936. *Some Chloride Alkoxides of Quadrivalent Vanadium and Quinquevalent Molybdenum.*

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Vanadium tetrachloride reacts with alcohols in cold benzene forming the dichloride dialkoxide alcoholates $VCl_2(OR)_2,ROH$ (I), where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, and *n*-pentyl. Under more vigorous conditions, and especially with tertiary alcohols, hydrolytic side reactions occur. Heating the dichloride dialkoxide alcoholates at 150°/0·1 mm. formed vanadium oxychloride alkoxides, $V_2OCl_3(OR)_3$. The alcoholates (I; R = Me or Pr^i) were dimeric in boiling benzene, suggesting hexaco-ordinated vanadium. Molybdenum pentachloride reacts with alcohols forming the dimeric trichloride dialkoxides $MoCl_3(OR)_2$ (II), where R = Me, Et, or Pr^n, in which molybdenum is probably hexaco-ordinated. These compounds decomposed at temperatures above 80° *in vacuo* and gave molybdenum oxychloride alkoxides. Both di- and tri-chloride alkoxides (I) and (II) exchanged alkoxide groups with alcohols.

THE tetrachlorides of titanium, zirconium, and thorium[1] show decreased reactivity towards alcohols with increase in atomic number of the metal. Little is known of the chemistry of vanadium tetrachloride because of its instability and it was of interest to study its reactivity with alcohols to compare it with the Group IVA tetrachloride.[3] Knowledge of the reactivity of vanadium tetrachloride was also required for the possible preparation of vanadium tetra-alkoxides. Similarly the reactivity of molybdenum pentachloride with alcohols was of interest for comparison with that of the pentachlorides of niobium and tantalum and in connection with the preparation of molybdenum penta-alkoxides.

Reactions of Vanadium Tetrachloride with Alcohols.—Vanadium tetrachloride reacted with several alcohols: $VCl_4 + 3ROH \longrightarrow VCl_2(OR)_2,ROH + 2HCl$; where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s or *n*-pentyl. It thus resembles titanium tetrachloride in reactivity and it appears that a change of one unit in atomic number has had little effect. Although vanadium tetrachloride dissociates to the trichloride at an appreciable rate even at room temperature the dichloride dialkoxide alcoholates are stable dark-green solids which are dimeric in boiling benzene. The dimers probably contain hexaco-ordinated vanadium with a structure consisting of two octahedra sharing a common edge through alkoxide bridges. None of these compounds could be sublimed *in vacuo* without decomposition, and in each case a black residue with the general formula $V_2OCl_3(OR)_3$ remained after heating at 150°/0·1 mm. However, the vanadium showed no change in valency as a result of the decomposition. The vanadium oxychloride alkoxides $V_2OCl_3(OR)_3$ were insoluble in benzene but soluble in the parent alcohols from which they were recovered unchanged. In the case of the methoxide, ethoxide, and *iso*propoxide molecular weights in the boiling alcohols suggested the presence of only one vanadium atom per molecular unit on the average and it appears that the oxychloride alkoxides are dissociated by solvation. The reaction between alcohols and vanadium tetrachloride was extremely rapid and exothermic and had to be moderated in order to obtain the dichloride dialkoxide alcoholate free from oxychloride alkoxide. With *tert.*-butyl or *tert.*-amyl alcohols the dichloride dialkoxides could not be prepared by this method because of side reactions and the products obtained contained appreciable proportions of quinquevalent vanadium. However, the *tert.*-amyl derivative was obtained by alcohol interchange from the *iso*propoxide. Other dichloride dialkoxides were also prepared by this method to establish its generality and to emphasize that the reactivity of vanadium tetrachloride is confined to disubstitution.

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[1] Bradley, Halim, and Wardlaw, *J.*, 1950, 3450.

Reactions of Molybdenum Pentachloride with Alcohols.—Molybdenum pentachloride reacts extremely vigorously with alcohols but under specially moderate conditions the reaction accords with: $MoCl_5 + 2ROH \longrightarrow MoCl_3(OR)_2 + 2HCl$; where R = Me or Et. The molybdenum trichloride dialkoxides are dimeric in boiling benzene; hence the molybdenum is probably hexaco-ordinated, with the dimer $Mo_2Cl_6(OR)_4$ consisting of two octahedra sharing a common edge through alkoxide bridges [cf. structure of $V_2Cl_4(OR)_4,2ROH$]. In view of the similar reactivity of titanium and vanadium tetrachlorides towards alcohols, a similarity was expected between niobium and molybdenum pentachlorides. However, niobium pentachloride forms[2] the dichloride trialkoxides $NbCl_2(OR)_3$ in contrast to the behaviour of molybdenum pentachloride. Moreover, there is a difference in behaviour towards *iso*propyl alcohol because, even under very mild conditions, the reaction involving molybdenum pentachloride produces a molybdenum oxychloride *iso*propoxide whereas niobium pentachloride forms the chloride *iso*propoxide. In fact it was not possible to prepare pure molybdenum trichloride di*iso*propoxide even by alcohol interchange involving the trichloride diethoxide, although the product was less hydrolysed than that obtained by direct reaction. On the other hand *n*-propyl alcohol exchanges with molybdenum trichloride diethoxide and forms the pure trichloride di-*n*-propoxide which is also dimeric in boiling benzene. This difference in behaviour of *n*- and *iso*-propyl alcohols is not surprising because it is a common feature of reactions involving metal chlorides and alcohols that hydrolytic side reactions occur when the alcohol has an alkyl group with a strong (+*I*) effect. We suggested that the side reaction was mainly caused by esterification of the alcohol by hydrochloric acid produced in the primary substitution reaction between metal chloride and alcohol.[3] However, the contrast in behaviour of niobium and molybdenum pentachlorides with *iso*propyl alcohol clearly reveals that the metal compound may also play a decisive rôle in the side reaction, perhaps as a catalyst for the esterification. Attempts to sublime the molybdenum trichloride dialkoxides *in vacuo* were unsuccessful owing to instability of the compounds. For example, prolonged heating of $MoCl_3(OEt)_2$ at 80°/0·1 mm. formed a molybdenum oxychloride ethoxide, soluble in benzene. At higher temperatures decomposition was more extensive but the products were still soluble in benzene until at 150°/0·1 mm. the product, approximating in composition to MoO_2Cl, was insoluble. The low average degrees of polymerisation (in benzene) of the oxychloride ethoxides suggest the presence of molybdenum–oxygen double bonds.

EXPERIMENTAL

All metal compounds described are extremely sensitive to hydrolysis and the usual special precautions[2] were taken to exclude moisture.

Vanadium Tetrachloride.—This was a viscous red liquid (Found: V, 26·3; Cl, 73·6. Calc. for VCl_4: V, 26·4; Cl, 73·6%) prepared by chlorination of vanadium at *ca.* 120° immediately prior to use.

Molybdenum Pentachloride.—The pure sublimed product (black crystals) was used as obtained commercially.

Analysis of Vanadium Compounds.—(a) *Vanadium.* The sample was dissolved in sulphuric acid (2N) and the quadrivalent vanadium titrated with standard permanganate after the addition of phosphoric acid (*ca.* 4 c.c.). Total vanadium was determined by reduction of a sample in sulphuric acid to the bivalent state in the Jones reductor. The solution from the reductor was passed directly into an excess of ferric alum solution and then titrated as before with permanganate. This procedure determined the percentage and valency of the vanadium.

(b) *Chloride.* The chloride was determined in nitric acid solution by Volhard's method.

(c) *Alkoxide.* Methoxide, ethoxide, or *iso*propoxide were determined by the chromic acid method,[1] which is unaffected by the presence of quadrivalent vanadium. In some cases carbon was determined by the Van Slyke method.[4]

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[2] Bradley, Chakravarti, and Wardlaw, *J.*, 1956, 2381.

[3] Bradley, Halim, Sadek, and Wardlaw, *J.*, 1952, 2032.

[4] Multani, Ph.D. Thesis, London, 1956, 65.

TABLE 1. $VCl_2(OR)_2$,ROH.

R	VCl_4 (g.)	C_6H_6 (c.c.)	ROH (g.)	Product (g.)	Found (%)				Calc. (%)			
					V	Cl	OR	C	V	Cl	OR	C
Me	5·3	40	50	5·5	23·2	33·1	43·0	16·4	23·6	32·9	43·1	16·7
Et	4·8	50	46	6·3	19·1	29·0	51·9	—	19·7	27·6	52·3	—
Pr^n	6·1	50	41	9·2	17·2	23·8	—	36·1	17·0	23·7	—	36·3
Bu^n	4·0	40	45	7·0	14·8	21·2	—	41·8	14·9	20·8	—	42·2
n-Pentyl	3·0	25	29	5·85	13·4	18·7	—	—	13·2	18·4	—	—
Pr^i	5·3	36	55	8·2	16·9	23·7	57·9	36·1	17·0	23·7	59·0	36·3
Bu^i	4·0	40	35	7·1	14·9	21·6	—	41·6	14·9	20·8	—	42·2
Bu^s	3·0	32	20	5·3	14·7	21·0	—	39·8	14·9	20·8	—	42·2
Bu^t	4·8	24	35	6·9	16·0 *	22·6	—	—	14·9	20·8	—	—
Am^t	5·1	40	30	9·3	14·1 †	20·3	—	9·4	13·3	18·5	—	47

* V^{IV} = 9·0%. † V^{IV} = 7·8%. In all other cases V (total) = V^{IV}.

TABLE 2. $VCl_2(OR)_2$,ROH.

R	Sample (g.)	$V_2OCl_3(OR)_3$ (g.)	Mol. wt.		Analysis							
					Found (%)				Calc. (%)			
			Found	Calc.	V	Cl	OR	C	V	Cl	OR	C
Me	10·0	7·4	164·2	317·5	31·4	33·1	27·2	—	32·1	33·5	29·2	—
Et	8·6	6·5	186·8	359·5	27·8	29·4	35·5	—	28·3	29·6	37·5	—
Pr^i	10·0	6·5	203	401·5	25·1	27·3	43·9	—	25·4	26·5	44·1	—
Pr^n	8·0	5·3	—	—	25·3	27·8	—	26·6	25·4	26·5	—	26·9

TABLE 4.

Starting material (g.)	C_6H_6 (c.c.)	ROH (g.)	Product (g.)	Found (%)				Calc. (%)			
				M	Cl	OR	C	M	Cl	OR	C
$VCl_2(OEt)_2$,EtOH (4·2)	—	Pr^iOH (225)	$VCl_2(OPr^i)_2$,Pr^iOH (4·9)	16·8	23·8	57·9	—	17·0	23·7	59·0	—
$VCl_2(OPr^i)_2$,Pr^iOH (5·0)	80	Pr^nOH (60)	$VCl_2(OPr^nOH$ (5·0)	17·2	24·0	—	36·4	17·0	23·7	—	36·3
,, (3·0)	—	MeOH (120)	$VCl_2(OMe)_2$,MeOH (2·1)	23·7	33·2	42·9	—	23·6	32·9	43·1	—
,, (4·2)	50	Bu^tOH (4·3)	$VCl_2(OBu^t)_2Bu^t$OH (4·5)	24·1 *	23·8	—	12·1	14·9	20·8	—	42·2
$VCl_2(OEt)_2$,EtOH (4·0)	50	,, (4·0)	,, (4·0)	23·2 †	24·1	—	11·8	14·9	20·8	—	42·2
,, (4·8)	40	Am^tOH (4·9) ‡	$VCl_2(OAm^t)_2$,Am^tOH (7·1)	13·5	19·0	—	44·8	13·3	18·5	—	47·0
$VCl_2(OPr^i)_2$,Pr^iOH (3·0)	32	,, (2·7)	,, (3·8)	13·7	18·9	—	46·0	13·3	18·5	—	47·0
$MoCl_3(OEt)_2$ (3·0) ...	80	Pr^nOH (25)	$MoCl_3(OPr^n)_2$ (3·3)	29·7	33·3	—	21·6	29·9	33·1	—	22·4
,, (3·0)	—	Pr^iOH (75)	$MoCl_3(OPr^i)_2$ (3·0)	33·4	32·1	32·0	—	29·9	33·1	36·9	—

* V^{IV} = 19·3%. † V^{IV} = 19·2%; in all other cases V (total) = V^{IV} and Mo (total) = Mo^V. ‡ Am^t = *tert.*-amyl.

TABLE 3.

R	ROH (g.)	$MoCl_5$ (g.)	$MoCl_3(OR)_2$ (g.)	Found (%) Mo	Cl	OR	C	Calc. (%) Mo	Cl	OR	C
Me ...	50	5·0	4·8	35·9	40·7	23·5	—	36·2	40·2	23·4	—
Et ...	75	5·0	5·5	32·1	37·8	30·9	16·3	32·8	36·4	30·8	16·4
Pr^i ...	75	5·0	6·0	40·9	27·8	21·9	—	29·9	33·1	36·9	—

TABLE 5.

Compound	Range of m (g.)	C_6H_6 (g.)	$\Delta T/m$ (°c/g.)	Mol. wt. Found	Calc.
$VCl_2(OEt)_2,EtOH$	0·0352—0·2948	17·25	0·325	525	258
$VCl_2(OPr^i)_2,Pr^iOH$	0·0318—0·3721	16·80	0·287	611	300
$MoCl_3(OMe)_2$	0·1412—0·4162	19·00	0·288	539	264·5
$MoCl_3(OEt)_2$	0·0862—0·3215	17·80	0·274	604	292·5
$MoCl_3(OPr^n)_2$	0·0521—0·3200	16·80	0·257	683	320·5

Analysis of Molybdenum Compounds.—(a) *Molybdenum.* Generally, molybdenum was determined volumetrically similarly to vanadium. Some analyses were checked and confirmed by the α-benzoin oxime method, but the method involving the precipitation of molybdenum sulphide was found unsuitable because it gave significantly low results.

(b) *Chloride.* The chloride was determined volumetrically by Volhard's method after we found that the gravimetric method (silver chloride) on the filtrate following the removal of molybdenum as sulphide gave the same result.

(c) *Alkoxide.* The chromic acid method was used for methoxide, ethoxide, and *iso*propoxide. However, it was necessary to allow for the chromic acid used in oxidising the molybdenum to the sexavalent state. Some carbon determinations were also made by the Van Slyke method.[4]

Reactions involving Vanadium Tetrachloride.—Vanadium tetrachloride was dissolved in benzene and the solution was cooled to *ca.* −78°. The alcohol was then added dropwise, causing a vigorous reaction. The solution was then evaporated to dryness under reduced pressure. This procedure was adopted throughout and the details are given in Table 1.

All of the vanadium dichloride dialkoxide alcoholates were green solids which were very soluble in alcohol or benzene, and attempts to recrystallise them were unsuccessful. In each experiment the volatile products, trapped (at −78°) during the evaporation of solvent, were yellow and contained traces of chloride and quinquevalent vanadium in the atomic ratio of 3 : 1, suggesting the presence of $VOCl_3$.

Action of Heat on Vanadium Dichloride Dialkoxide Alcoholates.—Each compound was heated at 150°/0·1 mm. until no more volatile products were condensed at *ca.* −78°. The residue was in each case black. Results are given in Table 2. The molecular weights were determined ebullioscopically in the parent alcohols.

The experiment was repeated several times on the dichloride diethoxide ethyl alcoholate but the black residue always had the composition $V_2OCl_3(OEt)_3$. The product was soluble in ethyl alcohol and the solution gave on evaporation of the solvent a *green* solid still having the composition $V_2OCl_3(OEt)_3$ (Found: V, 27·9; Cl, 29·3; OEt, 37·1. Calc. for $C_6H_{15}O_4Cl_3V_2$: V, 28·3; Cl, 29·6; OEt, 37·5%). At 250°/0·1 mm. further decomposition occurred and the black residue (Found: V, 34·4; Cl, 29·8; OEt, 27·8%) was insoluble in alcohol. In all these experiments traces of $VOCl_3$ were detected in the volatile products but the vanadium in the non-volatile residue was entirely quadrivalent.

Reactions involving Molybdenum Pentachloride.—The pentachloride, added cautiously to the cold (*ca.* −78°) alcohol, caused a vigorous reaction. The excess of alcohol was then removed under reduced pressure and left a brown solid. The results are given in Table 3. In each case all the molybdenum in the product was quinquevalent.

Alcohol-interchange Reactions.—The chloride alkoxide was usually dissolved in a mixture of benzene and the higher alcohol. The solution was then fractionally distilled until the lower alcohol was completely removed. When vanadium dichloride dimethoxide was prepared the fractional distillation was omitted for obvious reasons. The results are given in Table 4.

Action of Heat on Molybdenum Trichloride Diethoxide.—(a) *At* 80°. A sample was heated in a molecular still at 0·1 mm. until no more volatile products were trapped at *ca.* −78°. The compound did not sublime and analysis of the non-volatile residue (Found: Mo, 36·5; Cl, 33·2; OEt, 26·0%; *M*, 807) showed that decomposition had occurred. The residue was soluble in benzene and a molecular-weight determination in this solvent showed an average degree of polymerisation of 3·1.

(b) *At* 140°. The residue obtained similarly at 140°/0·05 mm. was further decomposed (Found: Mo, 49·4; Cl, 21·4; OEt, 15·6%; *M*, 1387) and had an average degree of polymerisation of 7·2 in boiling benzene.

(c) *At* 150°. Prolonged heating at 150°/0·05 mm. gave a residue which was insoluble in benzene (Found: Mo, 56·2; Cl, 20·2; OEt, 7·7%).

Molecular-weights.—These were determined ebullioscopically over a range of concentrations in the apparatus previously described.[2] The results are given in Table 5.

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