

## THE SYNTHESIS OF OXOBIS (2,4-PENTANODIONATO)VANADIUM (IV) REVISITED\*

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The synthesis of VO (acac)<sub>2</sub> from V<sub>2</sub>O<sub>5</sub> or VOSO<sub>4</sub> must be performed in anaerobic conditions. In contact with air impure products are obtained. A pH range of precipitation lower than previously reported is recommended.

## I – INTRODUCTION

Oxobis (2,4-pentanedionato)vanadium (IV), VO (acac)<sub>2</sub>, is known since 1876<sup>1</sup>. Its five coordinate structure, rather unusual in the early years, its ability to change to a six-coordinate complex by adding a further ligand, and its formulation as an oxycation, stable in aqueous solution, were controversial features which contributed to the development of new theoretical explanations<sup>2, 3</sup>.

VO (acac)<sub>2</sub> continues playing an important role in coordination chemistry until nowadays. Extensive investigation about its vibrational, electronic and ESR spectra in a variety of media has been performed<sup>4-11</sup>. It has been used as a reference acceptor for several bases in solution<sup>4, 12-17</sup> and in solid state<sup>18-20</sup>. It is also a widely used ESR spin probe<sup>11</sup>, an efficient catalyst for oxygen-transfer reactions<sup>4, 21-23</sup> and a starting material for mixed valence compounds<sup>22, 24</sup> and for the production of oxide films in electronic industry<sup>25</sup>.

In several attempts to synthesize VO (acac)<sub>2</sub> by reported procedures, from V<sub>2</sub>O<sub>5</sub><sup>26</sup> or VOSO<sub>4</sub><sup>27</sup>, we were not able to obtain samples suitable for spectrophotometric work. The complex precipitates easily but not in a pure form. Purification has been achieved by recrystallization from chloroform<sup>16, 26, 28</sup>, benzene<sup>6, 16</sup>, toluene<sup>11</sup>, acetone<sup>6, 21</sup> and other solvents<sup>28</sup> or by sublimation under reduced pressure. In the last case, a black residue was observed and a brown impurity sublimated along with the compound.<sup>29</sup>

VO (acac)<sub>2</sub> is commercially available, but there are reports of the bottled material leaving a black, gummy residue upon dissolution in organic solvents<sup>21</sup>.

This paper describes the problems we have encountered in the synthesis of VO (acac)<sub>2</sub> and emphasizes some essential precautions which allow the formation of pure samples, so that further purification is unnecessary.

## EXPERIMENTAL

## Materials

V<sub>2</sub>O<sub>5</sub> 99.5% was obtained from Riedel-de-Haen and VOSO<sub>4</sub>·2H<sub>2</sub>O from Fisher Scientific Co. All other chemicals were of analytical quality. 2, 4-pentanedione, Hacac, from Merck, was freshly distilled.

## Synthesis by Procedure A

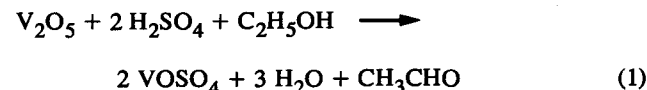
A mixture containing 5.0 g (27 mmol) V<sub>2</sub>O<sub>5</sub>, 13.0 mL H<sub>2</sub>O, 9.0 mL 96% (by weight) H<sub>2</sub>SO<sub>4</sub> (160 mmol) and 25.0 mL (430 mmol) ethanol was boiled for 30 min and filtered. The cold filtrate was treated with 13 mL (126 mmol) of Hacac. An aqueous Na<sub>2</sub>CO<sub>3</sub> solution (14% by weight) was added in small increments with vigorous stirring, the pH being measured after each addition. The resulting solid was filtered off, washed with cold water until negative test with barium and dried over P<sub>4</sub>O<sub>10</sub>.

## Synthesis by Procedure B

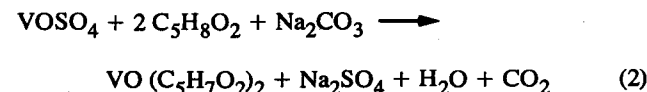
10.8 g (54 mmol) VOSO<sub>4</sub>·2H<sub>2</sub>O were dissolved in 80 mL 0.05 M H<sub>2</sub>SO<sub>4</sub> (4 mmol) in a nitrogen stream. 13.0 mL (126 mmol) Hacac were added, followed by ethanol just enough for homogenization (ca. 4 mL). The mixture was treated with Na<sub>2</sub>CO<sub>3</sub> solution as in procedure A, except that all solution and liquid reagents were pre-saturated with nitrogen.

## RESULTS AND DISCUSSION

The synthesis of VO (acac)<sub>2</sub> by the method of Rowe and Jones<sup>26</sup>, extensively used until nowadays, is based on the one-electron reduction of vanadium (V) by ethanol



followed by



Procedure A was essentially that of Rowe and Jones. The synthesis was carried out by this procedure in open vessel. Precipitation of the complex occurred at much lower pH values than the reported range of 3.5 to 5.5<sup>26, 30</sup>. Four crops of product were collected (Table 1, synthesis 1). At pH 2.2, 83% total yield was achieved. The formation of the fourth crop of VO (acac)<sub>2</sub> was accompanied by a steep increase in pH, without appreciably changing the yield.

The product was however contaminated by green colloidal particles insoluble in 1,2-dichloroethane, making it unsuitable

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for spectrophotometric work. The turbidity of mixtures with this solvent decreased for the successive crops, probably as a consequence of lowering concentration of mother liquor and reducing time of manipulation. Recrystallizations from chloroform were unsuccessful, the resulting solids being green instead of the characteristic blue-green VO(acac)<sub>2</sub>.

A difficulty in synthesis 1 was encountered during reaction (1). As the reaction proceeds, the initial slurry of V<sub>2</sub>O<sub>5</sub> darkens, becomes green and finally turns blue<sup>26</sup>. These color changes occur gradually, so that a criterion for distinguishing the "correct" blue tone is difficult to establish. After 30 min of vigorous boiling, the reaction was interrupted, but a small amount of V<sub>2</sub>O<sub>5</sub> remained unreacted.

The synthesis was therefore repeated, the reacting mixture being boiled under reflux, as in ref. 30. After about 5 hours, the solution was still dark green. By adding Na<sub>2</sub>CO<sub>3</sub> to this solution, appreciable quantities of a gummy dark material were formed, even before the beginning of precipitation of VO(acac)<sub>2</sub> and the synthesis was interrupted. The i.r. spectrum in KBr pellet shows strong and broad bands coincident with bands described<sup>31</sup> for uncoordinated Hacac (observed values 1630; 1420; 1240 cm<sup>-1</sup>), acetaldehyde (obsd. values 2850; 1700; 1440; 1360; 1110 cm<sup>-1</sup>) and the trimerized acetaldehyde, paraldehyde (obsd. values 2930; 1460; 1385; 1180; 1110 cm<sup>-1</sup>). Strong bands attributed to VO(acac)<sub>2</sub> (e.g.  $\nu_{\text{V}=\text{O}}$  at 995 cm<sup>-1</sup>)<sup>32</sup> and VO<sub>2</sub><sup>+</sup> group (ca. 915 and 890 cm<sup>-1</sup>)<sup>22</sup> were not observed. The acetaldehyde produced by reaction (1) was condensed (reported B.P. 21°C / 760 mmHg)<sup>31</sup>, originating polymeric species.

A synthesis by Procedure A was then performed under nitrogen atmosphere. V<sub>2</sub>O<sub>5</sub> reacted completely after 30 min. boiling. The final product (Table 1, synthesis 2) dissolved completely in 1,2-dichloroethane. The following analytical results were obtained: C, 45.4; H, 5.3; V, 19.2% (calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>5</sub>V: C, 45.30; H, 5.32; V, 19.21%).

Figure 1 shows typical pH variations during the addition of Na<sub>2</sub>CO<sub>3</sub> solution to the mixture obtained after reaction (1), in procedure A. This is a mixed-solvent solution with low water content (ca. 20 to 30% by weight, depending on losses of

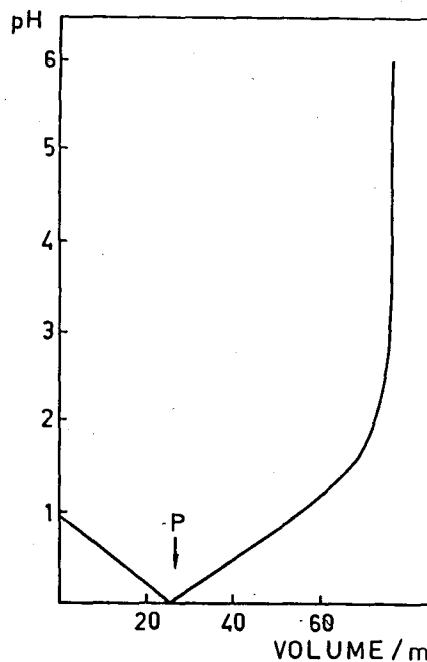


FIG. 1 - Effect of addition of Na<sub>2</sub>CO<sub>3</sub> solution on pH of reacting media (synthetic procedure A). P denotes the beginning of precipitation of VO(acac)<sub>2</sub>.

ethanol during boiling period) and H<sub>2</sub>SO<sub>4</sub> content in the range 16-22% by weight. The approximate molar ratio H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O is 1:8. Addition of an aqueous solution with 86% by weight H<sub>2</sub>O causes water-enrichment of the media, increasing the extent of dissociation of H<sub>2</sub>SO<sub>4</sub>. The opposite effects of enhanced dissociation and consumption by neutralization can be responsible for the observed curve shape in Figure 1.

Procedure B is based only on reaction (2), so that a high content of H<sub>2</sub>SO<sub>4</sub> is unnecessary. Contrarily to Procedure A, precipitation started when Hacac was added and pH readings increased continuously upon addition of Na<sub>2</sub>CO<sub>3</sub> solution. The pH range of precipitation is given in Table 1 (synthesis 3). Analytical results were: C, 45.3; H, 5.1; V, 19.1%.

In both cases where atmospheric oxygen was excluded (syntheses 2 and 3), the complex precipitated in pure form. Further purification was unnecessary.

Solutions of VO(acac)<sub>2</sub> are sensitive to oxygen, particularly in alcoholic media<sup>1, 4, 8, 10, 14, 33</sup>. The oxidation of vanadium (IV), d<sup>1</sup>, to vanadium (V), d<sup>0</sup>, is evidenced by the loss of d-d bands in the visible spectra, as the solution color gradually changes from blue to green to yellow to orange<sup>34</sup>. Physico-chemical measurements with solutions of VO(acac)<sub>2</sub> have been done immediately after their preparation<sup>16, 21, 28</sup> or under nitrogen<sup>10</sup> or argon<sup>11</sup> atmospheres. Exclusion of oxygen is also necessary in the synthesis of the compound. Flushing with an inert gas also helps removing acetaldehyde which is a source of contamination of the product.

The complex precipitated in good yields at pH values lower than 3. Further addition of Na<sub>2</sub>CO<sub>3</sub> caused a steep increase in pH. The solution lost its characteristic blue color, turning brown. The nature of the species present in vanadium (IV) solution at pH higher than 4 is still controversial. Polymeric species, such as (VO)<sub>4</sub>(OH)<sub>10</sub><sup>2-</sup> may be formed<sup>4</sup>, being responsible for the brown color. These solutions are increasingly susceptible to air-oxidation with raising pH<sup>4</sup>. In general, oxovanadium (IV) ions are stable for several months.

Table 1 - Results from the syntheses of VO(acac)<sub>2</sub>

| Synthesis and crop | Total volume of Na <sub>2</sub> CO <sub>3</sub> (ml) | pH range of precipitation | Color of filtrate | % yield |
|--------------------|--|---------------------------|-------------------|---------|
| 1. 1               | 50   | 0.2 - 0.6                 | blue              | 51      |
| 2                  | 70   | 1.1 - 1.4                 | blue              | 20      |
| 3                  | 81   | 1.8 - 2.2                 | green             | 12      |
| 4                  | 85 <sup>a</sup>                                      | 2.7 - 5.8                 | brown             | 5       |
| 2. 1               | 97 <sup>a</sup>                                      | 0.2 - 2.7                 | blue              | 77      |
| 3. 1               | 28 <sup>b</sup>                                      | 0.7 - 2.2                 | blue              | 63      |

<sup>a</sup>, <sup>b</sup>Stoichiometric amounts for neutralizing H<sub>2</sub>SO<sub>4</sub> = <sup>a</sup>70, <sup>b</sup>3 mL and Hacac (necessary for complex formation) = <sup>a</sup>, <sup>b</sup>36 mL

in concentrated strong acids, but they are rapidly oxidized above pH 2.5, especially in alkaline solutions<sup>1, 22</sup>. Synthetic procedures for VO(acac)<sub>2</sub> with adjustment of pH to 5<sup>33</sup> and 6<sup>35</sup> are thus criticized.

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