems probable that the formation of $(VOX_2)_3$ proceeds consecutively through Reactions (4) and (16).

On the other hand, by eliminating $VO^{2+}{}_{(a)}$ and $H^+{}_{(a)}$ from (4) and (15), one can obtain another equation, expressed as:

$$3VO(X_2H)_{2(o)} = (VOX_2)_{3(o)} + 3(HX)_{2(o)} \quad (17)$$

This indicates that the formation of $(VOX_2)_3$ is possible even in the organic phase; this is in contrast to Eq. (16), which formally shows the formation of $(VOX_2)_3$ on the boundary between aqueous and organic phases. As was described in the previous section, it was found experimentally that Reaction (17) actually took place reversibly and attained an equilibrium rapidly with the equilibrium constant $K=[VO(X_2H)_2]^3/[(VOX_2)_3]\text{-}[(HX)_2]^3=1.1\times10^{-1}$ l/mol. Accordingly, it also seems possible that $(VOX_2)_3$ is formed consecutively through Reactions (4) and (17).

Consequently, there are two possible reaction pathways, differing in the second reaction step, although it is not experimentally determinable which contributes to the formation of $(VOX_2)_3$. However, the mole ratio of $(VOX_2)_3$ to $VO(X_2H)_2$ formed in the organic phase should be ultimately determined by the equilibrium reaction (17), irrespective of the pathway. It can readily be seen from the equilibrium relation that the final mole ratio $[(VOX_2)_{3(o)}]/[VO(X_2H)_{2(o)}]$ is strongly dependent upon the HDBP concentrations, $[(HX)_{2(o)}]$, in the organic phase. That is to say, the trimer, $(VOX_2)_3$, is formed predominantly when $[(HX)_{2(o)}]$ is small, whereas the monomer, $VO(X_2H)_2$, is formed when it is large.

From the above considerations, the finding that $(VOX_2)_3$ is formed favorably in the presence of an excess of vanadyl ions is understandable, because $[(HX)_{2(o)}]$ can be expected to become small under such conditions because of the almost complete utilization of $(HX)_{2(o)}$ in Reaction (4).

On the other hand, $[(HX)_{2(o)}]$ is influenced not only by a complex formation reaction such as (4), (16), and (17), but also more strongly by the following dimerization, distribution, and dissociation reactions of HDBP:[23,24,29]

$$2HX_{(o)} = (HX)_{2(o)} \qquad K_2 = 10^{6.87} \quad (18)$$

$$HX_{(a)} = HX_{(o)} \qquad K_d = 10^{-2.30} \quad (19)$$

$$HX_{(a)} = H^+_{(a)} + X^-_{(a)} \qquad K_a = 10^{-1.00} \quad (20)$$

where K_2, K_d, and K_a denote the equilibrium constants for the respective reactions and where the numerical values, experimentally determined in hexane by Dyrssen *et al.*,[23,24] are each illustrated.

Accordingly, HDBP is present almost completely as the dimer in hexane, and its concentration, $[(HX)_{2(o)}]$, is strongly dependent on the pH values in the aqueous phase. For example, $[(HX_2)_{(o)}]$ is expected to decrease remarkably with an increase in $pH_{(f)}$ above 1.0 as a result of the displacement of Equilibrium (20) to the right, while the variation in $[(HX_2)_{(o)}]$ with $pH_{(f)}$ is small when $pH_{(f)}$ is below 1.0.

Thus, the experimental finding that $(VOX_2)_3$ is selectively formed at $pH_{(f)}>2$ can reasonably be interpreted on the above grounds, although it is not clear why $(VOX_2)_3$ is selectively formed in place of the chain polymer, $(VO)_nX_{2(n+1)}H_2$, or the monomer, VOX_2, proposed by the previous authors. In any event, one can conclude with reasonable certainty that the selectivity for the formation of the $(VOX_2)_3$ trimer or of the $VO(X_2H)_2$ monomer is governed by the equilibrium reactions, (17) or (12), in the organic phase and altered or enhanced by extraction conditions, such as $pH_{(f)}$ and $C_{HX(i)}/C_{V(i)}$.

Structure of the Trimeric Vanadyl Complex. In this section we wish to propose a structure for the trimeric vanadyl complex. It is assumed first that each vanadyl ion is tetragonally coordinated by oxygen atoms of di-*n*-butyl phosphate anions to form a tetragonal pyramidal structure with the vanadyl oxygen perpendicular to the square plane. This is the basic type of coordination known for many vanadyl complexes.[30] Next, each di-*n*-butylphosphate anion is assumed to act as a bidentate ligand through two vacant oxygens, either to form a four-membered chelate ring or to link pairs of vanadium atoms.

On the basis of these assumptions, we can discuss two types of possible structures; one is linear trimer, while the other is a cyclic one. Each structural model is illustrated schematically in Fig. 12.

The structural model (I), quite similar to the molecular structure previously proposed for the polymeric uranyl-HDEHP complex $(UO_2)_nX_{2(n+1)}H_2$,[25] was derived by first supposing that the trimer was formed according to the ion-exchange reaction (14). However this model was found to be inadequate in the case of the trimeric vanadyl-HDBP complex, because the chemical stoichiometry determined in this work was incompatible with the one expected from such a coordination model.

The other models (II and III) of the linear trimer are also compatible with the stoichiometry $(VOX_2)_3$. It can be expected from such linear models that a series of polymeric species, such as dimer, trimer, and tetramer, should be formed consecutively with a certain distribution *via* the reaction:

$$\begin{aligned}(VOX_2)_{n(o)} + (HX)_{2(o)} + VO^{2+}_{(a)}&\\ = (VOX_2)_{n+1(o)} + 2H^+_{(a)}&\end{aligned} \quad (21)$$

However, such reactions were not observed under the conditions employed in this work. On this basis, the models (II and III) were also ruled out. Consequently, a cyclic structural model was finally taken into consideration.

The structural model for the cyclic trimer is illustrated

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29) C. J. Hardy and D. Scargill, *J. Inorg. Nucl. Chem.*, **11**, 128 (1959).

30) R. J. H. Clark, "The Chemistry of Titanium and Vanadium," Elsevier Publishing Company, New York (1968), p. 202.

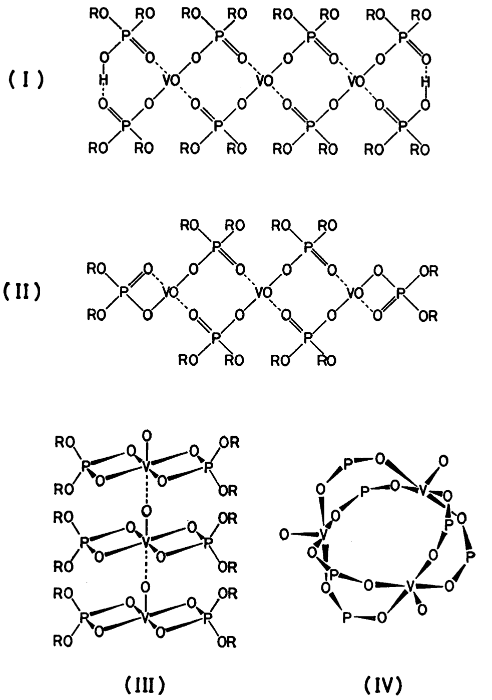

Fig. 12. Possible structures for trimeric vanadyl complex; (I) linear trimer for the stoichiometry $(VO)_3X_3H_2$, (II), (III) linear trimer for the stoichiometry $(VOX_2)_3$, (IV) cyclic trimer for the stoichiometry $(VOX_2)_3$, where each P represents $P(OR)_2$ with the two OR groups toward the outside.

in Fig. 12 (IV), where three vanadium atoms are assumed to be linked by the double-phosphate bridge in an equilateral triangle. A simple geometrical construction using a molecular structure model (HGS, D-type, Maruzen Co.), with the usual bond lengths, showed that this cyclic structure appeared reasonable, with no undue strain nor steric hindrance. Moreover, this cyclic structure can well explain the T-spectrum on the assumption that the magnitude of exchange interaction between vanadium ions satisfies the relation $|J| \gg |a|$.

A similar structural model has recently been proposed by Hasegawa *et al.*[13] for the trimeric vanadyl pyrophosphate complex, $Na_6(VOP_2O_7)_3 \cdot 12H_2O$, on the basis of ESR and magnetic susceptibility measurements, where magnetic electrons on the three vanadium atoms were found to interact antiferromagnetically with the exchange integral of $|J| \fallingdotseq 30\ \mathrm{cm}^{-1}$. It can, therefore, be presumed that the exchange integral for $(VOX_2)_3$ does not differ greatly from that determined for $Na_6(VOP_2O_7)_3 \cdot 12H_2O$, and that the relation $|J| \gg |a|$ is valid. Thus, we can consider that the cyclic model (IV) is most probable for the structure of the trimeric vanadyl di-*n*-butylphosphate complex, $(VOX_2)_3$.

It is interesting to note that the proposed structure is closely related to those determined by X-ray single-crystal studies of such trimeric complexes as $Pd_3(CH_3COO)_6 \cdot 1/2H_2O$[31] and $Cr_3(CH_3COO)_6OCl \cdot 5H_2O$.[32] Our complex differs from $Pd_3(CH_3COO)_6 \cdot 1/2H_2O$ only in that the three metal ions are linked together by double-phosphate bridges rather than by double-acetate bridges. Needless to say, the final proof of the structure must await study by X-ray diffraction.

This work was supported in part by a grant of the Ministry of Education, to which the authors' grateful acknowledgements are made. The authors wish to thank Dr. T. Ohama for his kind advices on the molecular-weight measurements and Dr. H. Uchida for his invaluable help in the differential scanning calorimetries.

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31) A. C. Skapski and M. L. Smart, *Chem. Commun.*, **1970**, 658.

32) B. N. Figgs and G. B. Robertson, *Nature*, **205**, 694 (1965).