

## High Catalytic Activity of Vanadium(V) Oxo-polymers for Oxidative Cleavage of Catechol

Yuzo Nishida\* and Hideki Kikuchi

Department of Chemistry, Faculty of Science, Yamagata University, Yamagata 990, Japan

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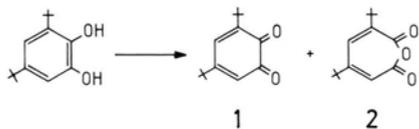
Vanadium(V) Oxo-Polymers, Catalytic Activity, Oxidative Cleavage of Catechol

Some vanadium(V) oxo-polymers such as *cis*-V<sub>2</sub>W<sub>4</sub>O<sub>19</sub><sup>4-</sup> and V<sub>10</sub>O<sub>28</sub><sup>6-</sup> exhibit high catalytic activity for the oxidative cleavage of 3,5-di-*t*-butylcatechol. A chelated species of catechol to two vanadium atoms has been assumed as an active intermediate based on the spectroscopic results.

### 1. Introduction

A variety of metal complexes have been reported that effect the oxidative cleavage of catechol [1–10]. These systems serve as models for the reaction catalyzed by catechol 1,2-dioxygenase and protocatechuate 3,4-dioxygenase, enzymes in which the proposed mechanism of oxygen incorporation involves substrate activation by the active site of ferric center [11].

In 1982, Otsuka *et al.* [6] have found that some oxovanadium(IV) complexes, such as [VO(acac)<sub>2</sub>] react with 3,5-di-*t*-butylcatechol to give the corresponding acid anhydride **2** in moderate yield (quinone **1** was also produced in this reaction),



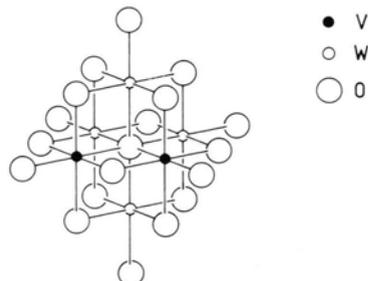
where H(acac) represents acetylacetonate. This has been considered to be one of the model reactions for catechol 1,2-dioxygenase, however, a detailed reaction mechanism catalyzed by oxovanadium(IV) complexes is not known at present. We have observed that some vanadium(V) oxo-polymers exhibit high catalytic activity for the formation of **2**, and in this article propose an active intermediate for this catalytic reaction.

\* Reprint requests to Dr. Y. Nishida.

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### 2. Materials and Methods

The vanadium(V) oxo-polymers used in this study were prepared according to published methods. All compounds were obtained as tetra(*n*-butyl)-ammonium salts; (a) W<sub>6</sub>O<sub>19</sub><sup>2-</sup> [12, 13], (b) VW<sub>5</sub>O<sub>19</sub><sup>3-</sup> [12], (c) *cis*-V<sub>2</sub>W<sub>4</sub>O<sub>19</sub><sup>4-</sup> [12], (d) 1,4,9-[PV<sub>3</sub>W<sub>9</sub>O<sub>40</sub>]<sup>6-</sup> [14], and (e) V<sub>10</sub>O<sub>28</sub><sup>6-</sup> [15], the structure of (c) being illustrated below.



In typical runs, the metal complex ( $1 \times 10^{-5}$  mol) and catechol (233 mg,  $1 \times 10^{-3}$  mol) were dissolved in 50 ml acetonitrile and the resulting solution was left to stand for 3 days. The acetonitrile was distilled off and the residue was eluted in chloroform in silica-gel column chromatography [6], and the yields of **1** and **2** were determined by spectrophotometry.

### 3. Results and Discussion

Interest in the speciation and reactivity of vanadium has been stimulated by reports of its activity in a number of biological systems. Many species of tunicates (*Ascidia*) concentrate free vanadium from sea water, although neither the mode of extraction nor the metabolic role of the element has been established [16, 17]. Vanadium has been shown to be an essential nutrient for higher animals. Cantley *et al.* [18] have established its endogenous presence in mammalian muscle tissue at levels sufficient to inhibit the sodium and potassium stimulated adenosine triphosphatase [(Na,K)-ATPase]. This specific inhib-

Table. Yield of **1** and **2** (%).

Complex	<b>1</b>	<b>2</b>
W <sub>6</sub> O <sub>19</sub> <sup>2-</sup>	0	0
VW <sub>5</sub> O <sub>19</sub> <sup>3-</sup>	0	0
<i>cis</i> -V <sub>2</sub> W <sub>4</sub> O <sub>19</sub> <sup>4-</sup>	5	15
1,4,9-[PV <sub>3</sub> W <sub>9</sub> O <sub>40</sub> ] <sup>6-</sup>	10	20
V <sub>10</sub> O <sub>28</sub> <sup>6-</sup>	19	39
[VO(acac) <sub>2</sub> ]	17	32



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ition can be removed by addition of catecholamine and catechol.

Previous work has revealed that in the reaction of vanadate and catechol, a blue solution forms only under conditions of high vanadate concentration, and this blue color has been assumed to be characteristic of the V(IV) chromophore [19]. In this study we have observed that oxo-polymeric vanadium(V) compounds containing more than two V(V) atoms react with catechol to yield the highly colored solution, whereas no color change was observed in the cases of  $W_6O_{19}^{2-}$  and  $VW_5O_{19}^{3-}$ . As a representative example, the absorption spectra of the reaction mixture of *cis*- $V_2W_4O_{19}^{4-}$  and catechol are shown in Fig. 1. New absorption bands appeared at 880 and

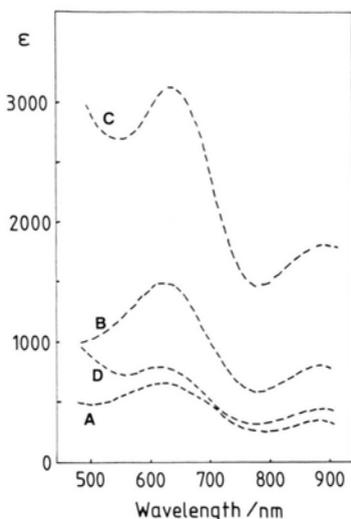
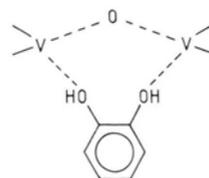


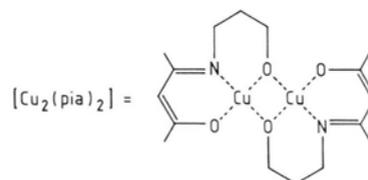
Fig. 1. Absorption spectra of the mixture of *cis*- $V_2W_4O_{19}^{4-}$  ( $10^{-5}$  mol) and catechol ( $10^{-3}$  mol) in acetonitrile. A: after 2 hours; B: after 5 hours; C: after 29 hours; D: after 53 hours.

610 nm, and disappeared after 3 days. Based on the above facts, we propose that the color change observed in some cases can be attributed to the formation of chelated species of catechol to two vanadium atoms, as illustrated below. We could not detect any ESR signals for these colored solutions, although



some mixed-valence V(V)–V(IV) oxo-polymers exhibit ESR signals at ambient temperature [20].

As shown in the table, only the compounds which give the highly colored solutions in the reaction of catechol show high catalytic activity for the formation of **2**. This clearly indicates that the catalytic activity of the compounds is closely related with the chelation of catechol to the two V(V) atoms, as suggested above. We already showed that some binuclear metal complexes react with catechols specifically [21]. However, it was found that these binuclear copper(II) complexes such as  $[Cu_2(pia)_2]$ , polynuclear iron(III) and manganese(III) such as  $[M_3O(CH_3COO)_6(py)_3]^+$  ((py) = pyridine, M = Fe(III) and Mn(III)) give only **1** in the reaction of 3,5-di-*t*-butylcatechol. These facts suggest that vanadium(V) is quite unique in its reaction with catechol.



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