

Catalytic Oxygenation of Pyrocatechols by O₂ in the Presence of Vanadium. Synthesis, Characterization, Electronic Structure and Reactivity of the Vanadium(IV)/Tetrachloro-*o*-quinone System

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(Received September 12, 1986)

Abstract

Complex **1**, VO(acac)(TCCat) (TCCat = tetrachlorocatecholate), was obtained from VO(acac)₂ and tetrachloro-*o*-quinone, and characterized by its IR, UV, visible, and NMR spectra; the molecular orbital diagram from EHT calculations on **1** was found to correlate well with (i) the preferred oxidation states of the metal and the ligand in **1**, and (ii) the experimental electronic transitions observed for **1**. In the presence of 1, 3,5-di-*tert*-butylcatechol is catalytically oxidized by molecular oxygen to the corresponding muconic acid anhydride and 2-pyrone.

Introduction

Interactions of *o*-quinones with transition metal complexes have been reported to lead to quinone, semiquinone and catecholato complexes, depending on the nature of the metal complex and the oxidizing potential of the quinone [1]. The only available data in the case of vanadium are concerned with the reduced metal: when the V(CO)₆⁻ anion and *o*-benzoquinone are made to react, tris(catecholato)-vanadium(V) complexes can be formed [2], while similar reactions carried out with neutral V(CO)₆ and tetrachloro-1,2-benzoquinone [3] gave tris(semiquinone)vanadium(III) species.

As part of our studies [4] on the redox behavior of vanadium/catechol and vanadium/quinone systems, we found that compound **1**, VO(acac)(TCCat), is obtained through the reaction of tetrachloro-*o*-quinone with VO(acac)₂. Compound **1**, which is itself inert towards molecular oxygen, allows for catalytic oxygenation of 3,5-di-*tert*-butylcatechol. We report here this oxygenation, which is very similar to that catalyzed by pyrocatechase [5], to-

gether with the synthesis, characterization and electronic structure, as calculated by EHT, of compound **1**.

Experimental

VO(acac)₂ was prepared according to literature procedure [6]. The solvents, the gases and all other compounds were purified by standard methods. The microanalyses were performed by the Service Central de Microanalyses of the Centre National de la Recherche Scientifique. IR spectra were recorded on a Perkin-Elmer 577, ¹H NMR on a WH90 Bruker spectrometer and ¹⁷O NMR spectra were obtained with a Bruker WM-400 spectrometer operating at 54.2 MHz. Optical spectra were recorded on a Beckman model 25 spectrophotometer. Mass spectra were obtained with a NERMAG-R-1010 spectrometer. ESR spectra were recorded on a VARIAN E9 spectrometer equipped with X-band (9 GHz). Magnetic data were obtained over a temperature range of 5-300 K with a SHE 900 susceptometer.

Preparation of VO(acac)(TCCat) (**1**)

VO(acac)₂ (0.56 g, 2 mmol) and tetrachloro-*o*-quinone (0.49 g, 2 mmol) were allowed to react for 48 h at room temperature in a CH₂Cl₂ (80 ml) solution. The reaction mixture was then concentrated under vacuum to 40 ml and filtered. The resulting dark blue powder was washed with hexane (1-3) and dried under vacuum (0.72 g; 87%). *Anal.* Calc. for VC₁₁H₇Cl₄O₅: C, 32.04; H, 1.69; Cl, 34.46; V, 12.37. Found: C, 32.35; H, 1.71; Cl, 35.38; V, 11.22%.

Oxidation Procedure and Product Analysis

In a typical procedure [7], a 0.1 M 3,5-di-*tert*-butylcatechol solution in CH₂Cl₂ containing 1:100 of **1** was placed under O₂ atmosphere for 60 h at

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room temperature. The reaction mixture was then chromatographed over SiO_2 with CHCl_3 as eluant: the weighted reaction products were characterized by the usual techniques (NMR, IR, melting point).

Theoretical Methodology

Molecular orbital calculations were carried out by the non-iterative 'Extended Huckel method' [8], using molecular geometries derived from published crystal structures. The $\{\text{VO}(\text{acac})\}$ moiety was taken from the crystal structure of $\text{VO}(\text{acac})_2$ [9]. The $\{\text{TCCat}\}$ fragment was derived from the structure of $\text{K}_2[\text{VO}(\text{cat})_2] \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ [10] and by replacement of the hydrogen atoms by chlorines. The TCSQ part was derived from the structure of $\text{Cr}[\text{O}_2(\text{C}_6\text{H}_2)(\text{C}_4\text{H}_9)_2]_3$ [11] and by replacement of the aromatic hydrogen atoms and the tertibutyl groups by chlorines, and the chromium atom by vanadium. The molecular geometry and the referential axis used are represented in Fig. 1.

Results and Discussion

Addition of one equivalent of tetrachloro-*o*-quinone to a CH_2Cl_2 solution of $\text{VO}(\text{acac})_2$ resulted in the dark blue compound **1**: elemental analysis of this complex indicated the formula $\text{VO}(\text{acac})(\text{TCQ})$. The same compound was obtained when the reaction was performed under O_2 atmosphere.

The IR spectra of **1** (KBr pellet) showed no absorption in the $1600\text{--}1800\text{ cm}^{-1}$ region where the coordinated quinone $\nu(\text{CO})$ vibrations are expected ($\nu(\text{CO}) = 1680\text{ cm}^{-1}$ in free TCQ), indicating that the quinone had been reduced. The complexity of the spectrum in the $1400\text{--}1600\text{ cm}^{-1}$ region did not however allow any further assignment to a semi-

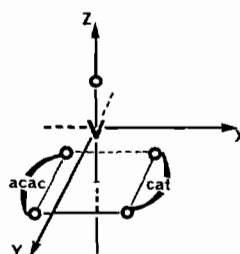


Fig. 1. Molecular geometry and referential axis used in the molecular orbital calculations.

quinone or to a catechol structure for the coordinated TCQ in **1**. ^{18}O labelling experiments allowed the 1008 cm^{-1} absorption to be attributed to the oxo stretching vibration $\nu(\text{V}=\text{O})$.

Magnetic moment measurements in the solid state and ESR spectra recorded both on the solid and on CH_2Cl_2 solutions of **1** showed the isolated complex to be diamagnetic. This was further confirmed in ^1H NMR by the sharpness of the signals attributable to the acac moiety ($\delta(\text{CH}_3) = 2.11\text{ ppm}$). The ^{17}O NMR spectrum recorded on THF solutions of **1**, after labelling of the $\text{V}=\text{O}$ group through exchange with $\text{H}_2\text{ }^{17}\text{O}$ [12], which occurs immediately, exhibits a single line at 1290 ppm in the region assigned to the $\text{V}(\text{V})=\text{O}$ moiety (Fig. 2) [13].

The absence of d-d transition in the optical spectra measured on both THF and CH_2Cl_2 solutions of **1** is in agreement with a d^0 configuration of the metal. The mass spectra (IC/ NH_3) of **1** exhibits a peak for $m/e = 412$, indicating a monomeric structure in the gas phase.

These data are all consistent with the formulation of **1** as a molecular $\text{V}(\text{V})$ -catecholate complex, as illustrated in Fig. 3.

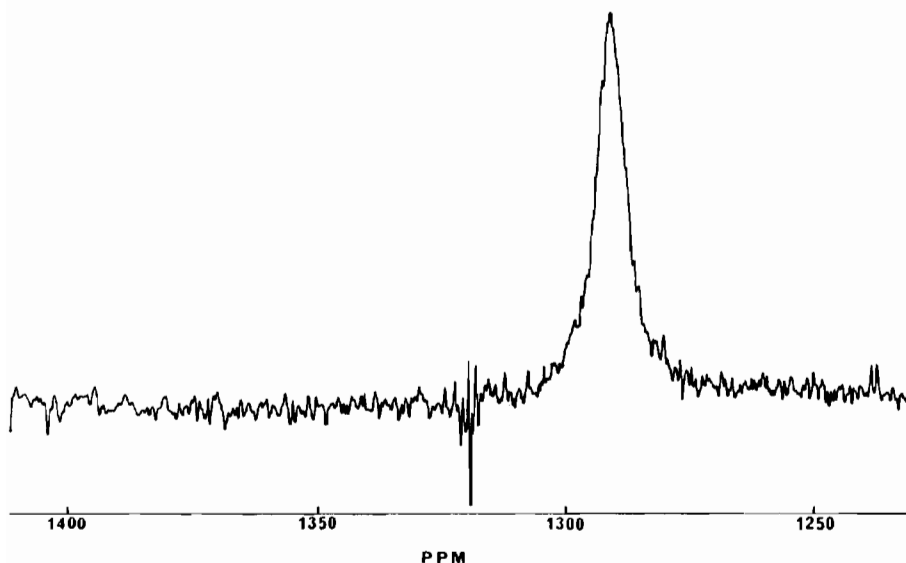


Fig. 2. ^{17}O NMR spectra measured on $\text{VO}(\text{acac})(\text{TCCat})$ in THF.

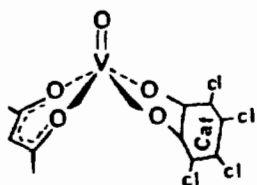


Fig. 3. Structure of compound 1.

There are many reports of vanadium–catechol complexes, but most of these are solution studies in which no compound was isolated. The extensive and often contradictory literature in the field has recently been rationalized by Cooper *et al.* [10]: the hitherto well-characterized catechol (L) vanadium complexes are mostly ionic species, such as (i) $-VL_3$ isolated for oxidation states III, IV and V, and (ii) VOL_2 derivatives characterized for oxidation states IV and V. The only molecular catechol complexes reported so far are V(IV) species [4, 10], except for the mixed catechol·semiquinone $VL_2(SQ)$ and $[VOL(SQ)]_2$ complexes [1, 10, 14, 15]. Compound 1 thus adds an example to the still limited series of known molecular catecholato vanadium complexes.

Molecular Orbital Calculations

The experimental data on compound 1 indicate that it is stable in the vanadium(V) catechol form A. We investigated the relative stability of form A with respect to the vanadium(IV) semiquinone form B through a theoretical approach, using EHT calculations on a semi-empirical basis, with the aim of

determining whether some properties of the complex could be accounted for by its electronic structure.

Figure 4(a, b) presents the results of our calculations on the two forms A and B, the catechol and the semiquinone moieties. Only the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals are represented in the C_s point group symmetry of the molecules.

We found that in form A the LUMO ($E = -10.233$ eV) is the pure $3d_{x^2-y^2}$ metal orbital and the two HOMOs ($E = -11.736, -11.785$ eV) are mainly built on the π^* catechol orbitals which are represented in Fig. 5. The non-bonding nature of these MOs is due to the poor overlap between the catechol ligand and metal orbitals. In the alternative electronic configuration B, the LUMO is a destabilized d_{xz} metal orbital. The two highest singly-occupied MOs (SOMO) are essentially built from the $3d_{x^2-y^2}$ metal orbital and from a $\pi^*(A')$ semiquinone orbital, respectively. The next two double

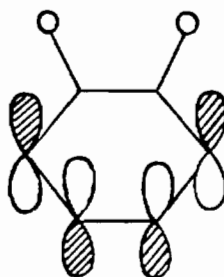
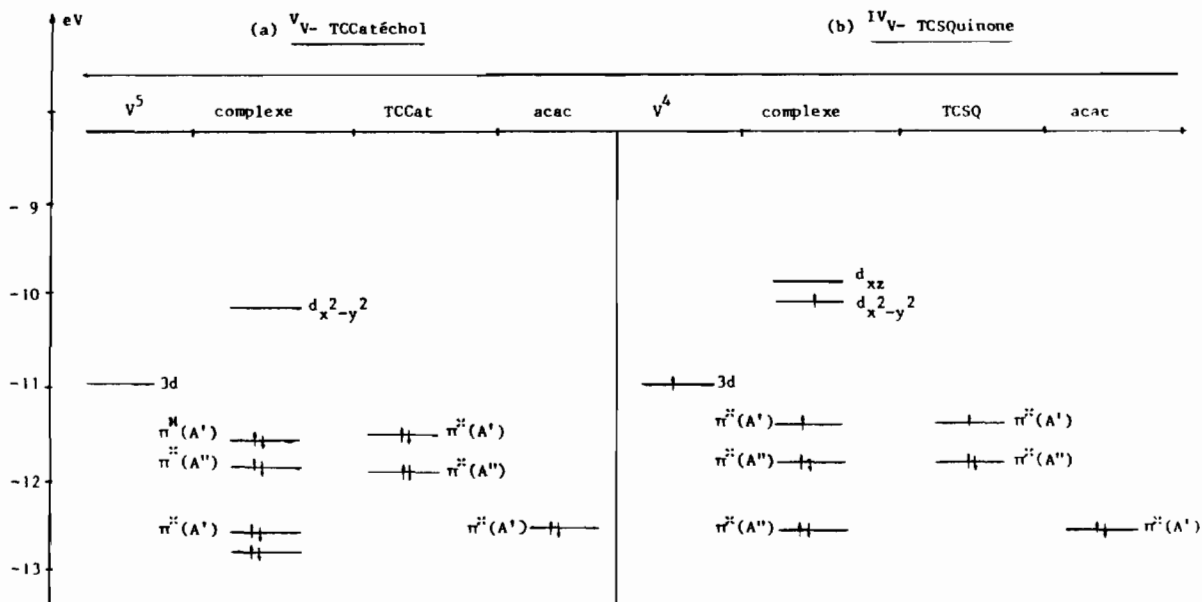
Fig. 5. π^* Catechol orbitals.

Fig. 4. Diagrams showing important molecular orbital levels for 1 in the vanadium(V) catechol form A (a) and vanadium(IV) semiquinone form B (b) on the basis of EHT calculations.

TABLE I. Calculated and Experimental Electronic Transitions for Compound **1** in the V(V) Catechol Form A and V(IV) Semiquinone Form B

Structures			Calculated ΔE (eV)	Experimental	
				ΔE (nm)	ΔE (eV)
A ($E_T = -2145.0$ eV) ^a	$\pi^*(A')\text{Cat}$	$d_{x^2-y^2}$	1.503	850	1.46
	$\pi^*(A'')\text{Cat}$	$d_{x^2-y^2}$	1.552		
	$\pi^*(A')\text{acac}$	$d_{x^2-y^2}$	2.346	575	2.15
B ($E_T = -2143.2$ eV) ^a	$\pi^*(A')\text{SQ}$	$d_{x^2-y^2}$	1.386		
	$\pi^*(A'')\text{SQ}$	$d_{x^2-y^2}$	1.706		
	$\pi^*(A')\text{SQ}$	d_{xz}	1.797		
	$\pi^*(A'')\text{SQ}$	d_{xz}	2.117		
	$\pi^*(A')\text{acac}$	$d_{x^2-y^2}$	2.418		
	$\pi^*(A')\text{Cat}$	d_{xz}	2.829		

^a E_T = calculated total energy.

occupied MOs are also quasi non-interacting π^* orbitals belonging to the semiquinone and acac ligands; as in form A, π -interaction is minimum and π -bonding and ionic contributions are chiefly responsible for vanadium–ligand bonding.

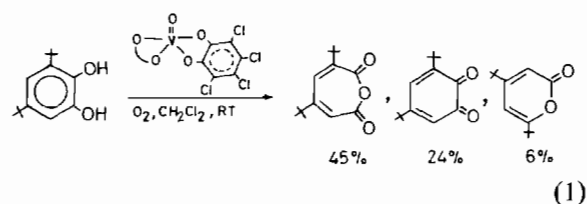
Although the total energy (ET) calculated by the EHT method is approximate in absolute scale, the sign of the energy difference between two structures is generally reliably related to their relative stability. The ET s of forms A and B are respectively -2145.0 and -2143.2 eV; the $S = 0$ species (form A) is stabilized by 1.8 eV over the $S = 1$ state (form B). This result is in agreement with the diamagnetism found for the complex isolated.

Table I presents the calculated electronic transitions for the two forms, and for $\text{VO}(\text{acac})_2$, along with the experimental data obtained for compound **1**. A reasonable agreement is observed between the calculated values for form A and the experimental values for **1**, while the agreement is poor between these and the values calculated for form B. This further confirms the tetrachlorocatecholate–oxovanadium(V) structure (form A) of compound **1**.

The electronic structure of the complex isolated is then described by Fig. 4 in which the HOMO is a non-bonding $\pi^*(A')$ catechol orbital.

Complex **1** as a Catalyst for the Oxygenation of 3,5-Di-tert-butylcatechol

In the presence of catalytic amounts (1 mol%) of **1**, 3,5-tert-butylcatechol is easily oxidized by molecular oxygen in CH_2Cl_2 under atmospheric pressure and at room temperature, to afford muconic acid anhydride (45%) and 2-pyrone (6%) together with 3,5-di-tert-butyl-*o*-benzoquinone (24%), as illustrated by eqn. (1)



The muconic acid anhydride is the main product in this reaction, indicating that vanadium catalyzes intra-diol cleavage of the pyrocatechol, with incorporation of one oxygen atom from molecular oxygen. On the other hand, pyrocatechol and 4-tert-butylcatechol are not oxidized by O_2 in the presence of **1**.

This catalysis compares well with the results recently reported in the literature for other vanadium systems [7, 16]. The characteristic features of the vanadium catalyzed oxygenation of 3,5-di-tert-butylcatechol are (i) the catechol is mainly oxygenated into the Hamilton intermediate [17], (ii) the formation of the 2-pyrone as a minor product can be attributed to the proximal extra-diol cleavage of the pyrocatechol ring and subsequent loss of a CO group [18], (iii) the active vanadium III, IV and V complexes show comparably high catalytic activity and (iv) the quinone is not oxidized. It is noteworthy that the vanadium systems, like those of ruthenium [19], catalyze the incorporation of one oxygen atom into the substrate, while pyrocatechase itself and its iron [19] and copper [20, 22] models allow incorporation of both oxygen atoms of molecular O_2 , through a dioxetan intermediate.

As we mentioned, compound **1** does not itself react with molecular oxygen; this implies that the first step in the oxygenation reaction is the replacement of the tetrachlorocatecholate moiety by the 3,5-di-tert-butylcatechol substrate in the coordination sphere of the metal.

We therefore added a threefold excess of di-tert-butylcatechol to a solution of **1** under argon atmosphere at ambient temperature to give a dark blue solution from which a dark blue powder could be obtained.

The IR spectrum measured for this residue shows, besides the vibrations due to the coordinated acac moiety and the typical print for the tert-butyl $\nu(\text{C-H})$ stretches, a strong $\nu(\text{V=O})$ absorption at 990 cm^{-1} , indicating that a new vanadyle compound (**2**) has formed from **1**. **2** was found to be paramagnetic.

We have not so far been able to isolate compound **2** in a pure state: the IR pattern always presented absorptions at 1680 and 1760 cm^{-1} , indicating that muconic anhydride and free di-tert-butylquinone have already been formed; the presence of these side products do not allow for any further characterization of **2**. More work is now in progress to obtain **2** by a different route.

Our results nevertheless indicate that in the oxygenation reaction reported herein, the vanadium species **2**, which reacts with oxygen, contains the $\text{VO}(\text{acac})$ moiety and affords muconic acid anhydride, 2-pyrone and di-tert-butylquinone. Pierpont *et al.* [15] have shown that, in the presence of excess 3,5-di-tert-butylcatechol, $\text{VO}(\text{acac})_2$ is first converted to $\text{V}(\text{SQ})_3$, which could be isolated under N_2 . This species is rapidly transformed into $[\text{VO}(\text{SQ})\text{(TBCat)}]_2$ and quinone in an O_2 atmosphere; further reaction with molecular oxygen gave V_2O_5 and the benzoquinone. On the other hand, Tatsuno *et al.* [23] proposed that the oxygenation of di-tert-butylcatechol in the presence of $\text{VO}(\text{Salen})$ proceeded through $\text{V}(\text{Salen})(\text{DBCatH})_2$. More work is obviously needed before these reactions are fully understood.

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