Dissociation of μ-Oxo-bis[oxobis(8-quinolinolato)vanadium(V)] and μ-Oxo-bis[oxobis(4-isopropyltropolonato)-vanadium(V)] in Chlorobenzene

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Dissociation of dimeric vanadium(V) complexes with 8-quinolinol(Hox) and 4-isopropyltropolone(Hipt), $V_2O_3(ox)_4$ and $V_2O_3(ipt)_4$, in organic solvents was studied spectrophotometrically. The equilibrium is found to be

$$V_2O_3L_4 + H_2O \rightleftarrows 2VO_2L + 2HL$$

with the following logarithmic equilibrium constants: log $K = -12.9$ for $L = ox^-$ and -12.8 for $L = ipt^-$ in chlorobenzene. VO_2L was synthesized and characterized by IR, UV, and visible spectroscopy for these ligands and also for 2-methyl-8-quinolinol.

Vanadium(V) reacts with 8-quinolinol(Hox) in weakly acidic media to form a black precipitate. This complex was thought to be $VO(OH)(ox)_2$ and has been the subject of a number of studies.[1-8)]

In the preceding papers we have studied the complexation of vanadium(V) with 8-quinolinolate ion in aqueous solutions, and established the formation of the following species: $VO_3(ox)^{2-}$, $VO_3H(ox)^-$, $VO_2(ox)$, and $VO_2(ox)_2^-$.[9)] Then taking these findings into consideration we have analyzed the extraction behavior of vanadium(V) with 8-quinolinol, and the extracted species from less acidic media is identified to be $V_2O_3(ox)_4$.[10)] Furthermore by IR spectroscopy in solid state this complex is shown to have an oxo-bridged dimeric structure, $VO(ox)_2$–O–$VO(ox)_2$.[10)]

In this paper dissociation of $V_2O_3(ox)_4$ dissolved in organic solvents are investigated spectrophotometrically. The 1:1 complex synthesized from $V_2O_3(ox)_4$ is characterized with UV, visible, and IR spectroscopy. Furthermore, 4-isopropyltropolone (Hipt) and 2-methyl-8-quinolinol(Hmeox) complexes are also studied and compared with the 8-quinolinolate complex.

Experimental

Reagent. 4-Isopropyltropolone was recrystallized twice from ligroin and dried under reduced pressure.

Chlorobenzene and nitrobenzene were shaken three times with sulfuric acid, sodium hydroxide solution, and finally with distilled water. Then the solvents were dehydrated over calcium chloride, refluxed over phosphorus pentaoxide, and distilled. The middle 80% was collected for use. The concentration of water in these solvents was about 4×10^{-3} mol dm^{-3}. Water saturated solvents were obtained by shaking these solvents with distilled water again, which contained about 2×10^{-2} mol dm^{-3} water. Solvents of different concentrations of water were obtained by mixing these two solvents.

Ammonium metavanadate, 8-quinolinol, and 2-methyl-8-quinolinol were purified as described previously.[10)]

Measurement. All the experiments were carried out in a room thermostated at 25±0.5 °C. All the measurements were performed in a thermoelectric circulating bath at 25±0.1 °C.

UV, visible, and IR spectra were recorded on a UNION High Sens spectrophotometer SM-401 with a thermostated cell compartment and a JASCO infrared spectrophotometer IR-S, respectively. The absorbance was measured with a Karl Zeiss spectrophotometer model 1 PMQ II.

Thermogravimetric analysis was performed using a Shimadzu thermogravimeter TGA-30 and a Shimadzu thermal analyzer DT-30B.

The concentration of water was determined by the Karl-Fischer method with the coulometric generation of iodine. Vanadium(V) was determined spectrophotometrically with PAR.[11)]

Preparation. *μ-Oxo-bis[oxobis(8-quinolinolato)vanadium(V)]*: $VO(ox)_2$–O–$VO(ox)_2$ was prepared as described previously.[3,4)]

Dioxo-8-quinolinolatovanadium(V): $VO_2(ox)$ was prepared by heating the above complex in Abderhalden's dryer with sodium hydroxide as a trap for vaporized 8-quinolinol. Crude complex was recrystallized from chlorobenzene.

μ-Oxo-bis[oxobis(4-isopropyltropolonato)vanadium(V)]: $VO(ipt)_2$–O–$VO(ipt)_2$ was prepared by mixing dioxovanadium(V) perchlorate solution and 4-isopropyltropolone and adjusting pH at 3.5 by the addition of ammonia. After standing overnight the precipitate was filtered off and dried at 80 °C. Prolonged heating over 100 °C resulted in the gradual weight loss.

Dioxo-4-isopropyltropolonatovanadium(V): $VO_2(ipt)$ was prepared as in the corresponding 8-quinolinolate complex.

Hydroxooxobis(2-methyl-8-quinolinolato)vanadium(V) Dihydrate: $VO(OH)(meox)_2 \cdot 2H_2O$ was prepared as described previously.[5)]

Dioxo-2-methyl-8-quinolinolatovanadium(V): $VO_2(meox)$ was prepared as in the case of $VO_2(ox)$.

Results

Vanadium(V)-8-quinolinolate complex, dissolved in chlorobenzene (about 10^{-4} mol dm^{-3}), shows a broad absorption maximum at around 550 nm. The spectrum of this solution changes under different conditions: the concentration of water, the concentration of excess 8-quinolinol, and the total concentration of the vanadium(V) complex.

Reaction with Water. The reaction of the complex with water results in the decrease of the absorbance in all the visible region. After the completion of this reaction (one or two hours) the absorbance was measured. Because of the limited change of water concentration (0.006—0.018 mol dm^{-3}), we were not able to obtain sufficient data for precise analysis. However, the reaction proceeds to a larger extent and more rapidly with increasing water concentration. It

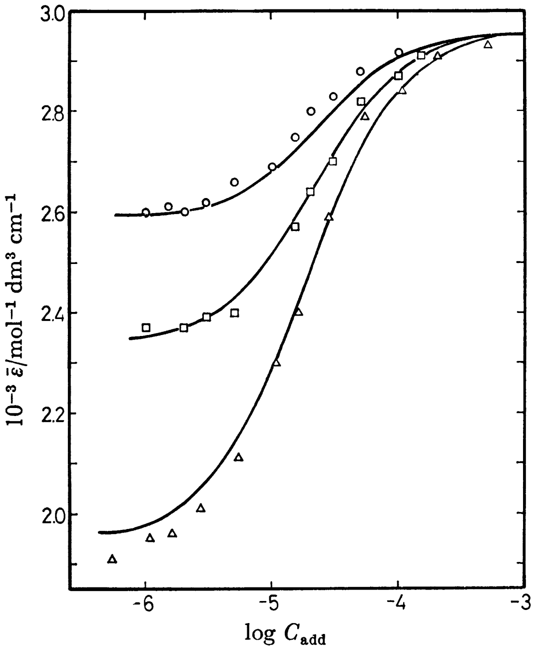

Fig. 1. Molar absorbance change at 480 nm as a function of log C_{add}.
$C_{H_2O}=1.13\times10^{-2}$ mol dm^{-3}; C_V/mol dm^{-3}: ○: 1.19 $\times10^{-4}$, □: 5.95×10^{-5}, △: 2.98×10^{-5}. The solid lines are curves calculated with the constants obtained.

should be noted that in the presence of excess amounts of 8-quinolinol we observe no reaction. The chlorobenzene solution of vanadium(V)-8-quinolinolate showed the absorption spectrum very similar to the reflection spectrum of the complex. Thus it may be concluded that we are dealing with the same compound in solution as in solid state.

Reaction with Excess 8-Quinolinol. The reaction of the complex with 8-quinolinol results in the increase of the absorbance in all the visible region. The reaction completes within a minute. The absorbance at 480 nm was then measured. Apparent molar absorbance, $\bar{\varepsilon}$, was plotted against the logarithmic concentration of added 8-quinolinol, log C_{add} (Fig. 1).

In the absence of the added 8-quinolinol, $\bar{\varepsilon}$ is smaller for lower total concentration of the complex and/or for higher water concentration. $\bar{\varepsilon}$ increases with increasing concentration of 8-quinolinol, and it becomes constant beyond 10^{-3} mol dm^{-3} regardless the conditions. These facts point to the presence of only one species, $V_2O_3(ox)_4$, under these conditions.

Dependence of the Absorbance on the Total Concentration of the Complex. Dependence of $\bar{\varepsilon}$ on the total concentration of the vanadium(V) complex, C_V, in the absence of excess 8-quinolinol and at constant amounts of water was studied using quartz cells with light path lengths of 10 and 50 mm (Fig. 2) Upon dilution of the complex solution Beer's law is not obeyed, and the apparent molar absorbance decreases. The limiting values of $\bar{\varepsilon}$ at lower ligand concentration in Fig. 1 are well accommodated in the plot given in Fig. 2.

On the other hand in the presence of sufficient amount of 8-quinolinol, as seen from Fig. 2, $\bar{\varepsilon}$ values are constant for different complex concentrations.

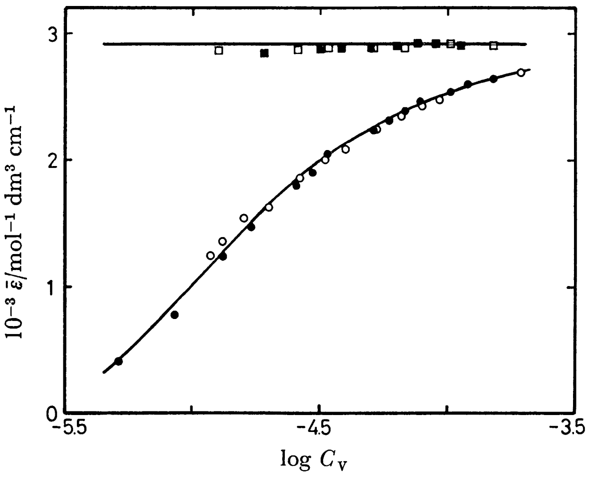

Fig. 2. Molar absorbance change at 480 nm as a function of log C_V.
C_{H_2O}/mol dm^{-3}: ○, □: 1.00×10^{-2}, ●, ■: 1.13×10^{-2}, C_{add}/mol dm^{-3}: ○, ●: 0, □, ■: 2.60×10^{-3}. The solid lines are curves calculated with the constants obtained.

Treatment of Equilibria. The reaction of $V_2O_3(ox)_4$ with water to its lower complex is expressed by Eq. 1 (see below about the composition of the lower complex).

$$V_2O_3(ox)_4 + H_2O \overset{K}{\rightleftarrows} 2VO_2(ox) + 2Hox \qquad (1)$$

The concentration of water being in large excess compared with the other species and kept constant, the conditional dissociation constant, K', is given by Eq. 2:

$$K' = K[H_2O] = \frac{[VO_2(ox)]^2[Hox]^2}{[V_2O_3(ox)_4]}. \qquad (2)$$

The apparent molar absorbance at 480 nm is expressed by Eq. 3:

$$\bar{\varepsilon} = \frac{\varepsilon_{24}[V_2O_3(ox)_4] + \varepsilon_{11}[VO_2(ox)]}{2[V_2O_3(ox)_4]+[VO_2(ox)]}, \qquad (3)$$

where ε_{11} and ε_{24} are the molar absorbances of $VO_2(ox)$ and $V_2O_3(ox)_4$, respectively. The value of ε_{11} and K' were refined to give minimum error square sum of data, $U=\sum(\bar{\varepsilon}_{\text{obsd}}-\bar{\varepsilon}_{\text{cald}})^2$, with an electronic computer. The value of ε_{11} approached to zero, which is consistent with the spectrum of $VO_2(ox)$.

Then the obtained logarithmic conditional dissociation constants under various conditions were plotted against

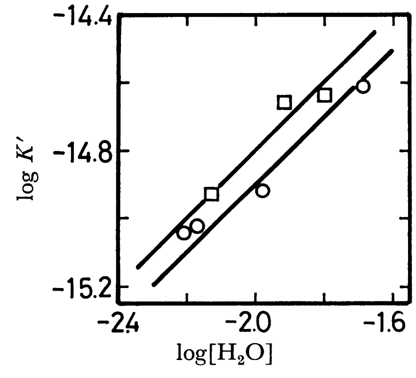

Fig. 3. The plot of log K' against log[H_2O].
○: 8-Quinolinolate complex, □: 4-isopropyltropolonate complex.

the logarithmic concentration of water (Fig. 3). The plot falls along a straight line with a slope of unity. This confirms the validity of Eq. 1. From the intercept the dissociation constant is obtained:

$$V_2O_3(ox)_4 + H_2O \rightleftarrows 2VO_2(ox) + 2Hox \quad : \log K = -12.9.$$

The possibility for the formation of the lower complex, $V_2O_4(ox)_2$, given by Eq. 4 was also examined. The assumption of this species lead to a systematic deviation from the experimental data.

$$V_2O_3(ox)_4 + H_2O \rightleftarrows V_2O_4(ox)_2 + 2Hox \qquad (4)$$

Dissociation of 4-Isopropyltropolonate Complex ($V_2O_3(ipt)_4$). Similar measurements were performed on 4-isopropyltropolonate complex under various conditions. All the data were analyzed by the same treatment as in the case of 8-quinolinolate complex to give K' and ε_{11}. The value of ε_{11} is close to zero, which is also consistent with the spectrum of $VO_2(ipt)$ (see below). The plot of log K' against log$[H_2O]$ falls along a straight line with a slope of unity (Fig. 3). From the intercept the following dissociation constant is obtained:

$$V_2O_3(ipt)_4 + H_2O \rightleftarrows 2VO_2(ipt) + 2Hipt \quad : \log K = -12.8.$$

Properties of Crystals. Thermogravimetry and Visible Spectroscopy: For the 8-quinolinolate complex, a weight loss was observed about 240 °C as reported by Borrel and Pâris.[1] (Fig. 4a) But the form of the thermogram depends upon the rate of heating, and no distinct plateau was observed at 240 °C at 0.5 °C min^{-1}. Thus no definite species can be found at this temperature. On the other hand, over 500 °C it approached to a constant weight corresponding to $VO_2(ox)$. At 240 °C we have a mixture of the species $VO_2(ox)$ with free 8-quinolinol, which gives a characteristic yellow solution just after dissolution in chlorobenzene. This solution, having an absorption maximum at 398 nm and no absorption at longer wavelength than 450 nm, returned to black in a day. The reaction was accelerated by the addition of 8-quinolinol. Thus the complex heated at 240 °C is the molten mixture of $VO_2(ox)$ and Hox, and vaporization of 8-quinolinol occurs at higher temperature.

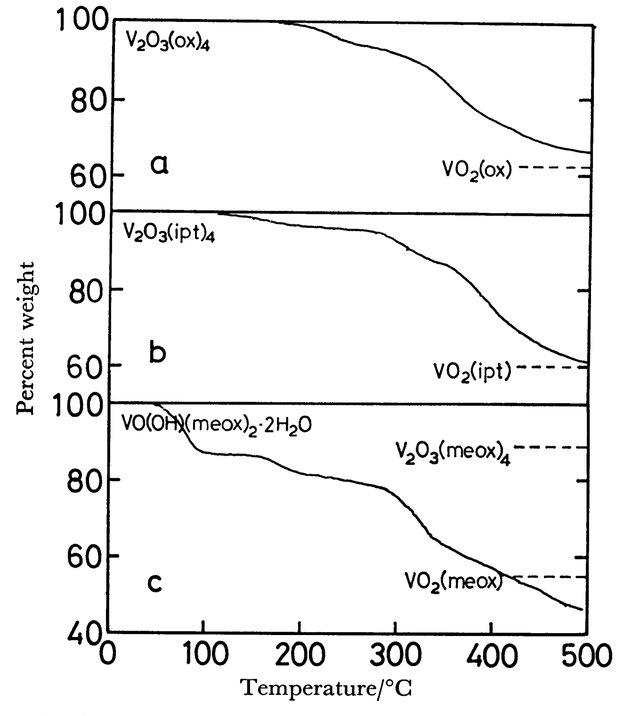

Fig. 4. Thermograms of vanadium (V) complexes.
a: 8-Quinolinolate complex, b: 4-isopropyltropolonate complex, c: 2-methyl-8-quinolinolinolate complex.

For the 4-isopropyltropolonate complex, the thermogram approached to a constant weight corresponding to $VO_2(ipt)$ beyond 500 °C (Fig. 4b). The complex dried at 240 °C, when dissolved in chlorobenzene, showed an absorption maximum at 366 nm and no absorption at longer wavelength than 450 nm, and also returned to black in a day.

For the 2-methyl-8-quinolinolate complex, a weight loss corresponding to 2.5 water molecules from $VO(OH)(meox)_2{\cdot}2H_2O$ to $V_2O_3(meox)_4$ was observed below 100 °C.[10,12] Further heating also dissociates the complex into $VO_2(meox)$ and Hmeox (Fig. 4c), which is overlapped with oxidative decomposition of the ligand.

TABLE 1. SUMMARY OF THE PROPERTIES OF VANADIUM(V) COMPLEXES

Complex	λ_{max}[a)] nm	ν(V=O)[b)] cm^{-1}	ν(V–O–V)[c)] cm^{-1}
8-Quinolinolate			
$V_2O_3(ox)_4$	550	950	715
$VO_2(ox)$	398	990[e)]	—
4-Isopropyltropolonate			
$V_2O_3(ipt)_4$	530	950	715
$VO_2(ipt)$	366	990[e)]	—
2-Methyl-8-quinolinolate			
$VO(OH)(meox)_2{\cdot}2H_2O$	340	925	—
$V_2O_3(meox)_4$	—[d)]	960	715
$VO_2(meox)$	388	980[e)]	—

a) λ_{max} is the wavelength of the absorption maximum in the UV and visible spectrum. b, c) ν(V=O) and ν(V–O–V) are the wavenumbers of the IR spectrum of V=O and V–O–V, respectively. d) The spectrum was unmeasurable in solution because of rapid change to the monomeric complex. e) The absorption was very broad and unsymmetric.

Infrared Spectra: IR bands of ν(V=O) and ν_{asym}(V–O–V) of the complexes are summarized in Table 1. All the dimeric compounds have ν(V=O) near 950 cm^{-1} in addition to ν_{asym}(V–O–V) at 715 cm^{-1} as in oxo-bridged dimeric Mo(V) complexes.[13]

The lower complexes are expected to have tetrahedral configuration. As the bonds between vanadium and oxo groups are much stronger than those of vanadium and organic ligands, the O–V–O skelton may be approximated as bent triatomic system and expected to have two vibrational mode in metal-oxo double bond region. But the symmetric and antisymmetric modes in bent triatomic system having similar wavenumber in many cases, the broad bands near 990 cm^{-1} seems to consist of these two bands and should not be compared with those of dimeric compounds. The absence of a band near 715 cm^{-1} excludes the possibility of a dioxo-bridged dimeric structure, $\mathrm{VO(ox)}\langle\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\rangle\mathrm{VO(ox)}$ for the lower complex.

Discussion

The visible spectrum of vanadium(V)–8-quinolinolate complex has been reported by many authors. The molar absorbance at 480 nm calculated from the literature are listed in Table 2. In the presence of excess amounts of 8-quinolinol the value of $\bar{\varepsilon}$ of extracted species or dissolved complex is well consistent with ours. In the absence of excess ligand the molar absorbance varies with experimental conditions, as evident from our findings.

TABLE 2. THE MOLAR ABSORBANCE OF VANADIUM(V)-8-QUINOLINOLATE COMPLEX IN THE LITERATURE

$\bar{\varepsilon}$ / mol^{-1} dm^3 cm^{-1}	C_v / mol dm^{-3}	C_add / mol dm^{-3}	Remarks	Ref.
2450—2500	1.96×10^{-4}	0	dissolved	3
2250—2500	—	0	dissolved	5
2950	2.0×10^{-4}	6.76×10^{-3}	dissolved	14
2640	1.1×10^{-4}	0	extracted	15
2910	1.1×10^{-4}	5.01×10^{-3}	extracted	15
3000	0.8×10^{-4}	7.94×10^{-3}	extracted	16

The dissociation constants of the two complexes, $V_2O_3(ox)_4$ and $V_2O_3(ipt)_4$, differ little: the difference is not large enough to discuss the effect of donor atoms: N and O for 8-quinolinolate, and O and O for 4-isopropyltropolonate. With this constant it is well understood that no lower complex was found in the extraction of vanadium(V) with 8-quinolinol.[10]

This type of ligand dissociation is anticipated to be promoted by heating. Actually the nitrobenzene solution of $V_2O_3(ox)_4$ changes to yellow when heated and it returns to black reversibly in cold.[17] The products of this reaction should not be identified as V_2O_5 and Hox but as $VO_2(ox)$ and Hox. Heating of solid complex also promote dissociation and, when the dissociated ligand is removed by NaOH, $VO_2(ox)$ is obtained.

We have shown the presence of $VO_2(ox)$ in aqueous solution, and proposed the structure of $VO(OH)_2(ox)(H_2O)$ from the comparison of pK_a between vanadic acid and complexes.[9] Accordingly the equilibria given by Eq. 5 is shifted completely to the right in aqueous solutions, while it is much favored to the left in organic solvents.

$$VO_2(ox) + 2H_2O \rightleftharpoons VO(OH)_2(ox)(H_2O) \qquad (5)$$

The 1:1 vanadium(V) complexes with β-diketonates have been reported.[18,19] They were identified as $\mathrm{VOL}\langle\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\rangle\mathrm{VOL}$ or VO_2L (L: β-diketonate) depending upon the presence or absence of infrared absorption near 715 cm^{-1} ascribed to the oxo bridging.

The visible spectrum of vanadium(V)-4-isopropyltropolonate complex has been reported from an analytical point of view by a few authors as $VO(OH)(ipt)_2$.[20—22] The spectrum of extracted species in the presence of excess amounts of 4-isopropyltropolone has an absorption maximum at 520 nm,[22] which is consistent with ours, whereas that of extracted species from strongly acidic media (6.6 mol dm^{-3} HCl) has an absorption maximum at 590 nm.[21] This blue shift is ascribed to the protonation of the complex, which has been found in the extraction of the 8-quinolinolate complexes.[10]

In the extraction of vanadium(V) with 4-isopropyltropolone, the extracted species was identified to be $VO(OH)(ipt)_2$.[23] The characteristics of UV, visible, and IR spectra,[10] however, point to the dimeric structure, $V_2O_3(ipt)_4$, as in the case of the 8-quinolinolate complex.

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