

Thermal studies of some niobium(V) phenoxides

Amit Pathania and Neeraj Sharma

Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla, India

ABSTRACT

The niobium (V) phenoxides of composition $NbCl_4(OAr^{1,2})$ and $Nb(OAr^{1,2})_5$ (where $OAr^1 = OC_6H_4-C_6H_5-2$ and $OAr^2 = OC_6H_3-Bu^t-2-OMe-4$) synthesized from the reactions of niobium pentachloride with 2-phenylphenol and 2-tert-butyl-4-methoxyphenol in metal : ligand 1:1 and 1:5 molar ratios in carbon tetrachloride have been studied by TG and DTA techniques. The TG profiles of complexes showed these to undergo decomposition in single step, yielding Nb_2O_5 as the final product of decomposition based on % mass loss and authenticated by IR spectra. The single step decomposition is substantiated by exothermic peaks in DTA curve.

Keywords: Niobium pentachloride, 2-phenylphenol, 2-tert-butyl-4-methoxyphenol, TG and DTA techniques.

INTRODUCTION

Although literature abounds with reports on metal alkoxides [1-8] and phenoxides [9-11] of main group elements, transition metals lanthanides and actinides [12-13] yet, in recent past these complexes have received renewed interest as precursors for metal oxides [14-15]. It is of interest to note that the early and late d-block metals have been exploited extensively for the synthesis of novel metal phenoxides using sterically hindered phenols in order to study the structural and chemical effects of π -donor properties of these ligands offering dramatic spectroscopic manifestations. Of group five compounds, niobium phenoxides have been reported to exhibit a range of fascinating structural complexities wherein the versatility of phenoxide ligands has been demonstrated [16-26]. As a part of our interest and an extension of our work on the synthesis of niobium phenoxides [27-31] we report herein our investigations on the thermal behaviour of newly synthesized niobium (V) complexes derived from 2-phenylphenol and 2-tert-butyl-4-methoxyphenol (Fig.1). The very objective of this work was to study the influence of the substituents on the thermal behaviour of the newly synthesized complexes besides the substantial modification of steric and electronic properties. Furthermore, these studies assume special significance in view of an ever-increasing interest of material scientists in alkoxides, heterobimetallic alkoxides and phenoxides of niobium as potential precursors to niobium oxides [32-35] owing to the considerable technological interest in niobium oxide powders and films [36-40].

MATERIALS AND METHODS

$NbCl_5$ (Fluka) was used without further purification and its purity was checked by chlorine analysis. 2-phenylphenol (Merck M.pt. 55.5-57.5°C) was recrystallized from benzene and purity was checked by its sharp melting point 56°C and the purity of 2-tert-butyl-4-methoxyphenol (Merck M.pt. 70-73°C) was checked by its sharp melting point 69°C. Solvents were made anhydrous before use by standard methods. The niobium content in the complexes was determined as Nb_2O_5 after decomposing the complexes with a mixture of conc. H_2SO_4 and HNO_3 followed by heating at 650-700°C. Chlorine was determined by Volhard's method.

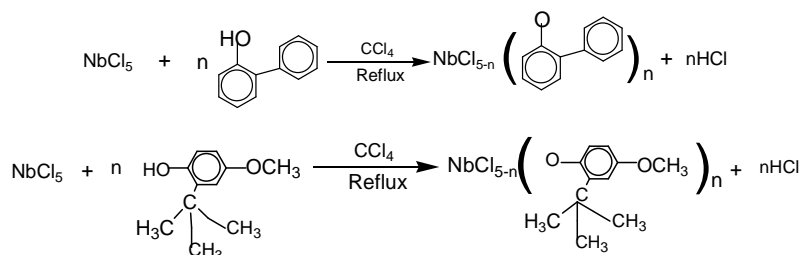
Microanalyses for carbon and hydrogen was performed on an Eager 300 NCH system Elemental Analyzer. Molar conductance (10^{-3} M solutions) in benzene/nitrobenzene were obtained at $25 \pm 0.1^\circ\text{C}$ on an Elico conductivity bridge (type Cm-82T). Molecular weights were determined cryoscopically in benzene (0.0015-0.0020M) using a Beckmann thermometer. IR spectra were recorded on a Nicolet-5700 FTIR spectrometer and ^{13}C -NMR spectra were recorded on a Bruker Avance II 400 spectrometer using CDCl_3 . The molecular dynamic simulation was done up to 1000K (relaxation time 1ps). Thermograms of complexes were recorded on simultaneous TG-DTA SHIMADZU DT-60 thermal analyzer in air at a heating rate of $20^\circ\text{C min}^{-1}$ using platinum crucible. Thermocouple used was Pt/Pt-Rh (10%). The temperature range of the instrument was from room temperature to 1300°C .

Synthesis

To a suspension of niobium pentachloride (3.0 g, 0.011 mol / 2.5 g, 0.009 mol) in CCl_4 (25 ml) were added one and five equivalents of 2-phenylphenol and 2-tert-butyl-4-methoxyphenol in the same solvent (25ml) in separate experiments. The mixing of reactants resulted in the formation of dark brown solution and evolution of HCl gas was observed. The reaction mixture refluxed till the evolution of hydrogen chloride gas ceased to ensure completion of the reaction. It was then filtered and solvent was distilled off. The resultant concentrate was then evaporated under vacuum. The addition of hexane yielded a dark brown complex. It was dried under vacuum.

RESULTS AND DISCUSSION

Complexes of composition $\text{NbCl}_4(\text{OAr}^{1,2})$ and $\text{Nb}(\text{OAr}^{1,2})_5$ (where $\text{OAr}^1 = \text{OC}_6\text{H}_4\text{-C}_6\text{H}_5\text{-2}$ and $\text{OAr} = \text{OC}_6\text{H}_3\text{-Bu}^t\text{-2-OCH}_3\text{-4}$) have been synthesized according to the scheme 1.



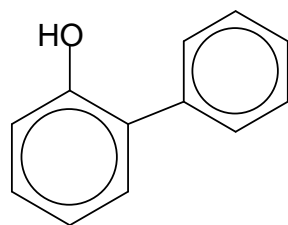
The newly synthesized complexes have been characterized by physicochemical, IR, ^1H and ^{13}C NMR spectral studies.

Thermal studies

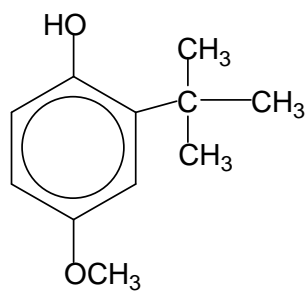
The thermal decomposition behaviour of complexes $[\text{NbCl}_4(\text{OC}_6\text{H}_4\text{-C}_6\text{H}_5\text{-2})]$ (I) $[\text{Nb}(\text{OC}_6\text{H}_4\text{-C}_6\text{H}_5\text{-2})_5]$ (II) $[\text{NbCl}_4(\text{OC}_6\text{H}_3\text{-C}(\text{CH}_3)_3\text{-2-OCH}_3\text{-4})]$ (III) $[\text{Nb}(\text{OC}_6\text{H}_3\text{-C}(\text{CH}_3)_3\text{-2-OCH}_3\text{-4})]$ (IV) has been studied by thermogravimetric and differential thermal analysis technique in air. The TG-DTA curves of niobium (V) phenoxides are illustrated in Figs 1-4 and thermal data is presented in table 1.

Table 1 Thermal data of niobium(V) phenoxides

Complex	Sample mass/mg	IDT/ °C	Stages of decomposition	TGA			DTA	
				Decomp. Range/°C	Mass Loss/% Obs./Calc.	Decomp. Product	Peak temp./°C	Peak Nature
NbCl ₄ (OC ₆ H ₄ -C ₆ H ₅ -2) (I)	6.60	51.9	Single	51.9-490.3	68.1	Nb ₂ O ₅	409.08	Exothermic
Nb(OC ₆ H ₄ -C ₆ H ₅ -2) ₅ (II)	6.30	48.50	Single	48.5-477.5	73.2	Nb ₂ O ₅	505.50	Exothermic
NbCl ₄ (OC ₆ H ₃ -C(CH ₃) ₃ -2-OCH ₃ -4) (III)	9.50	71.4	single	71.4-465.8	68.5	Nb ₂ O ₅	451.12	Exothermic
Nb(OC ₆ H ₃ -C(CH ₃) ₃ -2-OCH ₃ -4) ₅ (IV)	15.00	62.2	Single	62.2-525.1	86.5	Nb ₂ O ₅	490.24	Exothermic

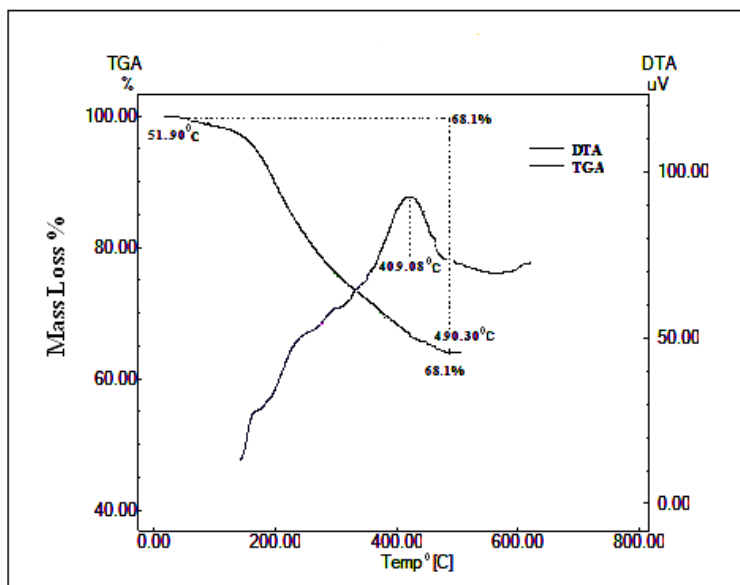


2-phenylphenol

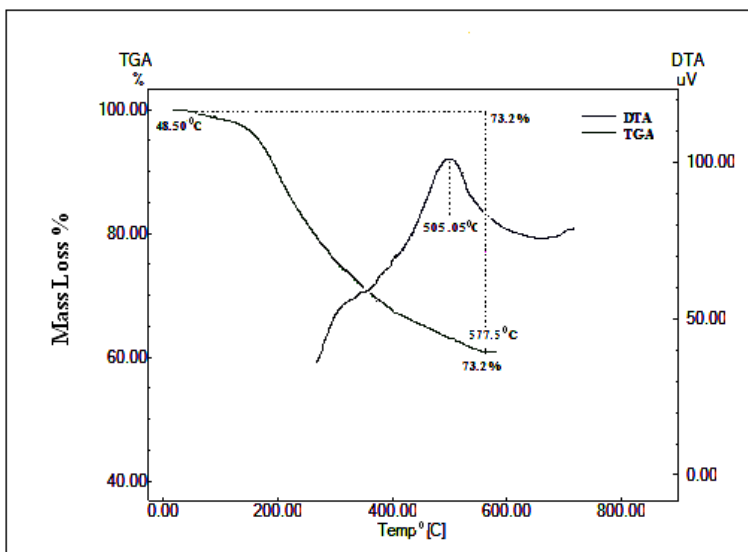


2-tert.butyl-4-methoxyphenol

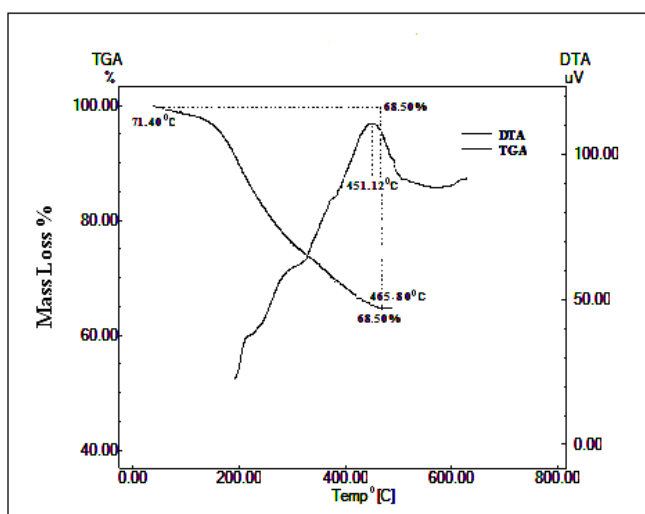
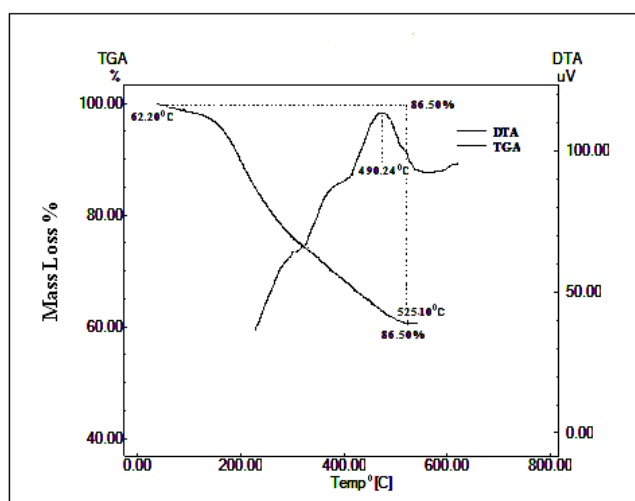
(Fig. 1) Structure of Ligands



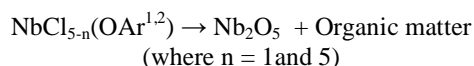
(Fig.2)TG and DTA curve of $\text{NbCl}_4(\text{OC}_6\text{H}_4\text{-C}_6\text{H}_5\text{-2})$



(Fig.3)TG and DTA curve of $\text{Nb}(\text{OC}_6\text{H}_4\text{-C}_6\text{H}_5\text{-2})_5$

(Fig.4) TG and DTA curve of NbCl₃(OC₆H₃-C(CH₃)₃-2-OCH₃-4)(Fig.5) TG and DTA curve of Nb(OC₆H₃-C(CH₃)₃-2-OCH₃-4)₅

The thermogravimetric curves of complexes (I-IV) (Figs. I-IV) have shown these to be thermally stable up to 51.9°C, 48.5°C, 71.4°C and 62.2°C respectively after which temperature the complexes have been found to undergo decomposition in a single step. Based upon initial decomposition temperature, the order of thermal stability of complexes has been inferred as III > IV > I > II. The complexes derived from 2-tert-butyl-4-methoxyphenol have been found to be more thermally stable than those derived from 2-phenylphenol. The mass loss of 68.1%, 73.2%, 68.5% and 86.5% respectively accounted for the formation of Nb₂O₅ as the final product of decomposition authenticated by white colour of residue formed in each case and absorption bands observed in 630-620 cm⁻¹ region in IR spectra. The scheme of decomposition may be represented as:



DTA curves of the complexes (I-IV) exhibited exothermic peak at 409.08°C, 505.5°C, 451.12°C and 490.24°C respectively thereby substantiating one step decomposition in TGA.

CONCLUSION

The two series of niobium (V) phenoxide complexes derived from 2-phenylphenol (I,II) and 2-tert-butyl-4-methoxyphenol(III,IV) studied by TG-DTA studies have been observed to decompose in one step. Based upon initial decomposition temperature, the order of thermal stability of complexes has been inferred as III > IV > I > II suggesting thereby that the complexes derived from 2-tert-butyl-4-methoxyphenol are thermally more stable than those derived from 2-phenylphenol. On the basis of mass loss, the formation of Nb₂O₅ as the final residue has been inferred for all the complexes suggesting these as potential precursors of niobium pentoxide.

Acknowledgement

This article is dedicated to the found memory of our worthy teacher Late Prof. K. C. Malhotra, Ex-Vice Chancellor H. P. University, Summerhill, Shimla (India).

REFERENCES

- [1] Heitz S, Aksu Y, Merschjann C, Driess M, *Chem Mater*, **2010**, 22, 1376–1385.
- [2] Aresta M, Dibenedetto A, Pastore C, *Inorg Chem*, **2003**, 42, 3256-3261.
- [3] Zemski KA, Castleman AW, Thorn DL, *J Phys Chem, A* **2001**, 105, 4633-4639.
- [4] Arai K, Lucarini S, Salter MM, Ohta K, Yamashita, Y, Kobayashi S, *J Am Chem Soc*, **2007**, 129, 8103-8111.
- [5] Boyle TJ, Alam TM, Dimos D, Moore GJ, Buchheit CD, Al-Shareef, HN, Mechenbier ER, Bear BR, Ziller JW, *Chem Mater*, **1997**, 9, 3187-3198.
- [6] Kumar RPC, Yao L, Fleming FF, *J Org Chem*, **2009**, 74, 7294-7299.
- [7] Cotton FA, Matonic JH, Murillo CA, *J Am Chem Soc*, **1997**, 119, 7889-7890.
- [8] Shcheglov PA, Drobot DV, Seisenbaeva GA, Gohil S, Kessler VG, *Chem Mater*, **2002**, 14, 2378-2383.
- [9] Steffey BD, Chesnut RW, Kerschner JL, Pellechia PJ, Fanwick PE, Rothwell IP, *J Am Chem Soc*, **1989**, 111, 378-380.
- [10] Michalczyk L, Gala SDe, Bruno JW, *Organomet*, **2001**, 20, 5547-5556.
- [11] Chesnut RW, Yu JS, Fanwick P E, Rothwell I P, *Polyhedron*, **1990**, 9(8), 1051-1058.
- [12] Aspinall HC, Bickley JF, Gaskell JM, Jones A C, Labat G, *Inorg Chem*, **2007**, 46, 5852-5860.
- [13] Berg JM, Clark DL, Huffman JC, Morris DE, Sattelberger AP, Streib WE, Sluys WGV, Watkin JG, *J Am Chem Soc*, **1992**, 114, 10811-10821.
- [14] Thurston J H, Trahan D, Ould-Ely T, Whitmire KH, *Inorg Chem*, **2004**, 43, 3299-3305.
- [15] John L, Utko J, Szafert S, Jerzykiewicz LB, Sobota P, *Chem Mater*, **2008**, 20, 4231–4239.
- [16] Vilardo JS, Salberg MM, Parker JR, Fanwick PE, Rothwell IP, *Inorg Chim Acta*, **2000**, 299(2), 135-141.
- [17] Matsuo T, Kawaguchi H, *Inorg Chem*, **2002**, (41)23, 6090-6098.
- [18] Yu JS, Felner L, Potyten MC, Clark JR, Visciglio VM, Fanwick PE, Rothwell IP, *J Organomet*, **1996**, 15, 4443-4449.
- [19] Chisholm MH, Rothwell IP, *Comprehensive coordination chemistry* G Wilkinson, R Gillard, McCleverty JAEDs, Pergamon Press Oxford UK **1987**, 2, 15.3.
- [20] Weinert CS, Fanwick PE, Rothwell IP, *Inorg Chem*, **2003**, 42, 6089-6094.

- [21] Davidson MG, Jones MD, Lunn MD, Mahon MF, *Inorg Chem*, **2006**, 45, 2282-2287.
- [22] Fischbach A, Herdtweck E, Anwander R, Eickerling G, Scherer W, *J Organomet*, **2003**, 22, 499-509.
- [23] Weinert CS, Fanwick PE, Rothwell IP, *Inorg Chem*, **2003**, 42(19), 6089-6094.
- [24] Coffindaffer TW, Steffy BD, Rothwell IP, Folting K, Huffman JC, Streibs WE, *J Am Chem Soc*, **1989**, 111, 4742-4748.
- [25] Kawaguchi H, Matsuo T, *J Organomet Chem*, **2004**, 689, 4228-4243.
- [26] Fuchibe K, Akiyama T, *J Am Chem Soc*, **2006**, 128(5), 1434-1435.
- [27] Sharma N, Sharma M, Meena, Chaudhry SC, *Polish J Chem*, **2009**, 83, 1265-1276.
- [28] Sharma N, Sharma M, Meena, Chaudhry SC, *Polish J Chem*, **2009**, 83, 1565-1573.
- [29] Sharma N, Sharma M, Pathania A, Kumar V, and Chaudhry SC, *Thermans*, **2010**, 165-167.
- [30] Sharma N, Sharma M, Bhatt SS, Chaudhry SC, *J Coord Chem*, **2010**, 63, 680-687.
- [31] Sharma N, Pathania A, Sharma M, *J Therm Anal Calorim*, **2012**, 107, 149-154.
- [32] Turevskaya EP, Turova NP, Korolev AV, Yanovsky AI, Struchkov YT, *Polyhedron*, **1995**, 14, 1531-42.
- [33] Boulmaaz S, Papiernik R, Hubert-Pfalzgraf LG, Septe B, Vaissermann J, *J Mater Chem*, **1997**, 7, 2053-2061.
- [34] Sobota P, Utko J, Szafert S, *Inorg Chem*, **1997**, 36, 2227-2229.
- [35] Geol SC, Hollingsworth JA, Beatty AM, Robinson KD, Buhro WE, *Polyhedron*, **1998**, 17, 781-790.
- [36] Serafim MJS, Bessler KE, Lemos SS, Sales MJA, *Trans Met chem*, **2007**, 32, 112-116.
- [37] Boffa V, castricum HL, Garcia R, Schmuhl R, Petukhov AV, Blank DHA, Elshof JET, *J Chem Mater*, **2009**, 21, 1822-1828.
- [38] Camargo ER, Kakihana M, *J Chem Mater*, **2001**, 13, 1905-1909.
- [39] McKarns PJ, Heeg MJ, Winter CH, *J Inorg Chem*, **1998**, 37, 4743-4747.
- [40] Anokhina EV, Duraisamy T, Lachgar A, *J Chem Mater*, **2002**, 14, 4111-4117.