

## Thermal decomposition of some nitroanilinoacetic acids

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**Abstract.** Thermal decomposition characteristics of 2,4 dinitroanilino acetic acid, 2,4,6 trinitro anilino acetic acid and their methyl and ethyl esters have been investigated by DTA. It is concluded from a study of the kinetic parameters of their decomposition, intramolecular hydrogen bonds existing in these compounds and mass spectral fragmentation characteristics of ethyl esters that these compounds decompose by the loss of OH through a cyclic intermediate formed by the intramolecular hydrogen bonding between the amino hydrogen atom and ortho nitro group.

**Keywords.** Explosives; nitroanilino acetic acids; thermal decomposition.

### 1. Introduction

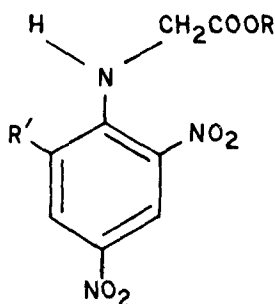
Nitro anilino acetic acids are the nitro derivatives of N-phenyl glycine. They are among the least studied explosive compounds. No data are available on the explosive or thermal properties of these compounds except for the report that their metallic salts are more explosive than the parent acids (Fedoroff 1960). The mode of thermal decomposition of 2,4 dinitro and 2,4,6-trinitro anilino acetic acids and their methyl and ethyl esters is discussed in this report in terms of their decomposition kinetic parameters and the nature of decomposition products formed, and confirmed from a study of mass spectral fragmentation of the ethyl esters.

### 2. Experimental

#### 2.1 Samples

2,4 Dinitro anilino acetic acid [glycine, N-(2,4 dinitrophenyl), (I); 2,4-DNAAA] was prepared by a minor modification of the procedure reported by Abderhalden *et al* (1910). 2,4,6 Trinitro anilino acetic acid [glycine, N-(2,4,6 trinitrophenyl) (II); 2,4,6-TNAAA] was obtained by an intramolecular rearrangement of N-(2,4-dinitro-phenyl), N-nitroglycine, synthesised in this laboratory (Rao 1982). Methyl (IA, IIA) and ethyl (IB, IIB) esters of the two acids were prepared by standard methods from the respective acids.

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	R	R <sub>1</sub>	Compound
I	H	H	2,4-DNAAA
IA	CH <sub>3</sub>	H	Methyl ester of I
IB	CH <sub>2</sub> CH <sub>3</sub>	H	Ethyl ester of I
II	H	NO <sub>2</sub>	2,4,6-TNAAA
IIA	CH <sub>3</sub>	NO <sub>2</sub>	Methyl ester of II
IIB	CH <sub>2</sub> CH <sub>3</sub>	NO <sub>2</sub>	Ethyl ester of II

## 2.2 Apparatus and methods

A micro DTA apparatus specially designed and fabricated in this laboratory for explosive materials was used for the thermal analysis. The temperature measurements were made using Pt/Pt-Rh (13%) thermocouples and the heating rate ( $\beta$ ) of the DTA furnace was monitored by a linear temperature variable rate programmer of M/s Stranton Redcroft, U.K. A multispan two-pen strip chart recorder was used for recording DTA results. Other details of the apparatus have been described elsewhere (Rao 1982). 10 mg samples were used for the kinetic studies. Peak temperature of decomposition ( $T_m$ ) of each of the compounds at different heating rates were determined and activation energies ( $E_a$ ) of decomposition calculated by the methods of Kissinger (1957) and Ozawa (1965). Mass spectra of ethyl esters were recorded using a Hitachi mass spectrometer. Temperature of the ion source: 150°C for IB and 100°C for IIB; Ion current 70 eV.

## 3. Results and discussion

Kinetic parameters of the thermal decomposition of the six compounds are tabulated in table 1. Arrhenius plots used for the calculation of activation energies are shown in figures 1 and 2.

A comparison of the thermal data of the six compounds suggests that the energy of activation and entropy of activation ( $\Delta S^*$ ) of each of the dinitro compounds are higher

**Table 1.** Physical constants and kinetic parameters of thermal decomposition of nitroanilino acetic acids and their esters.

Compound	m.p. (K)		$E_a$ (kJ/mole)		$\ln A$	$\Delta S^*$ (J mole <sup>-1</sup> K <sup>-1</sup> )	$k$ (sec <sup>-1</sup> )
	$\beta = 10$ K/min	$\beta = 5.17$ K/min	Kissinger's method	Ozawa's method			
I	478	469	130.1	131.6	28.45	-20.4	0.0061
IA	399	499	156.8	159.2	33.05	17.3	0.0066
IB	415	523	150.6	152.7	29.70	-10.9	0.0057
II	436	462	103.4	105.6	21.92	-74.6	0.0051
IIA	401	498	126.4	127.2	25.38	-46.4	0.0053
IIB	364	493	111.5	116.1	21.89	-75.4	0.0028

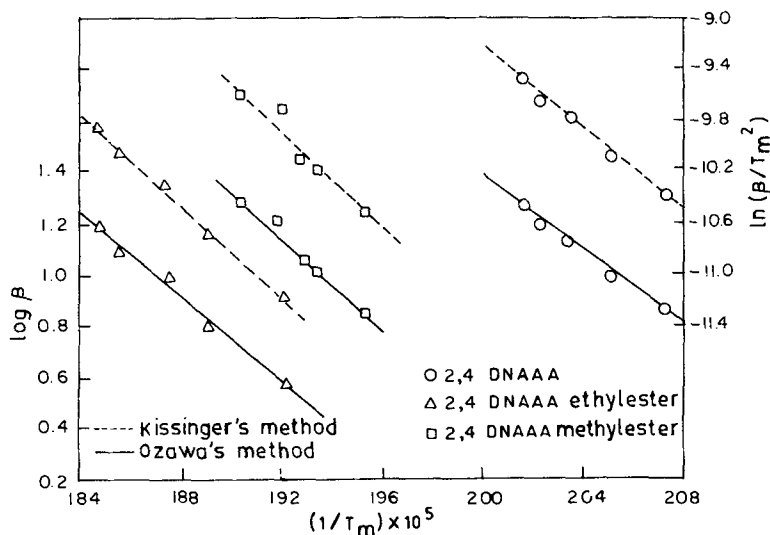


Figure 1. Arrhenius plots for determination of kinetic parameters – 2,4, DNAAA derivatives.

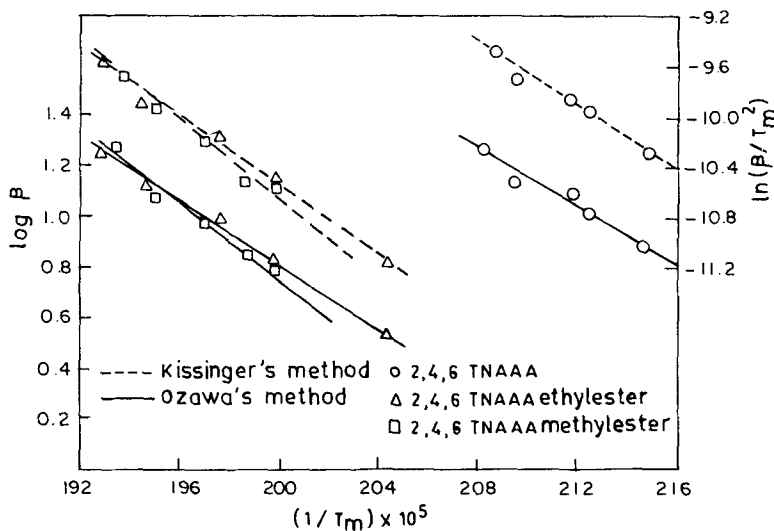


Figure 2. Arrhenius plots for determination of kinetic parameters – 2,4,6 TNAAA derivatives.

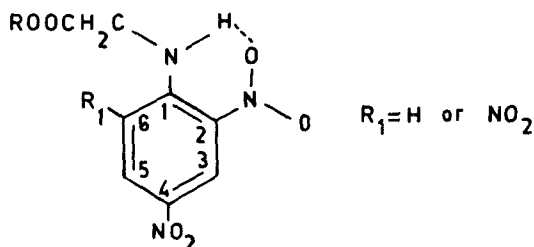
than those of the corresponding trinitro compounds thus forming two distinct groups. Except for the fact that the two acids I and II have relatively low activation energy, the nature of R appears to have little influence on the mode of decomposition. The second set of compounds differ from the first in having an additional nitro group in the 6 position which appears to facilitate decomposition as shown by the lower activation energies. If the nitro group in the 2 position is involved in the formation of any intermediate in the activated state, the availability of a second nitro group in the other

ortho position helps in the facile formation of this intermediate and thus improves the reactivity.

Decomposition reactions involving cyclic intermediates have been reported to have low entropies of activation (Kwart and Taagepara 1964; Maksimov 1969) which are of the same order as that observed for these compounds. The formation of a cyclic intermediate can thus be expected during these decompositions as well. The lower entropies of activation of the trinitro compounds suggest that the formation of this intermediate is further favoured by the introduction of the additional nitro group.

Another property involving the formation of a cyclic system whose strength increases by the introduction of a nitro group in the 6 position is intramolecular hydrogen bonding involving the amino H and the oxygen atom of the *o*-nitro group. A study of the influence of the solvent on the N-H stretching frequencies of IB and IIB by the method of Bellamy (1958) indicated that the introduction of the second nitro group strengthened this internal bond and resulted in shifting the N-H stretch to lower frequencies by  $9\text{ cm}^{-1}$  (Rao 1982).

As the amino H participates in the decomposition reaction and intramolecular hydrogen bonding and the two properties namely, the entropy of activation and the intramolecular hydrogen bonding are influenced by the introduction of an additional nitro group in a similar manner, it is reasonable to assume that the cyclic system formed as a result of the intramolecular hydrogen bonding is the cyclic intermediate formed in the activated state.



The primary step of decomposition then constitutes the cleavage of one or more of the endocyclic or exocyclic bonds of this cyclic system with the formation of relatively stable products. The different bonds that can be expected to undergo cleavage are  $\text{C}_1\text{-C}_2$ ;  $\text{C}_2\text{-C}_3$ ;  $\text{C}_1\text{-C}_6$ ;  $\text{C}_1\text{-N}_{\text{amino}}$ ;  $\text{C}_2\text{-N}_{\text{nitro}}$ ;  $\text{N}_{\text{amino}}\text{-H}$ ;  $\text{N}_{\text{nitro}}\text{-O}$ .

A comparison of the activation energy values of the two sets of compounds suggests that the formation of a stronger intramolecular hydrogen bond favours the decomposition. This requires the cleavage of two relatively strong bonds namely N-H and N-O, the average bond energies of these two bonds being  $350.4\text{ kJ mole}^{-1}$  and  $238.6\text{ kJ mole}^{-1}$  respectively (Roberts *et al* 1965). The depletion of electrons available in the ring as a result of the introduction of an additional nitro group reduces the strength of these two bonds by (i) increasing the bond length of N-H and thus weakening it and (ii) decreasing the bond order of the N-O bond of the  $\text{NO}_2$  group thus reducing its strength. Considering the fact that the O-H bond energy is  $460\text{ kJ mole}^{-1}$ , the lowest activation energy observed in these compounds *viz*  $104\text{ kJ mole}^{-1}$  for II can only be sufficient to bring about decomposition by the cleavage of N-H and N-O bonds.

From the above observations it is postulated that the primary step in the decomposition of these compounds involves the loss of the OH through a cyclic intermediate formed as a result of intramolecular hydrogen bonding between the amino H and the O atom of the *o*-nitro group. The higher activation energy of compounds I, IA and IB is due to the relatively strong N–H and N–O bonds present in them. The relatively high values of entropy of activation observed is ascribed to the greater degree of freedom available in the intermediates from these compounds due to their weaker internal hydrogen bonds.

A survey of literature indicated the absence of any reports on the mechanism of decomposition of *o*-nitroaniline derivatives. Zeman (1980) determined the kinetic parameters of the decomposition of picramide and its N-alkyl derivatives. Fields and Meyerson (1968), Maksimov (1971), Matveev *et al* (1976, 1978a) investigated the decomposition mechanism of mono- and poly-nitrotoluenes which are structurally related to the nitroanilines, Matveev *et al* (1976, 1978a) showed that the *m*- and *p*-nitrotoluenes decompose by a radical mechanism involving the cleavage of the C–NO<sub>2</sub> bond while the *o*-derivatives decompose through a six-membered cyclic intermediate. By a comparison of the kinetic parameters of decomposition and the study of the isotope effects of *o*-nitrotoluene and *o*-nitroaniline, Matveev *et al* (1978b) concluded that a similar mechanism operates in the case of *o*-amino nitrobenzenes as well.

Fields and Meyerson (1975) observed that the decomposition of nitro compounds under thermal conditions was similar to that under electron impact. Torssel and Ryhage (1965) and Musso (1967) have suggested that the decomposition reactions of explosives under electron impact closely parallel those in the early stages of explosions and that the mass spectra can therefore furnish helpful guidance in the study of such processes. Electron impact mass spectra of 2,4-DNAAA were reported by Studier *et al* (1970) and Hellberg *et al* (1972). Hellberg *et al* observed that the major fragmentation of 2,4-DNAAA was the loss of a carboxyl radical followed by the loss of an OH radical. Studier *et al* however did not report the presence of any ions corresponding to the loss of OH.

The electron impact mass spectral data of the compounds IB and IIB recorded during the present investigations are tabulated in table 2. The base peak in the mass spectra of these compounds is at *m/z* (*M*–COOCH<sub>2</sub>CH<sub>3</sub>). They have intense peaks

Table 2. Principal fragmentations of ethyl esters of 2,4-DNAAA and 2,4,6-TNAAA

Ethyl ester of 2,4-DNAAA		Ethyl ester of 2,4,6-TNAAA		Possible mode of formation of ion from <i>M</i> <sup>+</sup> or ( <i>M</i> +1) <sup>+</sup>
Fragment ion <i>m/z</i>	Relative intensity % base peak	Fragment ion <i>m/z</i>	Relative intensity % base peak	
269	28.7	314	13.19	<i>M</i> <sup>+</sup>
253	2.4	298	1.88	( <i>M</i> +1) <sup>+</sup> – OH
223	0.6	268	9.04	( <i>M</i> +1) <sup>+</sup> – OH – NO
197	26.03	242	22.62	( <i>M</i> +1) <sup>+</sup> – COOCH <sub>2</sub> CH <sub>3</sub>
196	100.0	241	100.0	<i>M</i> <sup>+</sup> – COOCH <sub>2</sub> CH <sub>3</sub>
179	5.91	224	8.92	<i>M</i> <sup>+</sup> – COOCH <sub>2</sub> CH <sub>3</sub> – NO <sub>2</sub>
150	35.5	195	22.62	<i>M</i> <sup>+</sup> – COOCH <sub>2</sub> CH <sub>3</sub> – NO <sub>2</sub>
149	12.4	194	16.7	<i>M</i> <sup>+</sup> – COOCH <sub>2</sub> CH <sub>3</sub> – OH – NO

corresponding to  $m/z$  ( $M-16$ ) followed by peaks at  $m/z$  ( $M-16-30$ ). It is known that the molecular ions capture hydrogen atoms from source walls. The formation of these two ions can be due to the loss of an OH from the ( $M + 1$ ) ion followed by loss of NO from the ( $M + 1 - OH$ ) ion. The formation of an ( $M + 1$ ) ion is also confirmed by the presence of relatively intense peaks at  $m/z$  197 and  $m/z$  242 in the mass spectra of IB and IIB respectively whose intensity cannot be accounted for by relative abundance of isotopes only. The peak corresponding to  $m/z$  ( $M - 16$ ) can also arise due to the loss of O from the molecular ion. The mass spectra show the loss of an OH from the ( $M-COOCH_2CH_3$ ) ion as well, as has been observed by Hellberg *et al* (1972) in the case of 2,4 DNAAA.

It can thus be concluded that these nitro anilino acetic acids and their esters decompose by the loss of an OH through a six-membered cyclic intermediate.

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