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Solid State Interaction of 4-Nitrophenol with Nickel, Zinc and Cadmium Carbonates

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Solid state interactions of 4-nitrophenol with basic carbonates of nickel and zinc and carbonate of cadmium have been examined. The reactions were followed by chemical analysis, TGA-DSC analysis, IR spectral studies and thermal and conductivity measurements. It has been ascertained that the metal carbonate moiety is quite strongly coordinated in the product and the complexes are quite stable upto 100 °C in ideal conditions.

Keywords: 4-Nitrophenol, Metal carbonate, Kinetics, Thermogravimetric analysis, Diffusion.

INTRODUCTION

Since the onset of the notion of green chemistry, solid state reactions have evoked considerable interest [1,2] due to the fact that many transformations afford a high yield in a short reaction time [3-5]. Solid state chemistry deals with the studies of synthesis, structure, reactivity and physical properties of solid materials. The synthesis of new solid state materials and kinetically stable compounds with optimum properties is crucial. The advantage of solid state reactions or mechano-chemical reactions is the elimination of the use of hazardous solvents. Repeated grinding and pulverization provide an increased surface contact to the reacting species, which enhances the reaction rate and, hence, mechano-chemistry [6,7] is very often used in solid state reactions. Grinding brings about a variety of changes such as heating, decreasing particle size or producing large surface area, dislocations in crystalline structure, phase transformations in polymorphic materials, local deformations and melting due to formation of an eutectic mixture [8]. An impressive range of reactions both with organic solids and inorganic solids have been demonstrated in solid state to utilize the advantages and unique characteristics of solid state reactions [9-15]. Mechano-chemistry is an effective tool for the efficient synthesis of a wide range of metal complexes, which varies from straight forward mononuclear complexes to coordination cages and even porous infinite frameworks.

The strong coordinating action of 4-nitrophenol (4-O₂NC₆H₄OH) in solution has been extensively studied and use in analytical applications [16] for a long time. Its biological, biochemical and medicinal studies have been the topic of interest [17,18]. The reaction of 4-nitrophenol with metal

carbonates in solid state forming coordination complexes seems to be *hitherto* unknown. This investigation reveals that it has a strong coordinating action in solid state as well.

EXPERIMENTAL

4-Nitrophenol (Sisco-chem Industries, Bombay, German product) was purified by recrystallization in alcohol, melting point 114 °C, basic nickel carbonate [NiCO₃·2Ni(OH)₂·4H₂O] and cadmium carbonate (CdCO₃) (Loba Chemie, Bombay, India) and basic zinc carbonate [ZnCO₃·2ZnO·4H₂O] (S.D. Fine-Chem Ltd., Bombay, India) were used without further purification. The reactants were powdered in an agate mortar and sieved to above 300 mesh size.

Kinetic studies: Lateral diffusion technique [14] was employed to study the kinetics for the reactions in solid state at different temperatures.

Lateral diffusion technique: Powdered 4-O₂NC₆H₄OH and metal carbonates (above 300 mesh) were packed in a sealed vertical pyrex glass tube of 0.5 cm internal diameter and was kept in an air thermostat maintained at desired temperatures, namely, 60, 65, 70, 75, 85 and 90 °C and controlled to ± 0.5 °C. The kinetics was followed by recording the isothermal growth of the product stratum at the interface at different intervals by a travelling microscope with a calibrated scale in its eyepiece (least count 0.001 cm). 1 g of each reactant (300 mesh) was taken each time and placed over one another under identical pressure as reported earlier [15]. Each reaction was run in triplicate and the average values of the isothermal kinetic data were used to calculate the temperature dependence of the kinetic parameters.

Elemental analysis of reaction products: Solid metal carbonates were finely ground with a large excess of 4-O₂NC₆H₄OH and heated to 85 °C for about 10 days. In another case, 1:1 molar mixtures of 4-O₂NC₆H₄OH and metal carbonates were ground in a mortar and heated at the same temperature for the same duration. The reaction products of both the reactions were washed repeatedly with chloroform (the products were insoluble in chloroform). The products were dried and the metal content (zinc, cadmium or nickel) was estimated gravimetrically [19]. Nitrogen, carbon and hydrogen were determined by micro analytical technique. The results of elemental analyses are as follows: Anal. calcd. for reaction product 4-O₂NC₆H₄OH-CdCO₃(%): Cd, 36.08; N, 4.97; C, 26.99; H, 1.62. Found: Cd, 36.21; N, 4.52; C, 26.93; H, 1.65. Anal. calcd. for reaction product 4-O₂NC₆H₄OH-ZnCO₃ (basic) (%): Zn, 40.76; N, 2.91; C, 17.45; H, 2.30. Found: Zn, 40.12; N, 2.25; C, 17.18; H, 2.62. Anal. calcd. for reaction product 4-O₂NC₆H₄OH-NiCO₃ (basic) (%): Ni, 34.17; N, 2.72; C, 16.30; H, 3.33. Found: Ni, 33.43; N, 2.42; C, 16.11; H, 3.80.

IR studies: Infrared spectra were recorded in KBr disks with a Beckman IR-20 spectrophotometer. Important infrared spectral bands are given in Table-1.

Thermal studies: Metal carbonate and 4-O₂NC₆H₄OH (all above 300 mesh size) were weighed separately and mixed thoroughly in 1:1 molar ratio and poured immediately into a Dewar flask, completely insulated and raise in temperature as a function of time was recorded using a Beckman thermometer reading to 0.01 °C. The plots of temperature against time are shown in Fig. 1. The reaction does not undergo completion as there is no repeated grinding and pulverization of the reaction mixture once kept in the Dewar flask. It appears that the heat evolved in the process is only due to reaction at the contact points of the reactants.

Conductivity measurements: Electrical conductivity measurements were made on powdered reaction mixtures, compressed into a disk, using a Teflon conductivity cell (self designed). Metal carbonates and 4-O₂NC₆H₄OH (all above 300 mesh size) were thoroughly mixed with each other in an equimolar ratio and poured immediately into a die and then pressed into a disk of 0.31 cm² surface area. The disk was hold between platinum electrodes of same surface area and the change in conductivity (σ) with time (t) at room temperature was measured by a GenRad (USA) 1657 model RLC Digibridge at a frequency of 120 Hz. Results of the studies are plotted in Fig. 2.

TGA/DSC analyses: TGA/DSC analyses were carried out by Perkin Elmer Simultaneous Thermal Analyzer (STA6000)

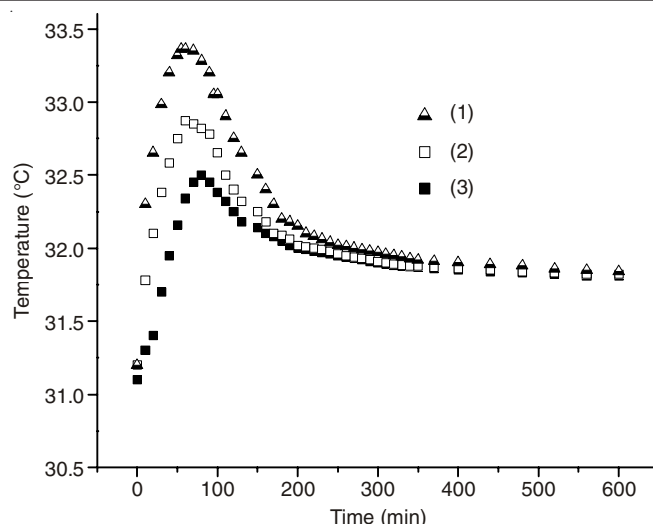


Fig. 1. Temperature rise as a function of time for the reactions: (1) 4-nitrophenol-NiCO₃ (basic), (2) 4-nitrophenol-ZnCO₃ (basic) and (3) 4-nitrophenol-CdCO₃

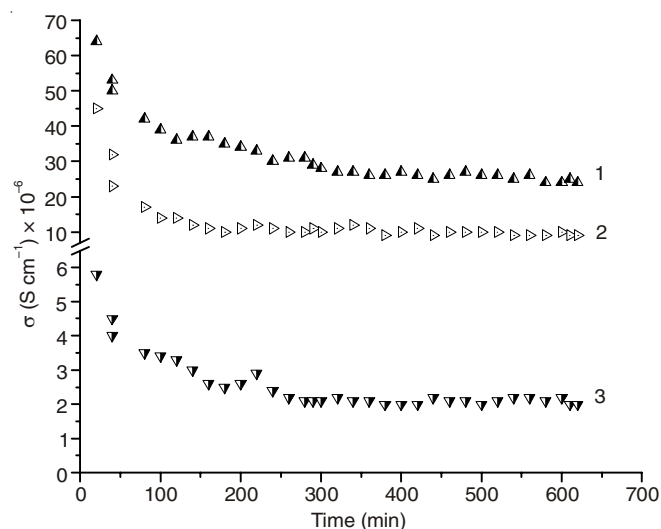


Fig. 2. Variation of electrical conductivity with time for the reactions: (1) 4-nitrophenol-ZnCO₃ (basic), (2) 4-nitrophenol-CdCO₃ and (3) 4-nitrophenol-NiCO₃ (basic)

offering simultaneous measurement and analysis of weight change and heat flow using high purity indium (m.p. 156.61 °C) as standard between 50 to 900 °C at a heating rate of 20 °C/min in nitrogen as a purge gas. The corresponding losses and heat flows are depicted in Figs. 3 and 4, which supports the purity. Thermo analytical data of 4-nitrophenol and the complexes for the corresponding steps are given in Table-2.

TABLE-1
IR SPECTRAL DATA (cm⁻¹) OF 4-NITROPHENOL AND ITS COMPLEXES WITH METAL CARBONATES

Compound/Frequency (cm ⁻¹)	ν_1	ν_2	ν_3	ν_4	$\nu(\text{OH})$	$\nu(\text{C-NO}_2)$	Ring vib.	$\nu(\text{C-O-H})$
4-O ₂ NC ₆ H ₄ OH	—	—	—	—	3300(s) 3160(m)	1600(s) 1540(s)	1550 1500 1480(s) 1440(s)	1260(s)
4-O ₂ NC ₆ H ₄ OH-CdCO ₃	1055(m)	850(s)	1485-1435(bs)	730(s)	3580-3160	1545 1500(s)	1490(m) 1430(m)	1275(s)
4-O ₂ NC ₆ H ₄ OH-ZnCO ₃ (basic)	1030(m)	830(s)	1335(s)	735(s)	3580-3180(bs)	1550(s) 1500(b)	1485(bs) 1435(w)	1275(s)
4-O ₂ NC ₆ H ₄ OH-NiCO ₃ (basic)		830(s)	1330(s)	750(s)	3450(s)	1580(s) 1570(s)	1480(m) 1440(m)	1280(s)

TABLE-2
THERMAL DATA OF 4-NITROPHENOL AND ITS COMPLEXES WITH METAL CARBONATES

Sample	Decomposition step	Weight loss (%)	Decomposition range (°C)	Heat flow peak temperature (°C)	ΔH^* (J/g)	Residue remain
4-O ₂ NC ₆ H ₄ OH	1	98.60	152-280	114.5	162.90	-
				271.4	368.70	
[4-O ₂ NC ₆ H ₄ OH·CdCO ₃]	1	29.06	165-302	108.3	43.55	CdO
				225.7	70.38	
	2	16.55	308-325	318.3	-173.35	
[4-O ₂ NC ₆ H ₄ OH·ZnCO ₃ ·2ZnO·4H ₂ O]	1	32.82	98-320	268.3	178.07	3ZnO
				348.0	-1435.59	
	2	18.75	330-644	555.7	-174.48	
[4-O ₂ NC ₆ H ₄ OH·NiCO ₃ ·2Ni(OH) ₂ ·4H ₂ O]	1	28.9	98-338	118.1	205.43	3NiO
				345.6	-556.76	
	2	26.9	342-600	365.2	-190.17	
				449.9	-816.93	

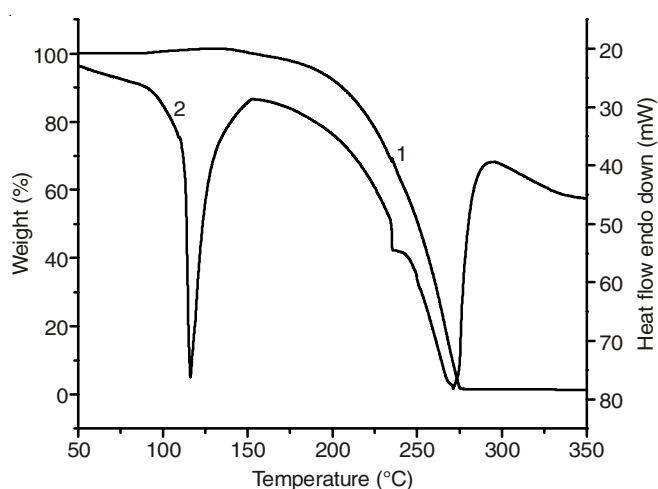


Fig. 3. TGA (1) and DSC (2) curve of 4-nitrophenol

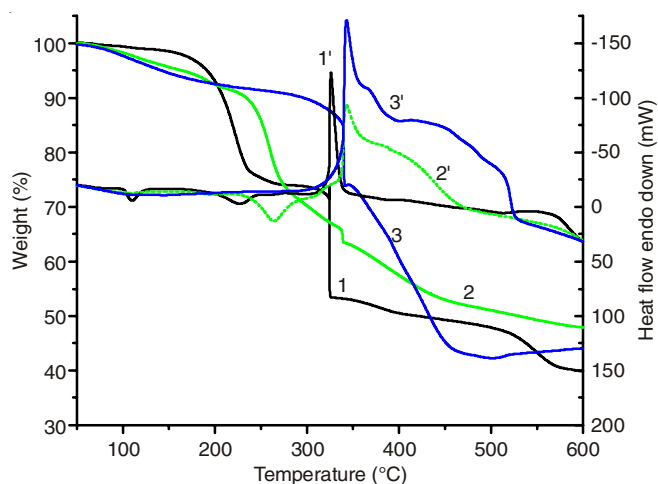


Fig. 4. TGA (1) and DSC (1'), TGA (2) and DSC (2') & TGA (3) and DSC (3') curves of the products of 4-nitrophenol and CdCO₃, 4-nitrophenol and ZnCO₃ (basic) & 4-nitrophenol and NiCO₃ (basic)

RESULTS AND DISCUSSION

Product analyses show that the metal carbonates and 4-O₂NC₆H₄OH react in the molar ratio of 1:1. In all thermal measurements, temperature rises sharply and then falls off gradually due to the dissipation of heat (Fig. 1) showing exothermicity. The plots of the conductivity (σ) versus time

(t) (Fig. 2) at room temperature show only single inflections due to the sharp fall in conductance attaining constancy, thereby, suggesting that all are one step reactions. Table-2 shows the TGA/DSC results of thermal decomposition of 4-O₂NC₆H₄OH and its products. The TGA curve (Fig. 3) of 4-O₂NC₆H₄OH refer to complete mass loss in temperature range 150-280 °C in a single step due to the evaporation of 4-O₂NC₆H₄OH. The DSC curve (Fig. 3) shows two endotherms with peaks at 114.5 °C and 271 °C respectively and ΔH as 162.90 and 368.70 J/g corresponding to the melting and vaporization of 4-O₂NC₆H₄OH.

TGA-DSC curves (Fig. 4) of the products of 4-O₂NC₆H₄OH with CdCO₃, ZnCO₃(basic) and NiCO₃(basic) show that the first loss in all the cases is due the loss of -C₆H₄OH moiety in the temperature ranges 165-302, 98-320 and 98-360 °C respectively. In case of the product [4-O₂NC₆H₄OH·CdCO₃], the loss of -C₆H₄OH moiety is followed by subsequent losses in the temperature ranges (308-325) °C and (330-612) °C corresponding to NO₂ and CO₂, respectively. In this case, 2 endotherms appears at 108.3 and 225.7 °C where the first endotherm seems to be a starting transient or an artifact and the second corresponds to the decomposition. The other 2 exotherm peaks observed at 318.3 and 550.4 °C corresponds to loss of NO₂ and CO₂ on further decomposition. In case of the products with basic carbonates, the first loss corresponds to the removal of -C₆H₄OH moiety along with the loss of 4 water molecules of hydration in the temperature ranges 98-320 and 98-338 °C, respectively with endotherm peaks at 268 °C and 118 °C for [4-O₂NC₆H₄OH·ZnCO₃·2ZnO·4H₂O] and [4-O₂NC₆H₄OH·NiCO₃·2Ni(OH)₂·4H₂O]. The subsequent decompositions for [4-O₂NC₆H₄OH·ZnCO₃·2ZnO·4H₂O] occur in the regions 330-644 °C with exotherm peaks at 348 °C and 555.7 °C corresponding to the loss of NO₂ and CO₂. In case of [4-O₂NC₆H₄OH·NiCO₃·2Ni(OH)₂·4H₂O] the subsequent decomposition occurs in the region 342-600 °C with exotherm peaks at 345.6, 365.2 and 449.9 °C corresponding to the loss of NO₂, H₂O and CO₂. However, after the first decomposition, the subsequent decomposition steps were almost continuous and hence posed ambiguity in identifying the exact steps. The TG/DSC data (Table-2, Fig. 4) show that the complexes are quite stable upto about 100 °C, the maximum temperature of performed kinetics. Further, the absence of melting endotherms

of 4-O₂NC₆H₄OH in products confirm the definite interaction between the organic compound and metal carbonates. The decomposition corresponding to NO₂ and CO₂ takes place only in the subsequent step(s) leaving behind residual metal oxides in stoichiometric proportions. This shows that the metal carbonate moiety is quite strongly held in the product.

Chemical analyses of the products also reveal that the metal carbonates and 4-O₂NC₆H₄OH react in 1:1 molar ratio. IR spectra of the products obtained by mixing the metal carbonates with (i) excess 4-O₂NC₆H₄OH and removing the unreacted 4-O₂NC₆H₄OH by treating with chloroform and (ii) equimolar amount of 4-O₂NC₆H₄OH are the same. The characteristic stretching vibrations of 4-O₂NC₆H₄OH [20,21] and those of its reaction products with basic NiCO₃, basic ZnCO₃ and CdCO₃ have been reported in Table-1. It is quite apparent from the table that the coordination basically takes place

through $\text{—N} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$ group as its characteristic vibrations are negatively shifted in the complexes. The $\nu(\text{C—O—H})$ frequency which should have been negatively shifted after coordination to metal ion, is rather showing a different trend. However, the expected increase in $\nu(\text{O—H})$ stretching vibration after complexation could not be ascertained with certainty probably because the release of hydrogen bonding upsets the expected change in $\nu(\text{O—H})$ stretching vibration. The chelation of CO[−] anion has also been indicated from the observed IR frequencies [22].

In lateral diffusion experiments, coloured boundaries formed at the interface grew only on the side of metal carbonates, indicating that 4-O₂NC₆H₄OH is the diffusing species. Growth of the thickness of product layer follows the equation:

$$\xi^n = kt$$

where ξ is the thickness of the product layer formed at time t and k and n are constants. The validity of the equation was tested by plotting $\log \xi$ versus $\log t$ where straight lines were

obtained. The fitting was done using linear least-squares curve fitting technique and the values of n and k were obtained by the best-fit plot. The extent of precision in k was calculated. As ξ is the experimental quantity, the error in k , if any, must be due to the error in the measured ξ values.

Therefore, the best-fit n value was substituted in equation $\xi^n = kt$ to obtain various k values for different ξ and its corresponding t values at the given temperature. The different k values so obtained were used to calculate the extent of precision. The values of n and k at different temperatures for each reaction are reported with their probable precision in Table-3. The values of n in $\xi^n = kt$ gradually falls with increasing temperature. However, the quantum of fall diminishes as it approaches higher temperature. The variation in the value of n and the plot of $\log k$ against $1/T$ (Fig. 5) clearly shows that the process occurring at lower temperatures is different from the one that occurs at higher temperatures. This has been reflected in the values of the activation energies (Table-4) calculated from Arrhenius reliance of rate constant (Fig. 5) for the low and high temperature ranges. It is observed that the activation energy, for all set of reactions, is high in the lower temperature range and low in higher temperature range. In any set of lateral diffusion experiment at a given temperature, the rate of growth of the product layer decreased with time. Initially the process is fast and reaction controlled. With the formation of product layer at the interface between two reactants, the reagent takes more and more time to diffuse through the product layer; the process becomes diffusion controlled and the rate thus falls continuously with the growth of product layer. At lower temperatures, the process is initially reaction controlled turning to be diffusion controlled with the passage of time with the increase in thickness of the product layer. However, at higher temperatures, the diffusion becomes comparatively faster even with the growth of product layer than the one observed at lower temperatures and, hence, does not play a significant role in controlling the rate of reaction at

TABLE-3
TEMPERATURE DEPENDENCE OF KINETIC PARAMETERS OF THE EQUATION $\xi^n = kt$

Reaction	Temperature (°C)	k (cm h ^{−1})	Standard deviation σ_{n-1}	n
4-O ₂ NC ₆ H ₄ OH-NiCO ₃ (basic)	(60 ± 0.5)	1.6427×10^{-4}	0.0385×10^{-4}	2.490
	(65 ± 0.5)	3.2531×10^{-4}	0.0603×10^{-4}	2.423
	(70 ± 0.5)	7.5444×10^{-4}	0.1460×10^{-4}	2.310
	(75 ± 0.5)	15.3230×10^{-4}	0.4940×10^{-4}	2.224
	(80 ± 0.5)	29.0410×10^{-4}	0.3849×10^{-4}	2.120
	(85 ± 0.5)	44.4920×10^{-4}	1.2928×10^{-4}	2.081
	(90 ± 0.5)	64.8260×10^{-4}	1.4489×10^{-4}	2.056
4-O ₂ NC ₆ H ₄ OH-ZnCO ₃ (basic)	(60 ± 0.5)	0.4373×10^{-4}	0.0081×10^{-4}	2.763
	(65 ± 0.5)	1.0497×10^{-4}	0.0273×10^{-4}	2.618
	(70 ± 0.5)	2.3767×10^{-4}	0.0585×10^{-4}	2.488
	(75 ± 0.5)	5.2775×10^{-4}	0.0818×10^{-4}	2.322
	(80 ± 0.5)	9.7063×10^{-4}	0.3377×10^{-4}	2.258
	(85 ± 0.5)	14.1710×10^{-4}	0.4868×10^{-4}	2.239
	(90 ± 0.5)	22.4250×10^{-4}	1.0058×10^{-4}	2.214
4O ₂ NC ₆ H ₄ OH-CdCO ₃	(60 ± 0.5)	0.9933×10^{-5}	0.0152×10^{-5}	2.943
	(65 ± 0.5)	2.2326×10^{-5}	0.1105×10^{-5}	2.833
	(70 ± 0.5)	6.5779×10^{-5}	0.3406×10^{-5}	2.646
	(75 ± 0.5)	14.3880×10^{-5}	0.8022×10^{-5}	2.532
	(80 ± 0.5)	29.0170×10^{-5}	0.8261×10^{-5}	2.425
	(85 ± 0.5)	51.6710×10^{-5}	0.6893×10^{-5}	2.351
	(90 ± 0.5)	81.5650×10^{-5}	1.8797×10^{-5}	2.316

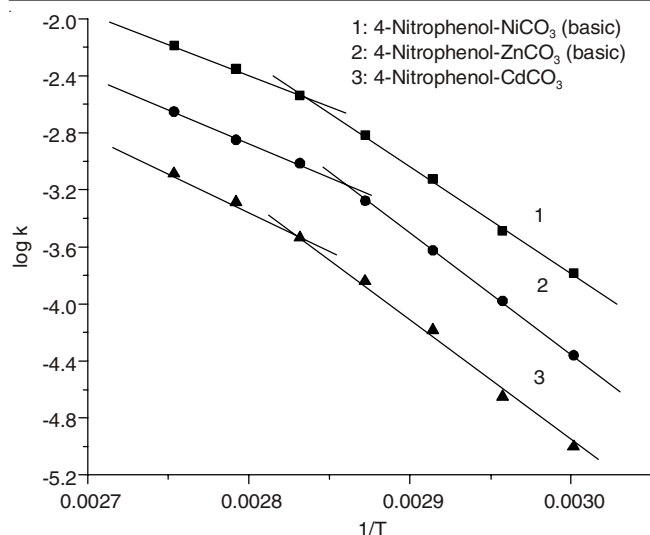


Fig. 5. Dependence of rate constant (k) on temperature (T)

TABLE-4
ACTIVATION ENERGIES OF THE REACTIONS

Reactions	Activation Energy (kJ mol ⁻¹)	
	Lower temperature range	Higher temperature range
4-O ₂ NC ₆ H ₄ OH-NiCO ₃ (basic)	143.90 ± 1.41	85.48 ± 1.72
4-O ₂ NC ₆ H ₄ OH-ZnCO ₃ (basic)	148.73 ± 1.42	89.13 ± 1.72
4-O ₂ NC ₆ H ₄ OH-CdCO ₃	174.28 ± 1.28	110.41 ± 1.45

any stage. At higher temperatures, the rate of the process most likely remains reaction controlled all through which is evident from n value that keeps decreasing with increase in temperature.

Conclusion

4-Nitrophenol appears to have strong coordinating action in solid state forming 1:1 addition product with metal carbonates in a single step which are quite stable upto 100 °C. Different rate controlling processes are involved in different range of temperatures. At lower temperatures, the process is initially

reaction controlled turning to be diffusion controlled with the formation of more and more products whereas the process remains reaction controlled all through at higher temperatures.

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