

Preparation, characterization and thermolysis of phenylenediammonium dinitrate salts[☆]

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Received 11 January 2007; received in revised form 5 May 2007; accepted 8 May 2007

Available online 18 May 2007

Abstract

Four phenylenediammonium dinitrate salts were prepared and characterized by elemental, Infrared spectroscopy (IR), Ultraviolet spectroscopy (UV) and gravimetric methods. These dinitrates find application in propellant, explosives and pyrotechnics. Their thermal decomposition has been studied using thermogravimetry (TG) and simultaneous thermogravimetry-differential scanning calorimetry (TG–DSC). Kinetics parameters were evaluated by model fitting and isoconversional methods. Their thermolytic pathways have also been suggested, which involves decomposition followed by ignition.

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Keywords: Phenylenediammonium dinitrate; Kinetics; Thermolysis; Proton transfer

1. Introduction

Interest in a systematic study of the characteristics of thermal decomposition of ring substituted aryl ammonium nitrates [1–3] and perchlorates [4–6] thrives due to the fact that the nitrogen base salts of inorganic acids like HNO₃ and HClO₄ find applications in explosives and pyrotechnics [7–9]. Because of the presence of both the oxidizer and the fuel groups in the same molecule; they have also been used in propellant formulations. Nitrates are powerful oxidizing agents and decompose at elevated temperature to give oxygen as one of the major products [10–13]. Extensive studies have been made on the thermal properties of alkyl [14–15] and ring substituted arylammonium nitrates [1–3]. Recently, we have studied thermal decomposition of phenylenediammonium sulfates [16]. The work on aromatic diammonium dinitrates is quite scanty and mechanism of their thermolysis is not yet reported in literature. Brill

et al. [17–22] have undertaken the thermal decomposition of aliphatic diammonium nitrate and perchlorate salts. As a part of our ongoing research programmes, we report here the preparation, characterization and thermolysis of dinitrates of various phenylenediamines.

2. Experimental

2.1. Materials

Following AR grade commercially available chemicals were used as received: phenylene-1,2-diamine (s.d.fine); phenylene-1,4-diamine (Alfa Aesar); phenylene-1,3-diamine (s.d.fine); 5-carboxyl-1,3-phenylenediamine (Merck); 70% Nitric acid (Ranbaxy) silica gel; iodine (s.d.fine) and nitron.

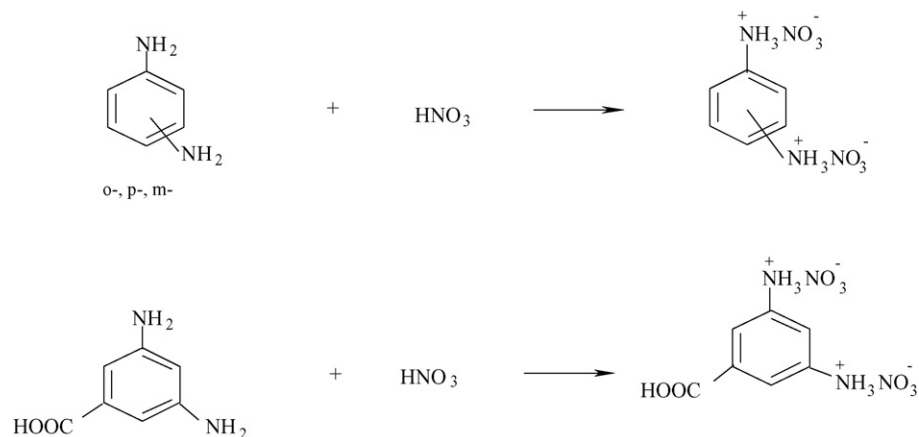
2.2. Preparation and characterization

Dinitrates (**CAUTION!** These are explosives of varying sensitivity and should be handled with appropriate precautions) were prepared at room temperature by treating cold 20% nitric acid with the corresponding phenylenediamine directly in 1:2 molar ratio (without using any solvent) in accordance with the reaction,

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It has been observed that interaction of isomeric three phenylenediamines with acid produce dinitrates immediately whereas precipitation was slow for carboxyl derivative. These dinitrates were recrystallized from aqueous solution and the crystals were vacuum dried. Their purity was checked by thin layer chromatography (TLC) using suitable solvents and compositions were confirmed by a gravimetric method using nitron reagent [23] as reported earlier [3]. The mp and analytical data of dinitrates are presented in Table 1 whereas elemental and spectral data are reported in Table 2.

2.3. Thermal decomposition of PDADN

2.3.1. Simultaneous TG–DSC studies

Simultaneous TG–DSC analysis on the dinitrates has been done by using NETZSCH, STA 409 PC instrument at

a heating rate of 10 °C min⁻¹ (sample mass ~ 10 mg, atmosphere = flowing nitrogen gas) and the thermograms are shown in Fig. 1.

2.3.2. Non-isothermal TG studies

Non-isothermal TG on dinitrates (wt. 33 mg, 100–200 mesh) were undertaken in static air at a heating rate of 10 °C min⁻¹ using home made TG apparatus [24] fitted with temperature cum controller. The accuracy of the furnace was ±1 °C. A round bottom platinum crucible was used as sample holder. The fractional decomposition (α) has been plotted against temperature (°C) and the thermograms are given in Fig. 2.

2.3.3. Isothermal TG studies

Isothermal TG studies (weight of the sample ~ 33 mg, 100–200 mesh) were taken in static air using indigenously

Table 1
Physical parameters, TLC and analytical data on PDADN

Compound	M. Wt.	Crystal colour	m.p./d (°C)	TLC		R _f	Yield (%)	% of NO ₃ ⁻	
				Eluent (a:b:c)	Spot colour			Experimental	Theoretical
P-1,2-DADN	234	Light brown crystals	157(d)	8:8:7	Brown	0.87	72	50	52.99
P-1,4-DADN	234	Dirty yellow crystals	145(d)	8:8:14	Grayish black	0.86	76	51.11	52.99
P-1,3-DADN	234	Black coloured amorphous	152(d)	8:8:4	Black	0.76	81	50.67	52.99
5-Carboxyl-P-1,3-DADN	278	Dark brown coloured crystals	164(d)	8:4:12	Grayish black	0.80	69	43.53	44.60

a:b:c = water:DMSO:methanol; locating reagent – iodine.

Table 2
Elemental and spectral parameters of PDADN

Compound	% Observed (calculated)			IR frequencies (cm ⁻¹)	UV absorbance
	C	H	N		
P-1,2-DADN	31.79 (30.77)	3.92 (4.27)	24.99 (23.93)	N–H str. 2947, N–H bend 1620, C–N str. 1307, NO ₃ ²⁻ 1377	197.43, 231.31, 302.60, 400.38, 479.26
P-1,4-DADN	29.75 (30.77)	4.17 (4.27)	22.84 (23.93)	N–H str. 2930, N–H bend 1612, C–N str. 1377, NO ₃ ²⁻ 1375	191.48, 238.89, 306.30, 378.80
P-1,3-DADN	28.52 (30.77)	3.89 (4.27)	24.78 (23.93)	N–H str. 2906, N–H bend 1750, C–N str. 1405, NO ₃ ²⁻ 1381	198.37, 218.37, 239.09, 306.83, 370.40
5-Carboxyl-P-1,3-DADN	31.86 (30.22)	3.89 (3.60)	21.25 (20.14)	N–H str. 2966, N–H bend 1537, C–N str. 1311, NO ₃ ²⁻ 1388	197.41, 237.25, 318.02, 359.11, 370.75, 373.99

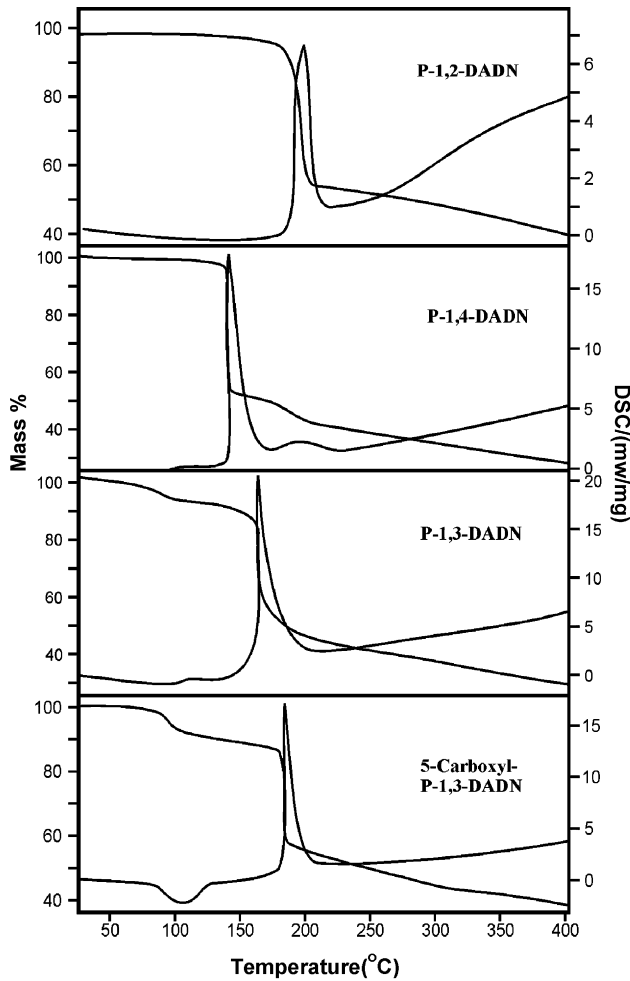


Fig. 1. Simultaneous TG–DSC curves of PDADN in N₂ atmosphere.

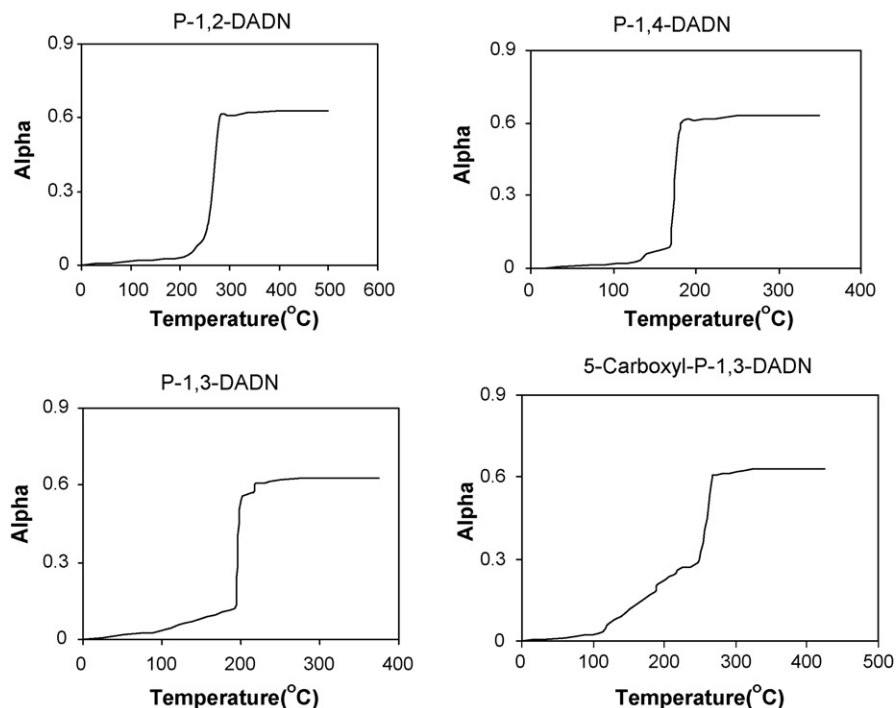


Fig. 2. TG curves of PDADN in air atmosphere.

fabricated TG apparatus at appropriate temperatures. The fractional decomposition (α) has been plotted against time (min) and plots are shown in Fig. 3.

2.3.4. Ignition delay measurements

The ignition delay (D_i) measurements were undertaken using tube furnace technique [25] in the temperature range 175–350 °C (± 1 °C). The D_i data were found to fit in the following equation [25–28]

$$D_i = A \exp\left(\frac{E}{RT}\right)$$

where E is activation energy for thermal ignition, A pre-exponential factor and T is absolute temperature. E was determined from the slope of a plot of $\ln(D_i)$ versus $1/T$ (Table 3).

2.4. Percent oxygen balance and velocity of detonation

The percent oxygen balance (OB) was calculated by following equation suggested by Martin and Yallop [29] and data are given in Table 3.

$$OB = \frac{(z - 2x - y/2)100}{n}$$

where x , y and z are the respective number of atoms of C, H, N, respectively, and n is the total number of atoms in the molecule. Furthermore, the velocity of detonation (VOD) was calculated by using Rothstein's method [30] and data are reported in Table 3.

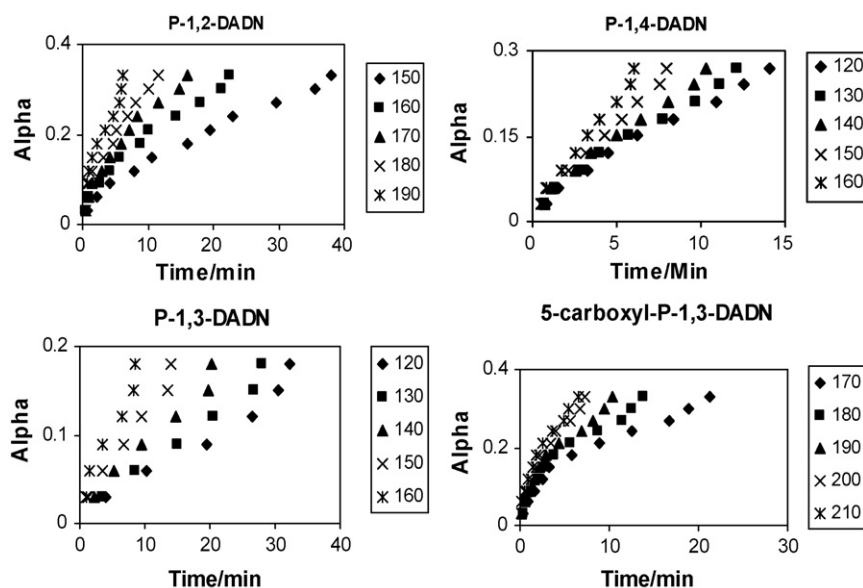


Fig. 3. Isothermal TG of PDADN.

2.5. Kinetic analysis of isothermal TG data

Kinetic analysis of solid state decomposition is usually based on a single step kinetic Eq. (1) [31]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where t is the time, T temperature, α extent of conversion ($0 < \alpha < 1$), $k(T)$ rate constant and $f(\alpha)$ is the reaction model [31], which describes the dependence of the reaction rate on the extent of reactions. The value of α is experimentally derived from the global mass loss in TG experiments. The reaction model may take various forms. The temperature dependence of $k(T)$ can be satisfactorily described by the Arrhenius equation, whose substitution into Eq. (1) yields:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a^*}{RT}\right) f(\alpha) \quad (2)$$

where A is the pre exponential factor, E_a^* the activation energy and R is the gas constant.

2.5.1. Model fitting method

Rearrangement and integration of Eq. (1) for isothermal conditions gives:

$$g_j(\alpha) = k_j(T)t \quad (3)$$

where $g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha$ is integrated form of the reaction model. The subscript j has been introduced to emphasize that, substituting a particular reaction model in Eq. (3) results in evaluating the corresponding rate constant, which is determined from the slope of a plot of $g_j(\alpha)$ versus t . For each reaction model selected, the rate constants are evaluated at several temperatures T_i , and Arrhenius parameters are determined using the Arrhenius Eq. (4) in its logarithmic form:

$$\ln k_j(T_i) = \ln A_j - \frac{E_j}{RT_i} \quad (4)$$

Arrhenius parameters were evaluated for isothermal experimental data by the model fitting method.

2.5.2. Model free isoconversional method

This method allows the activation energy to be evaluated without making any assumptions about the reaction model. Additionally, the method evaluates the effective activation

Table 3
Ignition delay (D_i), activation energy for thermal ignition (E), oxygen balance (OB) and velocity of detonation for PDADN

Compound	Mass (mg)	D_i (s) at Temperature.(°C)								E (kJ mol ⁻¹)	r	OB	VOD (mm μs ⁻¹)
		175 ± 1	200 ± 1	225 ± 1	250 ± 1	275 ± 1	300 ± 1	325 ± 1	350 ± 1				
P-1,2-DADN	15	271	192	158	105	69	58	49	42	25.9	0.9855	-42.31	6.91
P-1,4-DADN	15	173	117	79	60	50	42	29	18	27.5	0.9958	-42.31	6.91
P-1,3-DADN	15	350	256	177	118	93	56	45	38	30.9	0.9969	-42.31	6.91
5-carboxyl-P-1,3-DADN	15	395	323	278	209	157	104	93	79	22.8	0.9836	-37.93	6.25

energy as a function of the extent of conversion, which allows one to explore multistep kinetics.

The basic assumption of the isoconversional method [32] is that the reaction model as defined in Eq. (1) is not dependent on temperature or heating rate. Under isothermal conditions, on combining Eqs. (3) and (4) we get:

$$-\ln t_{\alpha,i} = \ln \left[\frac{A_{\alpha}}{g(\alpha)} \right] - \frac{E_a^*}{RT} \quad (5)$$

where E_a^* is evaluated from the slope of the plot of $-\ln t_{\alpha,i}$ against T_i^{-1} . Thus E_a^* at various α for dinitrates have been evaluated and the E_a^* dependencies on α are shown in Fig. 7.

3. Results and discussion

Dinitrates were characterized by Infrared (JASCO FT/IR-5300), Ultra violet (HITACHI U-2000 spectrometer), elemental (EUROEA elemental analyzer) and gravimetric methods. The molecular formula of the dinitrates was deduced by fitting the observed percent mass of the various elements with that of calculated (Table 2). The IR and UV data (Table 2) also signalize the proposed molecular formula of the dinitrates (IR bands in the range 1375–1388 cm^{-1} for NO_3^- ; 2906–2966 cm^{-1} for NH_3^+ and UV 191–198 nm; 231–400 nm).

TG taken in nitrogen atmosphere (Fig. 1) and static air (Fig. 2) reveals that each sample shows incomplete mass loss as they are highly fuel rich and a black residue remains in the crucible after completion of decomposition followed by ignition. Each sample was found to ignite during TG measurements at particular temperatures; phenylene-1,2-diammonium dinitrate (P-1,2-DADN) at 260 °C; phenylene-1,4-diammonium dinitrate (P-1,4-DADN) at 169 °C; phenylene-1,3-diammonium dinitrate (P-1,3-DADN) at 195 °C and 5-carboxyl-phenylene-1,3-diammonium dinitrate (5-carboxyl-P-1,3-DADN) at 251 °C (Fig. 2). All three isomeric dinitrates show only exotherms (Fig. 1) which may be due to the oxidation–reduction reactions occurring during thermolysis of these salts. Carboxyl derivative shows both an endotherm (possibly due to loss of CO_2) and an exotherm. Moreover 15% mass loss in TG also supports the loss of CO_2 . Isothermal TG in static air in different temperature ranges (the temperature from where decomposition starts and the temperature before ignition) gave acceleratory curves (Fig. 3) with mass losses; 18% for P-1,3-

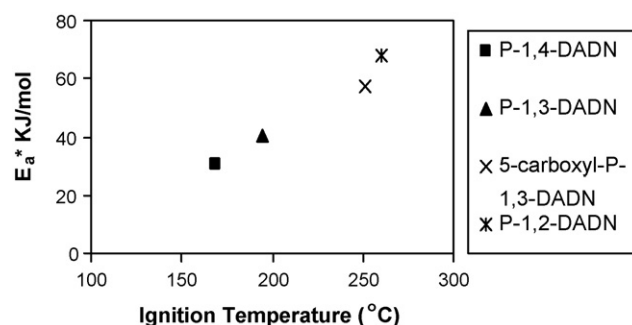


Fig. 5. Variation of E_a^* with ignition temperature.

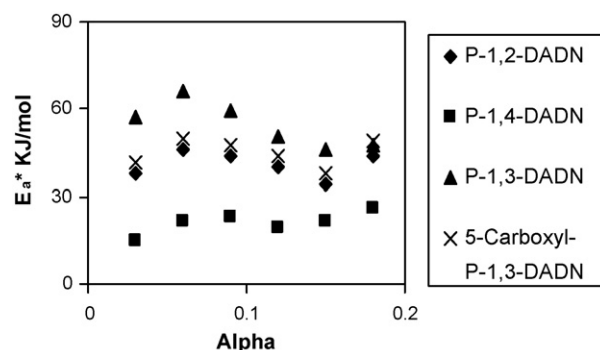


Fig. 6. Variation of activation energy with extent of conversion (α).

DADN, 28% for P-1,4-DADN and 37% for both P-1,2-DADN and 5-carboxyl-P-1,3-DADN.

The kinetics of thermal decomposition of PDADN was evaluated using 14 mechanism based kinetic models. In the model fitting method, the kinetics is analyzed by choosing a “best fit” model based on the value of correlation coefficient r close to 1. All 14 kinetic models are fitted in isothermal TG data. Values of activation energy obtained from different models for particular sample are nearly equal irrespective of the equation used. Average value of activation energy 67.8, 30.2, 40.2 and 57.0 kJ mol^{-1} were obtained, respectively, for P-1,2-DADN, P-1,4-DADN, P-1,3-DADN and 5-carboxyl-P-1,3-DADN from isothermal TG data (kinetic models and kinetic parameters can be seen in supplementary materials). A plot of activation energy versus $\ln A$ (Fig. 4) obtained from different models indicates that all these values fall in an almost straight line showing the existence of kinetic compensation

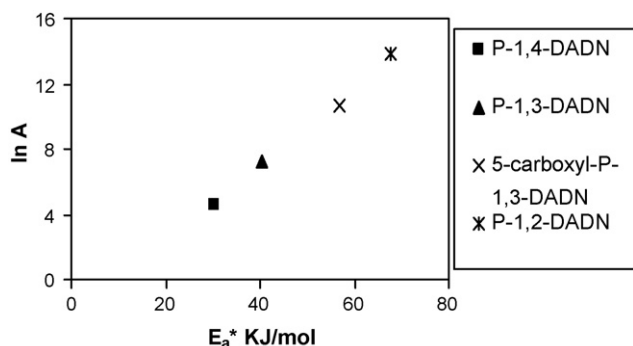


Fig. 4. Variation of $\ln A$ with E_a^* .

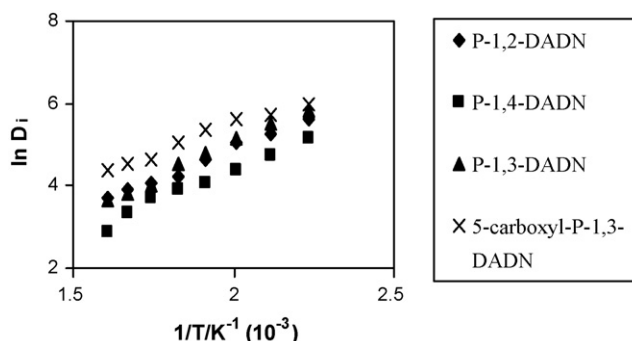
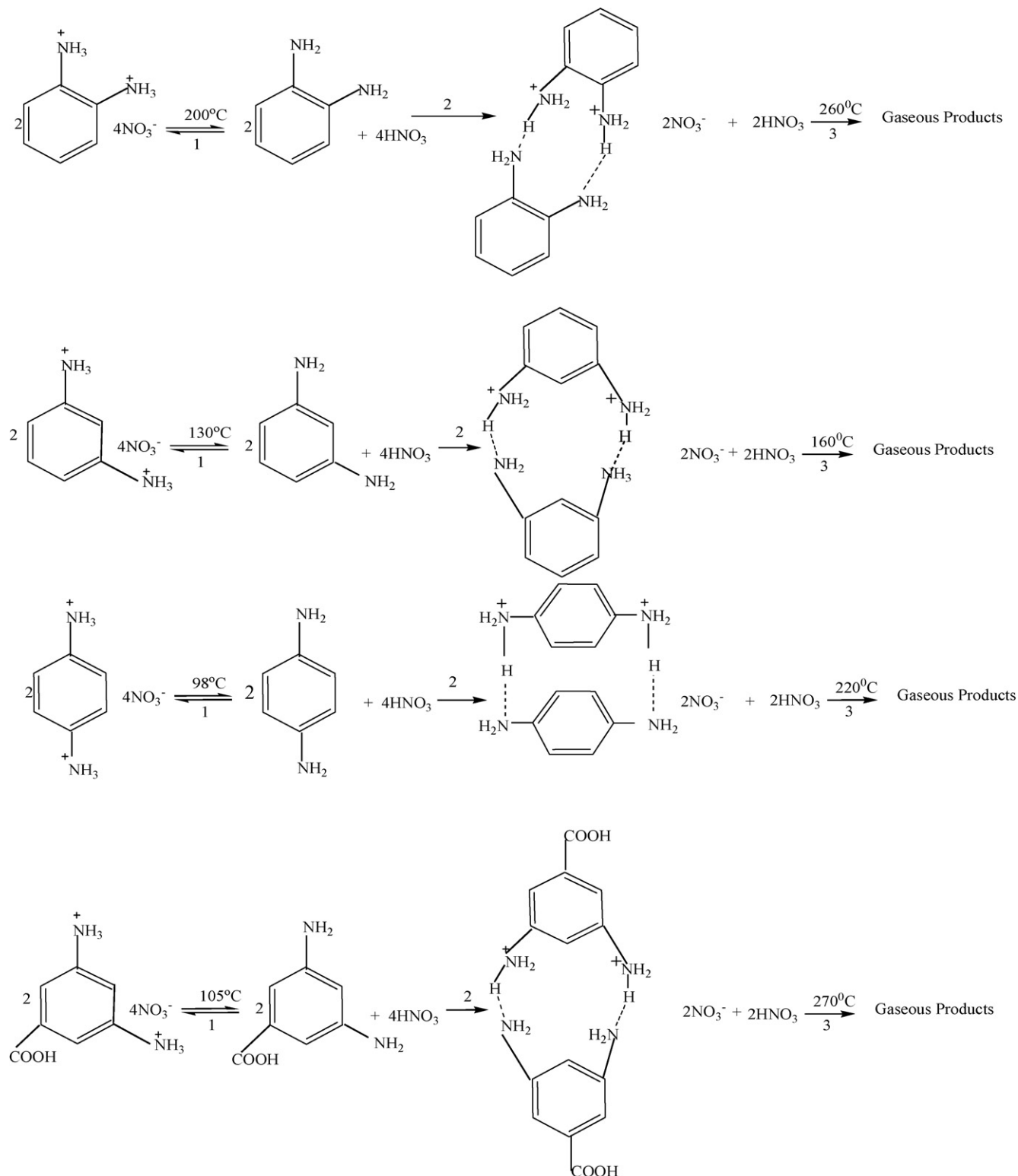


Fig. 7. Graph of $\ln D_i$ vs. $1/T$.

effect [33]. The overall activation energies for these dinitrates were found to follow the trend, P-1,2-DADN > 5-carboxyl-P-1,3-DADN > P-1,3-DADN > P-1,4-DADN. It has been observed that dinitrate having higher value of ignition (observed during

TG) temperature also have higher value of activation energy (Fig. 5).

Isoconversional method is known to permit estimation of activation energy independent of the model used. In this method,



Scheme 1. Thermolytic pathways of PDADN.

activation energy corresponding to the extent of conversion of the sample is evaluated. As it is clear from the Fig. 6 that for a particular sample, activation energy has different value at a different α . Although these dinitrates are stable at room temperature, but they ignite when subjected to sudden high temperatures. Ignition delay and activation energy in the temperature range 175–350 °C are reported in Table 3. Energy of activation for ignition E are in decreasing order, P-1,3-DADN > P-1,4-DADN > P-1,2-DADN > 5-carboxyl-P-1,3-DADN. The lowest value of E for P-1,2-DADN among three isomers is due to steric hindrance between *ortho*-substituent which favour proton transfer followed by ignition. This also support the contention [34] that *ortho*-substituted groups in substituted aniline generally exert the effect of same kind (N–H bond weakening) whether they are electron donating (+I) or electron withdrawing (–I). Similarly –I of –COOH group deactivate the ring, weaken N–H bond and favoring N–H bond heterolysis (proton transfer) hence shows lowest E . Highest value of E for P-1,3-DADN might be due to the strongest N–H bonds (among four nitrates prepared) as –NH₃⁺ group is *m*-directing and hence *m*-position have somewhat higher electron densities compared to *o*- and *p*-positions. Fig. 7 indicates that on increasing temperature, value of ignition delay decreases. Their oxygen balance and velocity of detonation are reported in Table 3. The VOD value of these dinitrates is very close to some common explosives such as trinitrocresol (6.80 mm μs^{-1}), hexanitrostilbene (6.84 mm μs^{-1}) and trimethylolethylmethane trinitrate (6.82 mm μs^{-1}) [30].

Thermal decomposition pathways of PDADN are shown in Scheme 1. All of the dinitrate salts liberate corresponding phenylenediamine (confirmed by co-TLC of heated sample and authentic sample) and HNO₃ by proton transfer [2–4] in the initial decomposition step 1 at corresponding temperatures. However, *m*-isomer evolves HNO₃ at a lower temperature (98 °C) than the other in accordance with the lower basicity of the parent amine compared to other salts. The greater basicity of *o*- and *p*-phenylenediamine appears to stabilize their salts towards the initial decomposition phase. The tendency to liberate HNO₃ (g) decrease as the basicity of amine increases. The more basic amine may produce HNO₃ in the condensed phase, but the HNO₃ engages in the oxidation–reduction with the aromatic amine before it desorbs. The salts appear to deprotonate (step 2) at both site in one molecule, but retain salt properties in the other molecule to form intermolecular hydrogen bonds (N–H \cdots N) then in the residue to maintain the condensed phase following release of ammonia molecule. The hydrogen bonded salts (I) then decomposes to small molecule products without releasing the parent amine (step 3). This type (I) of hydrogen bonded structure has also been reported by Brill et al. [17–22] in the thermolysis of ammonium salts. All the salts studied release NH₃ (confirmed qualitatively) indicating that C–N bond scission takes place in the residue. Moreover, O/H < 1 for these dinitrates also supports the release of NH₃ [2,35,36].

The final stage of the thermolysis process is ignition and involves redox reactions of the residue to give small gaseous products characteristics of other alkylammonium nitrate salts [2–3,17–22].

4. Conclusion

Thermolysis of PDADN salts involves proton transfer followed by intermediate formation formation of corresponding phenylenediamine, nitric acid and intermolecularly hydrogen bonded salt which ultimately undergo ignition to give gaseous products.

Acknowledgements

Thanks are due to Head, Department of Chemistry, DDU Gorakhpur University for providing laboratory facilities. Authors are also thankful to Dr. S.S. Das, Department of Chemistry, DDU Gorakhpur University, for providing TG–DSC facilities.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2007.05.022.

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