Alkoxides of Vanadium, I

# Synthesis of Trialkylorthovanadates by Alcohol Interchange Technique

By R. K. MITTAL and R. C. MEHROTRA

### Summary

A number of alkoxides of vanadium have been prepared more conveniently in higher yields by alcohol interchange technique.

# Inhaltsübersicht

Eine Reihe von Vanadin(V)-alkoxiden wurde in höheren Ausbeuten als bisher durch Umesterung hergestellt.

Vanadic acid esters were first prepared by PRANDTL and HESS<sup>1</sup>) in 1913 by refluxing vanadium pentoxide and the alcohol for 6-8 hours. In 1958, FUNK and collaborators<sup>2</sup>) and also VORONKOV and co-workers<sup>3</sup>) prepared trialkylvanadates by adding vanadium oxytrichloride to dry alcohol and then passing a stream of dry ammonia. More recently, ORLOV and VORONKOV<sup>4</sup>) prepared a number of trialkylorthovanadates by azeotropic removal of water from a reaction mixture of one mole of vanadium pentoxide and six moles of alcohol in benzene and refluxing for eight to twelve hours. The yield of the compounds prepared was only 10-32% by this method.

BRADLEY, MEHROTRA and WARDLAW<sup>5</sup>)<sup>6</sup>) and MEHROTRA and co-workers<sup>7-9</sup>) have employed the technique of alcohol interchange successfully in the preparation of higher alk-

<sup>1</sup>) W. PRANDTL and L. HESS, Z. anorg. Chem. 82, 103 (1913).

<sup>2</sup>) H. FUNK and W. WEISS, Z. anorg. allg. Chem. 296, 36 (1958).

<sup>3</sup>) M. G. VORONKOV and Yu. I. SKORIK, ИЗВЕСТИЯ АКАДЕМИИ НАУК СССР, ОТДЕЛЕНИЕ ХИМИЧЕСКИХ НАУК [Bull. Acad. Sci. URSS, Cl. Sci. chim.] 1958, 503.

<sup>4</sup>) N. F. ORLOV and M. G. VORONKOV, Известйя Академай Наук СССР, Отделение Химических Наук [Bull. Acad. Sci. URSS, Cl. Sci. chim.] 1959, 933.

<sup>5</sup>) D. C. BRADLEY, R. C. MEHROTRA and W. WARDLAW, J. chem. Soc. [London] 1952, 2027, 4204, 5020; 1953, 2025, 4204.

<sup>6</sup>) D. C. BRADLEV, R. C. MEHROTRA and W. WARDLAW, J. chem. Soc. [London] 1953, 1634.

<sup>7</sup>) I. D. VARMA and R. C. MEHROTRA, J. chem. Soc. [London] 1960, 2966.

8) R. C. MEHROTRA and G. SRIVASTAVA, J. Indian chem. Soc. 38, 1 (1961).

<sup>9</sup>) R. C. MEHROTRA, J. Indian chem. Soc. 30, 585 (1953) and 31, 55 (1954).

oxides of titanium<sup>5</sup>), zirconium<sup>5</sup>), boron<sup>8</sup>), aluminium<sup>9</sup>) and germanium<sup>10</sup>) and the same has now been extended to the alkyl orthoxanadates.

Ethylorthovanadate is treated with the required alcohol (slight excess) in the presence of benzene and the ethanol liberated in the reaction:

$$VO(OEt)_3 + 3 ROH \rightarrow VO(OR)_3 + 3 EtOH$$

is fractionated out azeotropically with benzene. The estimation of ethanol in the azeotrope by a simple oxidimetric process<sup>11</sup>) gives a ready check of the progress of the reaction. Methyl, isopropyl, tertiary butyl, secondary and tertiary amyl, secondary and tertiary hexyl and cyclohexyl orthovanadates have been prepared in about 70% yield. Using ethyl orthovanadate as the starting material, the chief advantages of azeotropic distillation technique in the preparation of higher alkoxides are: 1. the ethanol produced is continuously removed pushing the reaction to completion, 2. only slight excess of the higher alcohol is required which is of great importance in this specific case due to the reductive properties of alcohols towards pentavalent vanadium, 3. side reactions like formation of alkyl chloride and water are avoided; these side reactions lower the yields considerably in the case of branched alcohol, 4. the oxidation of the alcohol is much less by ethyl vanadate compared to that with vanadium oxytrichloride or vanadium pentoxide; this appears to be in general conformity with the lower oxidising capacity of the same oxidation state of a particular element when it is linked covalently.

The identity of the compounds has been established by estimation of vanadium (total as well as pentavalent vanadium separately) and by molecular weight measurements in benzene. The trialkylorthovanadates have been found to be monomeric. In this property, these compounds resemble the derivatives of titanium which also have been shown to be monomeric except in the case of ethylorthotitanate (average molecular complexity  $1.4^{5}$ )). The pentaethoxides of niobium and tantalum<sup>12</sup>) have been shown to be dimeric in benzene which is in line with similar derivatives of titanium<sup>5</sup>), zirconium<sup>5</sup>), and hafnium<sup>6</sup>) in which cases also the average molecular complexities observed are 1.4, 3.4 and 3.4 respectively.

## Experimental

All glass apparatus with standard interchangeable joints was used throughout the work, and special care was taken to exclude moisture.

Material. Vanadium oxytrichloride was prepared by refluxing vanadium pentoxide with thionyl chloride<sup>2</sup>) (Both B. D. H., L. R.).

<sup>10)</sup> D. C. BRADLEY, L. J. KAY and W. WARDLAW, J. chem. Soc. [London] 1956, 4927.

<sup>&</sup>lt;sup>11</sup>) D. C. BRADLEY and W. WARDLAW, J. chem. Soc. [London] 1950, 3450.

<sup>&</sup>lt;sup>12</sup>) D. C. BRADLEY, B. N. CHAKRAVARTI and W. WARDLAW, J. chem. Soc. [London] **1956**, 4439.

			Formula weight	Alkoxid	es of V Analvsis	anadiun	1 Etha	lou			
Ethylortho- Alcohol added and yie	Alcohol added and yie	and yie	ld of		ciequant. Total			 Cale,	Physical pron and R P	Molecula	ur weight
taken g. $g$ , the production $g$ , $(\%_0)$	g. the produc (%)	the produc (%)	<del>د</del> .	V+5 (%)	$\stackrel{(\%)}{\Lambda}$	Calc. (%)	Lib.	for 3 moles.g	M. P.	Found	Calcu- lated
2.02 Dimethyl-n- VO(C <sub>6</sub> H <sub>13</sub> O <sup>1</sup> ) propyl carbinol 2.59 g. 70 4.0	Dimethyl-n- VO(C <sub>6</sub> H <sub>13</sub> O <sup>1</sup> ) propyl carbinol 2.59 g. 70 4.0	V0(C <sub>6</sub> H <sub>13</sub> O <sup>†</sup> ) 2.59 g. 70		13.65	13.65	13.75	1,34	1.38	Light yellow liquid, 122°C/1.5 mm.	375.0	370,44
$\begin{array}{c ccc} 3.717 & Cyclohexanol & VO(C_6H_{11}O)_3 \\ 5.46 & 6.4 \text{ g. } 95 \end{array}$	Cyclohexanol $VO(C_6H_{11}O)_3$ 5.46 6.4 g. 95	$VO(C_6H_{11}O)_3$ 6.4 g. 95		14.09	13.95	13.98	2.54	2.54	Colourless solid, M. P. 80°C	368.5	364.39
3.168 Secondaryamyl VO(C <sub>5</sub> H <sub>11</sub> O <sup>8</sup> ) <sub>2</sub> alcohol 3.5 g. 70 5.5	Secondaryamyl VO(C <sub>5</sub> H <sub>11</sub> O <sup>8</sup> ) <sub>2</sub> alcohol 3.5 g. 70 5.5	$VO(C_5H_{11}O^8)_8$ 3.5 g. 70	<u>.</u>	15.54	15.45	15.51	2,10	2.11	Light yellow liquid, 118°C/1.5 mm.	317.0	328.36
2.778 Tertiaryamyl $VO(C_5H_{11}O^4)_3$ alcohol $3.0 \text{ g}.66$ 4.8	Tertiaryamyl $VO(C_5H_{11}O^4)_3$ alcohol $3.0 \text{ g}. 66$ $4.8$	VO(C <sub>5</sub> H <sub>11</sub> O <sup>t</sup> ) <sub>3</sub> 3.0 g. 66		15.55	15.46	15.51	2.00	1.90	Light yellow liquid, 118°C/2.5 mm.	316.0	328.3(
9.294 Tertiarybutyl VO(C <sub>4</sub> H <sub>9</sub> O <sup>1</sup> ) <sub>3</sub> , alcohol 9.5 g. 72 14.0	Tertiarybutyl VO(C4H_0 <sup>01</sup> ) <sub>3</sub> , alcohol 9.5 g. 72 14.0	VO(C <sub>4</sub> H <sub>9</sub> O <sup>t</sup> ) <sub>3</sub> , 9.5 g. 72		17.65	17.70	17.79	6.31	6.35	Colourless crystalline low melting solid, 118°C/12 mm.	289.5	286.28
14.100 Isopropylateohol VO(C <sub>3</sub> H <sub>7</sub> O <sup>1</sup> ) <sub>3</sub> ,   20.0 15.5 g. 90	Isopropylalcohol $VO(C_3H_7O^{1})_3$ , 20.0 15.5 g. 90	V0(C <sub>3</sub> H,O <sup>1</sup> ) <sub>3</sub> , 15.5 g. 90		20.60	20.75	20.86	}	ļ	Yellow liquid 102°C/9 mm.	240.5	244.2(
3.859 Methy1-alcohol VO(OCH <sub>s</sub> ) <sub>3</sub> , 15.0 1.52 g. 50 (sublimed)	$ \begin{array}{ c c c c } \mbox{Methyl-alcohol} & \mbox{VO(OCH_s)_3,} \\ \mbox{15.0} & \mbox{1.52 g. 50} \\ \mbox{15.0} & \mbox{(sublimed)} \\ \mbox{(sublimed)} \end{array} $	VO(OCH <sub>3</sub> ) <sub>3</sub> , 1.52 g. 50 (sublimed)		31.73	31.67	31.87	I	l	Yellow solid, sublimed in vac.		

1	Vanadi
Table	Alkoxides of

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Benzene (B. D. H.) was dried first with sodium and then azeotropically with small amount of ethanol. Alcohols (methyl, ethyl, isopropyl and tertiary butyl) were dried first over sodium and finally azeotropically with small amount of benzene. Higher alcohols (Pentanols, hexanols and cyclohexanol) were dried azeotropically with a small quantity of ethanol and benzene or distilled under reduced pressure. Ethylorthovanadate was prepared by the ammonia method<sup>2</sup>)<sup>3</sup>.

Analytical methods: Ethoxy and isopropoxy contents were estimated by standard dichromate method<sup>11</sup>).

Pentavalent vanadium was estimated by titrating it with standardised ferrous ammonium sulphate solution using N-phenylanthranilic acid as internal indicator. Total vanadium was determined by igniting the compound to vanadium pentoxide. The molecular weights of the compounds were found out ebullioscopically in benzene.

Reaction of ethylorthovanadate and methyl-isobutyl carbinol. Dry secondary hexanol (about 5 g.) and benzene (about 40 g.) were added to ethylorthovanadate (2.55 g.). The reaction mixture was refluxed at 80-90 °C for about four hours and then the azeotrope was slowly taken. Ethanol was estimated in the azeotrope. Excess benzene was removed under reduced pressure and then the compound (a light yellow liquid) was distilled at 139 °C/2 mm. The compound was analysed for the percentage of pentavalent as well as total vanadium. Weight of the distilled product = 3.5 g., yield = 70%.

Found:  $V^{+5}$ , 13.67; total V, 13.76; Calc. for  $OV(C_6H_{13}O^8)_3$ ; V, 13.753%. Alc. lib., 1.69 g., Alc. Calc., 1.74 g. for 3 moles. Mol. Wt. found, 372.0, Mol. Wt. Calc. 370.442. For brevity, details of other alkoxides prepared by alcoholic interchange technique are listed in the table.

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