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Easy Access to Molecular Vanadium Catecholates; Reactivity Towards Oxygen

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Abstract

Complexes **2**–**4**, VO(acac)(L), L = catecholate (Cat) (**2**), L = 3-tert-butylcatecholate (TBCat) (**3**), L = 3,5-di-tert-butylcatecholate (DTBCat) (**4**), were obtained from $V_2O_4(acac)_2$ and the corresponding catechol. Compounds **2** (L = Cat) and **3** (L = TBCat), were found to be inert towards O_2 and to be best formulated as vanadium(V) catecholate species. Complex **4** (L = DTBCat) does react with O_2 to yield 3,5-di-tert-butylquinone and, as a result of oxygen incorporation in the catechol ring, muconic acid anhydride and 2-pyrone.

Introduction

Pyrocatechase is an enzyme capable of catalyzing the oxidative ring cleavage of catechols by dioxygen [1]. Metal catalyzed oxygenations of catechols have received considerable attention in recent years to elucidate the enzymatic mechanism and mimic its reactivity [2], but these reactions still remain poorly understood.

As part of our studies on the behavior of vanadium/catechol [3] and vanadium/quinone [4] systems, we report here an easy access to molecular vanadium catecholates, starting from $V_2O_4(acac)_2$, and their reactivity towards O_2.

The following abbreviations will be used throughout the text: Cat = catecholate dianion; TBCat = 3-tert-butylcatecholate; DTBCat = 3,5-di-tert-butylcatecholate; TCCat = tetrachlorocatecholate; acac = acetylacetonate; SQ = semiquinone; Q = quinone.

Experimental

$V_2O_4(acac)_2$ was prepared according to the literature procedure [5]. 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 Bruker IFS 45, ^1H NMR on a Bruker WH-90 spectrometer. 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).

Preparation of VO(acac)L (L = Cat (2), TBCat (3), DTBCat (4))

In a typical procedure, $DTBCatH_2$ (0.61 g; 2.74 mmol) was added to $V_2O_4(acac)_2$ (0.50 g; 1.37 mmol) in CH_2Cl_2 (100 ml). The brown solution immediately became deep blue. After concentration to 20 ml, the dark blue product, **4**, was filtered, washed with CH_2Cl_2–hexane (1–3) and dried under vacuum (0.97 g; 90%).

The same procedure applied to $TBCatH_2$ or $CatH_2$ yielded 87% and 90% of compounds **3** or **2**, respectively. Analytical data are shown in Table 1.

Oxidation Procedure and Product Analysis

A *c.* 10^{-2} M CH_2Cl_2 solution of **4** was placed under O_2 atmosphere for 60 h at room temperature. The reaction mixture was then chromatographed over SiO_2 with $CHCl_3$ as eluant. The weighed reaction products were characterized by the usual techniques (NMR, IR, melting point).

TABLE 1. Analytical data

Compound	V		C		H	
	calc.	found	calc.	found	calc.	found
$VO_{5.5}C_{11}H_{12}$ (**2**)	18.0	17.1	46.64	46.83	4.24	4.07
$VO_{5.5}C_{15}H_{20}$ (**3**)	15.01	14.75	53.10	53.21	5.93	5.60
$VO_{5.5}C_{19}H_{28}$ (**4**)	12.87	12.46	57.73	57.75	7.38	7.19

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Results and Discussion

The reaction of catechol and its 3-tert-butyl and 3,5-di-tert-butyl derivatives with vanadium(V) taken as $V_2O_4(acac)_2$ is immediate and leads to the isolation of the dark blue complexes 2, 3 and 4. Elemental analysis indicated the formula VO(acac)(L)· $0.5H_2O$, where L = Cat (2), TBCat (3), DTBCat (4).

The IR spectra of 2, 3 and 4 (KBr pellets) showed strong vibrations at 1560 and 1360 cm^{-1} due to the coordinated bidentate acac moiety, and V=O absorption bands at 980 (2), 982 (3), 977 and 986 (4) cm^{-1}. No absorption was detected in the 1600–1800 cm^{-1} region, where the coordinated quinone CO vibrations are expected.

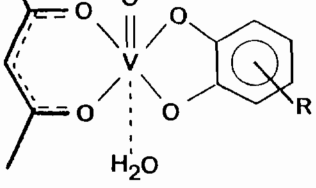
The presence of a half mole of solvated water in compounds 2, 3 and 4 was shown from the IR spectra, elemental analyses and, in the case of 2 and 3, ^{1}H NMR.

VO(acac)(Cat) (2) and VO(acac)(TBCat) (3)

Complexes 2 and 3 can be obtained easily in the presence of air. They are diamagnetic and their proton NMR spectra clearly indicate that the ligand is in the catecholate redox state: thus, the signals measured at 1.20 ppm (CH_3), 6.8 and 6.9 ppm (ring protons) in free $TBCatH_2$ are detected at 1.23 ppm (CH_3), 6.25 and 6.4 ppm (ring protons) in compound 3. The molecular peak is measured in their mass spectra (chemical ionization, NH_3).

All the data for compounds 2 and 3 are consistent with their formulation as molecular vanadium(V)/ catecholate complexes, as illustrated in Scheme 1. The same preferred redox state was already found for VO(acac)(TCCat) (5) [4].

Compounds 2, 3 and 5 are inert towards O_2 both in the solid state and in solution.



R = 3-tert-butyl, 3
R = H, 2

Scheme 1.

VO(acac)($O_2C_6H_2(tBu)_2$) (4)

In marked contrast with its analogues for the less basic catechols, 2, 3 and 5, compound 4 can only be isolated under strict argon atmosphere: diluted CH_2Cl_2 solutions of 4 were found to immediately change in colour from deep blue to green. However, once isolated, it is relatively stable in the solid state even in the presence of air.

The IR spectrum measured for 4 (KBr pellets) is very similar to that of 2 or 3 apart from a medium vibration at 1458 cm^{-1} detected only for 4, in the region assignable to a semiquinone structure of the coordinated catechol [2]. However, due to the complexity of the spectrum in the 1400–1600 cm^{-1} region, this assignment cannot be taken as conclusive. On the other hand, compound 4 was found to be diamagnetic in the solid state, which would rather favor a V(V)–catecholate redox state for the complex.

The FD mass spectrum recorded for 4 is easily interpreted as shown in Scheme 2, starting with trimeric $(VO(acac)(DTBSQ))_3$ in the gas phase.

The data for compound 4 led us to propose its formulation in the solid state as a molecular vanadium(V)/catecholate complex $[VO(acac)(DTBCat)]_3$ with vanadium atoms located at the apices of an equilateral triangle. Catechol may be thought to form the bridges between the vanadyle moieties, the acac ligands being either terminal or bridging (Scheme 3). A similar structure has been proposed by Shilov *et al.* [6] for the complex which forms when catechol is added to alcohol solutions of VCl_2.

An alternative, which takes into account the behaviour observed for 4 in solution (*vide infra*), is to consider a tetrameric structure.

Crystals suitable for X-ray analysis could not be obtained in our hands, which is probably to be attributed to the dissociation of 4 in solution.

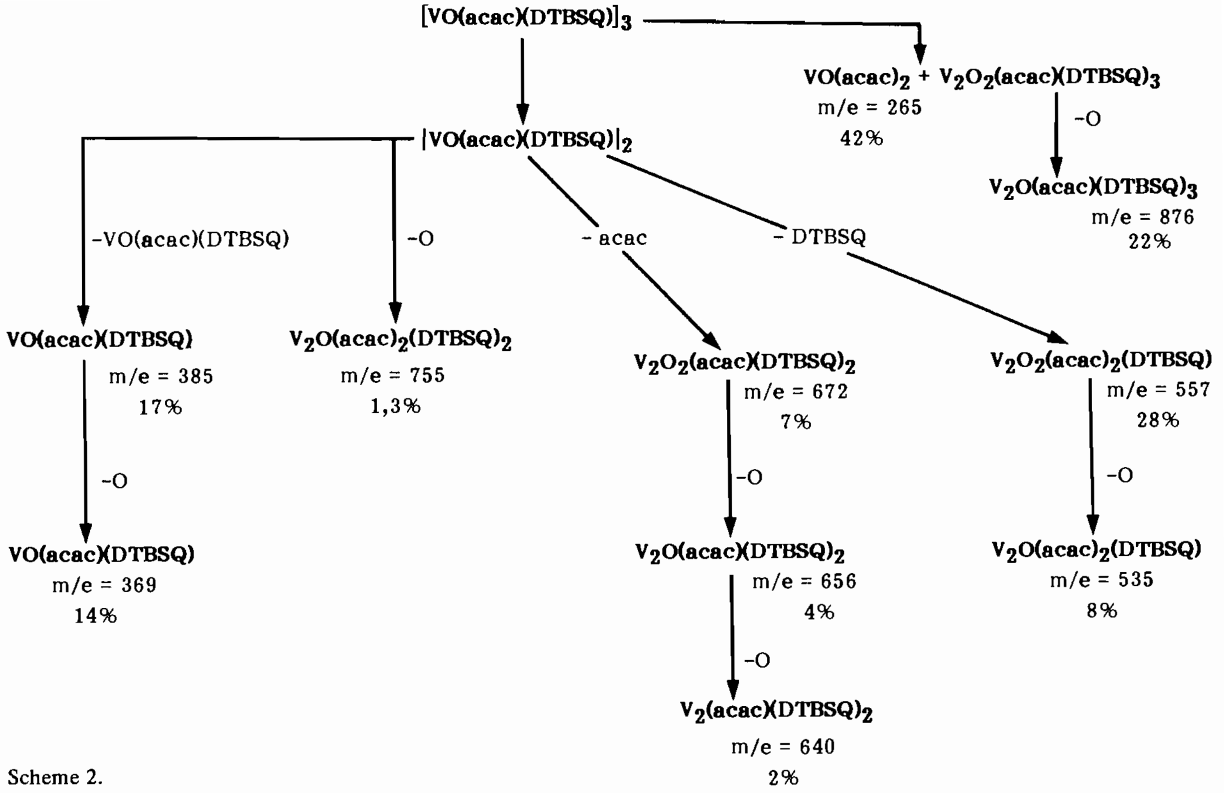
Reactivity Towards Oxygen

IR monitoring of *c.* 10^{-2} M CH_2Cl_2 solutions of the vanadium complexes 2, 3 and 4 showed on one hand that 2 and 3 remain unchanged after 24 h even in the presence of air. On the other hand, IR measured for the solutions of 4 in air indicates the immediate formation of $VO(acac)_2$, which is responsible for the green colour of the solution, and 3,5-di-tert-butylquinone; muconic acid anhydride becomes detectable in the IR after a *c.* 15 min contact with air at room temperature.

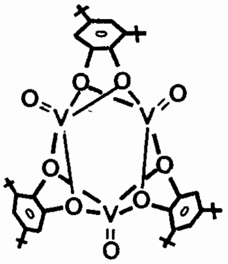
The EPR spectrum measured for 4 in CH_2Cl_2 (*c.* 10^{-3} M) shows the superposition of two signals: the eight line pattern typical for $VO(acac)_2$ (g = 1.97; A = 99 G) [7] and a second signal centered at about a g value of 2.007 which consists of nine lines with a 2.16 G separation, which suggests that the paramagnetic center is on an organic semiquinone radical [8].

Oxidation of catechol by O_2 in the presence of vanadium has been reported by Pierpont *et al.* [9] to occur without oxygen incorporation and to yield exclusively the quinone through the intermediate formation of a dimeric $[VO(Cat)(SQ)]_2$ species, according to eqn. (1)

$$2VO(acac)_2 + 4CatH_2 \longrightarrow [VO(Cat)(SQ)]_2 \xrightarrow{1.5O_2} V_2O_5 + 4Q \quad (1)$$



Scheme 2.



Scheme 3.

The same dimeric [VO(DTBCat)(DTBSQ)]$_2$ can form in our reactions starting from a tetrameric structure for **4**, through intramolecular redox reactions and dissociation (eqn. (2))

$$[\mathrm{VO(acac)(DTBCat)}]_4 \longrightarrow 2\mathrm{VO(acac)}_2 + [\mathrm{VO(DTBCat)(DTBSQ)}]_2 \qquad (2)$$

Its oxidation would be responsible for the formation of the quinone.

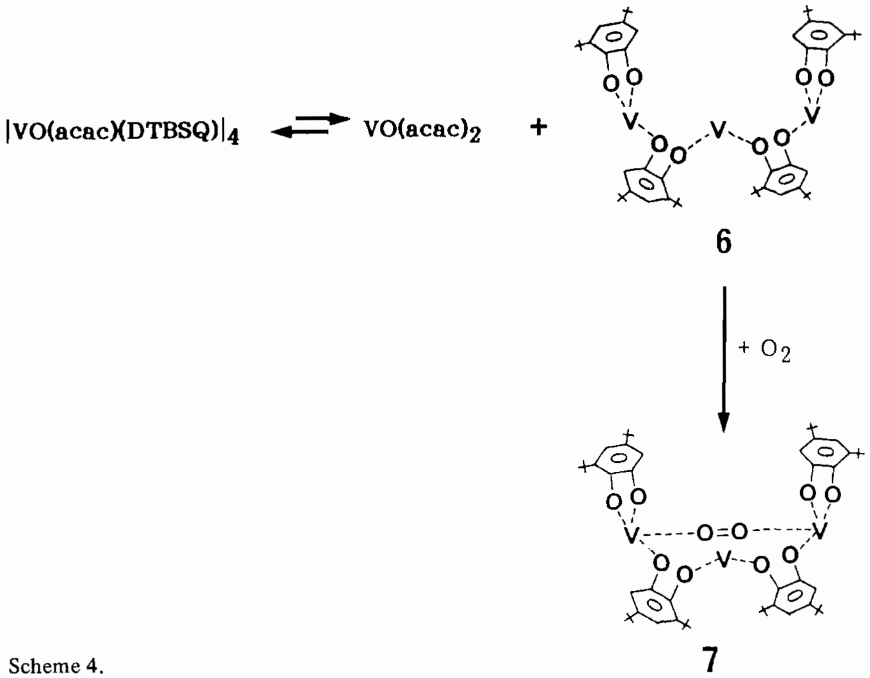
But the oxidation of catechol in compound **4** does not yield exclusively the quinone, as indicated by the IR monitoring experiment.

In a separate large scale experiment, the final products of this oxidation were found to be muconic acid anhydride (45% with respect to the starting catechol), 2-pyrone (6%) and 3,5-di-tert-butyl-*o*-benzoquinone (24%).

This distribution of oxidized products is identical to that found when 3,5-di-tert-butylcatechol is oxidized by O_2 in the presence of catalytic amounts of **5** [4]; it is very close to that observed with (VO(acac)OMe)$_2$ [10] or VO(salen) [11] as a catalyst. The muconic acid anhydride is the main product in these reactions, indicating intra-diol cleavage of the pyrocatechol, with incorporation of one oxygen into the substrate through the Hamilton intermediate [12]. The formation of 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 [13]. It is noteworthy that pyrocatechase itself allows for the incorporation of both oxygen atoms of molecular O_2 into the catechol ring through a dioxetan intermediate [14].

Incorporation of oxygen in the catechol ring obviously goes through a different intermediate from [VO(DTBCat)(DTBSQ)]$_2$. Tatsuno *et al.* [15] proposed as an intermediate in the oxidative ring cleavage of DTBCatH$_2$ with dioxygen catalyzed by VO(salen), the monomeric vanadium(IV) catecholate VO(salen)(DTBCatH)$_2$. Such an intermediate seems rather unlikely in our reactions where the VO moiety is maintained and the two OH functions on the catechol deprotonated.

As a reasonable hypothesis very close to that of Shilov *et al.* [6] in the N_2 activation by vanadium catecholates, we propose that **4** in solution dissociates



(3)

Scheme 4.

not only according to eqn. (2) but also according to eqn. (3) to yield $VO(acac)_2$ and the trimeric species **6** illustrated in Scheme 4, with two vanadium IV atoms at the end of an open chain. Complex **6** is most likely to react rapidly with dioxygen to form **7**, which could be the intermediate responsible for incorporation of oxygen in the catechol ring.

Conclusions

The reaction of $V_2O_4(acac)_2$ with catechol and its derivatives offers a new and very easy access to the molecular vanadium catecholates VO(acac)L.

The reactivity towards O_2 of the isolated complexes was found to depend on the substituents on the catechol ring.

With the less basic catechols (pyrocatechol, 3-tert-butylcatechol, tetrachlorocatechol), the molecular vanadium(V) catecholates **2** (L = Cat), **3** (L = TBCat) or **5** (L = TCCat) are obtained; they are unreactive or poorly reactive towards molecular O_2.

Compound **4**, which is obtained with the more basic 3,5-di-tert-butylcatechol, does react with oxygen in solution to yield not only quinone but also, as a result of oxygen incorporation in the catechol ring, muconic acid anhydride and 2-pyrone; this oxygenation is very similar to the pyrocatechase-catalyzed one [1].

Such an oxidation of catechol in the presence of vanadium is in full agreement with the results of Tatsuno *et al.* [11, 15, 16] and Fenton *et al.* [10], but differs from those of Pierpont *et al.* [9] where the only oxidation product of catechol is 3,5-di-tert-butylquinone.

Although further studies are necessary to clear up these reactions, our results show that, in the reaction with O_2, vanadium is capable of discrimination among various catechols depending on the substituents on the ring: only the more basic catechols, which are susceptible of favoring a vanadium(IV)–semiquinone redox state over the vanadium(V)–catecholate state, undergo incorporation of oxygen in the ring to give muconic acid anhydride.

Acknowledgements

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