

Potentiality and Kinetic thermal decomposition studies of optically nonlinear Rhodium- tetracyanoquinodimethan adducts

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ABSTRACT

Some nonlinear Rhodium- tetracyanoquinodimethan were synthesized from the reaction of different counters of Rhodium with tetracyanoquinodimethan. Chemical structure of the obtained products will be investigated and confirmed by using elemental analysis and spectroscopic techniques such as IR-, UV/Vis- and ¹H-NMR spectroscopy. In addition, the molecular structure of the obtained products determined. Described synthetic condition results in a significant improvement in both yield and reaction time of Z- β -(1-substituted-4-pyridinium)-α-cyano-4-styryldicyanomethanide chromophores. A decomposition study of the zwitterionic chromophores in solution is also described. The non-isothermal decomposition of rhodium adducts was studied on heating to the formation of rhodium metal at 400°C in N₂ atmosphere using thermogravimetry (TGA), derivatives thermogravimetry (DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC), X-ray powder diffraction and IR spectroscopy were used for identification of solid decomposition products. The variation of the rate of heating was used to calculate the activation energy(E_a) and the frequency factor (ln A) for the dehydration and the decomposition processes. In addition, the enthalpy(ΔH), heat capacity (C_p) and the entropy (ΔS) changes were also calculated from DSC measurements. The final mass loss after complete decomposition was found to increase appreciably with increasing the heating rate.

Key words: Kinetic thermal decomposition, non-linear Rhodium tetracyanoquinodimethan.

INTRODUCTION

B. Gillot¹ have used a quantitative analysis by DTG to obtain a direct measure of mixed-valent distribution over tetrahedral A and octahedral B sites, even when a given atom, such as iron or manganese, may have the M⁽ⁿ⁺¹⁾⁺/Mⁿ⁺ redox couple for A sites overlapping the M⁽ⁿ⁺¹⁾⁺/Mⁿ⁺ redox couple for B sites. The spinel oxide structure of the chemical formula AB₂O₄ is formed by a nearly close-packed face-centered cubic array of oxygen ions with tetrahedral A and octahedral B sites partly occupied by cations A and B².

The interest of this work is focused in studying the thermal behavior of many metal salts³⁻⁵ as well as the thermogravimetric studies and reactivity of polymeric metal complexes of poly (5-vinylsalicylidene-2-benzothiazoline) (PVSBH₂)^{6,7}. This imposes a tough challenge for oxidation catalysts. This problem is even more challenging if oxygen is added in stoichiometric amounts to CO and when significant amounts of water vapor are present⁸. Manganese has been a component of many oxidation catalysts, especially in Hopcalite-like compounds. Many studies have been devoted to studying catalytic effects in oxidation (especially for CO) of Mn in various crystallographic sites.

Calderbank et. al.⁹ studied the effect of using copper salts and copper bronzes instead of copper powder in the reaction but they came to the conclusion that precipitated copper powders were the most effective. High resolution X-ray diffraction analysis of the Diquat dication has been reported by three groups. Diquat dibromide has been analyzed by Ashton et. al. and the complex of the Diquat dication with 7,7,8,8-tetracyanoquinodimethane¹⁰. Paraquat is almost completely dissociated in solution into positive and negative ions. The toxic effect is promoted by the metabolic activities of the cells, which reduce the positive ion to form a relative stable free radical, via mitochondria¹¹. During the irradiation experiments with artificial light the temperature of the herbicides solutions remained below 40°C. The experiments showed that no degradation occurs when the solutions are irradiated without catalyst, or in the presence of catalyst but without irradiation. The adsorption/desorption equilibrium depends on the herbicide type and experimental conditions used.

The interest of this work is focused to study the thermal behavior of nonlinear Rhodium-tetracyanoquinodimethane as well as TGA, DTA and DSC studies. In addition, the enthalpy (ΔH), heat capacity (C_p) and the entropy (ΔS) changes were also calculated from DSC measurement.

MATERIAL AND METHODS

Compound I_a was prepared by first dissolving Li TCNQ (2.570 mol) in 20 mL of Me CN, followed by addition of a solution of N-octyl-4-methylpyridinium bromide (1.283 mmol) in 5 mL of Me CN. At reflux DBU (2.570 mmol) was added in increments of three drops every 15mm. After 14 h the reaction was stopped and the precipitate was filtered, washed with Me CN and dried under vacuum. The crude product was purified by washing with boiling methanol (70 ml) in a beaker, followed by filtering the undissolved portion. The process was repeated four times before the undissolved product was pure as analyzed by UV-vis.

The solvent selected for the reactions was Me CN since it resulted in the best yields by far. Reactions were also carried out using DMF, chlorobenzene and ethanol' chlorobenzene, but

these only produced the chromophores in very low yields (0.2%). The reaction of neutral TCNQ and a lepidiniurn salt in the presence of piperidine was found to proceed rapidly (e.g. 8 h)¹². However, it was later confirmed that a side reaction took place as the result of piperidine displacing cyano groups of TCNQ¹³ which is a known reaction for primary, secondary and tertiary amines with TCNQ¹⁴. Thus, in our work a number of tertiary amines were tested, including pyridine, 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), 1-(2-hydroxyethyl) piperidine and 1,4- diazabicyclo(2.2.2)octane. It was found that the strongest base, DBU, led to the most drastic improvement in reaction time.

In order to maximize the yield the syntheses of Ia and Ib were repeated several times, using the different amounts of starting materials for each reaction. The conditions providing the highest yield for Ia used 1 equiv. of N-octyl-4-methylpyridinium bromide, 2 equiv. of Rhodium TCNQ adduct (RhCl_2TCNQ) and 2 equiv. of DBU. Once the reactants were dissolved in refluxing Me CN, DBU was added slowly in intervals of three drops every 15 mm over a period of 1.5 h. The reaction proceeded for 14 h and the product that had precipitated from solution was collected. After washing the crude product repeatedly with boiling methanol, Ia was obtained in 97%.

Instruments

FTIR spectroscopic analysis was by means of a Mattson 5000 FTIR spectrophotometer, the reactant and solid decomposition products were carried out by the KBr disk technique. ¹HNMR spectra were recorded on a Varian EM-390 spectrometer (90 MHz). Elemental microdetermination was carried out using a Perkin-Elmer 2400 series IICHNS/ O Auto analyzer.

Analytical grade rhodium (II) acetate monohydrate product of Fluka AG (Switzerland), was used as received. Thermal analyses including TG,DTA and DSC, were carried out by means of a Shimadzu (Japan) [TGA-50H,DTA-50 and DSC-50],equipped with a TA-50WSI data station. Thermal analysis experiments were performed in a dynamic atmosphere (40 ml.min⁻¹) of N₂ at heating rates between 2 and 15oC.min⁻¹.

X-ray powder diffraction analysis of the solid decomposition products was carried out using a Model D5000 diffractometer (Germany), Ni-filtered CuK α radiation (λ , 1.5406 Å)

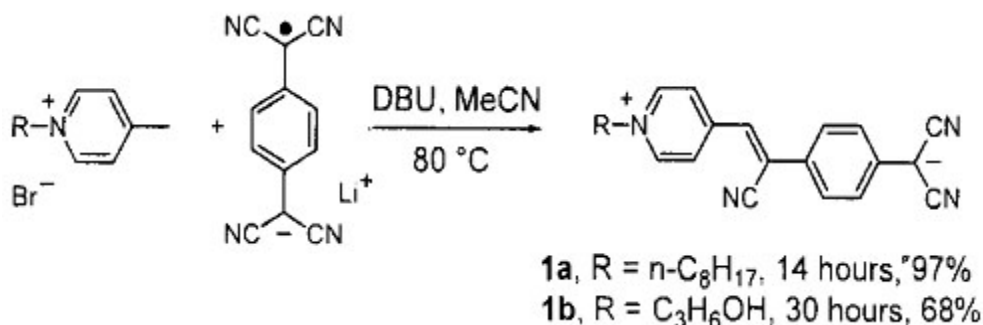
RESULTS AND DISCUSSION

The IR spectrum of 1a showed C=N peaks at 2132 and 2175 cm⁻¹, reinforcing that the compound is zwitterionic in character^{12,13}. The Uv-Vis absorption spectrum showed a broad peak at 654 nm (Fig. 1). The chromophore 1a was also characterized by ¹H-NMR.

Despite all, these nonlinear NLO chromophores have long been neglected, presumably due to the lack of availability. The literature procedures available reported low yields

of only 15 to 30%, and the reaction times when repeated were upwards of 5 to 14 days. In order to investigate the utility of these chromophores for EO device applications they need to be made more accessible. Thus, we report herein our findings that by varying the reaction conditions and with the use of an amine base, chromophores 1a and 1b were synthesized in 14 to 30 h with yields ranging from 68 to 97%.

To compare with the results achieved using RhCl₂TCNQ, two additional reactions were carried out using neutral TCNQ^[15]. The first involved 1 equiv. of N-octyl-4-methylpyridinium bromide, 2 equiv. of DBU and 2 equiv. of TCNQ. The reaction proceeded for 18.5 h and had a yield of only 34%. The second reaction used 1 equiv. of N-octyl-4-methylpyridinium bromide, 2 equiv. of DBU, 1 equiv. of RhCl₂TCNQ



Scheme 1: Synthesis of NLO chromophores 1a,b.

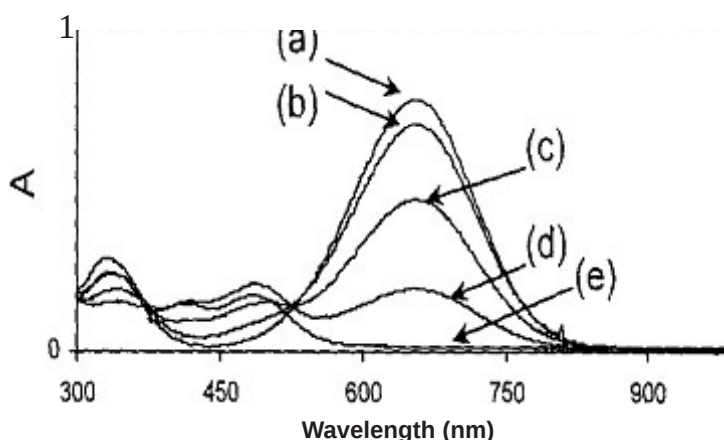


Fig. 1: Uv-vis absorption spectra of 1a in DMF (4.4×10^{-4} M, 0.1 cm path length) at 125°C, in dark, with the vessel open to air, heated for a period of (a) 2 min; (b) 50 min; (c) 90 min; (d) 122 min; (e) 144 min.

and 1 equiv. of neutral TCNQ. The reaction proceeded for 16 h and had a final yield of 50%. The results suggested that using RhCl_2TCNQ dicyano-p-toluoylcyanide anion (2, Scheme 3) has been shown to form readily and irreversibly in the presence of trace amounts of oxygen and it absorbs in the same region by UV vis (λ_{max} -490 nm).^{16,17}.

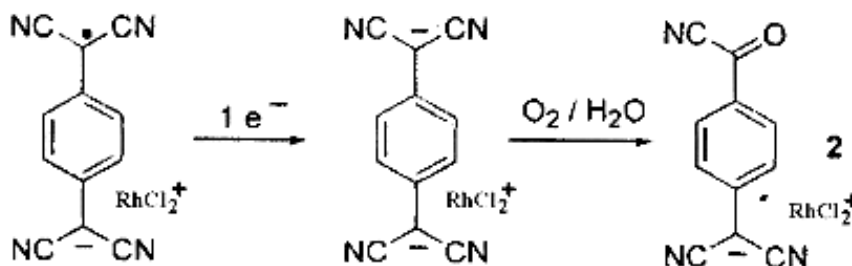
The results overall indicated that using both RhCl_2TCNQ and DBU in excess relative to the pyridinium salt provided shorter reaction times and higher yields than reported previously for type 1 chromophores. Based on these results we propose the reaction mechanism shown in Scheme 2. This radical mechanism seemingly explains why the second equiv. of RhCl_2TCNQ is required to achieve a yield greater than 50%, as well as the need for the second equiv. of DBU. A one-electron transfer from the first adduct to RhCl_2TCNQ is facilitated by the formation of the known TCNQ dianion¹⁸. For each synthesis outlined in Table 1, an additional peak would begin to form around 490 nm during the course of the reaction. This peak is attributed to the oxidation of TCNQ^{2-} formed during the reaction

following the one-electron transfer to the second equiv. of RhCl_2TCNQ as shown in Scheme 1&2.

Each reaction used chromophore 1a in DMF at the same concentration (4.4×10^{-4}). All the reactions were carried out in a closed system under nitrogen, at 125°C and in the dark unless stated otherwise (depending on the variable being investigated)

Fig.1 shows the effects of air on the chromophore decomposition. For this reaction the vessel was open to air, protected from light and maintained at 125°C. The peak at 490 nm began to form after only 90 min. The chromophore peak at 654 nm had disappeared completely within 144 min.

The relative effects of temperature, light and atmospheric oxygen are demonstrated in Fig.2. The absence of an inert atmosphere leads to the fastest rate of decomposition. The presence of light (from a 60 W white light lamp) focused on the reaction vessel increased the rate of decomposition as well but to a lesser degree.



Scheme 2: Formation of by-product 2 from RhCl_2TCNQ

Table 1: Effect of the rate of heating on the decomposition range and the total mass determined at 400 °C.

Rate of heating(°C min ⁻¹)	Decomposition range (°C)	Total mass loss %
2	241-271	45.5
5	245-279	53.1
7	265-291	54.5
10	268-297	55.1
15	271-302	55.3

There was no reaction at room temperature (under nitrogen and in the dark) after 45 h. A closer look at the temperature dependence is demonstrated in Fig.3. At both room temperature and 65°C the chromophore appears stable even after 45 h. At 80°C and above, the rate of decomposition increases with temperature.

The results show that exposure to atmosphere oxygen had the largest impact on chromophore decomposition similar to the one found for other TCNQ-tertiary amine adducts⁸. Since the chromophore syntheses were done without absolute exclusion of oxygen, water or light, there is still room for further improvement in the reaction yields.

Fig.4. shows the characteristic features of heating rhodium- tetracyanoquinodimethane [Rh-TCNQ].H₂O in nitrogen atmosphere from ambient temperature to 400°C. It shows the TGA,DTA and

DSC curves that were measured at 50C./min⁻¹. The TG curve implies the dehydration of the salt at 110-130°C with a mass loss of 7.5 % [expected mass loss, 7.64 %]. This was followed by a gradual, slow mass loss of 2.7 % up to 265°C leading to the main decomposition reaction occurring at 265-278°C with a mass loss of 45.3%. This makes the total mass loss of 54% at 400°C, which is close to [ca. 57.3%] expected for the formation of Rh metal only from the adduct. The slight disagreement observed [ca.4.2%] could be attributed to the presence of small amounts of oxide residue in the solid product.

Fig.5 monitors the effect of variation of the heating rate on the TG curve of the decomposition of Rh(TCNQ).H₂O. It is clear from Fig.5 that increasing of the heating rate shifts the temperature regimes of the dehydration and the decomposition processes towards higher values.

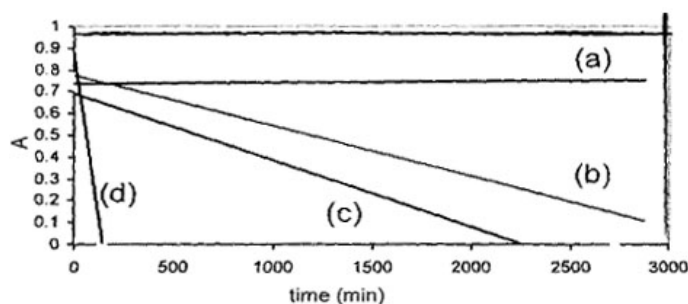


Fig. 2: Absorbance of max (654 nm) versus time for 1a under different conditions: (a) 25°C under N₂(g), dark; (b) 125°C under N₂(g), dark; (c) 125°C, under N₂(g), exposed to light; (d) 125°C, no N₂(g), dark.

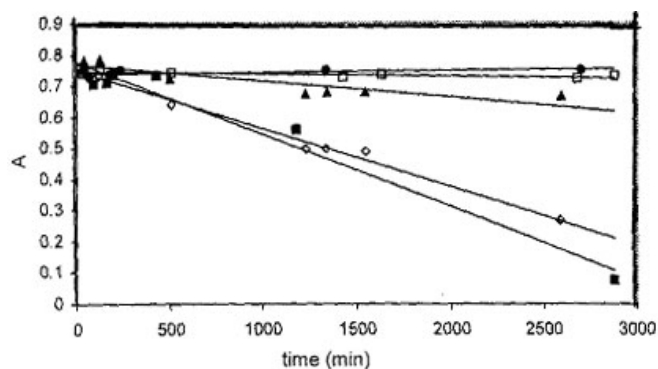


Fig. 3: Absorbance of max (654 nm) versus time of 1a at various temperatures, in the absence of light, under N₂(g); (filled circles) 25°C; (open rectangular) 65°C; (filled triangles) 80 °C; (filled squares) 100 °C; (filled rectangular) 125°C.

Moreover, as the heating rate increases, the total mass loss, leading to maximal recovery of the rhodium metal content, is shown to increase reaching a value of ca. 55.4% at $15^{\circ}\text{C}.\text{min}^{-1}$ which is close to the expected value (57.3%) for $\text{Rh}(\text{TCNQD}).\text{H}_2\text{O} \rightarrow \text{Rh}$. The variation of the final mass loss with the heating rate is reported in Table 1.

The corresponding DTA and DSC curves are broadly similar in displaying two endothermic peaks maximized at 119 and 120°C , respectively (due to the dehydration) and at 278 and 279°C respectively (due to the decomposition). The presence of rhodium oxide and rhodium metal in residual solid products was confirmed by X-ray diffraction of a sample heated to 400°C . Four diffraction lines were obtained at 2.20, 1.90, 1.15 and 1.35°A which matched well with the standard JCPDS data¹⁹ No. 5-685 for Rh metal and its oxide.

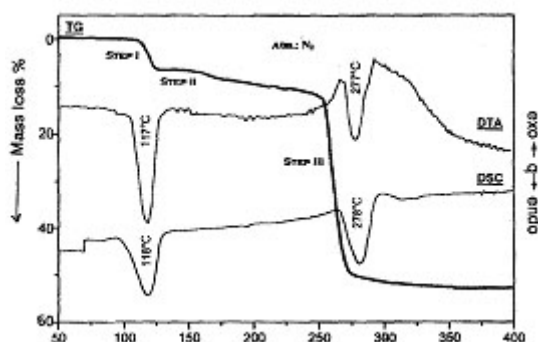


Fig. 4: TG, DTA and DSC curves for the decomposition of Rh (TCNQ). H_2O at a heating rate of $50^{\circ}\text{C}.\text{min}^{-1}$ under a dynamic (40 ml. min^{-1}) atmosphere of N_2 .

Fig.6 shows the IR transmission spectra of the reactant adduct (denoted room temperature) together with that for the solid decomposition product after heating at 400°C at $5^{\circ}\text{C}.\text{min}^{-1}$ in N_2 atmosphere. This can further explain the discrepancy between the calculated and found total mass loss.

Fig.7 display three DTG curves of the decomposition rh(tcnqd). H_2O in N_2 at different heating rates. A shift of the T_{max} values [T_{max} : The temperature of maximum rate of mass loss] towards higher temperatures has taken place as a result of increasing the heating rate. This variation in T_{max} . Experience was used to calculate the kinetic parameters of the dehydration and decomposition processes that are listed in Table 2

The variation of T_{max} of the DTA curves with heating rates was also used to calculate the kinetic parameters using Kissinger equation²⁰. The results

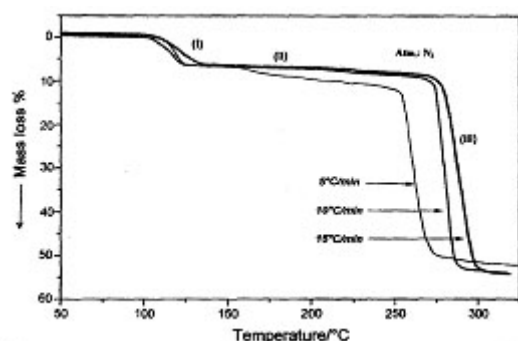


Fig. 5: Three TG curves for the decomposition of Rh (TCNQ). H_2O at different heating rates under a dynamic (40 ml. min^{-1}) atmosphere of N_2 .

Table 2: Kinetic and thermodynamic parameters of the dehydration and decomposition of rhodium $\text{Rh}(\text{TCNQ}).\text{H}_2\text{O}$ in N_2 atmosphere

Parameter	Dehydration process	Decomposition process
Ea. $\text{kJ}.\text{mol}^{-1}$	111.6 ± 5	156.5 ± 6
$\text{Ln}(A.\text{min}^{-1})$	34.0 ± 1.9	28.7 ± 1.7
Correlation coefficient	0.997	0.999
H. $\text{kJ}.\text{mol}^{-1}$	30.83 ± 2	28.32 ± 2
Cp. $\text{kJ}.\text{deg}^{-1}.\text{mol}^{-1}$	0.82 ± 0.09	0.82 ± 0.08
S. $\text{kJ}.\text{deg}^{-1}.\text{mol}^{-1}$	0.080 ± 0.005	0.052 ± 0.004

were in good agreement with those calculated from the DTG curves (given in Table 2).

The thermodynamic functions [i.e., ΔH , C_p and ΔS] for the dehydration and decomposition processes of $\text{Rh}(\text{TCNQ})\cdot\text{H}_2\text{O}$ in N_2 were calculated from a number of DSC experiments carried out at

different heating rates. These values are listed in Table 2.

Data analysis

The activation energy (E_a , $\text{kJ}\cdot\text{mol}^{-1}$) and the frequency factor ($\ln A$, min^{-1}) were calculated for the dehydration and the decomposition processes, by fitting the data, derived from derivative thermogravimetric curves (DTG), obtained at different heating rates, into the Ozawa equation²¹,

$$\ln(\Phi/Tm^2) = (E_a/RT) + \ln(R/0E_a)$$

where Φ is the rate of heating ($^{\circ}\text{C}\cdot\text{min}^{-1}$), T_m is the DTG peak maximum temperature, R is the gas constant ($8.314\text{J}\cdot\text{mol}^{-1}\cdot\text{C}^{-1}$) and 0 is the reduced time ($=1/A$). The enthalpy (H , $\text{kJ}\cdot\text{mol}^{-1}$), heat capacity (C_p , $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{deg}^{-1}$) and entropy (S , $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{deg}^{-1}$) change, were calculated from DSC experiments' was calculated from the amount of heat absorbed or released by each process, whereas C_p was obtained using the following equation¹² $C_p = H/T$, where $T = T_2 = T_1$, T_1 is the temperature at which the peak rejoins the baseline. S was calculated from the following relation²² $\Delta S = 2.303\cdot C_p \cdot \log T_2/T_1$. It is of interest to consider the value of the use of rhodium adduct as a precursor for the preparation of rhodium metal catalysts. One advantage is the low decomposition temperature (400°C) compared with the decomposition temperature required to obtain rhodium metal from the decomposition of the chloride precursor in N_2 atmosphere (near 1000°C)²³.

CONCLUSIONS

The results obtained in this research concerning the yield and reaction times for the syntheses of chromophores 1a and 1b were significantly improved by varying the amount of reactants and with the use of a strong tertiaryamine base making this interesting class of NLO chromophores available in tens of grams for the first time. This new method should also be applicable to similar NLO chromophores that are difficult to make such as those derived from TCNQ and lepidinium derivatives²⁴. Further studies involving chromophore 1a and corresponding EO devices may now be possible.

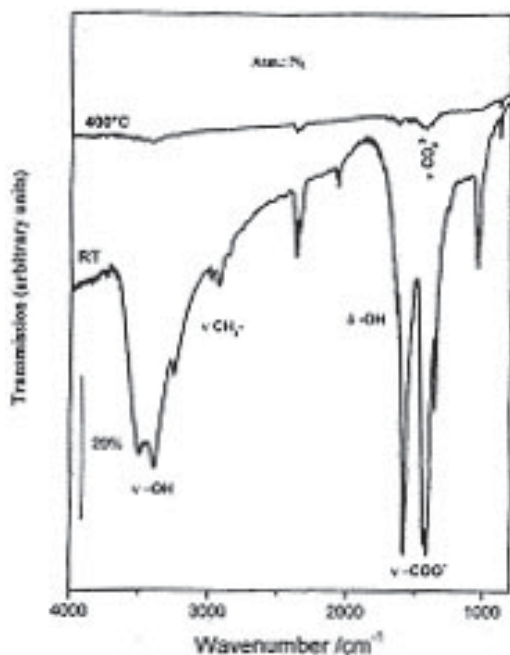


Fig. 6: IR transition spectra of unreacted $\text{Rh}(\text{TCNQ})\cdot\text{H}_2\text{O}$ (denoted RT) and its decomposition product at 400°C in N_2 .

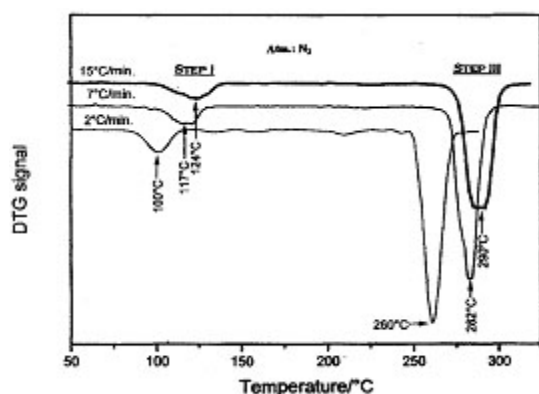


Fig. 7: DTG curves for the decomposition of $\text{Rh}(\text{TCNQ})\cdot\text{H}_2\text{O}$ at different heating rates under a dynamic (40 ml. min^{-1}) atmosphere of N_2 .

Some metal adducts can be used as precursors for the preparation of metal catalysts. Rhodium adduct is introduced as an alternative precursor for rhodium metal catalysts via thermal decomposition in N₂ near 400°C. This is based on its minimal heat demands compared with the commonly used rhodium chloride (produces rhodium metal near 100°C in N₂ atmosphere).

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