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THERMAL EXPLOSION OF NITROPHENATES OF TRANSITION METALS

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The thermal decomposition studies on nitrophenates of copper, nickel and cobalt have been undertaken. α-*t* curves show dehydration of these compounds at lower temperatures whereas dehydration cum decomposition seem to occur at higher temperatures leading to oxidative combustion of aromatic part. NO_2 gas is evolved during decomposition which seems to be responsible for oxidative reactions leading to detonation. The explosion temperature and velocity of detonation have been found to be linearly related with the number of nitro groups. The mechanism of thermal explosion has also been discussed.

Keywords: nitrophenates, thermal explosion, transition metals

Introduction

The thermo-explosive characteristics of the metallic salts of picric acid are of interest in the technology of explosives chiefly because of the ease with which picric acid combines with many metals and basic salts to form picrates and some of which are capable of direct detonation when subjected to heat or shock [1, 2]. Kast [3] reported that highly hydrated explosive compounds are less sensitive to heat and shock whereas anhydrous are the most sensitive ones. Thermal decomposition of energetic materials (explosives) at very high temperatures, cause spot initiation centres leading to explosion. Most of the explosive materials are decomposed by heat at relatively moderate temperatures. A kinetic investigation using thermogravimetry is an effective method of clarifying the mechanism of decomposition and/or explosion reactions [4–8].

Therefore, it was found appropriate to synthesize, several nitrophenates of transition metals. A detailed study of their behaviour on thermal decomposition

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and sensitivity towards heat is likely to yield valuable information regarding the mechanism of explosive reactions. Therefore, the thermal decomposition of these compounds was undertaken. The role of nitro group and water of crystallization present in the nitrophenate salts has also been discussed.

Experimental

Materials

Picric acid (CDH) and 2, 4-dinitrophenol (Thomas Baker) were used without any further purification whereas 2-nitrophenol (Loba) was recrystallised from hot water. Carbonates of cobalt, copper (BDH) and nickel (Thomas Baker) were taken for the preparation of metal hydroxides.

Preparation of nitrophenates of transition metals

Nitrophenates are generally prepared by the interaction of transition metal cations with mono-, di- and trinitrophenols [9–12]. Thus copper, nickel and cobalt nitrophenates were prepared by reacting suspension of nitrophenols in boiling water with freshly prepared hydroxides of these metals. Hydroxides were prepared by treating sodium hydroxide with carbonates of these metals. After completion of the reaction, the solution was filtered and concentrated with rotary evaporator (JSGW) at low temperature (60°C) and pressure (200 mm Hg) in order to achieve crystalline solids. These were separated and recrystallised from aqueous solution. The metal trinitrophenates (TNP) are bright yellow, dinitrophenates (DNP) are yellow or orange and mononitrophenates (MNP) are bright red crystals. Their purity was checked by TLC (mobile solvent ethylacetate) and coloured spots were obtained on TLC plates without any developing reagent.

Metal percentage in the mononitrophenates was confirmed by mass loss method. However, very small amount of carbon was also found to be formed during heating at a very slow rate upto 600°C. Di- and trinitrophenate samples were mixed with Al_2O_3 in 1:3 ratio and decomposed to metal oxide at a very slow heating rate as pure compounds undergo explosion prior to the formation of metal oxides. The formation of metal oxide was found to be within experimental error. The molecular formula of the nitrophenates are given in Table 1.

Thermogravimetric (TG) studies on metal nitrophenates

Thermogravimetric studies were undertaken on a home made apparatus assembled in our laboratory [13]. The temperature of the furnace was controlled to ±1°C. The sample of about 10 mg, (Particle size 100 –200 mesh) was taken in a

Table 1 Oxygen balance, number of water molecules, explosion temperature, and velocity of detonation of metal nitrophenates

Sample	Molecular formula	No. of water molecules	Explosion temperature / °C	Oxygen balance	Velocity of detonation / m·sec^{-1}
Cu–MNP	$Cu[(NO_2)C_6H_4O]_2$	1	330 ± 4	–103.68	5080
Cu–DNP	$Cu[(NO_2)_2C_6H_3O]_2$	2	312 ± 2	–63.33	6442
Cu–TNP	$Cu[(NO_2)_3C_6H_2O]_2$	2	300 ± 3	–36.96	7331
Ni—MNP	$Ni[(NO_2)C_6H_4O]_2$	1	356 ± 2	–104.30	5059
Ni–DNP	$Ni[(NO_2)_2C_6H_3O]_2$	3	325 ± 4	–64.08	6416
Ni–TNP	$Ni[(NO_2)_3C_6H_2O]_2$	2	309 ± 2	–37.30	7320
Co–MNP	$Co[(NO_2)C_6H_4O]_2$	2	300 ± 5	–105.12	5032
Co–DNP	$Co[(NO_2)_2C_6H_3O]_2$	2	225 ± 1	–64.02	6418
Co–TNP	$Co[(NO_2)_3C_6H_2O]_2$	1	220 ± 2	–37.29	7320

gold crucible. For isothermal TG, samples were run at 100°, 125°, 140°, 160°, 180° and 200°C. The data were repeated three times and plots of fractional decomposition (α) *vs.* time (t) are given in Figs 1–3. Non-isothermal TG data were undertaken at a heating rate of 2 deg·min^{-1} and repeated three times. The α *vs.* T (Temp. °C) plots are given in Fig. 4. The low rate of heating was selected on

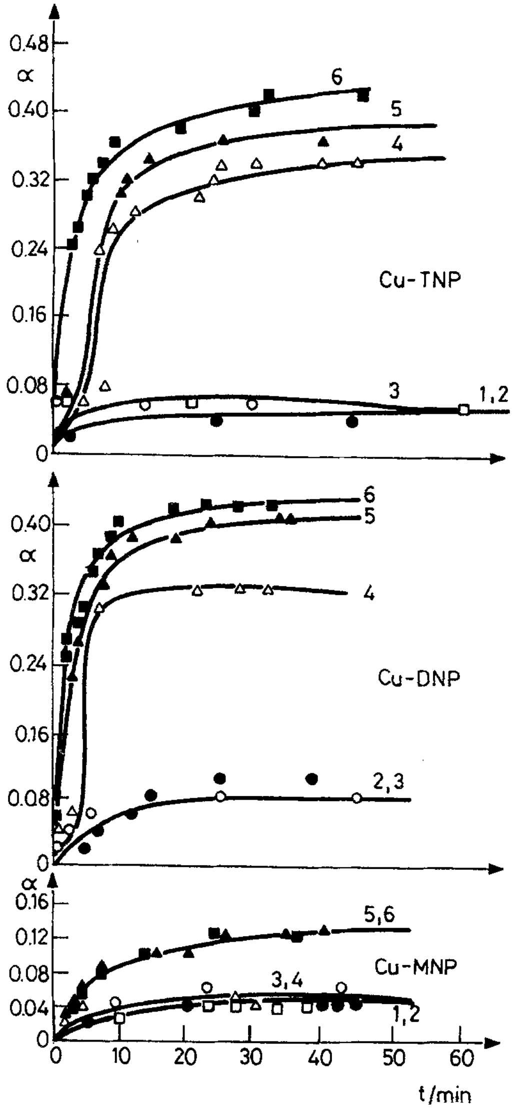

Fig. 1 Isothermal decomposition of Cu-nitrophenates (100–200 mesh), plots of α *vs.* t: (1)100°, (2)125°, (3)140°, (4)160°, (5)180° and (6) 200°C

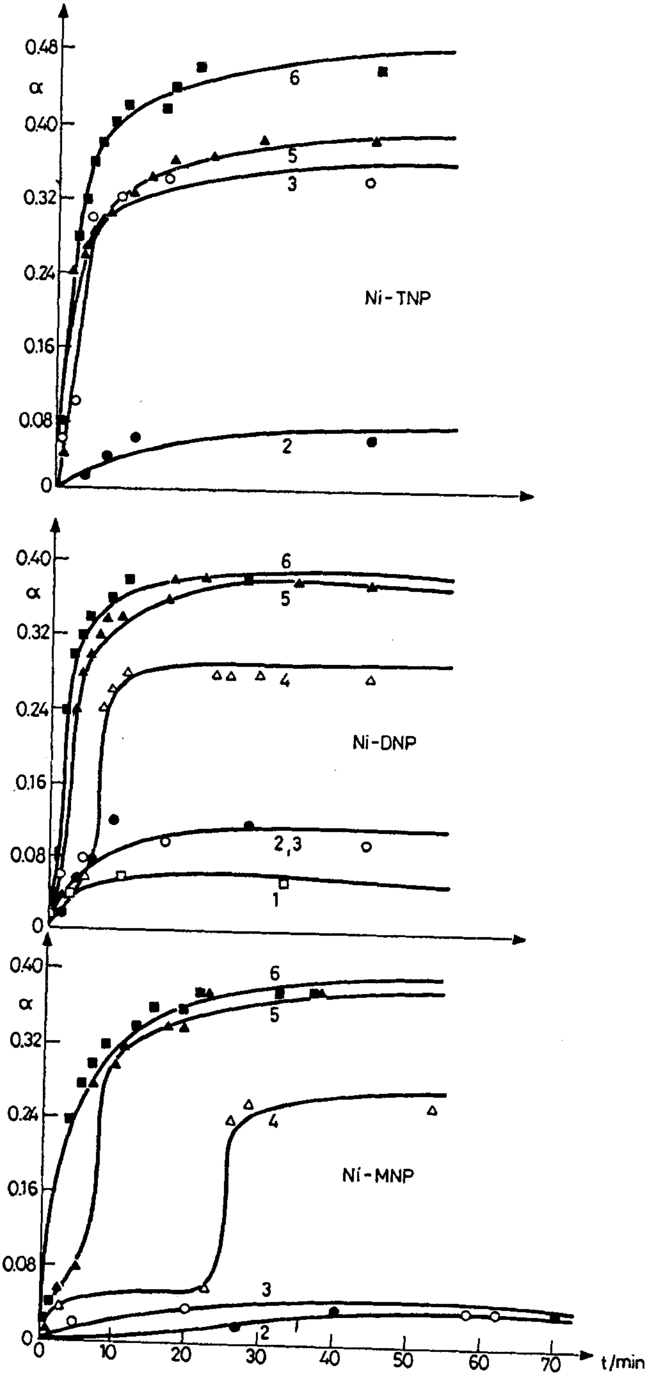

Fig. 2 Isothermal decomposition of Ni-nitrophenates (100–200 mesh), plots of α *vs*. *t*: (1)100°, (2)125°, (3)140°, (4)160°, (5)180° and (6) 200°C

account of the fact that samples detonate at higher heating rates without undergoing appreciable mass loss.

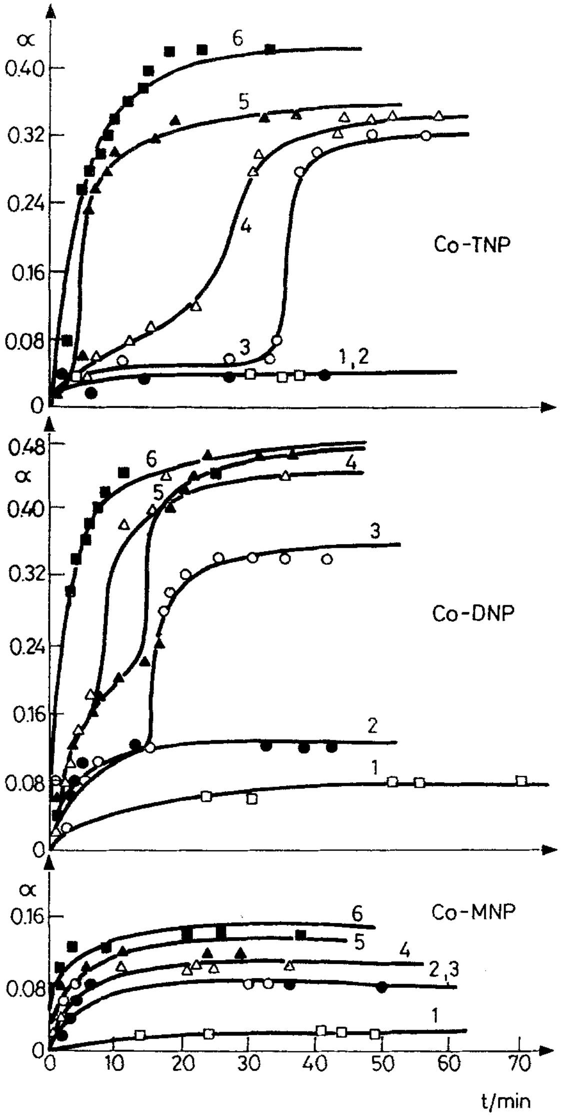

Fig. 3 Isothermal decomposition of Co-nitrophenates (100–200 mesh), plots of α *vs.* *t*: (1)100°, (2)125°, (3)140°, (4)160°, (5)180° and (6) 200°C

Results and discussion

Figures 1–3 clearly show that the rate of decomposition of each compound increases with increase in the temperature and induction period was absent in all the cases which may be due to grinding. On careful examination of the α –*t* curves reported in Figs 1–3, it has been found that these compounds are dehydrated at

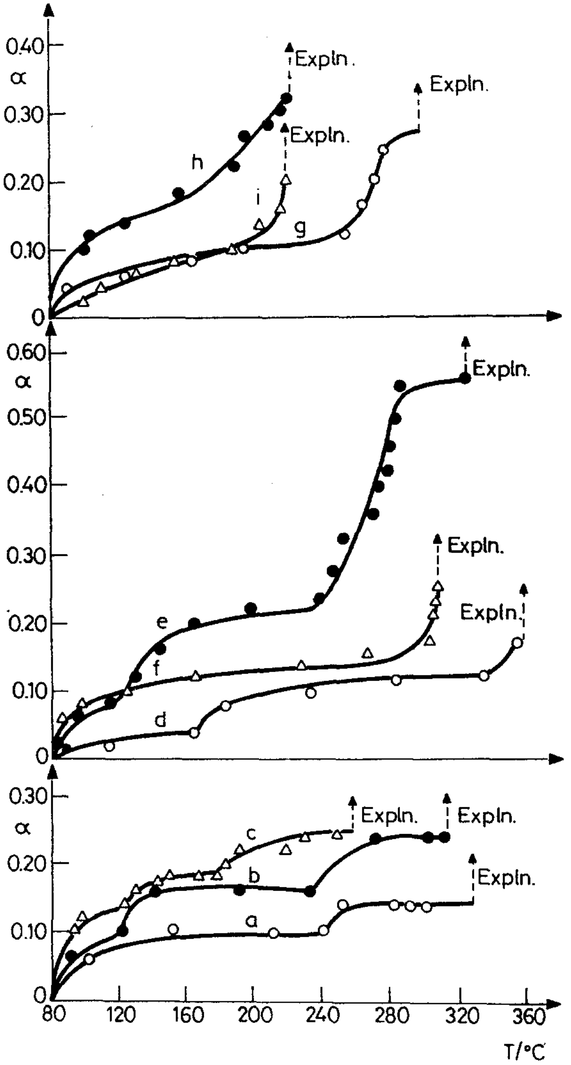

Fig. 4 Dynamic TG of (a) Cu-MNP, (b) Cu-DNP, (c) Cu-TNP, (d) Ni-MNP, (e) Ni-DNP, (f) Ni-TNP, (g) Co-MNP, (h) Co-DNP and (i) Co-TNP: heating rate = 2 deg·min^{-1}, weight of the sample = 10 mg (100–200 mesh)

lower temperatures whereas dehydration is coupled with decomposition at higher temperatures. The number of water molecules present in each compound are calculated and data are given in Table 1.

NO_2 gas is expected to be liberated as these compounds undergo decomposition and it was confirmed by chemical analysis.

Evolution of NO_2 and other oxides of nitrogen have been reported by Hara *et al.* [14, 15] when tetryl and TNT samples were heated at high temperature.

It was thought to investigate the kinetics of dehydration cum decomposition by theoretical model functions [16, 17] given in Table 2, which are applicable to most of the salts [18–20]. The kinetics of solid state reactions can be represented by the general equation.

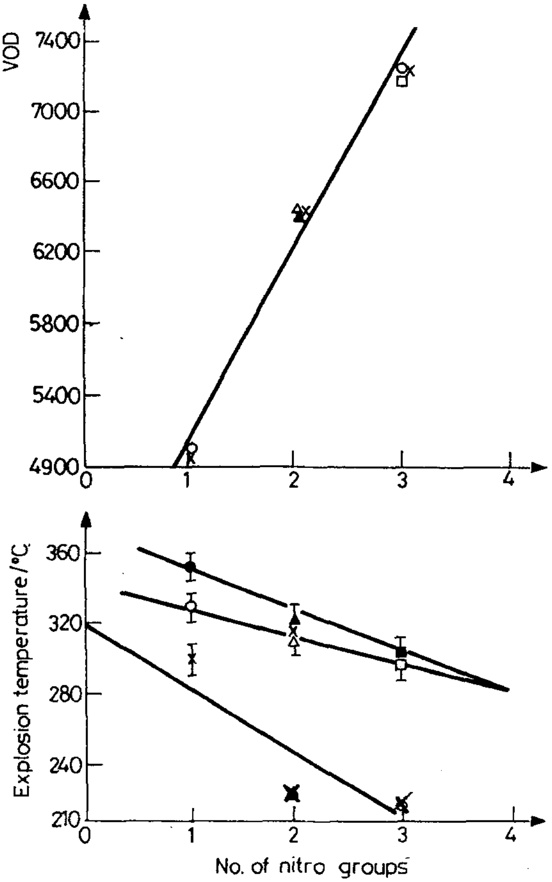

Fig. 5 Plots of explosion temperature and velocity of detonation (VOD) against number of nitro groups: ○ — Cu-MNP, △ — Cu-DNP, ⊡ — Cu-TNP, ● — Ni-MNP, ▲ — Ni-DNP, ■ — Ni-TNP, x — Co-MNP, ✖ — Co-DNP and ✖ — Co-TNP

$$G(\alpha) = kt \tag{1}$$

where k is a rate constant, t is the reaction time and $G(\alpha)$ is a function of the macroscopic reaction mechanism. No $G(\alpha)$ function (Eq. (1)) gave linear plots with isothermal TG data. It seems that the mechanism of thermal decomposition of these salts change with temperature. It is clear from the plots reported in Figs 1–3 that dehydration is occurring between 100°–125°C in case of Ni-TPN, Co-DNP, Co-TNP; 100°–140°C in case of Cu-MNP, Cu-DNP, Cu-TNP, Ni-MNP, Ni-DNP, Co-MNP and above these temperatures, dehydration is accompanied by decomposition (evolution of NO_2). Further, oxidative decomposition reactions with NO_2 seem to be responsible for the rupture of the hydrocarbon part of these compounds [21, 22]. Thus non-applicability of Eq. (1) seems plausible due to varied nature of plots (dehydration and dehydration cum decomposition at various temperatures).

Table 2 Commanly used $G(\alpha)$ functions for solid-phase reactions

$G(\alpha)$	Rate-controlling process
$1-(1-\alpha)^{1/2}$	Two dimensional phase boundary reactions: contracting square equation
$1-(1-\alpha)^{1/3}$	Three dimensional phase boundary reactions: contracting cube equation
$[-\ln(1-\alpha)]^{1/n}$	Random nucleation: Avrami-Erofeev equation (n = 1, 2, 3).
$[1-(1-\alpha)^{1/3}]^2$	Three dimensional diffusion: Jander equation

Non-isothermal TG data reported in Fig. 4 also showed mass losses (seems to be due to dehydration) comparable with the isothermal TG data upto 100°C, for all the samples. The explosion temperature for each compound, reported in Table 1, were noted from Fig. 4, at a constant heating rate of 2 $\text{deg}\cdot\text{min}^{-1}$. It may be noted that decomposition will overlap with dehydration process during isothermal TG studies, whereas dehydration will be completed prior to the start of decomposition in case of non-isothermal decomposition.

The percent oxygen balance (Ω) was calculated by the following relation (2) suggested by Martin and Yallop [23] and data are given in Table 1.

$$\Omega = \frac{\left(z - 2x - \frac{y}{2}\right)1600}{\text{mol. weight}} \tag{2}$$

where x, y and z are the respective number of atoms of carbon, hydrogen and oxygen in the molecule. Furthermore, the velocity of detonation (VOD) was calculated by the relation (3) and data are reported in Table 1.

$$\mathrm{VOD} = 8578 + 33.74\,\Omega \tag{3}$$

Figure 5 clearly shows that VOD increases with the increase in the number of nitro groups whereas explosion temperature is lowered with the increase in the number of NO_2 group. However, linear relationships are observed in each case (Fig. 5).

It seems that all the nitrophenate salts undergo dehydration followed by decomposition and nuclei are formed at the corners and edges of the particles within a very short time (within the time in which the sample is heated up to the furnace temperature). However, all the salts have been found to decompose without melting. Thus evolution of gaseous products induce strain in the crystal lattices of these salts and the rate of decomposition is enhanced in the solid state. NO_2 gas evolved oxidise the hydrocarbon ring and metal ions seems to catalyse the oxidative reactions culminating in detonation. However, the catalytic oxidation by metal ions was observed in the order Co > Cu > Ni.

We therefore propose the following stages as probable ones depicted in scheme 1.

$$\mathrm{M[(NO_2)_xC_6H_{5-x}O]_2\cdot yH_2O} \xrightarrow[-y\,\mathrm{H_2O}]{<140^\circ\mathrm{C}} \mathrm{M[(NO_2)_xC_6H_{5-x}O]_2} \xrightarrow{>140^\circ\mathrm{C}}$$

$$\{\mathrm{M[C_6H_{5-x}O]_2}+x\mathrm{NO_2}\} \xrightarrow[\text{decomposition reactions}]{\text{Oxidative}} \text{Detonation} \longrightarrow \text{Gaseous products}$$

Intermediates

where x = No. of NO_2 groups, y = No. of water molecules, and M = Cu, Ni or Co.

Considerable amount of heat would be liberated during decomposition due to exothermic oxidative autocatalytic reactions and when the rate of decomposition is sufficiently high, explosion will take place.

Conclusions

Nitrophenates of copper, nickel and cobalt undergo audible thermal explosion. The explosive properties of these salts are controlled by the number of nitro groups attached to the hydrocarbon nucleus. NO_2 gas, evolved during thermal decomposition, seems to be responsible for oxidative reactions.

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Zusammenfassung — Es wurde die thermische Zersetzung von Kupfer-, Nickel- und Cobalt-Nitrophenaten untersucht, die α-t Diagramme zeigen die Dehydratation dieser Verbindungen bei niedrigeren Temperaturen, während höhere Temperaturen zur Dehydratation und Zersetzung zu führen scheinen, was zur Verbrennung des aromatischen Teiles führt. Während der Zersetzung wird NO_2-Gas freigesetzt, was für die zur Detonation führenden Oxidationsreaktionen verantwortlich zu sein scheint. Man fand, daß Explosionstemperatur und Detonationsgeschwindigkeit sich proportional zur Anzahl der Nitrogruppen verhält. Auch der Mechanismus der thermischen Explosion wurde diskutiert.