Bromide Alkoxides of Tantalum

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Abstract

Reactions of tantalum pentaalkoxides (ethoxide, isopropoxide and tertiarybutoxide with acetyl bromide give the products: $Ta(OEt)_4Br$; $Ta(OEt)_3Br_2$; $Ta(OEt)_2Br_3 \cdot MeCO_2Et$; $Ta(OEt)Br_4 \cdot MeCO_2Et$; $Ta(OPr^i)_4Br$; $Ta(OPr^i)_3Br_2$; $Ta(OPr^i)_2Br_3 \cdot MeCO_2Pr^i$; $TaOBr_3$. $MeCo_2Pr^i$; $Ta(OBu^t)_4Br$ and $TaOBr_3 \cdot MeCO_2Bu^t$. These products were found to be viscous liquids or solids. All these bromide alkoxides except the tertiarybutoxide derivatives were found to be soluble in benzene. The tetraalkoxide monobromide derivatives could either be distilled or sublimed unchanged under reduced pressure. The tetraalkoxide monobromide derivative was found to be dimeric in boiling benzene.

Introduction

Considerable amount of work has been carried out on the reactions of alkoxides of samarium[2]), aluminium[3–4]), titanium[5]), zirconium[6]), tin[7]), vanadium[8]) and niobium[9]) with acyl halides (chloride and bromide). Mehrotra et. al.[9]) have studied the reactions of niobium pentaalkoxides with acetyl chloride and acetylbromide. Recently Kapoor and Prakash[10]) have reported the synthesis of a number of chloride alkoxides of tantalum. In view of the interesting results obtained in the case of acetyl chloride, it was considered of interest to study the reactions of tantalum pentaalkoxides with acetyl bromide.

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Tantalum pentaethoxide and pentaisopropoxide undergo exothermic reactions with acetyl bromide in anhydrous benzene and can be represented by the following equations:

$$Ta(OR)_5 + MeCOBr \rightarrow Ta(OR)_4Br + MeCO_2R$$

$$Ta(OR)_5 + 2MeCOBr \rightarrow Ta(OR)_3Br_2 + 2MeCO_2R$$

$$Ta(OR)_5 + 3MeCOBr \rightarrow Ta(OR)_2Br_3 \cdot MeCO_2R + 2MeCO_2R$$

$$Ta(OEt)_5 + 4MeCOBr \rightarrow Ta(OEt)Br_4 \cdot MeCO_2Et + 3MeCO_2Et$$

(or excess) (Where R is Et or Pr^i).

In the reactions of tantalum pentaisopropoxide and pentatertiarybutoxide with acetyl bromide, the replacement of the first alkoxy group is straightforward. Further replacement is slow and with an excess of acetyl bromide an oxytribromide derivative was the end product.

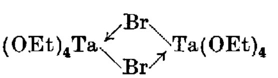
$$Ta(OR)_5 + 4MeCOBr \rightarrow TaOBr_3 \cdot MeCO_2R + 3MeCO_2R$$

(or excess) (Where R is Pr^i or Bu^t).

These reactions were found to be exothermic, the amount of heat evolved increases with the concentration of acetyl bromide. Similar to the chloride alkoxides of tantalum these bromide alkoxides also have an increasing tendency to add on a molecule of the organic ester formed in the reaction itself.

Except the tertiarybutoxide derivatives, all these alkoxide bromides were soluble in benzene and were isolated from the reaction mixtures by evaporating the solvent under reduced pressure.

The tantalum tetraethoxide monobromide was found to be dimeric in boiling benzene and can be assigned the following bridge type of structure:



Experimental

Apparatus: An all glass apparatus fitted with interchangeable standard joints was used and adequate precautions were taken to enclude moisture. Fractionations were carried out in a column packed with Raschig rings and fitted to a stillhead.

Materials: Tantalum pentaalkoxides were prepared as reported[11][12]. Organic solvents were dried carefully by conventional methods. Acetyl bromide (B. D. H A.R.) was distilled at 76.5 °C before use.

Analytical Methods: Tantalum and bromine were estimated gravimetrically as Ta_2O_5 and AgBr. Molecular weights were determined ebullioscopically in boiling benzene and the apparatus was Caliberated internally with fluorene.

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Table 1
Reactions of Tantalum penta-ethoxide with acetyl bromide

Molar Ratio	Tantalum penta-ethoxide (g)	Acetyl bromide (g)	Product and State	Molecular complexity	Boiling point	Analysis Found % Tantalum	Analysis Found % Bromine	Analysis Calculated % Tantalum	Analysis Calculated % Bromine
1:1	2.50	0.76	$TaBr(OEt)_4$ Yellowish white solid molecular weight: 926	2.1	160 °C/1 mm.	41.2	18.3	41.0	18.1
1:2	1.73	1.05	$TaBr_2(OEt)_3$ Yellowish white solid	—	—	37.1	33.6	38.0	33.5
1:3	2.05	1.86	$TaBr_3(OEt)_2 \cdot MeCO_2Et$ Brown liquid.	—	—	29.6	39.4	30.2	40.0
1:4,5 or excess	1.91	2.35	$TaBr_4(OEt) \cdot MeCO_2Et$ Dark brown liquid.	—	—	28.4	51.1	28.5	50.4

Table 2
Reactions of Tantalum pentaalkoxides with acetyl bromide

Molar Ratio	Alkoxide (g)	Acetyl bromide (g)	Product and State	Action of heat	Analysis			
					Found %		Calculated %	
					Tantalum	Bromine	Tantalum	Bromine
1:1	$Ta(OPr^i)_5$ 1.02	0.26	$Ta(OPr^i)_4Br$ Dirty white solid	—	36.9	16.0	36.4	16.0
1:2	$Ta(OPr^i)_5$ 1.00	0.52	$Ta(OPr^i)_3Br_2$ Light brown liquid	—	34.6	30.4	34.9	30.8
1:3	$Ta(OPr^i)_5$ 0.85	0.67	$Ta(OPr^i)_2Br_3 \cdot MeCO_2Pr^i$ Light brown viscous liquid	—	28.1	37.0	28.2	37.4
1:4,5 or excess	$Ta(OPr^i)_5$ 0.52	0.80	$TaOBr_3 \cdot MeCO_2Pr^i$ Dark brown viscous liquid	—	32.9	44.8	33.6	44.4
1:1	$Ta(OBu^t)_5$ 0.60	0.14	$Ta(OBu^t)_4Br$ Yellowish white solid	Sublimes at 120—125 °C/0.4 mm.	32.2	13.8	32.7	14.4
1:4,5 or excess	$Ta(OBu^t)_5$ 1.45	3.00	$TaOBr_3 \cdot MeCO_2Bu^t$ Yellowish white solid	—	33.0	43.1	32.7	43.3

Reactions

I. Reaction of tantalum pentaethoxide with acetyl bromide in the molar ratio of 1:1.

Acetyl bromide (0.76 g) was added to a benzene (20 g) solution of tantalum pentaethoxide (2.50 g). An exothermic reaction took place at the room temperature. The mixture was boiled under reflux for an hour. The excess of solvent was distilled out under reduced pressure. A yellowish solid (b.p. 160°/0.5 mm) was obtained.

Found: Ta 41.2; Br 18.3. $TaBr(OEt)_4$;
requires: Ta 41.0; Br 18.1%.

II. Reactions of tantalum penta tert-butoxide with acetyl bromide in molar ratio 1:Excess

When acetyl bromide (3.0 g) was admitted to a benzene solution of tantalum penta tert-butoxide (1.45 g), an exothermic reaction occurred. The reaction mixture was refluxed for an hour at a bath temperature of 110 °C. Excess of benzene and the ester were evaporated under reduced pressure. A yellowish white solid was abtained.

Found: Ta 33.0; Br 43.1. $TaOBr_3 \cdot MeCO_2Bu^t$;
requires: Ta 32.7; Br 43.3%.

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