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옥소바나듐(IV)과 벤조히드로옥사믹산 간에 형성되는 착물의 전기화학적 성질에 관한 연구

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Electrochemical Behavior of Oxovanadium(IV) Complex of Benzohydroxamic Acid

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요 약. 벤조히드로옥사믹산(Hben)과 이의 옥소바나듐(IV) 착화합물, $VO(Ben)_2$의 전기화학적 거동을 폴라로그래피와 순환 전압 전류법을 이용하여 조사하였다. Hben의 경우, 아세톤 용매중에서 얻은 폴라로그램은 Ag/AgCl 전극에 대해 −0.05V와 −1.78V에서 두개의 환원파를 나타내었다. 첫번째 환원파는 단일 라디칼 음이온의 생성에, 그리고 두번째 환원파는 이중 라디칼 음이온의 생성에 기인하는 것으로 해석되었다. $VO(Ben)_2$ 착물의 폴라로그램은 +0.55V에서 한개의 산화파를, 그리고 −0.15V와 −1.30V에서 각각 한개씩의 환원파를 나타내었다. +0.55V의 전극반응은 1전자 산화과정이었다 ($VO(Ben)_2 \rightleftharpoons VO(Ben)^+ + e$). −0.15V에 나타난 환원파는 준가역적인 역시 1전자 과정이었으며 $VO(Ben)_2^-$ 라디칼 형성에 의한 것으로 해석되었다. −1.30V에서 나타난 환원파는 비가역적이며 이 과정에서는 바나디움(III) 이온을 생성하는 것으로 믿어진다. 산소 주게 원자를 갖는 Hben 리간드는 황이나 질소를 포함하는 다른 리간드들과 비교해 볼 때 중심금속인 바나듐의 +4가 산화상태의 안정성을 감소시키는 것으로 믿어진다.

ABSTRACT. The redox proprties of benzphydroxamic acid (Hben) and its oxovanadium complex, $VO(ben)_2$ has been studied by the use of polarograpy and cyclic voltammetry. The radical anions of ben seem to be generated in acetone. The wave at −0.05V *vs.* Ag/AgCl electrode might be attributed to the formation of radical anion and the wave at −1.78V *vs.* Ag/AgCl electrode might be attributed the formation of radical dianion. The $VO(ben)_2$ exhibits one oxidation wave at +0.55V and two reduction waves at −0.15V and −1.30V *vs.* Ag/AgCl electrode; the oxidation is reversible one electron process ($VO(ben)_2 \rightleftharpoons VO(ben)_2^+ + e$). The reduction wave at −0.15V is quasireversible and is arised from the formation of radical anion, $VO(ben)_2^-$. The second reduction wave at −1.30V is irreversible and this reduction process produces vanadium(III). This oxygen containing ligand of Hben seems to reduce the stability of +4 oxidation state of vanadium while the sulfur or nitrogen donor of the ligands stabilize the +4 oxidation state of vanadium when comparisons are made among several oxovanadium complexes.

INTRODUCTION

Although the chemistry of vanadium is now quite well understood, its biological role in some living species still remains uncertain. In sea water, vanadium exists as the vanadium anion, $H_2VO_4^-$

(+5), at a concentration of $5 \times 10^{-8} M$.[1] In vanadium containing blood cell of some ascidian, the intracellular vanadium is mainly in the V(III) state, with about 10% in V(IV) state.[2,3] Accumulation of vanadium occurs in some sort of ascidian and it is believed that accumulation appears to be driven by the redox processes in a specific vanadate transport system of the blood cells of ascidian.[4] It seems to be essential to understand the electrochemical behavior of vanadium to elucidate its biological role and accumulation machanism in living species. However, a few electrochemical studies in vanadium(IV) or vanadium (III) complexes have been made.[5-10] This may be attributed to the fact that oxovanadium (IV) complexes do not seem to warrent an electrochemical investigation since most oxovanadium(IV) complexes are unstable and/or insoluble in most organic solvents as well as in water. Pervious works have been carried out on some oxovanadium complexes with bidentate[5-8] ligand. In this study, oxovanadium complex with bidentate ligand having oxygen as a donor atom has been carried out. Electrochemical investigation of oxovanadium complex of benzohydroxamic acid seemed to provide a better understanding of redox chemistry of vanadium. This study is carried out in aprotic solvent mainly due to the poor solubility of this complex in water.

EXPERIMENTAL

Preparation of Complex. Potassium benzohydroxamate was prepared as prescribed by C. R. Houser *et al.*. One gram of potassium benzohydroxamate is dissolved in 25 m*l* of distilled water in a milk dilution botter and deoxygennated by bubbling through nitrogen. To this solution, $0.01M$ $VOSO_4 \cdot 3H_2O$ solution was added dropwise with a syringe while the solution was being warmed and stirred. The mixture was digested in a boling water bath for several minutes. The violet colored crystals precipitated. They were isolated by filteration and washed successively with warm water, and ethanol. The crystals were dried in a vacuum oven. Anal. Calcd. for $VO(ben)_2$; C = 49.57, H = 3.57, N = 8.26, Found; C = 48.45, H = 3.61, N = 8.02(%).

Electrochemical Measurement. Conventional dc polarograms of free ligand and metal complex in acetone were recorded with a Yanaco P-8 type polarograph using $0.1M$ tetraethylammonium perchlorate as supporting electrolyte. A three electrode system was employed for all conventional dc measurements. The Ag/AgCl electrode ($0.1M$ LiCl in acetone) was constructed, and was used as the reference electrode. The galss capillary dropping mercury electrode has the following characteristics; mercury column height was 67cm in open circuit, flow rate of mercury, m was 1.645 mg/sec, drop time, t was 4.60 sec and $m^{2/3}t^{1/6}$ was 1.797. The dropping mercury electrode (DME) has responed quite accurately in the acetone/0.1 M Et_4NClO_4 medium, and exhibited the useful measureable range starting from +0.8V *vs.* Ag/AgCl electrode. This range observed is in good agreement with previous results.[11] All test solutions were throughly degassed with nitrogen gas saturated with acetone and a contineous stream of nitrogen was passed over the solution while measurements were being taken. This solutions were thermostated at 25 ± 0.1°C and H-type cell was used.

Cyclic voltammetric measurements were made with a three electrode system. The working electrode were glassy carbon electrode (GCE, Tokai Co., area = 7.2 mm^2) and hanging mercury drop electrode (HMDE). The auxiliary electrode was platinum wire and the reference was Ag/AgCl electrode ($0.1M$ LiCl in acetone). The potentiostat used in cyclic voltammetric and coulometric measurement was EG & G model 273 (PAR. Co., USA) and cyclic voltammograms were recorded

with Kipp&Zonen model 13 BD 90 XY recorder. The working electrode used for controlled pontential electrolysis was mercury pool electrode. All test solutions were degassed with nitrogen to prevent from air oxidation.

RESULTS AND DISCUSSION

Electrochemical Behavior of Benzohydroxamic Acid. *Fig.* 1 shows dc polarogram of the ben ligand. The ben ligand generated two reduction waves; the first wave is appeared at -0.05V and the second wave is appeared at -1.78V *vs.* Ag/AgCl electrode, respectively. For two reduction waves appeared at -0.05V and -1.78V, a plot of difussion current, i_d *vs.* concentration are linear, and a plot of i_d *vs.* the square root of the mercury column height, $h^{1/2}$ is also linear. These indicated that two reduction waves are difussion controlled. The plot of $E_{1/2}$ *vs.* log $i/(i_d-i)$ of the first and second waves are linear and the slope of the plots are 57 mV and 70 mV, respectively. The number of electrons involved in the redox processes were determined by the controlled potential coulometric measurements. The electrode processes both for wave 1 and wave 2 involve one-electron transfer. These results indicate that on electrode reaction is reversible and the other one is quasireversible. The $(E_{1/4}-E_{3/4})$ values are independent of DME drop time. These value equal to 60 ± 5 mV and 80 ± 5 mV (see *Table* 1), also indicating reversible nature of the electrode reaction. In aprotic solvents, many aromatic hydrocarbons and their derivatives are reported to be reduced electrolytically in two successive one-electron steps[11]; the first step is the formation of radical anion and the second step produces the dianion from the radical anion produced in the first step. As a result, a polarogram of such hydrocarbon usually consists of two one electron waves, and the second wave generally occurs at potential about 0.5V more negative than the first. The electrochemical result of ben is consistent with these facts. These reduction processes are diffusion controlled and are found to be an one electron processes being judged from the result of coulometric measurement. The first wave at

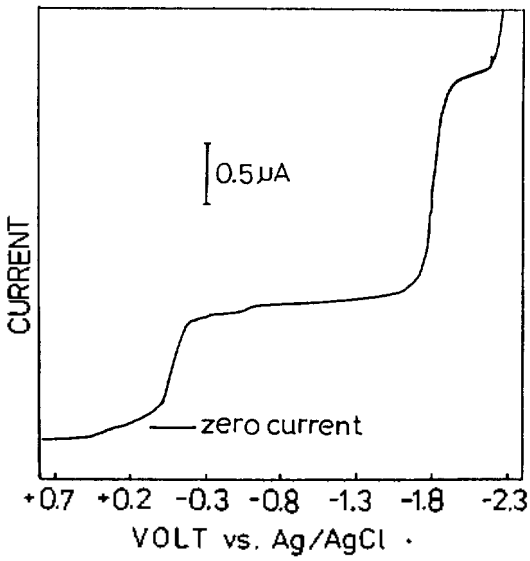

Fig. 1. The dc prolarogram of ben in 0.1M tetraethylammonium perchlorate/acetone solution at 25°C.

Table 1. Variation of $E_{1/2}$ and $(E_{1/4}-E_{3/4})$ values with drop time for the benzohydroxamic acid ($5\times10^{-4}M$)

Drop time (sec)	$E_{1/2}$ (V *vs.* Ag/AgCl)		i_d (uA)		$E_{1/4}-E_{3/4}$ (mV)	
	wave 1	wave 2	wave 1	wave 2	wave 1	wave 2
0.2	-0.05	-1.77	0.77	1.75	60	85
0.4	-0.04	-1.76	0.85	1.81	65	80
0.8	-0.04	-1.77	0.91	1.82	60	80
1.6	-0.04	-1.78	0.98	1.93	60	80
3.2	-0.04	-1.77	1.05	1.89	70	85

Table 2. The peak potential values (E_p) *vs.* Ag/AgCl electrode in cyclic voltammograms for $VO(ben)_2$ and Ben

		Glassy Carbon electrode		HMDE	
		E_{pc}	E_{pa}	E_{pc}	E_{pa}
$VO(ben)_2$	peak 1	+0.63	+0.75		
	peak 2	-1.52			
Ben	peak 1	-1.65		0.01	-0.52
	peak 2		-0.02	0.064	-1.74
	peak 3		+0.16		

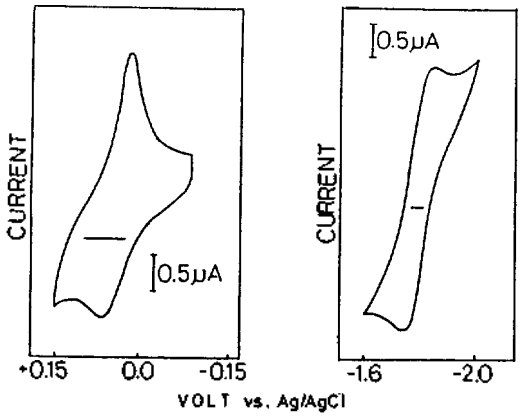

Fig. 2. The cyclic voltammogram of ben with HMDE (in acetone/0.1 *M* tetraethyl ammonium perchlorate).

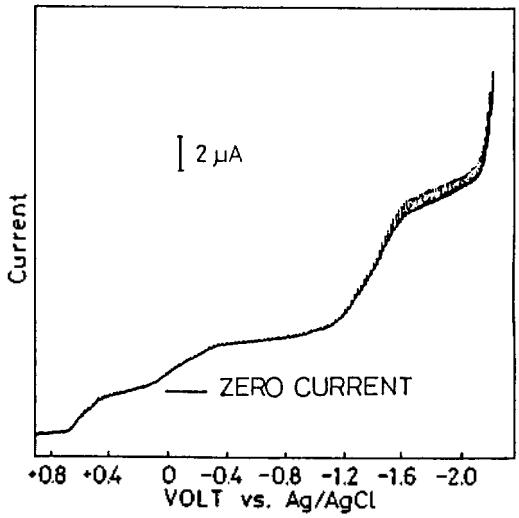

Fig. 3. The DC polarogram of $VO(ben)_2$ complex in 0.1 *M* Et_4NClO_4/acetone solution at 25 °C.

−0.05V might be attributed to the formation of radical anion and the second wave at −1.78V might be due to the formation of the dianion. Cyclovoltammograms of the ben are obtained by the use of glassy carbon electrode and HMDE (see *Table* 2). The peak seperations between cothodic and anodic peak are 56 mV and 75 mV, respectively. The reductions are found reversible and are both one electron processes (see *Fig.* 2).

Electrochemical Behavior of $VO(ben)_2$. The polarogram of oxovanadium complex shows three polarographic waves *i.e.*, one oxidation wave (wave 1; +0.55V *vs.* Ag/AgCl electrode) and two reductive waves (wave 2; +0.05V and wave 3; −1.30V *vs.* Ag/AgCl electrode) (see *Fig.* 3). The plots of diffusion current, i_d *vs.* concentration are linear in the range of $1\times10^{-3}\times10^{-4}M$ for the wave 1, wave 2 and wave 3. The plots of i_d *vs.* the square root of the mercury column height, $h^{1/2}$ are linear. Therefore the wave 1, wave 2 and wave 3 are diffusion controlled. The plot of E *vs.* log $i/(i_d-i)$ are also linear for the three waves. The slopes of these plots are 56 ± 3 mV, 83 ± 3 mV and 92 ± 2 mV, respectively. These results indicate that the electrode reaction of wave 1 is a reversible one-electron process while that of wave 2 and wave 3 are irreversible electrode processes. The number of electrons involved in the redox processes are also determined by the coulometric measurements. The reversible nature of the electrode reaction of wave 1 is evidenced further by the fact that ($E_{1/4}$-$E_{3/4}$) value of wave 1 is 60 ± 5 mV and is independent of DME drop time. The variation of $E_{1/2}$ and ($E_{1/4}$-$E_{3/4}$) values against drop time are summerized in *Table* 3. When a reversible electrode processes is observed, it implies that the charge transfer is rapid compared to the time

Table 3. Variation of $E_{1/2}$ and ($E_{1/4}$-$E_{3/4}$) values with drop time for the $VO(ben)_2$

drop time (sec)	$E_{1/2}$(V *vs.* Ag/AgCl)			i_d(uA)			$E_{1/4}$-$E_{3/4}$(mV)		
	wave 1	wave 2	wave 3	wave 1	wave 2	wave 3	wave 1	wave 2	wave 3
3.20	0.55	−0.15	−1.30	1.05	1.40	3.81	60	90	95
1.60	0.57	−0.15	−1.31	0.98	1.26	4.1	60	90	95
0.80	0.55	−0.18	−1.33	0.94	1.19	4.06	65	90	95
0.40	0.55	−0.18	−1.35	0.91	1.12	4.69	60	95	95
0.20	0.55	−0.15	−1.36	0.87	0.98	4.2	60	95	95

scale of the dc polarographic experiment. The oxidized form in this case generally has the same molecular structure and differ only in their electronic populations. Therefore, we can suggest that following electrode reaction might take place in the $VO(ben)_2$ complex;

$$VO(ben)_2 \rightleftharpoons VO(ben)_2^+ + e \text{ (wave 1)}$$

The $VO(ben)_2$ exhibits an oxidation wave with $E_{1/2}$ value of +0.55V *vs.* Ag/AgCl electrode while the free ligand does not exhibit any oxidation wave. This clearly indicates that the oxidation wave is attributed to the oxidation of vanadium complex. Also the polarogram of $Hg(ben)_2$ does not exhibit oxidation wave but only shows reductive waves.

The electroreduction reaction of wave 2 is one electron process. This is confirmed by controlled potential coulometry and the reduced form should essentially has the same five or six coordinate structure like $VO(ben)_2$. The electroreduction reaction of $VO(ben)_2$ for wave 2 can be described by the following;

$$VO(ben)_2 + e \rightarrow VO(ben)_2^- \text{ (wave 2)}$$

For wave 3, the large ($E_{1/4}$-$E_{3/4}$) value indicates that the irreversible nature of the process. The electrode process for wave 3 involves one electron reduction and this is confirmed by controlled potential coulometry. This process might involve the dissociation of metal-ligand bond and produces vanadium ion of +3 oxidation state. The following mechanism can be postulated for the reduction of wave 3 as below;

$$VO(ben)_2^- + e \rightarrow \text{decomposition (wave 3)}$$

products

The dissociation of metal-ligand bond was previously suggested by Kitamura[8a] and Asri Nawi[8b] for the similar redox process of $VO(acac)_2$ in acetonitrile and dimethylsulfoxide. The cyclic voltammetric result for the complex is consistent with the dc polarographic results. The cyclic voltammogram of $VO(ben)_2$ is shown in *Fig.* 4. The first peak of voltammogram exhibits its reversible nature, but the second peak does clearly exhibit their irreversibility. The peak potential values of cathodic and anodic peak (E_{pc} and E_{pa}) are summarized in *Table* 2.

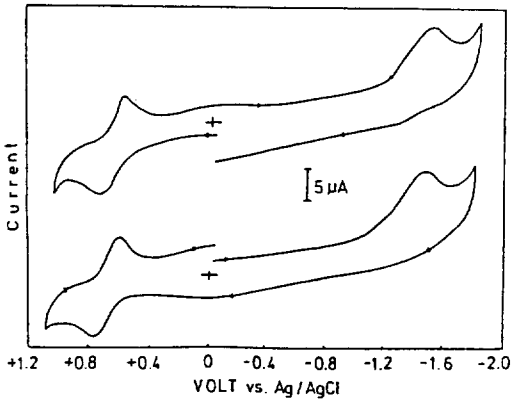

Fig. 4. Cyclic voltammogram of $VO(ben)_2$ complex with glassy carbon electrode ($5 \times 10^{-4}M$ in acetone).

Table 4. Polarographic date for oxidation and reduction of some oxovanadium complexes

Compound	$E_{1/1}$(V *vs.* Ag/AgCl) wave 1	wave 2	wave 3	Remark
VO(ben)	+0.55(ox,R)	-0.15	-1.30(I)	Acetone
ben	-0.05	-1.78		Acetone
$VO(mpno)_2$[a]	+0.57(ox,R)	-1.18	-1.76	Acetone
$V(dtc)_3$[b]	+0.35(ox,I)	-1.08(R)		DMF
VQ_3[b]	+0.45(ox,I)	-1.48(R)	DMF	
$VO(dtc)_2$[b]		-1.35(I)	DMF	
VOQ_2[c]	+0.76(ox,I)		DMF	
$VO(salene)_2$[d]	+0.3(ox,R)	-1.55(R)		Acetone

[a]reference 14, [b]reference 5, [c]reference 6, [d]reference 9 R = reversible, I = irreversible, ox = oxidation Q = 8-quinolinol, dtc = dithiocarbamate.

In ascidian, the intracellular vanadium is reported to be mainly in the form of V(III) state and with up to 10% in the VO(IV) state. Also Dingley[13] reported that the reduction of V(V) to V(IV) is reversible and fast in the whole blood cell of ascidian, and they suggested VO^{2+} species in the ascidian cell are reduced to V(III) species irreversibly and this non-transpotable cation species, V(III) are

accumulated in the blood cell of ascidian. These results are well constent with the electrochemical behaviors of $VO(ben)_2$. Polarographic results for oxidation and reduction of VO(ben) along with other oxovanadium(IV) complexes are summarized in *Table* 4.

The half-wave potential of the first reduction wave (wave 2) of oxovanadium (IV) complexes containing oxygen atom is less positive than those of the complexes having sulfur donor atoms when the comparisons are made among oxovanadium (IV) complexes.

Oxygen containing ligand of benzohydroxamic acid seem to reduce the stability of +4 oxidation state of vanadium while sulfur containing ligands stabilize the +4 oxidation state of vanadium.

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