

Reactions of Pyruvitrile with Nb(V) & Ta(V) Alkoxides

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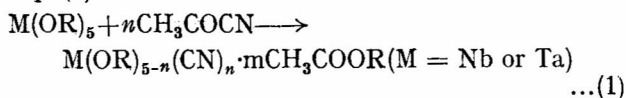
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Received 20 June 1975; accepted 1 September 1975

Reaction of pyruvitrile with the alkoxides (isopropoxides and ethoxides) of Nb(V) and Ta(V) give products of the type $M(OR)_{5-n}(CN)_nPX$ (where $M=Nb, Ta$; $R=Pr^i, Et$; $n=1$ to 5 ; $P=0.5$ to 2.5 ; $X=CH_3COOR$). The reverse reaction of pentacyanide derivatives of these metals with excess of isopropanol has been studied.

IN recent years a number of cyanide complexes¹⁻³ of different metals have been synthesized and characterized. There is no reference available in the literature on the cyanide complexes of metal alkoxides. We have now synthesized the cyanide derivatives of Nb(V) and Ta(V) alkoxides by the reaction of pentaalkoxides of these metals with pyruvitrile, similar to the reaction of acyl halides⁴ in the synthesis of halide derivatives (mainly chloride and bromide) of metal alkoxides.

The reaction of pyruvitrile with these alkoxides have been carried out in different molar ratios in cyclohexane and are found to be exothermic in nature. These can be represented by the general Eq. (1):



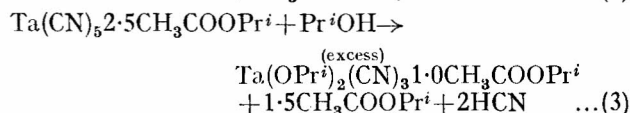
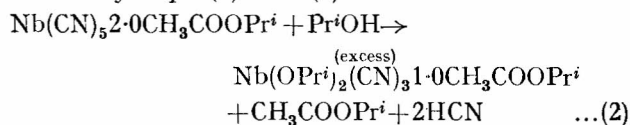
When $R = Pr^i$; $n = 1, m = 0$; $n = 2, m = 0.5$; $n = 3, m = 1$; $n = 4, m = 1.5$; $n = 5, m = 2.0$ (for $M = Nb$) and 2.5 (for $M = Ta$) and when $R = Et$; $n = 1, m = 0$; $n = 5, m = 2.0$ (for $M = Nb$) and 2.5 (for $M = Ta$).

All the products are reddish brown, crystalline solids or pasty solids (in some cases) (Table 1).

It appears that as the isopropoxy groups of the Nb(V) and Ta(V) isopropoxides are replaced by the cyanide groups, the new complexes formed exhibit an increasing tendency to add on additional molecules of the ester. The penta-derivative of niobium adds two molecules of the ester, while in the case of tantalum, the corresponding penta derivative adds 2.5 molecules of the ester. The ester molecules cannot be removed even when the compound is heated up to 80° (bath temperature) under reduced pressure (0.1 mm) for a long time.

To study the reversibility of these reactions, isopropanol was added to $Nb(CN)_5 \cdot 2 \cdot 0CH_3COOPr^i$ and $Ta(CN)_5 \cdot 2 \cdot 5CH_3COOPr^i$ and the reaction mixtures were refluxed for 1 hr. The compounds obtained were the same as obtained by the reactions of $Nb(OPr^i)_5$ and $Ta(OPr^i)_5$ with CH_3COCN in

the molar ratio 1:3. The reactions can be represented by Eqs. (2) and (3):



It seems that the above reactions proceed only up to 1:2 molar ratio. It may be of interest to record that similar reactions of $NbCl_5$ and $TaCl_5$ with Pr^iOH proceed with the formation of dichloride tri-isopropoxide derivatives⁵.

IR spectra (nujol, ν_{max} in cm^{-1}) of the mixed cyanide derivatives of the Nb(V) and Ta(V) alkoxides show peaks $\sim 2070, 2170, 2220$ in the CN stretching region. The first two bands may be attributed to the isocyanide⁶ and cyanide forms respectively. The position of the CN absorption band of isocyanide is approximately 100 lower than the corresponding position for a nitrile. In some cases the absence of the band near about 2070 does not exclude the possibility of the isocyanide isomer being present in very low concentration. Thus we can assume that these alkoxy cyanide derivatives consist of equilibrium mixtures of the iso (M-NC) and normal (M-CN) structures similar to the trimethyl derivatives^{7,8} of silicon and germanium. The band ~ 2220 may be assigned to the bridging cyanide (M-CN-M) group similar to those observed in the compounds $K_2Ni(CN)_4 \cdot 4BF_3$ (ref. 9) and $(NH_3)_5CONCCO(CN)_5$ (ref. 10).

Molecular weights of few of these freshly prepared complexes have been determined ebullioscopically (Table 1). These data depict that molecular association increases with the replacement of isopropoxy groups. All the penta derivatives are polymeric and are sparingly soluble in refluxing benzene. The association of the molecules can be explained on the basis of cyanide bridge formation. This is supported by IR data (peak $\sim 2220 \text{ cm}^{-1}$).

All the alkoxy metal cyanide complexes undergo disproportionation when heated under vacuum to give corresponding alkoxides. When

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TABLE 1 — CYANIDES OF Nb(V) AND Ta(V) ALKOXIDES

Molar ratio	Product*	Found (%) (calc.)		Mol. complexity
		Metal	N	
REACTION OF Nb(OPr ⁱ) ₅ WITH CH ₃ COCN				
1:1	Nb(OPr ⁱ) ₄ (CN), brown viscous	25.64 (26.17)	4.07 (3.94)	2.0
1:2	Nb(OPr ⁱ) ₃ (CN) ₂ 0.5 X, brown viscous	25.20 (24.99)	7.45 (7.50)	—
1:3	Nb(OPr ⁱ) ₂ (CN) ₃ X, brown solid	24.31 (23.75)	11.12 (10.74)	2.34
1:4	Nb(OPr ⁱ) ₂ (CN) ₄ 1.5 X, reddish solid	22.75 (22.72)	13.79 (13.69)	2.62
1:5	Nb(CN) ₅ 2X, reddish solid	21.75 (21.76)	16.00 (16.40)	Polymer
REACTION OF Nb(OEt) ₅ WITH CH ₃ COCN				
1:1	Nb(OEt) ₄ (CN), reddish semi-solid	30.78 (31.08)	4.50 (4.68)	do
1:5	Nb(CN) ₅ 2Y, reddish solid	23.24 (23.29)	17.00 (17.54)	do
REACTION OF Nb(CN) ₅ 2X WITH Pr ⁱ OH				
1: excess	Nb(OPr ⁱ) ₂ (CN) ₃ X, brown solid	25.30 (23.75)	10.71 (10.74)	—
REACTION OF Ta(OPr ⁱ) ₅ WITH CH ₃ COCN				
1:1	Ta(OPr ⁱ) ₄ (CN), yellow solid	41.68 (40.85)	3.25 (3.16)	3.0
1:2	Ta(OPr ⁱ) ₃ (CN) ₂ 0.5 X, brown semi-solid	40.55 (39.25)	5.85 (6.07)	—
1:3	Ta(OPr ⁱ) ₂ (CN) ₃ X, brown solid	38.24 (37.77)	8.54 (8.77)	4.0
1:4	Ta(OPr ⁱ) ₂ (CN) ₄ 1.5X, reddish solid	37.15 (36.40)	11.12 (11.27)	4.0
1:5	Ta(CN) ₅ 2.5X, reddish brown solid	31.97 (31.96)	12.10 (12.37)	Polymer
REACTION OF Ta(OEt) ₅ WITH CH ₃ COCN				
1:1	Ta(OEt) ₄ (CN) reddish semi-solid	46.20 (46.78)	3.50 (3.61)	do
1:5	Ta(CN) ₅ 2.5Y, reddish solid	35.84 (34.10)	12.88 (13.18)	do
REACTION OF Ta(CN) ₅ 2.5X WITH Pr ⁱ OH				
1: excess	Ta(OPr ⁱ) ₂ (CN) ₃ X, brown solid	37.67 (37.70)	8.37 (8.77)	—

X = CH₃COOPrⁱ; Y = CH₃COOC₂H₅.

*Near quantitative yield.

Nb(CN)₅2.0CH₃COOPrⁱ and Ta(CN)₅2.5CH₃COOPrⁱ are heated (0.5 mm) up to 300° (bath temperature), these decompose slowly.

Experimental Procedure

Stringent precautions were taken to exclude moisture throughout these investigations.

Pyruvonnitrile (Fluka) was used after distillation (b.p. 93°). Molecular weights were determined in a semimicro ebulliometer (Gallenkamp) in refluxing benzene. IR spectra were recorded in the range 4000-400 cm⁻¹ on a Perkin-Elmer 337 spectrophotometer using KBr plates.

Niobium and tantalum were estimated as their oxides and nitrogen was estimated by Kjeldahl method.

Reaction of Nb(OPrⁱ)₅ with CH₃COCN (1:1)—An exothermic reaction took place when Nb(OPrⁱ)₅ (2.17 g, 0.055 mole) is treated with CH₃COCN (0.38 g, 0.055 mole) in cyclohexane (50 ml). The reaction mixture was refluxed for 20 min. Removal of the solvent under reduced pressure gave a brownish viscous liquid which tended to solidify on long standing.

Reaction of Nb(OPrⁱ)₅ with CH₃COCN (1:5)—To a solution of Nb(OPrⁱ)₅ (2.77 g, 0.07 mole) in cyclohexane (50 ml), CH₃COCN (2.46 g, 0.35 mole) was added and the reaction mixture refluxed for 20 min. The solvent was removed under reduced pressure and the product dried for 8 hr (0.1 mm/70°C bath temp.). A reddish solid compound was obtained.

To Nb(CN)₅2.0CH₃COOPrⁱ (0.49 g), excess of isopropanol was added and the reaction mixture is refluxed for 1 hr. The brown solid was dried under reduced pressure [Found: Nb, 25.50; N, 10.71. Nb(OPrⁱ)₂(CN)₃·CH₃COOPrⁱ requires Nb, 23.75; N, 10.74%].

The products obtained by the reactions of Nb(V) and Ta(V) isopropoxides and ethoxides with CH₃COCN are given in Table 1.

Acknowledgement

One of the authors (B.L.G.) thanks the UGC, New Delhi, for the award of a junior research fellowship.

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