

Thermal decomposition of 2,4,N-trinitro anilino acetic acid and its esters

K U B RAO* and S R YOGANARASIMHAN†

Explosives Research and Development Laboratory, Armament Post, Pune 411 021, India
† Present address: IDL Chemicals Ltd, Sanathnagar (IE) P.O., Hyderabad 500 018, India

MS received 29 September 1983; revised 15 December 1984

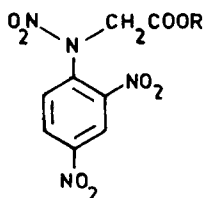
Abstract. The mode of decomposition of 2,4,N-trinitro anilino acetic acid [Glycine, N-(2,4 dinitrophenyl), N-nitro] and its methyl and ethyl esters has been determined from a study of the kinetic parameters of their thermal decomposition using DTA, isolation and identification of some of the nonvolatile products of decomposition, and confirmed from a mass spectral study. It is concluded that these compounds decompose through the scission of N-NO₂ bond.

Keywords. Explosives; nitramines; nitro anilino acetic acids; thermal decomposition.

1. Introduction

A number of polynitro aromatic nitramines which are potential high explosives have been reported in the literature (Fedoroff 1960). A majority of them for example pentryl, heptyl etc., have low thermal stability due to the presence of nitrate ester groups in them. Thermal decomposition characteristics of only the tetryl, of the various stable aromatic nitramines have been studied. No thermal data of any of the related aromatic nitramines are available.

Tetryl and the other aromatic nitramines reported have an alkyl group on the amino Nitrogen. Hence, the explosive properties of these compounds cannot be varied extensively by bringing about small changes in the nature of the alkyl group. A compound of the structure I can be expected to offer the following advantages over tetryl and other related compounds.



- I (R = H)
II (R = CH₃)
III (R = CH₂CH₃)

- (i) being an aromatic nitramine with three nitro groups its explosive and thermal characteristics will be similar to those of the tetryl. But the explosive power is expected to be less.
(ii) Its derivatives can find use in different explosive formulations; Metal salts can be

* To whom all correspondence should be addressed.

used in delay compositions and as burning rate modifiers in propellants. Esters are useful as energetic plasticisers.

A survey of the literature revealed that only the 2,4 dinitro and the 2,4,6 trinitro derivatives of N-phenyl glycine have been synthesised so far and the N-nitro compound is as yet unreported.

In this laboratory 2,4,N-trinitro anilino acetic acid [Glycine, N-(2,4 dinitro phenyl), N-nitro (I); 2,4,N-TNAAA] and its methyl (II) and ethyl (III) esters were synthesised for the first time. Incorporation of III as the plasticiser in a cast double base propellant composition gave a propellant with improved density, burning rate and specific impulse (Rao 1982). To understand the role of this compound during the combustion of the propellant, the thermal decomposition characteristics of the acid and the two esters were studied. The results are presented in this report.

2. Experimental

2.1 Materials

2,4,N-TNAAA was synthesised by the selective N-nitration of glycine, N-(2,4 dinitro phenyl) (1084-76-0) in the presence of acetic anhydride at -7 to -5°C . Methyl and ethyl esters were obtained by the esterification of I by standard methods (Rao 1982). 2,4,N-TNAAA m. p. 161°C (decomposition) C 34.83; H 1.96; N 19.36; $\text{C}_8\text{H}_6\text{N}_4\text{O}_8$ requires C 33.56; H 2.097; N 19.58. IR (KBr) 3100, 1737, 1600, 1555, 1550, 1530, 1525, 1425, 1390, 1340, 1325, 1305 cm^{-1} . NMR Acetone d_6 δ 5 (2H); 8.1 to 8.2 (1H); 8.54 (1H); 8.7 to 8.8 (1H) and 9 (1H). Methyl ester of 2,4,N-TNAAA m. p. $126-127^{\circ}\text{C}$ C 36.8; H 2.6; N 18.4; $\text{C}_9\text{H}_8\text{N}_4\text{O}_8$ requires C 36; H 2.67; N 18.67. IR (KBr) 3125, 3000, 1745, 1610, 1565, 1560, 1550, 1535, 1422, 1355, 1320, 1300, 1240 cm^{-1} . NMR (CDCl_3) δ 3.83 (3H); 8.0 to 8.15 (1H); 8.5 to 8.6 (1H) and 8.95 (1H); signal corresponding to methylene protons not observed. Ethylester of 2,4,N-TNAAA m. p. $99-100^{\circ}\text{C}$ C 38.92; H 3.12; N 17.52; $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_8$ requires C 38.22; H 3.18; N 17.83. IR (KBr) 3122, 3000, 1755, 1615, 1562, 1555, 1545, 1535, 1422, 1357, 1345, 1315, 1295, 1240 cm^{-1} . NMR (CDCl_3) δ 1.25 to 1.45 (3H); 4.15 to 4.45 (2H); 4.8 to 5.2 (2H); 7.9 to 8.1 (1H); 8.5 to 8.6 (1H) and 8.9 (1H).

2.2 Apparatus and methods

The apparatus and experimental methods used have been described earlier (Rao *et al* 1985). Activation energies (E_a) of decomposition of the three compounds were calculated by the methods of Kissinger (1957) and Ozawa (1965). Pre-exponential factor (A), entropy of activation (ΔS^*) and the rate of decomposition (k) were also calculated. The mass spectrum of III was recorded using a Hitachi mass spectrometer; temperature of ion source- 100°C and ion current-70 eV. The major components of the nonvolatile residue obtained by the controlled decomposition of about 10 g of III were separated by column and thin layer chromatographic techniques. The components were identified by TLC and their identity confirmed by derivative preparation and IR spectroscopy (Rao 1982).

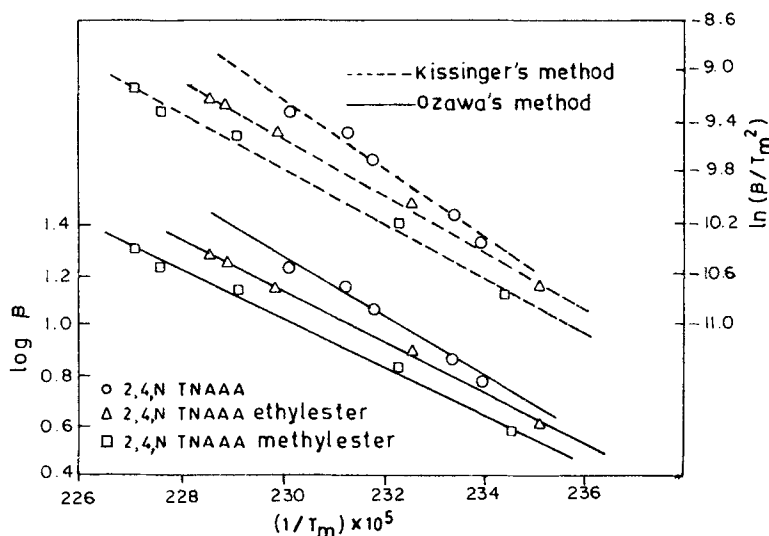
3. Results and discussion

Kinetic parameters of thermal decomposition of 2,4,N-TNAAA, its methyl and ethyl esters are tabulated in table 1. Arrhenius plots used for the calculation of activation

Table 1. Physical constants and kinetic parameters of thermal decomposition of 2,4,N-TNAAA and its esters.

Compound	m.p. (K) $\beta = 10 \text{ K/min}$	T_m (K) at $\beta = 5.17 \text{ K/min}$	E_a (kJ/mole)		$\ln A$	ΔS^* ($\text{J mole}^{-1} \text{ K}^{-1}$)	k (sec^{-1})
			Kissinger's method	Ozawa's method			
I	434 (d)	424	207.9	204.2	54.74	199	0.03511
II	399-400	425	182.2	179.7	46.62	131.5	0.01204
III	372-373	426	191.8	192.8	49.76	157.5	0.01248

T_m = peak temperature of decomposition; β = heating rate; d = decomposition

**Figure 1.** Arrhenius plots for the determination of kinetic parameters 2,4,N-TNAAA derivatives.

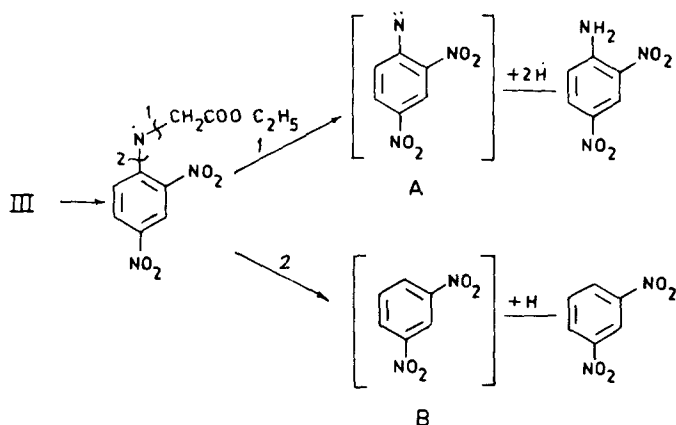
energies are shown in figure 1. All the compounds decompose at the same temperature and have kinetic parameters of the same order suggesting that irrespective of the nature of R, they undergo decomposition by the same mechanism. The acid decomposes three times as fast as either of the esters. The ethyl ester of 2,4-dinitro anilino acetic acid, 2,4-dinitro aniline and *m*-dinitrobenzene are among the nonvolatile products of the decomposition of III. The formation of these products suggests that one of the three bonds N-NO_2 , $\text{N-C}_{\text{methylene}}$ or $\text{N-C}_{\text{aromatic}}$ should rupture in the primary step of the decomposition.

The activation energy for the decomposition of the compounds I, II and III is much lower than the bond energy of the N-C bond 295 kJ mole^{-1} (Roberts and Caesario 1965) and is of the same order that can be expected for the strength of the N-NO_2 bond. Llewellyn and Whitmore (1948) determined the N-NO_2 bond energy in ethylene dinitramine to be $223.4 \text{ kJ mole}^{-1}$. It has partial double bond character due to 1,3 migrations. The compounds I, II and III which lack a H atom on the amino N cannot

exhibit such tautomerism and the N-NO₂ bond in them should have a much lower strength. Further, Delpuech and Cherville (1948) observed that when aromatic nitramines are irradiated, the excitation energy is preferentially transferred to N-NO₂ bond. Free rotation around the N-NO₂ bond in these compounds is restricted in the ground state. The preferential absorption of energy during excitation increases the bond length. This facilitates free rotation around the bond and accounts for the high energy of activation and pre-exponential factor values observed during the decomposition. These findings suggest that the cleavage preferentially takes place at the N-NO₂ bond. The NO₂ formed catalyses further decomposition accounting for the high rates of decomposition of these compounds. The preferential cleavage of the N-NO₂ bond in the nitramine decompositions is corroborated by the results of a number of workers, Flournoy (1962), Korsunski and Dubovitskii (1964), Korsunski *et al* (1967a, b, 1974) who investigated the decomposition mechanism of aliphatic nitramines with different substituents on the amino N. Several investigators using different thermoanalytical techniques studied the decompositions of nitramino explosives HMX (Robertson 1949; Rogers and Smith 1967; Maycock and Pai Vernekar 1969; Kimura and Kubota 1980), RDX (Robertson 1949; Hall 1971; Cosgrove and Owen 1974; Batten and Murdie 1970) and Tetryl (Robertson 1948; Dubovitskii *et al* 1960; Dubovitskii *et al* 1961; Merzhanov *et al* 1967). They observed that these compounds also decompose by a similar mechanism.

During the decomposition studies of tetryl, Dubovitskii *et al* (1960) isolated N-methyl 2,4,6 trinitro aniline, picric acid and 2,4,6-trinitro anisole from its decomposition products. Analogous products that can be expected from III are the ethyl ester of 2,4-dinitro anilino acetic acid, 2,4 dinitro phenol and 2,4 dinitro anisole. We have isolated the first of these compounds. A careful TLC analysis of the decomposition products of III failed to show the presence of 2,4-dinitro phenol. The formation of the other two compounds isolated in the present study can be explained as follows by the cleavage of the respective bonds and consequent reorientations arising from the high exothermicity of the primary reactions.

Thus,



The formation of intermediate products A and B is substantiated by the presence of peaks corresponding to the ions of mass m/z 181 (A) and m/z 167 (B) in the mass spectrum of III.

The electron impact (Volk and Schubert 1968) and chemical ionisation (Zitrin and Yinon 1976) mass spectra of nitramines show intense peaks corresponding to m/z ($M-\text{NO}_2$) while the aromatic nitro compounds have negligible or no peaks at that value.

The electron impact mass spectrum of III has an intense peak (16.7% of base peak) at m/z 269 ($M-45$) corresponding to the parent amine *viz.* ethyl ester of 2,4 DNAAA compared to a weak peak (5%) at m/z 268 ($M-46$). The formation of the parent amine in the source of the mass spectrometer has been observed earlier (Wilson *et al* 1970 and Larsen *et al* 1975). Larsen *et al* observed that the intensity of parent amine impurity thus arising increases with the temperature of the ion source and the length of the time elapsing from the introduction of the sample to the actual recording of the spectrum. The lower intensity of the peak at m/z 268 in comparison with that at m/z 269 can be attributed to this phenomenon. A rerecording of the mass spectrum of III using the visigraph method in which the time lapse is minimum gave peaks with the following intensities: m/z 269 (7.2%) and m/z 268 (30%).

It can thus be concluded that the primary step in the decomposition of 2,4,N-TNAAA and its esters is the scission of the nitramine bond.

References

- Batten J J and Murdie D C 1970 *Aust. J. Chem.* **23** 737
Cosgrove J D and Owen A J 1974 *Combust. Flame* **22** 13, 19
Delpuech A and Cherville J 1976 *Symp. Chem. Probl. Connected Stab Explos (Proc)* **4** 179
Dubovitskii F I, Rubtsov Yu I and Manelis G B 1960 *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk.* 1763 (*Chem. Abstr.* 1962 **56** 14969 b)
Dubovitskii F I, Manelis G B and Smirnov L P 1961 *Zh. Fiz. Khim.* **35** 521 (*Chem. Abstr.* 1961 **55** 17564)
Fedoroff B T (ed.) 1960 *Encyclopedia of explosives and related items* (New Jersey: Picatinny Arsenal, Dover) vol. 1, p. A 420
Flournoy J M 1962 *J. Chem. Phys.* **36** 1106
Hall P G 1971 *Trans. Faraday Soc.* **67** 556
Kimura J and Kubota N 1980 *Propellants and Explos.* **5** 1
Kissinger H E 1957 *Anal. Chem.* **29** 1702
Korsunskii B L and Dubovitskii F I 1964 *Dokl. Akad. Nauk. SSSR* **155** 402 (*Chem. Abstr.* 1964 **61** 558 d)
Korsunskii B L, Dubovitskii F I and Sitonina G V 1967a *Dokl. Akad. Nauk. SSSR* **174** 1126 (*Chem. Abstr.* 1968 **68** 29067 s)
Korsunskii B L, Dubovitskii F I and Shurygin E A 1967b *Izv. Akad. Nauk. SSSR. Ser. Khim.* 1452 (*Chem. Abstr.* 1968 **68** 38798 h)
Korsunskii B L, Kiselava L Ya, Ramushev V I and Dubovitskii F I 1974 *Izv. Akad. Nauk. SSSR* 1778 (*Chem. Abstr.* 1974 **81** 168S12 v)
Larsen B S, Becher J, Hammerum S and Schroll G 1975 *Acta Chim. Scand.* **B29** 41
Llewellyn F J and Whitmore F E 1948 *J. Chem. Soc.* 1316
Maycock J N and Pai Vernekar V R 1969 *Explosivstoffe* **17** 5
Merzhanov A G, Abramov V G and Abramova L T 1967 *Zh. Fiz. Khim* **41** 179 and (*Chem. Abstr.* 1967 **66** 76355 C)
Ozawa T 1965 *Bull. Chem. Soc. Jpn.* **38** 1881
Rao K U B 1982 *Studies on nitro anilino acetic acids* Ph.D. thesis, University of Poona, Pune
Rao K U B and Yoganasimhan S R 1985 *Proc. Indian Acad. Sci (Chem. Sci)*
Roberts J D and Caeserio M L 1965 *Principles of organic chemistry* (New York: Benjamin Inc) p. 77
Robertson A J G 1948 *Trans. Faraday Soc.* **44** 627
Robertson A J G 1949 *Trans. Faraday Soc.* **45** 85
Rogers R N and Smith L C 1967 *Anal. Chem.* **39** 1024
Volk F and Schubert H 1968 *Explosivstoffe* **16** 2
Wilson J G, Barnes C S and Goldsack R J 1970 *Org. Mass Spectrom.* **4** 365
Zitrin S and Yinon J 1976 *Org. Mass Spectrom.* **11** 388