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Organic Compounds of Niobium and Tantalum. Reactions of Niobium and Tantalum Pentaethoxides with Dibenzoylmethane

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Following three types of new compounds have been isolated: $M(OEt)_4(Dbm)$, $M(OEt)_3(Dbm)_2$ and $M(OEt)_2(Dbm)_3$ (where M is niobium or tantalum) by the reactions of niboum and tantalum pentaethoxides with dibenzoylmethane. These derivatives interchange their ethoxy groups with tertiary butanol. The molecular weights of the few compounds have been determined ebullioscopically in benzene.

There has been considerable interest in the chemistry of coordination compounds of niobium and tantalum. Recently reactions of niobium and tantalum penta-alkoxides with β-diketones[1-3] and β-ketoesters[4,5] have been studied and interesting results have been reported. In view of the above, it was considered of interest to study the reactions of niobium and tantalum pentaethoxides with dibenzoylmethane.

A systematic study of the reactions of niobium and tantalum pentaethoxides with dibenzoylmethane in molar ratio of 1 : 1, 1 : 2 and 1 : 3 has been carried out in benzene solution. The ethanol produced in these reactions has been fractionated out azeotropically with benzene and estimated by an oxidation method.[6] These reactions can be represented by the following equation:

$$M(OEt)_5 + xL \rightarrow M(OEt)_{5-x}L_x + xEtOH$$

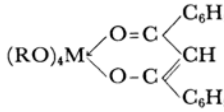
(Where M is niobium or tantalum; $x=1, 2$ or 3 and L is dibenzoylmethane).

All these products are yellow brown pastes and soluble in benzene (solubility goes on decreasing from $M(OEt)_4(Dbm)$ to $M(OEt)_2(Dbm)_3$. It has been found that reaction upto the replacement of the two ethoxy groups is comparatively facile, but further reaction is slow and requires several hours of refluxing. The reactions of the pentaethoxides of these two elements with dibenzoylmethane in molar ratio of 1 : 5 yielded only 3 mol of ethanol in the azeotrope, there by indicating the formation of trisubstituted derivatives. The non replacement of the further ethoxy groups of niobium and tantalum pentaethoxides with 5 mol of dibenzoylmethane, could be ascribed either to steric hindrance or saturated coordination state of the metal in trisubstituted derivatives. Only mono substituted derivatives can be distilled with slight decomposition while all other derivatives decompose when heated under reduced pressure.

Further alcoholysis reactions of mono-, di- and trisubstituted derivatives with tertiary butanol in the presence of benzene provided a good method for the synthesis of the corresponding tertiary butoxide derivatives. Estimation of ethanol liberated gave not only a check on the completeness of the reaction but also provided a means of analysis of ethoxide contents in the original derivatives. These reactions proceeded comparatively more readily in case of tantalum.

These derivatives are yellow crystalline solids and soluble in benzene. All these products can be purified by sublimation (except the trisubstituted derivatives) under reduced pressure. The molecular weights of the mono- and disubstituted derivatives have been determined ebullioscopically in benzene and found to be monomeric.

On the basis of the analyses of the products formed, the following plausible structures can be ascribed to the various new compounds isolated during the present investigation:



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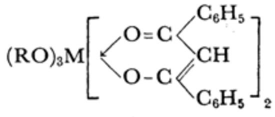

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1) P. N. Kapoor and R. C. Mehrotra, *J. Less-Common Metals*, **8**, 339 (1965).

2) Miss A. Whitley, Ph. D. Thesis London University (1955).

3) R. Gut, H. Buser and E. Schmid, *Helv. Chim. Acta*, **48**, 878 (1965).

4) R. C. Mehrotra and P. N. Kapoor, *J. Less-Common Metals*, **7**, 176, 453 (1964).

5) R. C. Mehrotra, R. N. Kapoor, S. Prakash and P. N. Kapoor, *Australian J. Chem.*, in press.

6) D. C. Bradley, F. M. A. Halim and W. Wardlaw, *J. Chem. Soc.*, **1950**, 3450.

TABLE 1. REACTIONS OF NIOBIUM AND TANTALUM PENTAETHOXIDES WITH DIBENZOYLMETHANE IN BENZENE

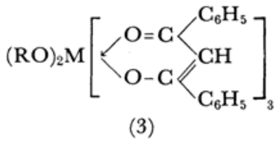
Alkoxide g	Dibenzoyl methane g	Molar ratio	Amount of alcohol in azeotrope		Product, yield and state	Action of heat	Analysis				Mol weight	
							Found %		Calcd. %			
			Found g	Calcd. g			Metal	Alkoxy	Metal	Alkoxy	Found	Calcd.
$Nb(OEt)_5$												
1.88	1.34	1 : 1	0.26	0.27	$Nb(OEt)_4(Dbm)$(2.9 g) yellow viscous paste	170°/0.5 mmHg	18.8	36.9	18.7	36.3	468	496
2.57	3.63	1 : 2	0.71	0.75	$Nb(OEt)_3(Dbm)_2$(5.3 g) brown viscous paste	decomposes on distillation	13.9	19.0	13.8	20.0	610	675
1.48	3.13	1 : 3	0.64	0.65	*$Nb(OEt)_2(Dbm)_3$(3.9 g) brown viscous paste	decomposes on distillation	10.8	10.7	10.9	10.6	—	—
$Ta(OEt)_5$												
2.97	1.64	1 : 1	0.33	0.34	$Ta(OEt)_4(Dbm)$(4.3 g) yellow viscous paste	173°/0.8 mmHg	30.3	30.3	30.9	30.8	554	584
2.12	2.34	1 : 2	0.44	0.48	$Ta(OEt)_3(Dbm)_2$(4.0 g) brown viscous paste	decomposes on distillation	23.7	18.3	23.7	17.7	683	763
1.64	2.72	1 : 3	0.54	0.56	*$Ta(OEt)_2(Dbm)_3$(3.8 g) brown viscous paste	decomposes on distillation	19.6	9.8	19.2	9.6	—	—

* Molecular weights could not be determined due to poor solubility in benzene.

TABLE 2. INTERCHANGE WITH TERTIARY BUTANOL*

Compound g	Bu^tOH g	Amount of alcohol in azeotrope		Product formed and yield	Bp°C/mmHg	Analysis		Molecular weight	
		Found g	Calcd. g			Found metal, %	Calcd. metal, %	Found	Calcd.
$Nb(OEt)_4(Dbm)$ 1.07	6.2	0.40	0.40	$Nb(OBu^t)_4(Dbm)$(1.3 g)	Sublimes 160—170/1.5	15.3	15.2	511	609
$Nb(OEt)_3(Dbm)_2$ 3.64	9.8	0.70	0.74	$Nb(OBu^t)_3(Dbm)_2$(4.1 g)	155—165/0.3	12.6	12.2	701	759
$Nb(OEt)_2(Dbm)_3$ 3.27	8.3	0.36	0.35	$Nb(OBu^t)_2(Dbm)_3$(3.5 g)	decomposes	10.8	10.2	—	—
$Ta(OEt)_4(Dbm)$ 1.35	7.9	0.42	0.43	$Ta(OBu^t)_4(Dbm)$(1.6 g)	160—165/0.9	26.0	26.0	630	697
$Ta(OEt)_3(Dbm)_2$ 3.00	8.6	0.56	0.54	$Ta(OBu^t)_3(Dbm)_2$(3.2 g)	170—175/1.5	21.6	21.4	763	847
$Ta(OEt)_2(Dbm)_3$ 3.80	11.2	0.38	0.36	$Ta(OBu^t)_2(Dbm)_3$(4.0 g)	decomposes	19.6	18.2	—	—

* All the products are yellow crystalline solids.



(3)

(Where R is Et or Bu^t group and M is niobium or tantalum).

It appears that in mono-, di- and trisubstituted derivatives, the niobium and tantalum each has achieved the coordination number six, seven and eight respectively, which is now well known.[7]

Experimental

Experimental techniques, reagents and analytical methods were similar to those described previously.[1,4] The dibenzoylmethane was distilled under reduced pressure before use.

Reaction of Niobium Pentaethoxide with Dibenzoylmethane in the Molar Ratio of 1 : 1. To the benzene (40 g) solution of niobium pentaethoxide (1.88 g), dibenzoylmethane (1.34 g) was added. The colour of the solution became light yellow. The solution was refluxed under a fractionating column and binary azeotrope of ethanol-benzene was collected at 68—80°C. After about eight hours, the excess of the solvent was distilled off at a high reflux ratio. A yellow solution was obtained which was concentrated under reduced pressure. A yellow viscous paste (2.9 g) was obtained which distils at 170°C/0.5 mmHg (Ethanol in the azeotrope 0.26 g: replacement of the 1 equivalent requires 0.27 g).

Found: Nb, 18.8; EtO, 36.9%; mol wt, 468. Calcd for $\mathrm{Nb(OEt)_4(Dbm)}$: Nb, 18.7; EtO, 36.3%; mol wt, 496.

Reaction of Tantalum Tetraethoxide Monodibenzoylmethane Derivative with Tertiary Butanol. Tertiary butanol (7.9 g) was added to a solution of the above compound (1.35 g) in benzene (40 g). The reaction mixture was refluxed under a fractionating column as above with slow fractionation of the azeotrope. Excess of the solvent was removed and a yellow solid (1.6 g), which sublimes at 160—165°C/0.9 mmHg, was obtained. (Ethanol in the azeotrope, 0.42 g; replacement of 4 equivalent requires 0.43 g).

Found: Ta, 26.0%; mol wt, 630. Calcd for $\mathrm{Ta(OBu^t)_4(Dbm)}$: Ta, 26.0%; mol wt, 697.

Further reactions are summarised in Table 1 and 2 respectively.

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[7] R. J. H. Clark, D. L. Kepert, and R. S. Nyholm, *J. Chem. Soc.*, **1965**, 2877.