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Studies on energetic compounds
Part 3. Kinetics of thermolysis of dimethylanilinium nitrates ☆

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Abstract

Thermolysis of dimethylanilinium nitrates (DMAN) has been carried out by TG, DTA, ignition delay, impact and friction sensitivity measurements. Although kinetics of the thermal decomposition of these salts were evaluated by fitting TG data in nine-mechanism-based kinetic models, only Avrami–Erofeev ($n = 2, 3$) and contracting area ($n = 2$) gave the best fits. A reaction scheme accounting for the decomposition products is proposed; it involves proton transfer leading to the formation of an arylamine and HNO_3. The other probable routes (evolution of NH_3) have also been suggested. The aryl nucleus seems to be oxidized by NO_2, HNO_3 or its decomposition products prior to ignition, and gaseous products are formed.

Keywords: Dimethylanilinium nitrates (DMAN); Energetic compounds; Friction sensitivity; Ignition delay; Impact sensitivity; Kinetics; Thermolysis

1. Introduction

Nitrates [1, 2] are powerful oxidizing agents and decompose at elevated temperatures to give oxygen as one of the major products. Extensive studies have been made on the thermal properties of ammonium nitrate [3–6], alkyl [7–10] and aryl mono (ring) substituted [11–13] ammonium nitrates, because of the technological use of these compounds, especially in pyrotechnics, explosives and solid propellants. Studies on

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☆ Preceding paper Ref. [20].

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dimethylanilinium nitrates (DMAN) are quite scanty [11] and the mechanism of their thermolysis is not yet reported in literature. As a part of our research programmes of preparation, characterization and thermolysis of energetic materials, studies on nitrates of dimethyl (ring) substituted anilines are reported in the present communication. TG, DTA, ignition delay, impact and friction sensitivity studies on these salts were undertaken and decomposition pathways for their thermolysis are suggested.

2. Experimental

2.1. Materials

2,4-, 2,5- and 3,4-dimethylanilines (Merck); nitric acid (AR, Qualigens) and Nitron (Loba) were used as received.

2.2. Preparation and characterization of DMAN

The nitrates of dimethylanilines were prepared by reacting cold 20% nitric acid with the corresponding dimethylaniline, in 1:1 molar ratio. The nitrates of 2,4- and 2,5-dimethylaniline readily precipitated out, whereas 3,4-DMAN crystallized out when the volume of the reaction mixture was concentrated under reduced pressure and then cooled. All these nitrates were recrystallized from aqueous solution and their purity was checked by thin layer chromatography (TLC). The percentage of NO_3^- anion was confirmed by a gravimetric method using nitron reagent [12] as reported in our earlier publication [13]. UV spectra were taken on an Hitachi U-2000 spectrophotometer using doubly distilled water, which also proved the formation of DMAN salts. Density measurements were made by a pycnometric method using benzene as the displaceable liquid. The gravimetric, UV and density data are given in Table 1. All the nitrates have been found to decompose without melting.

2.3. TG/DTA studies on DMAN

Simultaneous TG/DTA thermograms were recorded from 25 to 250°C (wt of sample = 10 mg, 100–200 mesh) on a thermal analyzer (Netsch STA-409) in a continuous flow of N_2 (75 ml min^{-1}) at a heating rate of 10°C min^{-1} and the traces are given in Fig. 1.

2.4. DTA studies on DMAN in static air

DTA were recorded in static air at a heating rate of 10°C min^{-1} using a DTA apparatus fabricated at Explosives Research and Development Laboratory (ERDL), Pune. The DMAN samples (wt = 10 mg, 100–200 mesh) were placed in a Pt crucible by taking Al_2O_3 as the reference material. A Pt–Pt (Rh 13%) thermocouple was used to record ΔT with the help of two-pen strip chart recorder. Their exothermic peak temperatures (T_d) are given in Table 1.

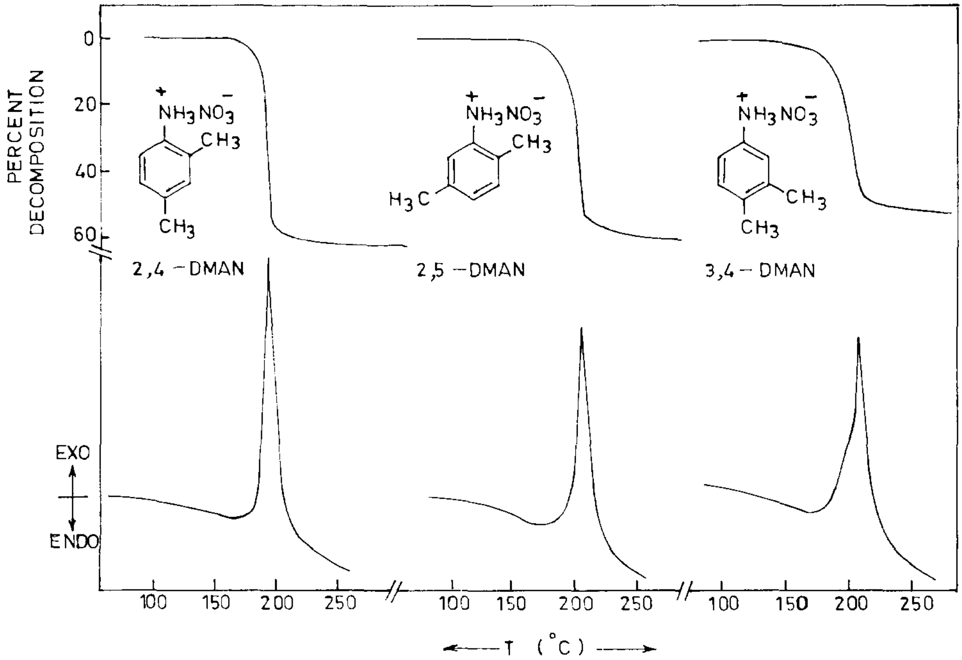

Fig. 1. TG/DTA thermograms of dimethylanilinium nitrates under nitrogen atmosphere.

2.5. *TG studies on DMAN*

Isothermal TG studies (Sample wt = 30 mg, 100–200 mesh) were undertaken in static air in the temperature range 145–205°C using an indigenously fabricated TG apparatus in our laboratory [14]. The accuracy of the furnace was ± 1°C. The plots of fractional weight loss (α = wt loss at time, t/final wt loss) versus time (min) are given in Fig. 2.

2.6. *Ignition delay measurements on DMAN*

The ignition delay (t_{id}) measurements were undertaken by the tube furnace (TF) technique [15–17], in the temperature range 500–900°C. Each run was repeated three times and mean t_{id} values are reported in Table 2. The ignition temperature (IT) for these salts was taken at t_{id} of 5 s, and data are given in Table 2. Ignition dealy data were found to fit in the following equation [18, 19]

$$[t_{id} = \mathrm{B}e^{E_i/RT}]$$

where B is a constant. The activation (or ignition) energy (E_i) was assessed from the above equation and typical plots are shown in Fig. 3. The values of E_i and the correlation coefficient (r) are given in Table 2.

Table 1
Analytical, UV, thermal analysis, impact and friction sensitivity data for dimethylanilinium nitrates

Compound	% of NO_3^-		λ_{max}/nm	Density/ (gm cm^{-3})	DTA peak temp. (T_d)/°C		TG weight loss/%		Impact sensitivity/ (% of explosion at 170 cm)	Friction insensitive limit/kg
	Theor.	Exp.			In air	In N_2	In air	In N_2		
2,4-DMAN	33.66	32.88	261, 269, 286	1.246	176	192	62.5	60.0	20	28.2
2,5-DMAN	33.66	33.45	264, 271, 282	1.198	181	203	63.0	61.0	10	35
3,4-DMAN	33.66	33.05	261, 269, 286	1.140	190	210	51.0	52.0	40	35

Table 2
Ignition delay (t_{id}), ignition temperature (IT) and kinetic parameters for dimethylanilinium nitrates

Compound	Ignition delay (s) at								IT/(°C) for t_{id} of 5s	E_i/ (kJ mol^{-1})	r
	500°C	550°C	600°C	650°C	700°C	750°C	800°C	900°C			
2,4-DMAN	13.2 ± 0.4	9.6 ± 0.3	7.6 ± 0.4	6.5 ± 0.1	4.8 ± 0.4	4.3 ± 0.3	3.7 ± 0	2.9 ± 0.2	685	29.3	0.9961
2,5-DMAN	16.0 ± 0.4	11.0 ± 0.5	8.3 ± 0.1	7.1 ± 0.2	5.5 ± 0.1	4.9 ± 0.2	4.1 ± 0	3.1 ± 0.2	725	30.9	0.9691
3,4-DMAN	DNI[a]	12.3 ± 0.1	9.3 ± 0.5	8.0 ± 0.3	6.4 ± 0.1	5.1 ± 0.2	4.6 ± 0	3.5 ± 0.2	742	29.4	0.9978

[a] DNI-did not ignite.

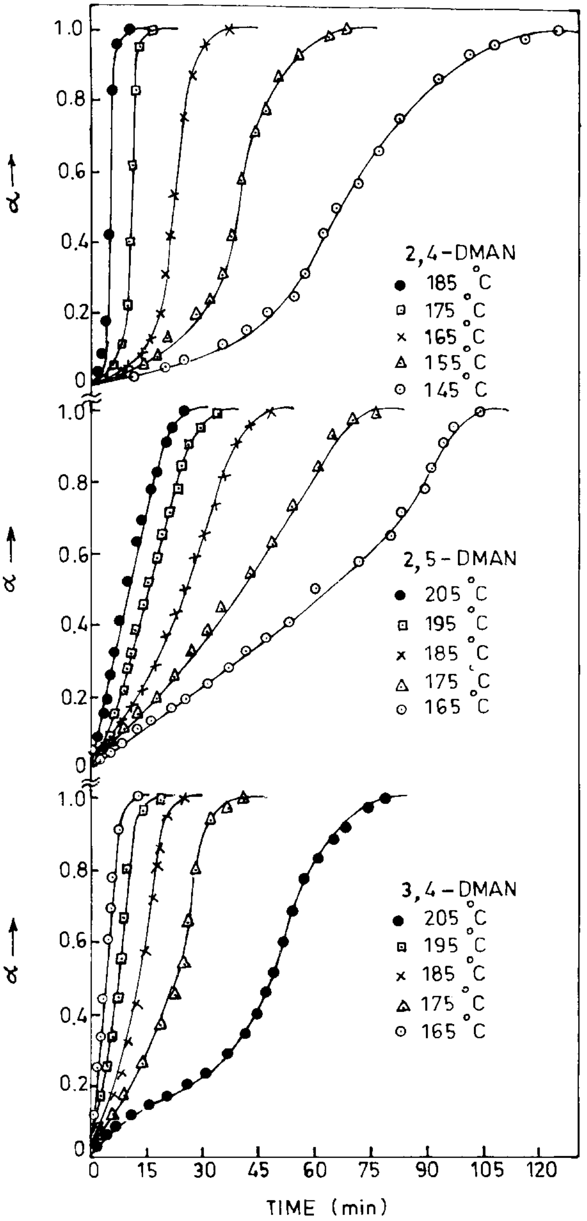

Fig. 2. Thermal decomposition of dimethylanilinium nitrates.

2.7. Impact and friction sensitivity measurements on DMAN

Impact sensitivity measurements were carried out by means of an impact machine at EDRL, Pune. The description of the device used has already been given in our earlier paper [20]. As the DMAN are less sensitive, the conventional Bruceton "stair case"

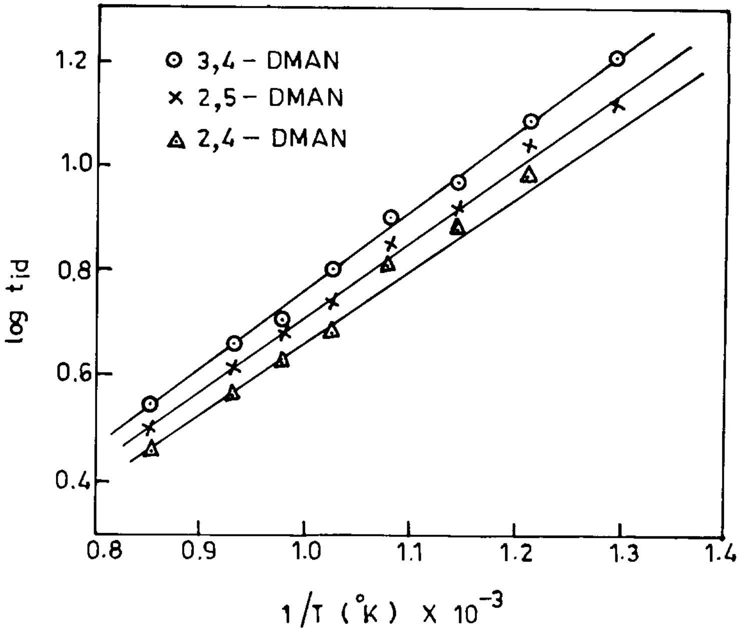

Fig. 3. Plot of log t_{id} versus $1/T$(K) for dimethylanilinium nitrates.

method could not be adopted. Hence, ten impact trials were conducted from 170 cm and the number of events of explosion was taken as the percentage of explosion (Table 1).

Friction sensitivity measurements were carried out by means of a friction-sensitive apparatus (Julius Peters, Berlin-21) at ERDL, Pune to find out the friction insensitive limit in kg, by adopting the same procedure as adopted earlier [20]. The data are given in Table 1.

3. Results and discussion

The exothermic decomposition temperature (T_d) reported in Table 1 clearly shows that the thermal sensitivity of DMAN, both in air and N_2, is in the order 2,4- > 2,5- > 3,4-DMAN. The density of these compounds falls in the same order. However, mass loss for 3,4-DMAN was quite low as compared to other nitrate salts. It is well known that ammonium salts decompose via a proton-transfer process [13, 17, 20–23]. Accordingly, 3,4-DMAN is less sensitive due to its high pK_a value (5.17) [24] as compared to 2,4- (4.89) and 2,5-dimethylanilines (4.53). It is reported that the *ortho* [25–27] and the *meta* [13, 17, 28, 29] methyl groups exert −I effects; and *para* exert +I, due to hyperconjugation [25]. Thus in *ortho* substituted nitrates (2,4- and 2,5-) this −I together with the *ortho* [25–27] and steric strain [25] effects causes weakening of the N–H bond, favouring proton transfer and consequently the rate of decomposition would be enhanced. Nevertheless, the low acidity of 3,4-DMAN may be due to the comparatively weaker −I effect of *m*-CH_3 than that of *o*-CH_3. About 40% residue was found left over in each case both in air and nitrogen atmosphere at the end of TG/DTA experiments.

The reaction mechanism can be derived by applying mechanism-based kinetic models [30–36] which gave the best fit with the isothermal TG data. Thus the kinetics of thermolysis of these nitrate salts were evaluated using nine kinetic models (Table 3). Only Avrami–Erofeev ($n = 2$, 3) and contracting area equations gave the best fits, as is clear from their correlation coefficients (r) given in Table 4. Thus it is inferred that random nucleation followed by the growth of nuclei and phase boundary reactions are rate-controlling processes in the thermolysis of DMAN. The calculated kinetic parameters are given in Table 4. A very high E_d value was obtained for 2,4-DMAN whereas not much variation in E_d was observed for 2,5- and 3,4-DMAN.

The performance of a potential new energetic material [37–40] can be determined by drop-weight impact and friction sensitivity tests [41, 42]. Moreover, it is well known that both impact and friction sensitivity depend on the chemical structure of the explosive molecule [41], and hence impact and friction sensitivity of these salts have been measured. It is very clear from Table 1 that all the three nitrates have almost the same sensitivity to impact and friction. However, DMAN are less sensitive as compared to mono (ring) substituted anilinium nitrates reported in our earlier publication [20]. This observation is also consistent with the contention of Mullay [43].

All the DMAN are quite stable at room temperature, and ignite when subjected to a sudden high temperature. Therefore, it was deemed to be of interest to undertake ignition delay studies on DMAN. 3,4-DMAN did not ignite at 500°C whereas the other two salts ignited. Table 2 shows that the ignition delay (t_{id}) and ignition temperature

Table 3
Mechanism-based kinetic models

Eq. no.	Form of $g(\alpha)$	Symbol	Rate-controlling process
1.	α^2	D_1	One-dimensional diffusion
2.	$\alpha + (1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion
3.	$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion, spherical symmetry; Jander equation
4.	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion, spherical symmetry; Ginstling–Brounshtein equation
5.	$1-(1-\alpha)^{1/2}$	R_2	Two-dimensional phase boundary reaction; contracting area (CA) equation
6.	$1-(1-\alpha)^{1/3}$	R_3	Three-dimensional phase boundary reaction; contracting cube (CC) equation
7.	$-\ln(1-\alpha)$	F_1	First-order reaction; Mample equation
8.	$[-\ln(1-\alpha)]^{1/2}$	A_2	Random nucleation; Avrami–Erofeev equation ($n = 2$)
9.	$[-\ln(1-\alpha)]^{1/3}$	A_3	Random nucleation; Avrami–Erofeev equation ($n = 3$)

Table 4

Kinetic parameters for the thermolysis of dimethylanilinium nitrates using Avrami–Erofeev ($n = 2, 3$) and contracting area equations

Compound	Avrami–Erofeev equation						Contracting-area equation			Mean	
	$n = 2$			$n = 3$			$n = 2$				
	E_d/(kJ mol^{-1})	A	r	E_d/(kJ mol^{-1})	A	r	E_d/(kJ mol^{-1})	A	r	E_d/(kJ mol^{-1})	A
2,4-DMAN	100.4	3.02×10^{10}	0.9739	119.6	5.75×10^{11}	0.9863	131.7	2.29×10^{11}	0.9914	117 ± 12.9	2.78×10^{11}
2,5-DMAN	86.6	1.90×10^{8}	0.9824	81.5	5.75×10^{7}	0.9828	90.6	3.98×10^{6}	0.9777	86 ± 3.7	8.38×10^{7}
3,4-DMAN	80.7	6.31×10^{8}	0.9694	75.4	3.31×10^{8}	0.9726	88.1	3.16×10^{8}	0.9918	81 ± 5.2	4.26×10^{8}

(IT) are in the order 2,4- < 2,5- < 3,4-DMAN. However, average E_i (for ignition) values turn out to be 29.8 ± 0.7 kJ mole^{-1}. The satisfactory correlation coefficient values support the fitting of t_{id} data.

Chemical (qualitative) analysis of the species formed during decomposition, and gaseous products evolved, was carried out in order to determine the thermal decomposition pathways (Fig. 4) of DMAN salts. It seems that the overall decomposition process takes place by the transfer of a proton (N–H bond cleavage) from dimethylanilinium ion (DMAI) (I) to NO_3^- ion to form the corresponding dimethylamine (III) and nitric acid molecules in the adsorbed phase prior to oxidation–reduction reactions causing ignition. However, the proton transfer (a primary step) [5, 13, 17, 20–23] from cation to NO_3^- ion (step $1a_1$) seems to occur through an activated complex (II), is destabilized by the activation of the benzene ring. This clearly supports the contention that the E_d values for 3,4-DMAN are comparatively low. It is reported [44, 45] that the basicity of the anion (NO_3^-) increases with a rise in temperature until it reaches the base strength of dimethylamine. At this temperature, the anion base removes the proton from the DMAI to form the corresponding amine and HNO_3 molecules in the condensed phase. It has been found that the addition of a drop of arylamine to the sample during TG measurement suppresses the rate of reaction (wt loss was lowered) which also proves the formation of the corresponding arylamine in the condensed phase. Addition of a drop of dil. HNO_3 increased the rate, which may be due to the enhancement of the oxidation step. The proton transfer is followed by the oxidation of amine by HNO_3 or its dissociation products (step $1a_2$). The proton transfer process is quickly joined by the other definable degradation reactions. The HNO_3 may also rapidly react with the aryl backbone, liberating

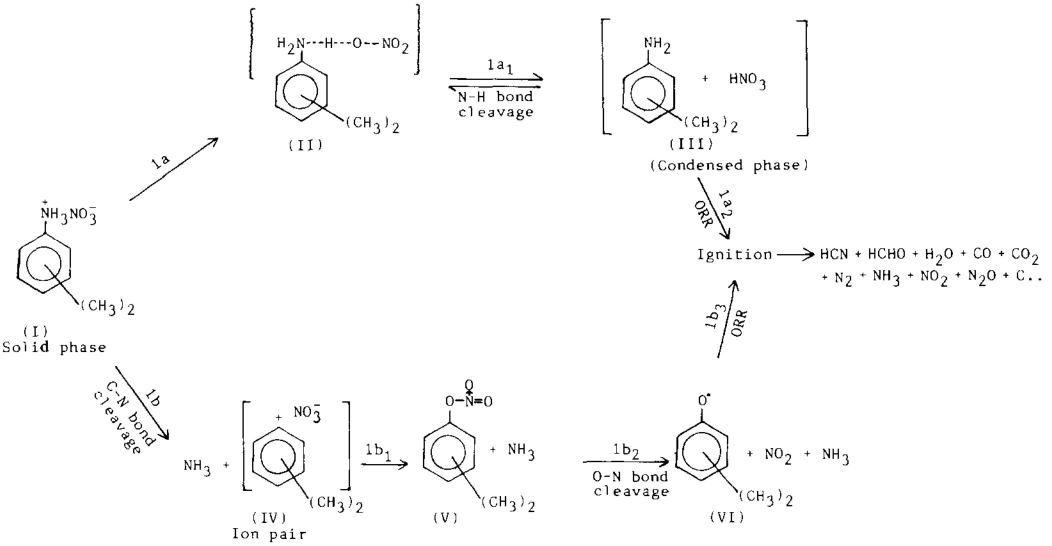

Fig. 4. Schematic representation of thermal decomposition pathways of dimethylanilinium nitrates (ORR = oxidation–reduction reactions).

secondary oxidation and reduction products of carbon and nitrogen as reported by many workers [5, 46].

The second possibility may be that DMAN decompose by C–N bond cleavage (step 1b) forming an ion pair (IV) and NH_3 (confirmed by chemical analysis). Ammonia is the expected product of decomposition [20, 37, 47, 48] of DMAN since the O/H ratio for all these nitrate salts is less than one. Nambiar et al. [49] have also reported the evolution of NH_3 during thermolysis of methylammonium perchlorates. The rate of evolution of ammonia for 3,4-DMAN was comparatively low compared to 2,4- and 2,5-DMAN which may be due to strengthening of C–N bond in the former.

The ester of nitric acid (V) is supposed to be formed by the attack of NO_3^- on the carbonation (step $1b_1$); this then decomposes ($1b_2$) via a free radical mechanism [50] leading to ignition (step $1b_3$). It may be noted that 2,4- and 2,5-DMAN yield more weight loss (60–63%) than 3,4-DMAN (51–52%) both in air and N_2 (Table 1). This may be due to an α-CH bond *ortho* to $-O-NO_2$ in the former, which activates the thermal decomposition process [51]. Rate of evolution of NO_2 (confirmed by qualitative analysis) was also found to be slow for 3,4-DMAN because of the strengthening of the O–N bond. It may be noted that the intermediates at higher temperatures are transitory prior to ignition.

4. Conclusions

The thermolysis of DMAN involves complex reaction paths, and proton transfer seems to control the overall thermolysis. Electron-donating groups ($-CH_3$) reduce the sensitivity of the energetic compounds within a class.

Acknowledgements

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References

[1] B.T. Fedoroff, Encyclopedia of Explosives and Related Items, Picatinny Arsenal, New Jersey, 1960, Vol. 1, pp. A311–379.
[2] J.H. Koper, O.G. Jansen and P.J. Vanden Berg, Explosivestoffe, 8 (1970) 181.
[3] M.S. Shaw and T.M. Oza, J. Chem. Soc., (1932) 725.
[4] D.G. Patil, S.R. Jain and T.B. Brill, Propellants, Explosives, Pyrotechnics, 17 (1992) 99.
[5] T.B. Brill, P.J. Brush and D.J. Patil, Combust. Flame, 92 (1993) 178.
[6] A. Biskupski and A. Kolaczkowski, Chem. Stosow., 27 (1983) 179.
[7] Y. Oyumi, T.B. Brill, A.L. Rheingold and C. Lowe-Ma, J. Phys. Chem. 89 (1985) 2309.
[8] T.P. Russell and T.B. Brill, Combust. Flame, 76 (1989) 393.

[9] S.R. Jain, M.V. Rao and V.R. Pai Vernekar, Proc. Indian Acad. Sci., 87A, No. 1. (1978) 31.
[10] S.R. Jain, M.V. Rao and V.R. Pai Vernekar, Propellants and Explosives, 3 (1978) 83.
[11] S.R. Jain, M.V. Rao and V.R. Pai Vernekar, J. Chem. Soc., Perkin Trans. 2, (1979) 406.
[12] Vogel's Text Book of Quantitative Inorganic Analysis, 4th edn., Longman, London, 1985, p. 497.
[13] G. Singh and I.P.S. Kapoor, Combust. Flame, 92 (1993) 283.
[14] G. Singh and R.R. Singh, Res. Ind., 23 (1978) 92.
[15] G. Singh, S.K. Vasudeva and I.P.S. Kapoor, Indian J. Tech., 26 (1991) 589.
[16] G. Singh, R.R. Singh, A.P. Rai and I.P.S. Kapoor, J. Therm. Anal. 36 (1990) 2539.
[17] G. Singh and I.P.S. Kapoor, J. Phys. Chem., 96 (1992) 1215.
[18] N. Semenov, Chemical Kinetics and Chain Reactions, Clarendon Press, Oxford, 1935, Chap. 18.
[19] E.S. Freeman and S. Gordon, J. Phys. Chem., 66 (1962) 2646.
[20] G. Singh, I.P.S. Kapoor, S.M. Mannan and J.P. Agrawal, combust. Flame, 97 (1994) 355.
[21] G. Singh and I.P.S. Kapoor, J. Chem. Soc., Perkin Trans. 2, (1989) 2155.
[22] G. Singh, I.P.S. Kapoor and M. Jain, J. Chem. Soc., Perkin Trans. 2, (1993) 1521.
[23] W.A. Rosser, S.H. Inami and H. Wise, J. Phys. Chem., 67 (1963) 1753.
[24] J.C. Dean, Lange's Hand Book of Chemistry, 13th edn., McGraw-Hill, New York, 1985.
[25] H.C. Brown and A. Cohn, J. Am. Chem. Soc., 72 (1950) 2930.
[26] Bennett and Mosses, J. Chem. Soc., (1930) 2367.
[27] Thomson, J. Chem. Soc., (1946) 113.
[28] P.V.R. Schleyer and G.W. Woodworth, J. Am. Chem. Soc., 90 (1963) 6530.
[29] T.H. Lowry and K.S. Richardson, Mechanism and Theory in Organic Chemistry, Harper and Row, New York, 1976, pp. 226; 229–250.
[30] V. Satava, Thermochim. Acta, 2 (1971) 423.
[31] J.H. Sharp, G.W. Brindley and B.N.N. Achar, J. Am. Ceram. Soc., 49 (1966) 379.
[32] Y. Masuda, K. Iwata, R. Ito and Y. Ito, J. Phys. Chem., 91 (1987) 6543.
[33] K.N. Somasekharan and V. Kalpagam, J. Phys. Chem., 91 (1987) 6543.
[34] M. Avrami, J. Chem. Phys., 7 (1939) 1103; 8 (1940) 212.
[35] B.V. Erofeev, C.R. Acad. Sci., USSR, 52 (1946) 5111.
[36] A.K. Galway, Chemistry of Solids, Chapman and Hall, London, 1967.
[37] G. Singh, I.P.S. Kapoor and S.M. Mannan, J. Therm. Anal. (1995) in press.
[38] G. Singh, I.P.S. Kapoor and S.M. Mannan, Part 1, J. Energ. Mater., 12 (1994) 113.
[39] G. Singh, I.P.S. Kapoor and S.M. Mannan, Part 2, J. Energ. Mater., 12 (1994) 123.
[40] G. Singh and I.P.S. Kapoor, J. Energ. Mater., 11 (1993) 293.
[41] D.E. Bliss, S.L. Christian and W.S. Wilson, J. Energ. Mater., 9 (1991) 319.
[42] M.J. Kamlet and H.G. Adolph, Propellants and Explosives, 4 (1979) 30.
[43] J. Mullay, Propellants, Explosives, Pyrotechnics, 12 (1987) 60.
[44] L. Erdey, S. Gal and G. Liptay, Talanta, 20 (1964) 913.
[45] L. Erdey and S. Gal, Talanta, 10 (1969) 23.
[46] W.A. Rosser, S.H. Inami and H. Wise, J. Phys. Chem., 67 (1963) 1753.
[47] Y. Oyumi and T.B. Brill, J. Phys. Chem., 89 (1985) 4325.
[48] Y. Oyumi and T.B. Brill, J. Phys. Chem., 91 (1987) 3657.
[49] P.R. Nambiar, P. Verneker and S.R. Jain, J. Therm. Anal., 7 (1975) 587.
[50] R. Bachan, R.T. Merrow and R.W.V. Dolah, Chem. Rev., (1955) 485.
[51] T.B. Brill and K.J. James, Chem. Rev., 93 (1993) 2667.