# Thermoanalytical investigations of niobium(V) complexes of 4-isopropylphenol

**Neeraj Sharma · Amit Pathania · Mala Sharma**

**Abstract** Thermal behaviour of newly synthesized niobium(V) aryloxides of composition $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}4)_n]$ (where $n = 1 \rightarrow 5$) synthesized by the reactions of niobium pentachloride with 4-isopropylphenol in predetermined molar ratios in carbon tetrachloride has been studied by thermogravimetric (TG) and differential thermal analysis (DTA) techniques. The results showed that thermal decomposition of complex of composition $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)]$ resulted in the formation of $NbOCl_3$ as the ultimate decompositional product while all other complexes yielded $Nb_2O_5$ as the final product of thermal decomposition. From the mathematical analysis of TG data, the kinetic and thermodynamic parameters viz. energy of activation, frequency factor, entropy of activation, etc. have been evaluated using Coats–Redfern equation.

**Keywords** Niobium (V) complexes · 4-Isopropylphenol · TG and DTA · Kinetic and thermodynamic parameters · Coats–Redfern equation

## Introduction

Over the years, an ever-increasing research interest in chemistry of niobium has aroused not only from the striking structural novelties and complexities exhibited by niobium compounds but also from their unique applications as catalysts [1–9] and in material science [10–16]. Most of the earlier work reported the synthesis of mono-, di- or trivalent metal niobates viz. lead magnesium niobate (PMN) and niobium doped lead zirconate titanate (PNZT) as ferro- or piezoelectric resonator materials. The rare earth niobates and tantalates are useful class of materials as photocatalysts, host lattices for phosphors and ion conductors [17]. The synthesis of lithium niobate has drawn much attention in recent years owing to its excellent piezoelectric, pyroelectric, electro-optic and photo-refractive properties.

The niobium(V) catalysts bearing di- and tri-phenolate ligands have been demonstrated to polymerize ethylene in the presence of an organoaluminium cocatalyst [18]. Owing to the utility of niobium oxides and mixed oxides as effective catalysts in many processes, the synthesis of metal–organic precursors affording these oxides has assumed remarkable importance. In this context, phenomenal interest in niobium chemistry has centred on complexes derived from alkoxo and aryloxo ligands which can be easily modified in steric bulk by substitution. Furthermore, niobium alkoxides, chloroalkoxides, heterometallic alkoxides and aryloxides have been extensively studied as precursors for the preparation of mixed metal oxides with potential utility as electro-optic materials [19–22]. In view of our continuing interest on niobium aryloxides [23–25], we report herein thermal studies of niobium(V)isopropylphenoxides with an objective to study their thermal behaviour, formation of intermediate if any and ultimate thermolytic product. The kinetic parameters evaluated from TG data using Coats–Redfern equation are also described.

## Experimental

Synthesis of niobium(V)4-isopropylphenoxides $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}4)_n](n = 1 \rightarrow 5)$

A suspension of niobium pentachloride (2.0 g, 0.007 mol) in $CCl_4$ (20 mL) was treated with a solution of one, two,

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three, four and five equivalents of 4-isopropylphenol (1.0 g, 0.007 mol; 1.90 g, 0.014 mol; 2.86 g, 0.021 mol; 3.81 g, 0.028 mol and 4.76 g, 0.035 mol) in dry carbon tetrachloride (15 mL) in separate experiments. The mixing of reactants resulted in an immediate colour change from yellow to dark orange with the evolution of HCl gas. The reaction contents were initially stirred for 3–4 h and were then refluxed till the evolution of hydrogen chloride gas ceased which ensured the completion of the reaction. No separation of any solid was observed during the course of the reaction in the mixture solution. It was filtered and the filtrate was then concentrated by distilling off the solvent. The resultant concentrated solution was treated with petroleum ether whereupon the formation of solids was observed. It was dried under vacuum.

Thermograms of complexes were recorded on simultaneous TG-DTA SHIMADZU DT-60 thermal analyzer in air at a heating rate of 20 °C/min using platinum crucible. Thermocouple used was Pt/Pt–Rh (10%). The sample size for TG-DTA analysis was 5–7 mg. The temperature range of the instrument was from room temperature to 1300 °C. IR spectra were recorded as (KBr pellets) on Nicolet-5700 FTIR spectrometer. The kinetic and thermodynamic parameters viz. energy of activation, frequency factor, entropy of activation, etc. have been computed using Coats–Redfern equation from mathematical analysis of TG data.
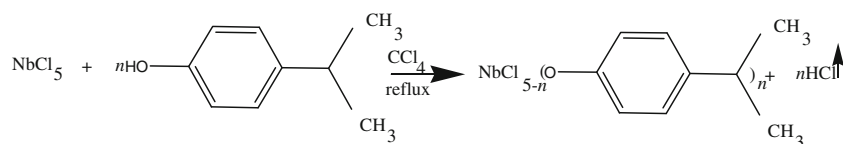
## Results and discussion

Complexes of composition [NbCl$_{5-n}$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_n$] (where $n = 1 \rightarrow 5$) have been synthesized according to the Scheme 1

The complexes are yellow to dark brown solids and have been thoroughly characterized by physicochemical, IR, $^1$H and $^{13}$C NMR, UV–vis and mass spectral studies [26].
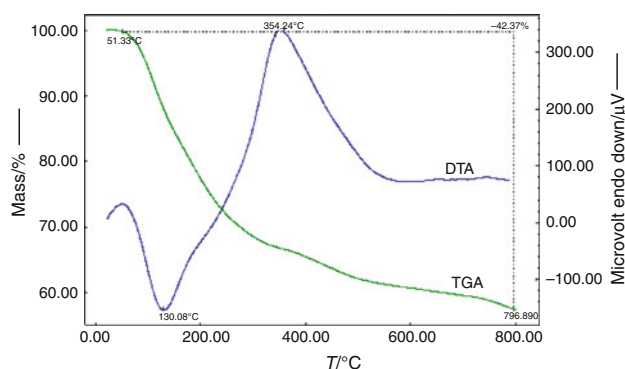
Thermal studies

The thermal decomposition behaviour of complexes, [NbCl$_4$OC$_6$H$_4$CH(CH$_3$)$_2$-4)] (I), [NbCl$_3$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_2$] (II), [NbCl$_2$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_3$] (III), [NbCl(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_4$] (IV) and [Nb(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_5$] (V)



**Fig. 1** TG-DTA curve of NbCl$_4$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)

has been studied by thermogravimetric and differential thermal analysis techniques in air. The TG-DTA curves of niobium(V)4-isopropylphenoxides are illustrated in Figs. 1, 2, 3, 4 and 5 and thermal data is presented in Table 1.
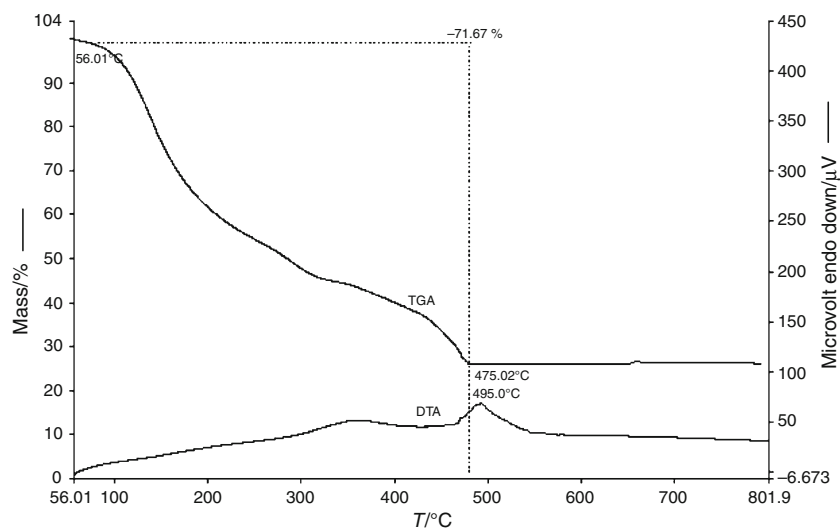
The thermogravimetric curve of [NbCl$_4$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)] (Fig. 1) has shown it to be thermally stable up to 51.33 °C after which temperature the complex has been found to undergo continuous decomposition in single step. The observed mass loss of 42.37% in 51.33–796.89 °C temperature range has been ascribed to the formation of NbOCl$_3$ as the ultimate residue as:

$$NbCl_4\left(OC_6H_4CH(CH_3)_2-4\right) \rightarrow NbOCl_3 + Organic\,matter$$
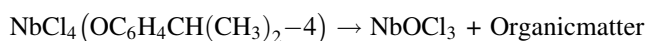
The formation of NbOCl$_3$ was authenticated from its white colour and infrared spectrum which showed a strong absorption band at 775 cm$^{-1}$ assigned to Nb–O–Nb stretching vibration and absorption bands at 432, 402 and 290 cm$^{-1}$ due to $\upsilon$(Nb–Cl) mode. The DTA curve of [NbCl$_4$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)] has shown both endothermic and exothermic peaks at 130.08 and 354.24 °C, respectively.

The TG curves of [NbCl$_3$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_2$], [NbCl$_2$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_3$], [NbCl(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_4$] and [Nb(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_5$] in Figs. 2, 3, 4 and 5, respectively, have depicted these to be thermally stable up to 56.01, 55.4, 54.92 and 30.06 °C, respectively, after which temperature the complexes undergo decomposition in single step. The complex of composition [Nb(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_5$] has been observed to be least thermally stable. The mass loss of 71.04, 76.07, 79.41 and 80.53% in respective complexes against theoretical mass loss of 71.67, 76.62, 80.10
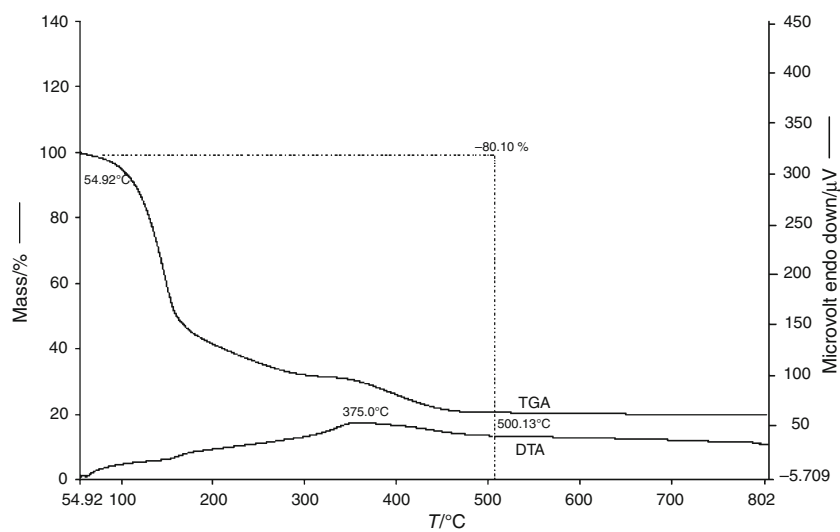
**Scheme 1** Synthesis of complexes

NbCl$_5$ + $n$HO—⟨C$_6$H$_4$⟩—CH(CH$_3$)(CH$_3$) $\xrightarrow[\text{reflux}]{\text{CCl}_4}$ NbCl$_{5-n}$(O—⟨C$_6$H$_4$⟩—CH(CH$_3$)(CH$_3$))$_n$ + $n$HCl↑

(where $n = 1 \rightarrow 5$)

**Fig. 2** TG-DTA curve of
$NbCl_3(OC_6H_4CH(CH_3)_2-4)_2$



**Fig. 3** TG-DTA curve of
$NbCl_2(OC_6H_4CH(CH_3)_2-4)_3$
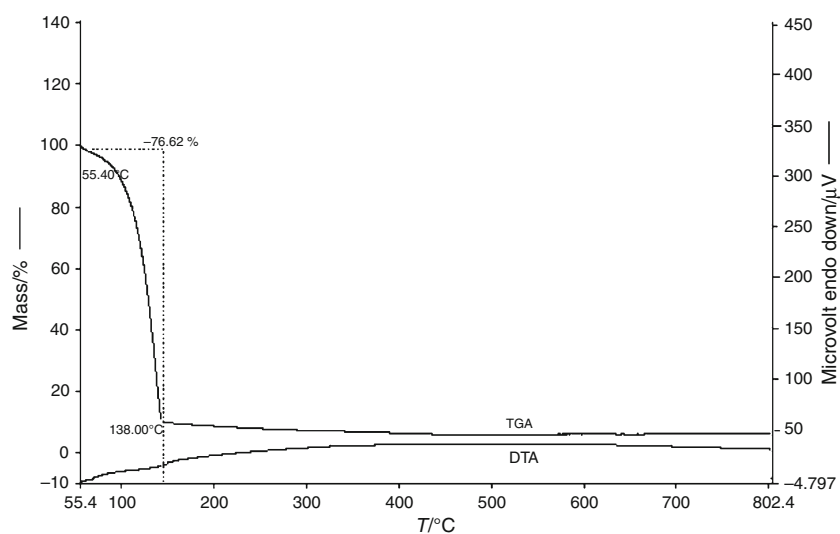


**Fig. 4** TG-DTA curve of
$NbCl(OC_6H_4CH(CH_3)_2-4)_4$
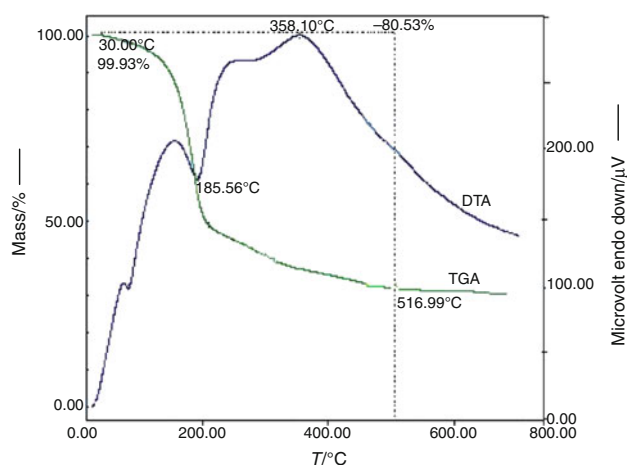
**Fig. 5** TG-DTA curve of Nb(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_5$

and 82.68% has accounted for the formation of Nb$_2$O$_5$ as the ultimate product of decomposition according to the equation.

$$NbCl_5(OC_6H_4CH_3)_2 \rightarrow Nb_2O_5 + Organic matter$$
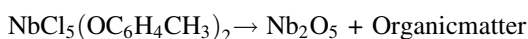
where $n = 2 \rightarrow 5$.

The white colour of residue formed in each case substantiated the formation of niobium pentaoxide. The DTA curves of [NbCl$_3$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_2$] and [NbCl(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_4$] showed an exothermic peak at 495 and 375 °C, respectively. The complex [NbCl$_2$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_3$] did not show any physical change in its DTA curve corresponding to thermal decomposition. The DTA

curve of [Nb(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_5$] depicted a sharp endothermic peak at 185.56 °C and a feeble exothermic peak at 358.10 °C.

It is important to mention here that the mass loss corresponding to feeble inflexions appeared in TGA curves of complexes did not account for the proposition of a stable intermediate suggesting thereby single decompositional step for complexes. The variation in the magnitudes of endothermic and exothermic peaks may be ascribed to the different sample size of complexes.

## Kinetic parameters

The evaluation of kinetic parameters such as rate constant, apparent activation energies, reaction order and pre-exponential factors has been one of the widespread quantitative applications of thermogravimetry. Compared to many reported methods for the evaluation of kinetic parameters from TG data, Coats–Redfern equation has been described to be less tedious, giving satisfactory kinetic analysis of thermogravimetric data. Hence, the mathematical analysis of TG data was computed using Coats–Redfern equation [27, 28] as:

$$\log\left[In\frac{W_\alpha}{\frac{W\alpha - W}{T^2}}\right] = \log\left[\frac{ZR}{\phi E^*}\left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT}$$

where $W\alpha$ is the mass loss at the completion of the reaction, $W$ is mass loss at time $t$ and $\Phi$ is the linear rate of heating.

**Table 1** Thermal data of niobium(V)4-isopropylphenoxides

| Complex | Sample mass/mg | IDT/°C | Stages of decomp. | TGA | | | DTA | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | | Decomp. range/°C | Mass loss/% | Decomp. product | Peak temp./ °C | Peak nature |
| NbCl$_4$(OC$_6$H$_4$CH(CH$_3$)$_2$-4) (I) | 6.18 | 51.33 | Single | 51.33–796.89 | 42.37 | NbOCl$_3$ | 354.24 | Exothermic |
| | | | | | | | 130.08 | Endothermic |
| NbCl$_3$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_2$ (II) | 5.25 | 56.01 | Single | 56.01–475.02 | 71.67 | Nb$_2$O$_5$ | 495.0 | Exothermic |
| NbCl$_2$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_3$ (III) | 6.36 | 55.40 | Single | 55.40–138.00 | 76.62 | Nb$_2$O$_5$ | – | – |
| NbCl(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_4$ (IV) | 6.40 | 54.92 | Single | 54.92–500.13 | 80.10 | Nb$_2$O$_5$ | 375.0 | Exothermic |
| Nb(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_5$ (V) | 6.77 | 30.06 | Single | 30.06–516.99 | 80.53 | Nb$_2$O$_5$ | 358.10 | Exothermic |
| | | | | | | | 185.56 | Endothermic |

**Table 2** Kinetic parameters of niobium(V)4-isopropylphenoxides

| Complex | Activation energy $E^*$/kJ mol$^{-1}$ | Frequency factor $Z$/s$^{-1}$ | Entropy $\Delta S^*$/kJ mol$^{-1}$ K$^{-1}$ | Free energy $G^*$/kJ mol$^{-1}$ K$^{-1}$ | Enthalpy $H^*$/kJ mol$^{-1}$ |
| --- | --- | --- | --- | --- | --- |
| NbCl$_4$(OC$_6$H$_4$CH(CH$_3$)$_2$-4) (I) | 22.29 | 1.68 × 10$^{-6}$ | −361.65 | 24.94 × 10$^4$ | 22.29 |
| NbCl$_3$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_2$ (II) | 5.20 | 1.02 × 10$^{-4}$ | – | – | 5.20 |
| NbCl$_2$(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_3$ (III) | 10.69 | 2.63 × 10$^{-5}$ | −338.79 | 22.35 × 10$^4$ | 10.68 |
| NbCl(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_4$ (IV) | 4.92 | 1.06 × 10$^{-4}$ | – | – | 4.92 |
| Nb(OC$_6$H$_4$CH(CH$_3$)$_2$-4)$_5$ (V) | 23.17 | 1.67 × 10$^{-6}$ | −361.70 | 25.03 × 10$^4$ | 23.17 |

The plots of $\log\{\ln[W\alpha/(W\alpha - W)/T^2]\}$ vs. $1/T$ were drawn and straight lines were obtained. The activation energy was calculated from the slope $-E^*/2.303R$. The kinetic parameters viz. entropy $(S^*)$ [29], free energy $(G^*)$ [30] and enthalpy of activation $(H^*)$ have been calculated from the relations:

$$S^* = 2.303 \log_{10}\left(\frac{Zh}{kT_s}\right)$$

$$G^* = E^* - T_s S^*$$

$$H^* = E^* - k_r T_s$$

where '$k$' is Boltzmann's constant, '$h$' Planck's constant, '$Z$' frequency factor, '$T_s$' the peak temperature computed from DTG and $k_r$ is the specific reaction rate constant calculated from the relation

$$k_r = Z \exp^{\frac{E^*}{RT}}$$

From the perusal of data (Table 2), the negative values of '$S^*$' indicate that the activated complex has a more ordered structure than the reactants [31]. The low values of '$Z$' suggest that the reactions are slower than normal [32, 33]. The non-observance of any correlation between the kinetic parameters and order of thermal stability may be ascribed to the fact that decisive criteria in kinetics are different from those determining thermal stability.

## Conclusions

The TG-DTA studies of newly synthesized niobium(V)4-isopropylphenoxides have demonstrated these to undergo decomposition in single step. The thermogravimetric analysis of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)]$ (I) gave $NbOCl_3$ as the ultimate product of decomposition authenticated by its colour and IR spectra while thermal study of complexes of composition $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2]$ (II), $[NbCl_2(OC_6H_4CH(CH_3)_2\text{-}4)_3]$ (III), $[NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4]$ (IV) and $[Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5]$ (V) yielded $Nb_2O_5$ as the final decompositional product suggesting these to be potential precursors of niobium pentoxide. The kinetic and thermodynamic parameters have been computed from TG data using Coats–Redfern equation.

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