

ELECTROCHEMICAL STUDY OF SOME VANADIUM COMPLEXES

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ABSTRACT

The electrochemical behaviour of some vanadium complexes with ester ligands, of the types $[V_2(\mu\text{-Cl})_2Cl_4(L)_4]$ [$L=\text{CH}_3\text{CO}_2\text{Et}$ (1) or $\frac{1}{2}\text{CH}_2(\text{CO}_2\text{Et})_2$ (2)], and $[V_4(\mu\text{-O})_4Cl_8\{\text{CH}_2(\text{CO}_2\text{Et})_2\}_4]$ (3), was investigated in aprotic media by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) at platinum electrodes. They exhibit, by CV, ill-defined anodic processes which, by CPE, appear to involve one electron per vanadium atom.

INTRODUCTION

Vanadium complexes with O-ligated ligands are promising catalysts for olefin polymerisation reactions as well as for dinitrogen activation processes which are dependent on the metal redox state. Hence, the investigation of their electrochemical behaviour should provide a significant contribution to the understanding of their reactivity. We now report the results of our study, by cyclic voltammetry (CV), at a Pt disc working electrode ($\phi=1$ mm), and controlled potential electrolysis (CPE), at a platinum gauze working electrode, in 0.2 M $[NBu_4][BF_4]/CH_2Cl_2$, of the chloro-bridged bimetallic V(III) complexes $[V_2(\mu\text{-Cl})_2Cl_4(\text{CH}_3\text{CO}_2\text{Et})_4]$ (1) and $[V_2(\mu\text{-Cl})_2Cl_4\{\text{CH}_2(\text{CO}_2\text{Et})_2\}_2]$ (2), as well as the oxo-bridged tetrametallic V(IV) compound $[V_4(\mu\text{-O})_4Cl_8\{\text{CH}_2(\text{CO}_2\text{Et})_2\}_4]$ (3) (Fig.1).

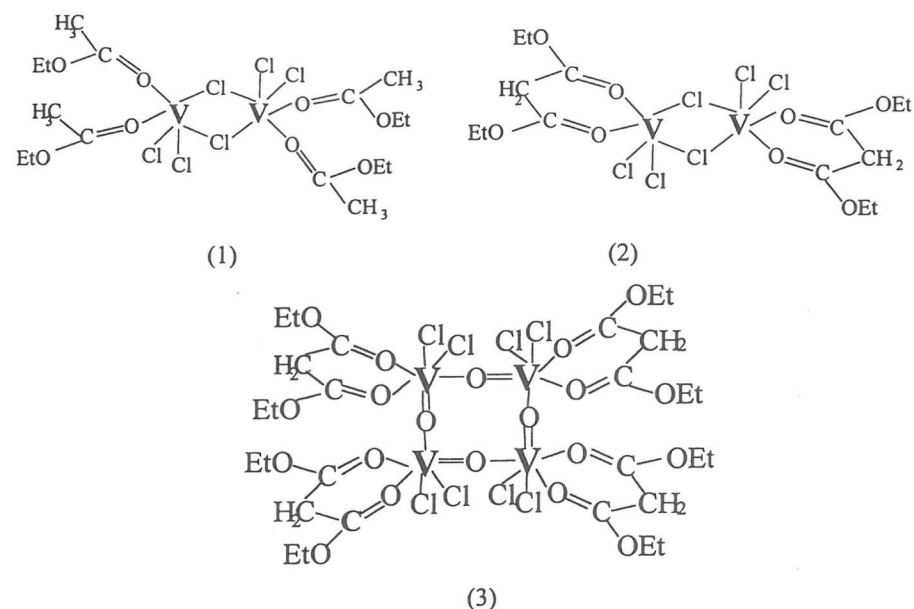


Fig.1- Vanadium complexes with O-ligated ligands: $[V_2(\mu\text{-Cl})_2Cl_4(\text{CH}_3\text{CO}_2\text{Et})_4]$ (1) , $[V_2(\mu\text{-Cl})_2Cl_4\{\text{CH}_2(\text{CO}_2\text{Et})_2\}_2]$ (2) and $[V_4(\mu\text{-O})_4Cl_8\{\text{CH}_2(\text{CO}_2\text{Et})_2\}_4]$ (3).

All the complexes were prepared according to published procedures [1] and were handled in an inert atmosphere and all the redox potentials are quoted relative to the SCE by using as internal reference the $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^{0/+}$ redox couple ($E_{1/2}^{\text{ox}} = 0.53$ V vs. SCE, in 0.2 M $[\text{NBu}_4][\text{BF}_4]/\text{CH}_2\text{Cl}_2$).

RESULTS AND DISCUSSION

The V(III) complexes (1) and (2), in CH_2Cl_2 , present by CV two successive irreversible anodic processes at peak potentials (table 1) *ca.* 1.0 and 1.2 V vs. SCE, which are believed to be centred at the metal since no redox process has been detected, in the range of potentials studied (up to 1.8 V vs. SCE), for free diethylmalonate, $\text{CH}_2(\text{CO}_2\text{Et})_2$.

Moreover, with the exception of the second anodic wave of complex (2) which corresponds to a single-electron process, each oxidation wave of compounds (1) and (2) involves *ca.* two electrons *i.e.* one electron per vanadium atom, as indicated by CPE,

being assigned to the V(III)→V(IV) (first wave) and V(IV)→V(V) (second wave) oxidations.

The cyclic voltammogram of the V(IV) compound $[V_4(\mu\text{-O})_4Cl_8\{\text{CH}_2(\text{CO}_2\text{Et})_2\}_4]$ also exhibits two irreversible oxidation waves (Fig.2) although at more anodic potentials (table 1) than those of the complexes (1) and (2). They involve, by CPE, an overall transfer of *ca.* four electrons which appear to correspond to monooxidation of each of the vanadium (IV) centres. The appearance of two distinct anodic waves for the V(IV)→V(V) conversion is an indication of the interaction between the vanadium centres in the tetranuclear complex (3).

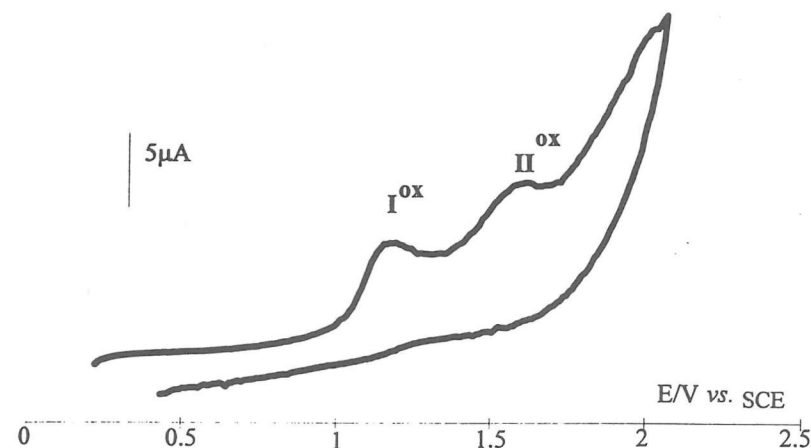


Fig. 2- Cyclic voltammogram for complex $[V_4(\mu\text{-O})_4Cl_8\{\text{CH}_2(\text{CO}_2\text{Et})_2\}_4]$ (3) ($C=0.55$ mM) in 0.2 M $[\text{NBu}_4][\text{BF}_4]/\text{CH}_2\text{Cl}_2$, at a Pt disc electrode ($\phi=1$ mm); scan rate= $200\text{mV}\cdot\text{s}^{-1}$; potential in V vs. S.C.E.

In addition, the number of electrons involved in each anodic wave of the cyclic voltammograms of the complexes (1), (2) and (3) was estimated from the slope of the plot of E_p^{ox} vs. $\log v$ (v = scan rate) ($\Delta E_p/\Delta \log v = 30/(\alpha \cdot n)$, diagnostic criterium [2] for an irreversible wave), assuming $\alpha = 0.5$. The values estimated in this way are comparable with those obtained by CPE, indicating the involvement of identical numbers of electrons in the CV and CPE time scales.

Table 1

Electrochemical data^a for complexes $[V_2(\mu-Cl)_2Cl_4(CH_3CO_2Et)_4]$ (1), $[V_2(\mu-Cl)_2Cl_4\{CH_2(CO_2Et)_2\}_2]$ (2) and $[V_4(\mu-O)_4Cl_8\{CH_2(CO_2Et)_2\}_4]$ (3).

Complex	$E_p^{ox^a}$	$E_p^{ox^a}$	I_n^b	π_n^b	$I_n + \pi_n$
(1)	1.02 ^c	1.22	2.4 (-) ^d	1.8 (1.5)	4.2 (-)
(2)	0.92	1.25	2.0 (2.0)	0.7 (1.0)	2.7 (3.0)
(3)	1.17	1.60	- ^e (2.4)	- ^e (1.6)	3.7 (4.0)

^a Values in Volt vs. SCE, measured at a Pt-disc electrode ($\phi=1$ mm), in 0.2M $[Bu_4N][BF_4]-CH_2Cl_2$, by using as internal reference the $[Fe(\eta^5-C_5H_5)_2]^{0/+}$ redox couple; scan rate of 200 mV.s⁻¹.

^b Number of electrons as obtained by CPE; in parentheses are given the values derived from the application of the diagnostic criterium for an irreversible wave, $\Delta E_p/\Delta \log v = 30/(\alpha.n)$.

^c Wave not detected at scan rates higher than 0.2 V.s⁻¹.

^d Not possible to estimate (see footnote c).

^e Not possible to estimate because only one broad wave at an intermediate potential (between those of the anodic waves I and II) was observed in the CPE cell.

No cathodic processes were detected for any of the complexes and no products could be isolated from the anodically electrolysed solutions.

The ready decomposition of the complexes in common solvents other than CH_2Cl_2 precluded the investigation of the effects of the solvent on the electrochemical behaviour. However, in DMSO all the vanadium complexes behave quite similarly, suggesting their decomposition to a common product whose anodic CPE led to an unexpected high number of electrons per vanadium atom, suggesting the occurrence of a catalytic anodic process.

A preliminary cyclic voltammetric study of the complexes in CH_2Cl_2 with addition of increasing amounts of DMSO appears to corroborate not only the catalytic oxidation of the sulfoxide but also to indicate its coordination to the vanadium centre. A study of the mechanism involved in the process will be attempted.

REFERENCES

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