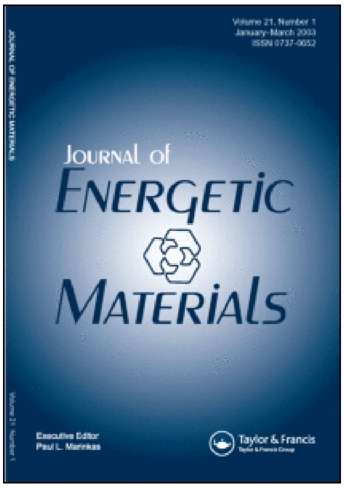

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Nitrophenates of transition metals[1] part II. DTA, explosion delay, impact and friction sensitivity studies

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NITROPHENATES OF TRANSITION METALS[1]
PART II. DTA, EXPLOSION DELAY, IMPACT AND FRICTION SENSITIVITY STUDIES

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ABSTRACT

Thermolysis of nitrophenates ($C-NO_2$ explosives) of transition metals of 3d-series have been studied by DTA, impact, friction, and explosion delay measurements. Explosion delay (D_E), explosion temperature (ET), activation energy for explosion (E^*), and height for 50% explosion ($h_{50\%}$) have been found to be in the order: trinitro$<$dinitro$<$mononitrophenates of transition metals. Only trinitrophenates have been found to be friction sensitive. It has been observed that these salts dehydrate below 140°C and at higher temperatures corresponding metal oxide and nitrosubstituted diphenylethers(as intermediates) are formed. The oxidative decomposition reactions seem to occur in adsorbed phase between NO_2, MO, and radical species leading to explosion.

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INTRODUCTION

As part of ongoing programme to understand the machanism of thermolysis of energetic materials[2-13] we have synthesised and characterised the nitrophenates of transition metals (NPTM) of 3d-series and these studies are reported in our previous paper.[1] Studies on thermolysis of NPTM are quite meagre and machanism of their thermolysis is far from understood.[14-24] Therefore, DTA, explosion delay, impact and friction sensitivity investigations on NPTM have been undertaken, which are discussed in this present communication. It has been observed that explosion temperature (ET) is linear with O/H, H/NO_2 ratios, number of nitro groups and velocity of detonation (VOD). A detailed thermolytic pathways leading to explosion have also been elucidated.

EXPERIMENTAL

DTA Studies on NPTM

DTA studies were carried out from 20°C to 450°C at static air, by using a DTA apparatus fabricated at Explosives Research & Development Laboratory (ERDL), Pune, at a heating rate of 10°C/min. 5 mg of NPTM sample (100-200 mesh) was taken in an open platinum cup and calcined alumina was taken in another platinum cup as reference sample. The ΔT was recorded with the help of Pt-Pt(Rh 13%) thermocouple. The DTA curves for all NPTM are presented in Figure 1 and recorded decomposition temperatures (T_d) are reported in Table 1.

Explosion Delay Measurements on NPTM

The explosion delay measurements were undertaken by the tube furnace (TF) technique as described in our earlier publications.[2,3,5,6] The sample (wt. = 10 mg, 100-200 mesh) was taken in an ignition tube (5 cm length and 0.4 cm diameter) and the time interval between the insertion of the ignition tube into the TF and the moment of an audible explosion, noted with the help of a stop watch with accuracy to 0.1 s, gave the value of explosion delay (D_E). The ignition tube loaded with the sample, clamped in a bent wire, was inserted manually into the TF upto a fix depth (7 cm) just above the probe of the temperature-indicator cum controller (Century, CT808T). The time taken for insertion of the ignition tube was also kept constant throughout the measurements. The accuracy of the TF was ± 1°C. Each run was repeated three times, and mean D_E values are reported in Table 2. The explosion temperature (ET) for these compounds were taken at D_E of 10 s and data are given in Table 1. D_E data were found to fit in the following equation[2,25-27].

$$1/D_E = A\ e^{\overset{\bullet}{E}/RT} \qquad (1)$$

where E^* is the activation energy for explosion and T is the absolute temperature. Typical plots are shown in Figure 2. The E^* and correlation coefficient (r) values are reported in Table 2.

Impact Sensitivity Measurements on NPTM

Impact sensitivity measurements were carried out by an impact machine for high explosives at ERDL, Pune. It consists of 1 inch long striker and a 1 inch long anvil machined to 1.5 cm diameter and hardened to the base. A conical heap, comprising about 10 mg of the sample (100-200 mesh) is centered on the anvil over a piece of aluminium foil (thickness 0.005-0.01 mm) and the sample was also covered with foil. The striker is then hit by a 2 kg weight dropped from heights, which are varried according to the Bruceton "staire case" method. This design permits the calculation of height from which drops will cause 50% explosions. The $h_{50\%}$ data reported in Table 1 was determined from 25 shot sequences.

Friction Sensitivity Measurements on NPTM

Friction sensitivity measurements were carried out by friction sensitive apparatus for high explosives (Julius Peters, Berlin-21) at ERDL, Pune, to find out the friction insensitive limit in kg and that limit was confirmed by five runs. The sample (wt. = 5 mg, 100-200 mesh) was placed over the ceramic friction plate (hardness 7-9 mho's scale, Roughness profile = 12.3 mμ). The predetermined weight was applied over the sample through the friction pin and the sample was subjected to friction. The friction insensitivity data are given in Table 1.

RESULTS AND DISCUSSION

DTA (Figure 1) data presented in Table 1 clearly show that decomposition temperature (T_d) is in the order: mononitrophenate (MNP) > dinitrophenate (DNP) > trinitrophenate (TNP), except Mn, Ni and Zn-TNP, the deviation may be due to their highly hydrated forms. All nitrophenates gave single exotherm (Zn-TNP showed two exotherms), which confirm the involvement of exothermic decomposition reactions just prior to explosion.

Although, nitrophenates are quite stable at room temperature but they explode when subjected to sudden high temperatures. Therefore, it was thought of great interest to undertake explosion delay (D_E) measurements on these salts. At 300°C, all TNP and few DNP (Ni & Mn) get exploded (Table 2), whereas, MNP of all metals did not explode at all. Only colour change and melting in few cases where observed. The D_E values measured in the temperature range 325-600°C are found to be in the order: MNP>DNP>TNP. The metal ions seem to exert the catalytic effect during thermolysis of NPTM in the order: Mn>Fe >Ni>Zn>Co>Cu. The number of nitro groups, O/H & H/NO_2 ratios and VOD (calculated using Martin and Yallop's relations[28]) for NPTM have been found to be linear with the ET (Figures 3-5). These findings suggest that the thermal stability of NPTM decreases with the increase in the number of nitro groups, which is contradictory to Agrawal.[19,20] However, number of water of crystallisation was also found to depend upon the number of nitro groups. This may be due to the possibility of hydrogen bonding between the water molecules and nitro groups. The fitting of D_E data in equation (1) gave very high correlation coefficient values (r) (Table 2) and E^* values are in the range 24.8 - 36.9 kj mol^{-1}. In order to understand the machanism of explosion, chemical analyses of the intermediate gaseous and solid products were done and machanistic pathways for the thermolysis of NPTM has been proposed in the Scheme.

The NPTM undergo complete dehydration below 140 °C (Scheme, step 1) to form anhydrated species (I), (II) & (III) (confirmed by TG). The negative charge on phenolic oxygen atom is directly conjugated with the benzene ring. The electron withdrawal by $-NO_2$ group(s) would deactivate the benzene ring and consequently the C-O bond in the nitrosubstituted phenoxy ion gets weakened. This protocol favours the formation of corresponding metal oxides and dinitrodiphenylether (IV), tetranitrodiphenylether (V), and hexanitrodiphenylether (VI) from (I), (II) and (III) respectively. However, MO formation will be facilitated in case of (III) and decreases from (II) to (I) via step 2. The temperature for step 2 were found to be lowered from MNP to TNP. Thus TNP are found to be thermally least stable and MNP are the most one. Step 2 seems to be the rate-controlling step in the thermolysis and explosion of NPTM.

Nitrosubstituted diphenylethers (IV), (V) & (VI) formed "in situ" are transitory and their stability is governed by many factors: (i) free rotation about C-O-C linkage is totally restricted due to the presence of nitro group(s) at ortho position(s) and steric hinderence increases from MNP to TNP (ii) repulsion between loan pair of etherial oxygen and C-O-C bonding pairs may lead to destabilisation (TNP >DNP> MNP) of these molecules (iii) furthermore, resonance interaction between unshared electron pairs of etherial oxygen and the nitrosubstituted rings would enhance the positive charge on etherial oxygen atom from (IV) to (VI).

Step 3 involves the formation of diphenylether radicals and NO_2 molecules alongwith MO (confirmed by TG) in adsorbed phase. It has been reported[29,30] that NO_2 reacts with carbon to produce NO and CO_2. Subsequently, NO and water react to form NH_3 and O_2. It has been observed that the rate of evolution of ammonia (confirmed by chemical analysis) is more in case of TNP and decreases from DNP to MNP. Theoretically, the formation of NO_2 (confirmed by chemical analysis) would be higher in (VI) as compared to (IV) & (V) and consequently, the rates of oxidative reactions would be in the order: TNP>DNP>MNP. This is because one $-NO_2$ group facilitates the removal of other $-NO_2$ group by electron withdrawal. The oxidative degradation reactions between NO_2 and diphenylether radical cause ring rupture which leads to explosion (step 4) and gaseous products are formed. It has been reported[31-33] that explosion products of C-H-N-O explosives are primarily water, nitrogen and carbon oxides and simple organic molecules like formaldehyde. It is also reported[34] that the initial reaction is the cleavage of $C-NO_2$ bond in polynitroaromatics and an increase in the number of nitro groups leads to increase in the number of potential initiation sites. In NPTM, MO fromation would also catalyse condensed phase reactions in step 4.

The impact sensitivity of NPTM was found to be in the order: MNP$<$DNP$<$TNP (Table 2). All the TNP have been found to be friction sensitive whereas, MNP and DNP are insensitive. Fe-TNP seems to be more sensitive towards impact and friction whereas, Zn-TNP is the least one.

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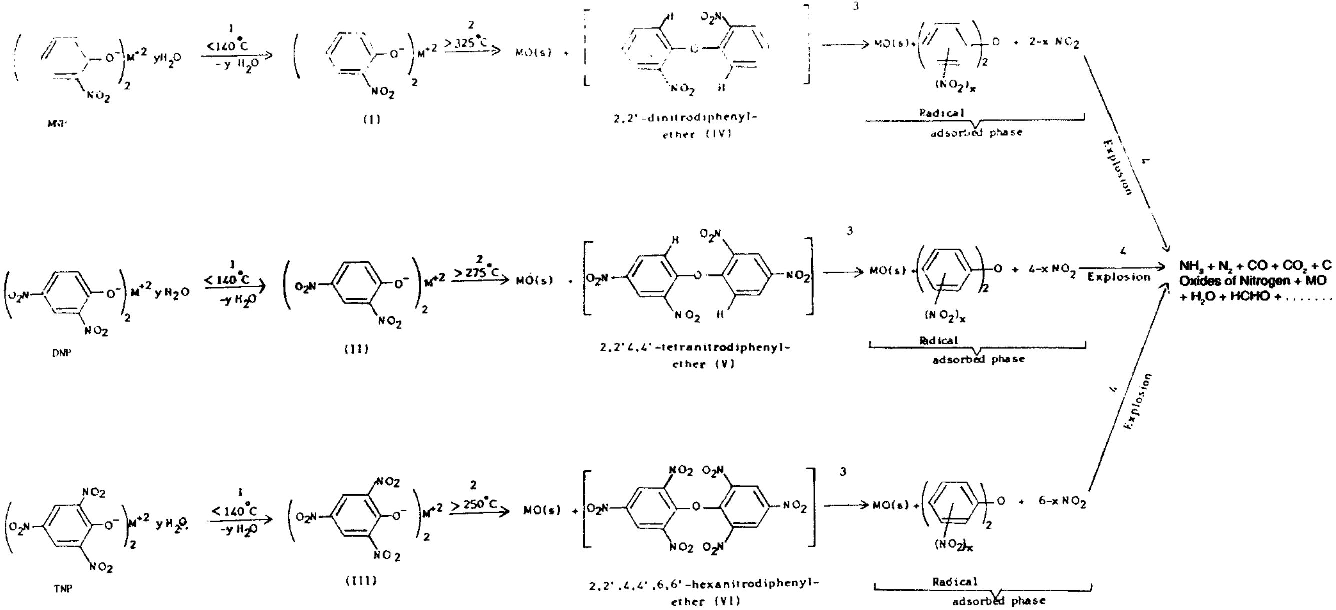

Scheme

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x = 0-6

y-No. of water of crystallisation

s-solid

TABLE 1

Molecular Formula, Decomposition Temperature(T_d), Impact($h_{50\%}$) & Friction Sensitivities and Velocity of Detonation(VOD) for Nitrophenates of Transition Metals.

Compound	Molecular Formula	DTA Peak Temp. T_d(°C)	$h_{50\%}$ (cm)	Friction Insensitive Limit (kg)	VOD (ms^{-1})
Mn-MNP	$Mn[(NO_2)C_6H_4O]_2$	331	180	36.0	4959
Mn-DNP	$Mn[(NO_2)_2C_6H_3O]_2.2H_2O$	264	175	36.0	6399
Mn-TNP	$Mn[(NO_2)_3C_6H_2O]_2.2H_2O$	295	145	25.2	7259
Fe-MNP	$Fe[(NO_2)C_6H_4O]_2$	326	180	36.0	5001
Fe-DNP	$Fe[(NO_2)_2C_6H_3O]_2.2H_2O$	292	176	36.0	6403
Fe-TNP	$Fe[(NO_2)_3C_6H_2O]_2.2H_2O$	285	54	12.0	7313
Co-MNP	$Co[(NO_2)C_6H_4O]_2.H_2O$	345	153	36.0	5032
Co-DNP	$Co[(NO_2)_2C_6H_3O]_2.3H_2O$	304	140	36.0	6418
Co-TNP	$Co[(NO_2)_3C_6H_2O]_2.4H_2O$	297	135	25.2	7320
Ni-MNP	$Ni[(NO_2)C_6H_4O]_2$	341	130	36.0	5059
Ni-DNP	$Ni[(NO_2)_2C_6H_3O]_2.2H_2O$	279	110	36.0	6416
Ni-TNP	$Ni[(NO_2)_3C_6H_2O]_2.5H_2O$	291	85	28.8	7320
Cu-MNP	$Cu[(NO_2)C_6H_4O]_2$	327	180	36.0	5080
Cu-DNP	$Cu[(NO_2)_2C_6H_3O]_2.2H_2O$	298	158	36.0	6442
Cu-TNP	$Cu[(NO_2)_3C_6H_2O]_2.2H_2O$	294	122	25.2	7331
Zn-MNP	$Zn[(NO_2)C_6H_4O]_2.H_2O$	334	162	36.0	5101
Zn-DNP	$Zn[(NO_2)_2C_6H_3O]_2.2H_2O$	294	173	36.0	6452
Zn-TNP	$Zn[(NO_2)_3C_6H_2O]_2.5H_2O$	324	180	36.0	7336

TABLE 2

Explosion Delay(D_E), Explosion Temperature(ET), Activation Energy for Explosion(E^*) and Correlation Coefficient(r) of Nitrophenates of Transition Metals.

Compound	Explosion Delay(s) at								ET(°C) for D_E of 10s	E^* (kJ mol^{-1})	r
	300°C	325°C	350°C	375°C	400°C	450°C	500°C	600°C			
Mn-MNP	DNE	79.5±3.2	57.4±2.7	40.1±1.8	35.0±1.0	24.1±1.7	17.3±0.5	10.1±0.5	630	31.9	0.9965
Mn-DNP	72.0±2.1	55.4±2.1	47.8±1.4	35.3±2.4	28.6±1.2	21.6±1.6	15.7±1.3	9.0±0.3	594	28.7	0.9986
Mn-TNP	68.4±3.3	51.8±2.2	41.1±0.9	29.2±0.7	24.3±1.6	17.8±0.9	14.1±0.7	8.9±0.8	546	28.3	0.9952
Fe-MNP	DNE	99.8±3.5	75.5±2.6	65.3±1.2	45.8±2.9	33.3±1.1	22.1±0.5	13.9±0.1	645	31.8	0.9974
Fe-DNP	106.2±4.4	88.1±3.0	64.6±1.3	52.4±0.9	38.3±1.6	27.4±1.0	20.0±0.3	12.0±0	603	31.1	0.9982
Fe-TNP	93.4±3.7	74.9±3.1	55.3±2.7	43.7±1.0	33.8±2.0	22.9±0.7	16.4±0.5	10.9±0.2	561	30.9	0.9976
Co-MNP	DNE	89.5±3.6	65.7±2.1	54.9±2.5	38.2±1.1	27.3±0.7	20.4±0.9	11.8±0.3	648	32.0	0.9971
Co-DNP	92.8±2.2	66.0±3.1	52.4±3.6	42.1±4.0	34.7±0.9	22.0±1.8	18.7±0.5	10.0±0.3	618	30.7	0.8982
Co-TNP	80.1±3.0	57.7±2.0	46.0±2.9	38.0±1.4	30.2±4.4	21.1±2.0	15.8±0.6	9.5±0.5	580	29.3	0.9995
Ni-MNP	DNE	101.5±4.5	76.7±2.4	67.0±1.7	55.3±2.0	32.7±3.1	25.1±0.6	13.9±0.3	651	31.6	0.9972
Ni-DNP	82.9±3.1	67.9±2.6	49.7±1.2	39.3±0.8	37.2±1.7	29.9±0.8	19.5±0.8	13.4±0.6	609	25.1	0.9936
Ni-TNP	73.8±4.3	55.9±3.1	42.9±2.2	36.0±2.8	30.5±1.4	22.7±0.8	18.2±0.6	12.0±0.5	567	24.8	0.9969
Cu-MNP	DNE	112.1±3.0	92.0±2.1	74.6±1.9	54.2±3.6	34.9±2.4	25.8±1.7	15.6±0.3	666	31.8	0.9789
Cu-DNP	DNE	76.1±2.1	64.5±1.2	56.9±2.0	42.4±2.5	29.6±1.8	21.3±1.2	13.7±0.1	630	28.3	0.9969
Cu-TNP	87.9±4.1	66.3±1.5	58.0±2.3	47.0±1.8	36.2±2.6	26.8±1.4	19.2±0.8	13.0±0.2	591	27.0	0.9983
Zn-MNP	DNE	113.4±4.1	83.9±2.0	59.8±2.6	51.6±2.8	31.6±1.4	21.7±0.7	10.7±0.8	634	36.9	0.9991
Zn-DNP	DNE	87.5±4.5	67.8±3.1	52.6±2.4	37.8±3.0	25.5±1.0	19.5±1.3	10.1±0	600	34.1	0.9981
Zn-TNP	90.7±3.8	65.9±1.7	50.9±2.2	42.6±1.6	31.3±1.2	21.4±1.3	17.4±0.5	9.5±0.5	561	30.8	0.9999

DNE - Did Not Explode.

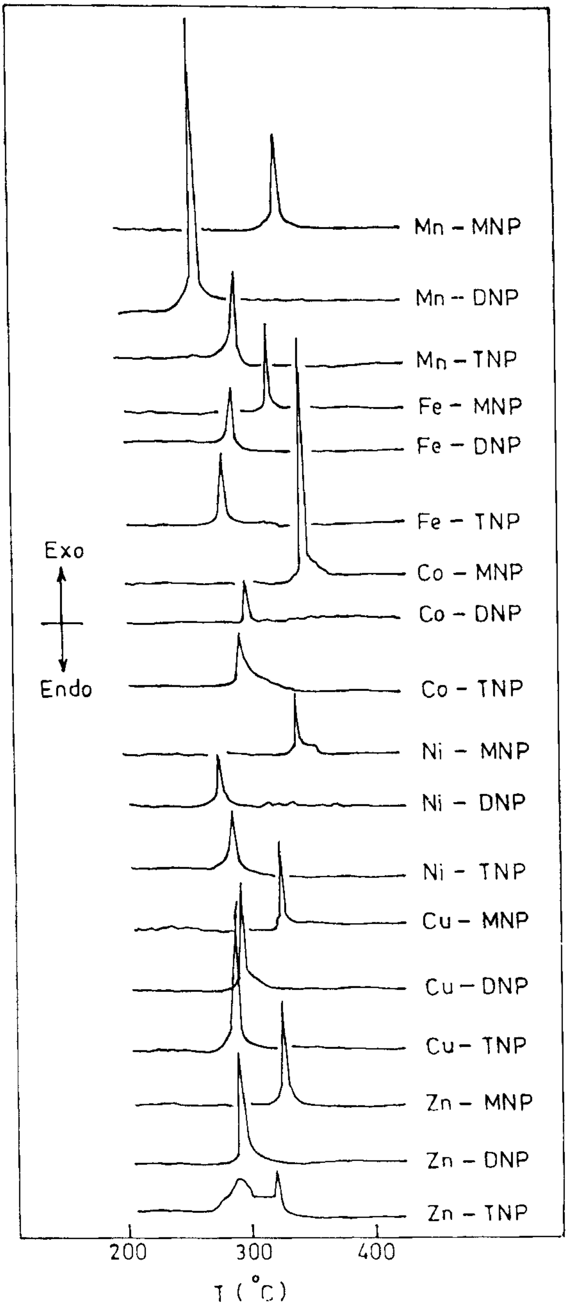

FIGURE 1

DTA Traces of Nitrophenates of Transition Metals.

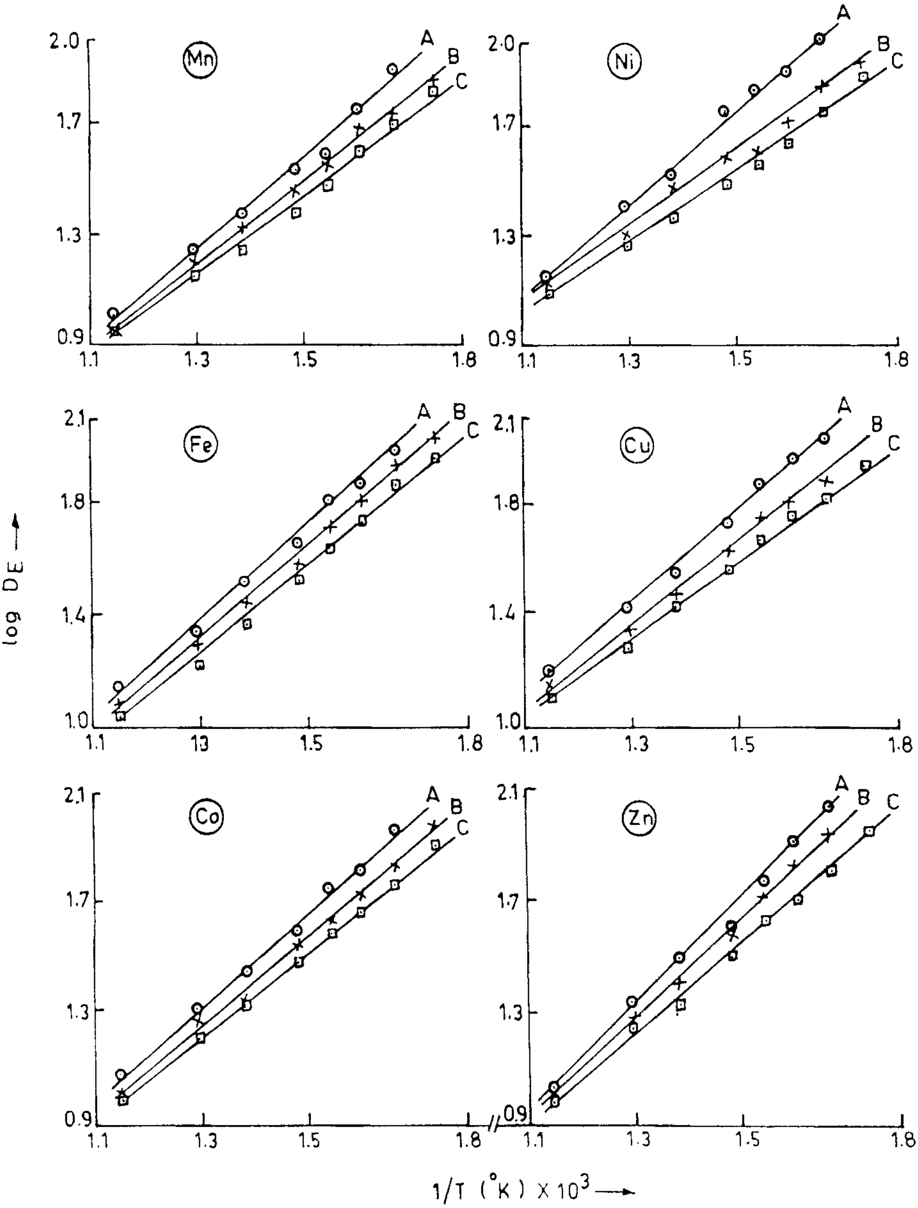

FIGURE 2

Plots of log (D_E) versus 1/T (°K) for Nitrophenates of Transition Metals.

(A) -MNP (B) -DNP (C) -TNP.

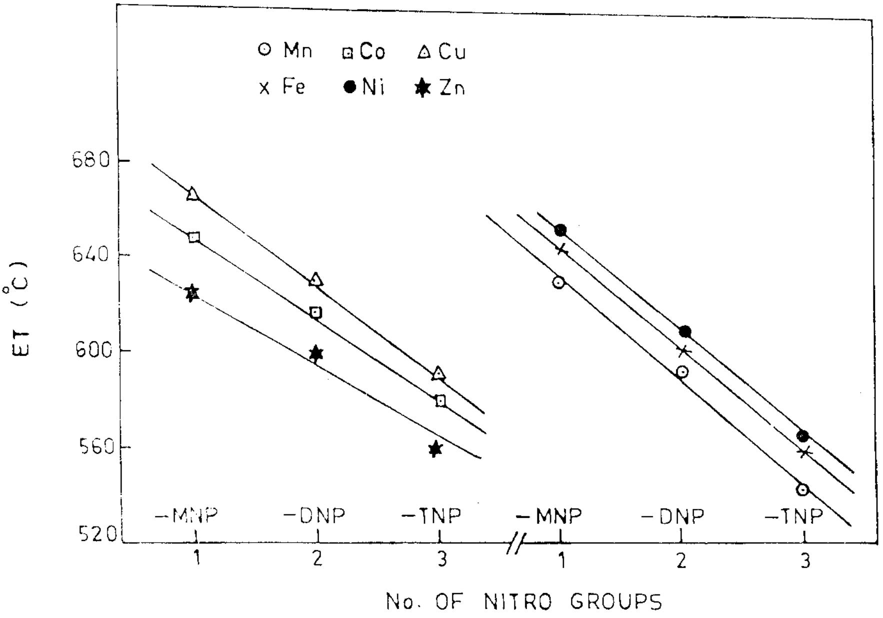

FIGURE 3

Plots of ET versus Number of Nitro groups for Nitrophenates of Transition Metals.

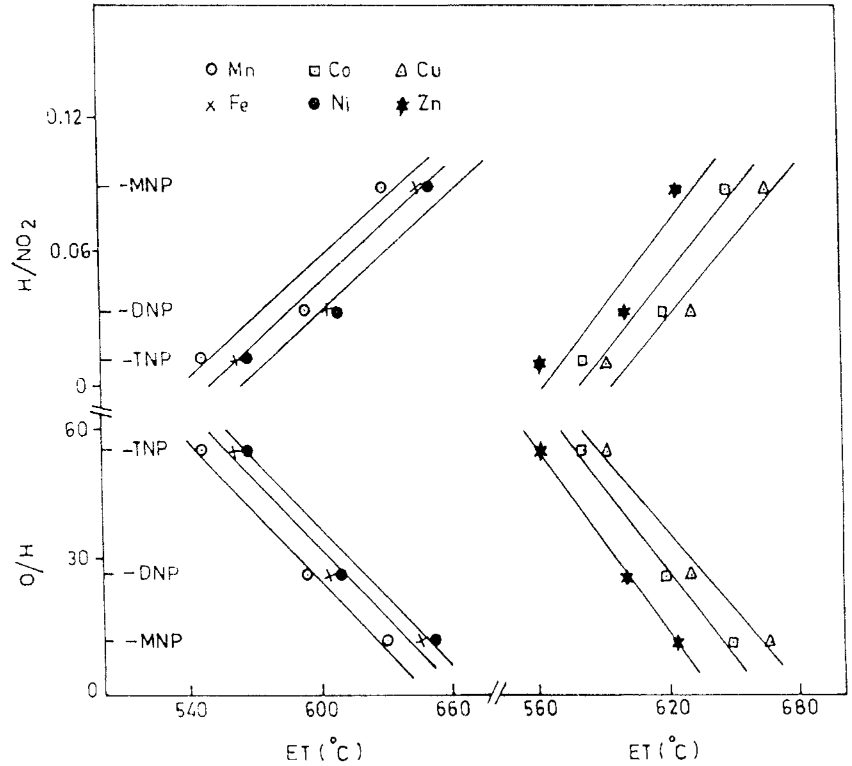

FIGURE 4

Plots of O/H and H/NO_2 versus ET (°C) for Nitrophenates of Transition Metals.

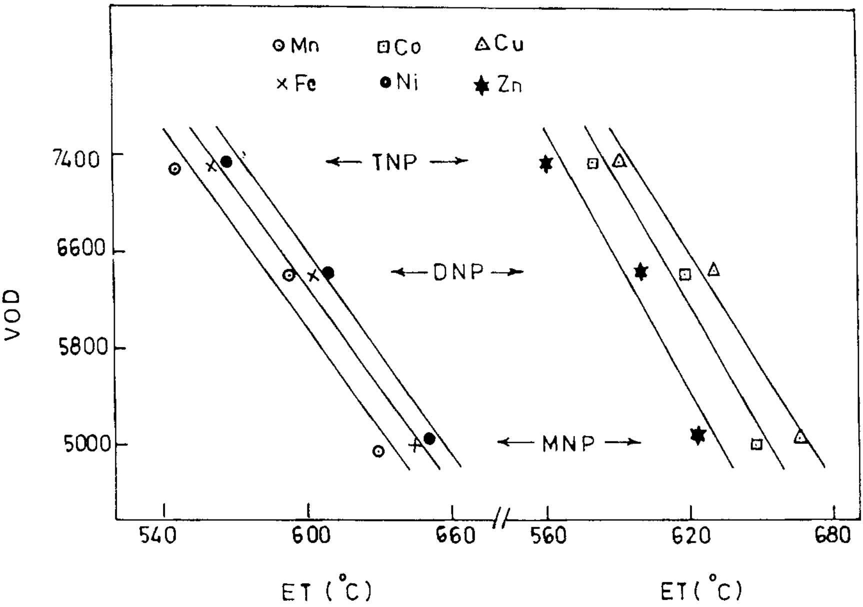

FIGURE 5

Plot of Velocity of Detonation (VOD) versus ET (°C) for Nitrophenates of Transition Metals.

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