# Kinetics and mechanism of thermal decomposition of tetramethylammonium nitrate

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**Abstract.** The mechanism of thermal decomposition of tetramethylammonium nitrate has been investigated by thermogravimetry and mass spectrometry. The activation energy for the decomposition has been determined by isothermal decomposition technique using thermogravimetry and by monitoring mass spectrometrically the formation of trimethylamine. The activation energies determined in both the cases compare well, suggesting that the decomposition proceeds via dissociation of tetramethylammonium nitrate into trimethylamine and methylnitrate.

**Keywords.** Thermal decomposition; tetramethylammonium nitrate.

## 1. Introduction

The importance of thermal decomposition studies on ammonium salts having oxidizing anions like perchlorate, nitrate, etc., arises because of their extensive usage in propellants and explosive compositions. The thermal characteristics of partially substituted methylammonium perchlorates (Nambiar *et al* 1975a, 1975b) and nitrates (Jain *et al*, in press) were recently studied in our laboratories for a similar reason. The decomposition mechanism of these compounds was explained assuming a dissociation step involving proton transfer prior to decomposition. The thermal behaviour of tetramethylammonium nitrate (TMAN) appears to be similar to these compounds in the sense that it decomposes exothermically in air and endothermically under reduced pressure as shown by its differential thermal analysis (DTA) by Nambiar and Jain (1974). A sublimate is also formed when the DTA is carried out under reduced pressure. Whereas the decomposition exotherm in air may be explained to be due to the reaction between the oxidizer and the fuel groupings in the molecule, the simultaneous appearance of an endotherm and a sublimate shows that the compound undergoes dissociation (sublimes) under reduced pressure. It is conceivable therefore that the decomposition of TMAN may proceed via a dissociation process and the overall exotherm may be the result of the two processes namely, an endothermic process due to dissociation/sublimation and subsequent exothermic reaction between the oxidizer and the fuel groupings (decomposition). The dissociation process which possibly involves a methyl group transfer, will be predominant at reduced pressures. In order to ascertain whether methyl group transfer is involved in the rate determining step, we have carried out the kinetics of thermal decomposition of TMAN

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by employing isothermal thermogravimetry and mass spectrometry techniques, the results of which are being reported in this paper.

## 2. Experimental

### 2.1. *Materials*

Tetramethylammonium nitrate was prepared by treating equimolar solutions of silver nitrate and tetramethylammonium iodide. Silver iodide precipitate was removed and the clear solution of tetramethylammonium nitrate was evaporated to reduce the volume when white crystals separated out. The salt was recrystallized from water, vacuum dried and characterized by its DTA and proton magnetic resonance spectrum in $D_2O$.

### 2.2. *Apparatus*

The mass spectrometric investigation was carried out with a mass spectrometer (AEI–MS 10) connected to a constant volume system via a molecular leak. For qualitative identification of decomposition products, 25 mg of the substance was heated for 15 min at 350°C and the evolved gases were analysed. The isothermal runs were made by monitoring the evolution of mass number 58, the major peak of trimethylamine fragmentation at various intervals of time. The isothermal thermogravimetric analysis (TG) was carried out using platinum bucket in a set up as that used by Jain and Nambiar (1974).

## 3. Results and discussion

The gaseous products of thermal decomposition of TMAN as analysed by the mass spectrometer (initial pressure of $1 \times 10^{-6}$ torr) are presented in table 1. Trimethylamine, nitric oxide and formic acid were identified earlier in the decomposition products of TMAN by Lawson and Collie (1888). Mass numbers 58 and 59 in the ratio 2·5 : 1 in the mass spectrum shows the presence of trimethylamine (Stenhagen *et al* 1974). The presence of trimethylamine and fragmentation/decomposition species of methylnitrate as reported by Stenhagen *et al* (1974) and Appin *et al* (1936), apparently shows that TMAN undergoes decomposition as follows:

$$(CH_3)_4\, NNO_3 \xrightarrow{\triangle E_1} (CH_3)_3\, N + CH_3\, NO_3 \xrightarrow{\triangle E_2} \text{products}$$
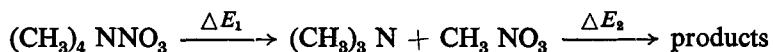
where $\triangle E_1$, is the dissociation energy and $\triangle E_2$ is the decomposition energy resulting from the reaction between trimethylamine and methylnitrate and/or its decomposition products. Methylnitrate has been shown by Appin *et al* (1936) to decompose above 200°C to give formaldehyde, methyl alcohol, water, carbon monoxide, nitric oxide and nitrogen dioxide. The mass spectrum appears to show the presence of all these products. Some of the decomposition products may also be due to the reaction between trimethylamine and decomposition products of methylnitrate. However,

under the mass spectral conditions (high vacuum), the dissociation process is favoured. This is also borne out by the reported DTA of TMAN under reduced pressure by Nambiar and Jain (1974) where an overall endothermic effect was observed. The endotherm obviously is a net effect of the exothermic decomposition process and the endothermic dissociation (sublimation) process, the latter process being prevalent at reduced pressures.

**Table 1.** Mass spectrometric data

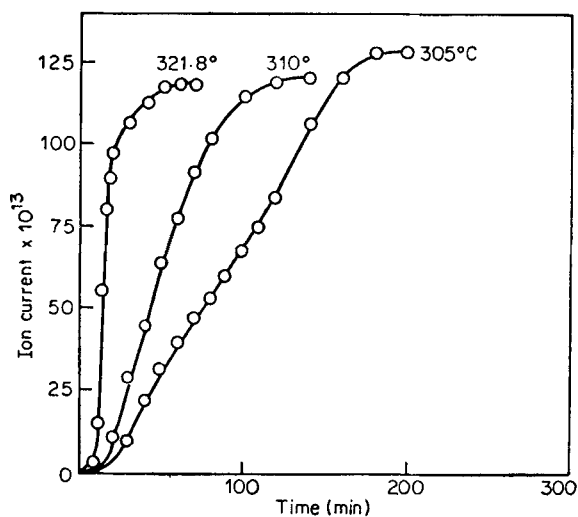| m/e | Probable assignments | Ion current $\times 10^{13}$ |
|---|---|---|
| 2 | $H_2^+$ | 0·78 |
| 12 | $C^+$ | 0·31 |
| 14 | $N^+$ | 0·83 |
| 15 | $CH_3^+$ | 2·44 |
| 16 | $O^+$, $CH_4^+$ | 0·4 |
| 17 | $OH^+$ | 0·22 |
| 18 | $H_2O^+$ | 1·20 |
| 26 | $C_2 H_2^+$ | 0·34 |
| 28 | $CO^+$, $N_2^+$ | 11·2 |
| 29 | $C_2H_5^+$ | 2·0 |
| 30 | $NO^+$, $HCHO^+$, $C_2H_6^+$ | 12·96 |
| 31 | | 3·0 |
| 32 | $O_2^+$, $CH_3OH^+$ | 2·22 |
| 40 | | 0·16 |
| 42 | | 1·28 |
| 44 | $CO_2^+$, $N_2O^+$ | 5·0 |
| 45 | | 0·10 |
| 46 | $NO_2^+$, $HCOOH^+$ | 0·95 |
| 52 | | 0·10 |
| 58 | $H_2C{=}N^+(CH_3)_2$ | 2·40 |
| 59 | $(CH_3)_3N^+$ | 0·9 |



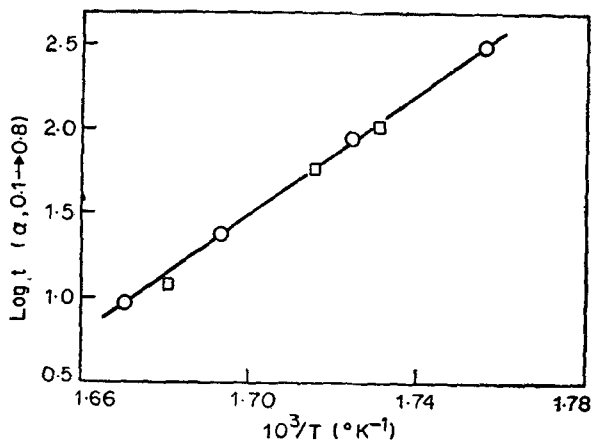**Figure 1.** Isothermal mass spectrometric curves for evolution of mass number 58, of TMAN.

**Figure 2.** log rate vs 1/T plot for the determination of activation energy for TMAN, $t$ is the time taken for decomposition to go from $a$, 0·1 to 0·8. □, mass spectrometric and ○, thermogravimetric data.
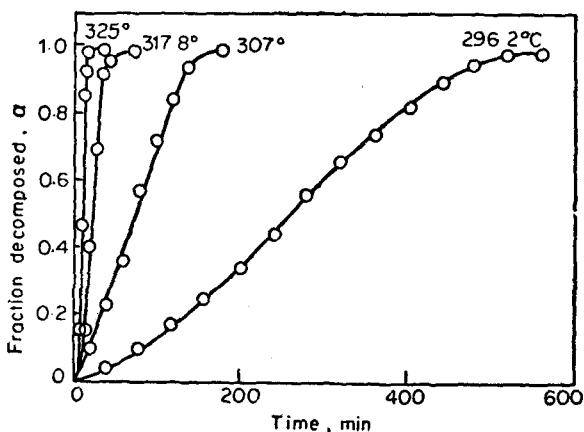


**Figure 3.** Isothermal TG curves of TMAN.

In order to determine the activation energy of the dissociation process, we followed the kinetics of the formation of trimethylamine, by monitoring the intensity of its major fragmentation peak at m/e, 58 at various time intervals. The isothermal mass spectral data, plots of ion currents vs time at various temperatures have been presented in figure 1. An activation energy of 88 kcal/mole was obtained using the Jacobs-Kureishy (1964) equation where one plots the logarithm of the time taken for fractional decomposition $a$, to go from one value to another versus reciprocal of the absolute temperature as shown in figure 2. The activation energy obtained, compares well with the dissociation energy of the $H_3C$—N bond which is reported to be 80·0 kcal/mole by Cottrell (1958). The rate determining step in the dissociation process therefore appears to be transfer of a $CH_3$ group, as expected.

**Table 2.** Kinetic Data for the decomposition of $(CH_3)_4 NNO_3$

| Kinetic equation | Activation energy (kcal/mole) | Rate constant ($k \times 10^3$) at various temperatures (°C) | | |
|---|---|---|---|---|
| | | 296·2 | 307 | 317·8 |
| Avrami-Erofeyev equation $(-\log(1-\alpha))^{1/3} = k_1 t + c_1$ | 83·6 | 1·74 | 5·96 | 25·0 |
| Prout-Tompkins equation $\log \alpha/1-\alpha = k_2 t + C_2$ acceleratory | 75·8 | 13·60 | 49·41 | 133·68 |
| Deceleratory | 86·0 | 4·89 | 16·80 | 70·0 |
| Jacobs-Kureishy equation $\log t\ (\alpha, 0\cdot1 \to 0\cdot8)$ $= \dfrac{E}{2\cdot303\ RT} + C_3$ Isothermal gravimetry | 82·0 | — | — | — |
| Isothermal mass spectrometry | 88·0 | — | — | — |

In air, at atmospheric pressure the DTA of TMAN shows an overall exotherm at 373°C indicating the predominance of decomposition rather than dissociation (sublimation) step. The kinetics of thermal decomposition in solid state in air was carried out by isothermal TG technique. There may be some uncertainty involved in the value of activation energy because of sublimation which may occur along with decomposition at atmospheric pressure. However the amount sublimed appears to be negligible as shown by the transparency of the TG tube after isothermal runs. The $\alpha$ vs $t$ plots are shown in figure 3. The calculation of activation energy by Jacobs-Kureishy method as well as by other topochemical methods (table 2) given by Garner (1955), gave an average value of 84 kcal/mole. It is interesting to note that in the log rate vs $1/T$ plot, shown in figure 2, the thermogravimetry and mass spectrometry data fall nearly on the same line, indicating the magnitude of the activation energy of the decomposition process to be virtually the same as that of the dissociation process. This result further suggests that the decomposition of TMAN occurs via dissociation of the compound, which is also the rate determining step.

## 4. Conclusion

The initial step in the thermal decomposition of tetramethylammonium nitrate has been shown to be the dissociation of the compound into trimethylamine and methylnitrate involving a methyl group transfer. The kinetic data show dissociation of the compound as the rate determining step in the thermal decomposition.

## References

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