lying along the trigonal axis.  Other stoichiometrically similar complexes which are likewise trigonal bipyramidal include $TiBr_3 \cdot 2N(CH_3)_3$[4] and $VCl_3 \cdot 2P(C_2H_5)_3$.[5,6]  Assignments for both the electronic spectra[7-9] and the V—N and V—Cl stretching frequencies[9,10] have been given.  The magnetic moment of the complex is 2.69 B.M. at 291°K and is almost independent of temperature.[9]  The compound sublimes at 100°.

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## 37. VANADYL(IV) ACETATE, VO(CH₃CO₂)₂
### [Bis(acetato)oxovanadium(IV)]

$$V_2O_5 + xs(CH_3CO)_2O \rightarrow VO(CH_3CO_2)_2$$
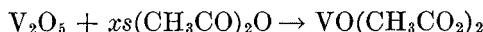
**Submitted by RAM CHAND PAUL,\* SAROJ BHATIA,\* and ASHOK KUMAR\***
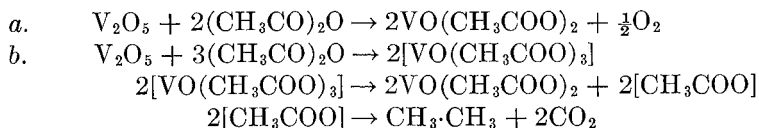**Checked by J. T. MAGUE† and C. W. WESTON†**

A method for the preparation of vanadyl(IV) acetate in non-aqueous media, as reported earlier,[1] involves solvolysis of vanadyl(V) chloride in acetic anhydride.  However, a quicker

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and more convenient method for its preparation has been developed by using vanadium(V) oxide in place of vanadyl(V) chloride. The simplicity of the procedure lies in the fact that vanadium(V) oxide need not first be converted to vanadyl(V) chloride which is the starting material for the earlier method. The present method is, therefore, economical in respect to both time and cost and gives a quantitative yield of the product.

The process whereby vanadium(V) is reduced to vanadium(IV) has not been established with certainty, but it takes place spontaneously, without addition of a reducing agent.[2] The following two postulates could be made[3] to account for this:

$a.$    $V_2O_5 + 2(CH_3CO)_2O \rightarrow 2VO(CH_3COO)_2 + \frac{1}{2}O_2$

$b.$    $V_2O_5 + 3(CH_3CO)_2O \rightarrow 2[VO(CH_3COO)_3]$

$\qquad 2[VO(CH_3COO)_3] \rightarrow 2VO(CH_3COO)_2 + 2[CH_3COO]$

$\qquad\qquad 2[CH_3COO] \rightarrow CH_3 \cdot CH_3 + 2CO_2$

Postulate $a$ may be ruled out since evolution of oxygen could not be detected while the reaction was in progress. Postulate $b$ seems more likely since the evolution of carbon dioxide is indicated.

### Procedure

Vanadium(V) oxide (18.2 g.) is added to acetic anhydride (50 ml.) in a round-bottomed flask fitted with a reflux condenser and a silica gel guard tube. The amount of acetic anhydride added should be in excess of that required theoretically for the reaction. This prevents the solid fluffy product from charring during refluxing of the contents. The contents are heated under reflux using an oil bath or an electric mantle maintained at $140 \pm 5°$. The start of the reaction is indicated by a change in the color from the reddish brown of vanadium(V) oxide to light gray. During the reaction, the contents may need to be shaken occasionally to prevent caking of vanadium(V) oxide. The reaction is complete in an hour as indicated by the separa-

tion of a product which does not change its gray color even on prolonged refluxing. The contents are cooled and filtered through a sintered-glass funnel. The solid product is then transferred to a 200-ml. round-bottomed flask containing carbon tetrachloride and the mixture refluxed for 10–15 minutes to remove traces of acetic anhydride from the compound. The product is again filtered, and washed with carbon tetrachloride. After it has been allowed to stand in the air for 2 hours, it is dried in vacuum at room temperature for about an hour. The excess acetic anhydride may be recovered by distillation of the filtrate. Yield is 35 g. (95%). *Anal.* Calcd. for $VO(CH_3CO_2)_2$: V, 27.57; C, 25.94; H, 3.29. Found: V, 27.3; C, 25.9; H, 3.20. Vanadium was determined by ignition to $V_2O_5$ and confirmed by thermogravimetric analysis.

### Properties

The compound is a gray, nonhygroscopic, odorless powder. It does not melt but decomposes on heating. Its pyrolysis curve reveals that it is stable up to 214°. It loses weight between 214 and 388° and attains a constant weight at 388°, leaving a residue of vanadium(V) oxide. It is insoluble in common organic solvents, e.g., carbon tetrachloride, benzene, chloroform, and cyclohexane. It does not form any addition compounds with tertiary organic bases like pyridine, picolines, etc. Its infrared absorption spectrum (Nujol mull) has the following characteristic bands: 2845(s), 1495(s), 1450(s), 1065(w), 1040(m), 900(s), and 665(s).

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