

## Evolved gas analysis for the study of reaction kinetics: thermal decomposition of thorium tetrapropyl ammonium nitrate

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### Abstract

TG–DTA–EGA measurements on thorium tetrapropyl ammonium nitrate (Th-TPAN) showed the compound to decompose in a single step to form thorium oxide. EGA peaks for the evolution of volatiles corresponding to mass to charge ratios of 30 and 59 have been analysed for kinetic parameters. Since the kinetic parameters obtained from the analysis of both the peaks are identical, it is concluded that nitrate and tetrapropyl ammonium moieties of the complex dissociate in the same thermal activation process.

### INTRODUCTION

The usefulness of TG–DTA/DSC techniques in the study of kinetics of multistep reactions is limited by the resolution of individual reaction steps on the temperature axis. Methods such as that of Kissinger [1] are useful in this context if the temperature of maximum reaction rate can be measured accurately. However, the use of such methods by assuming coincidence of temperature of a DTA peak ( $T_p$ ) with the temperature of maximum reaction rate ( $T_m$ ) is without sufficient justification in view of the possible variation of the difference between  $T_p$  and  $T_m$  with heating rate [2]. Further, the occurrence of multiple reactions in the same temperature interval is not amenable to study by TG–DTA measurements since these techniques respond to the cumulative effect of the reactions on the mass or heat content of the sample. In the case of multistep reactions involving gaseous components in the reaction equilibrium, evolved gas analysis (EGA) measurements enable observation of simultaneous evolution or consumption of multiple gaseous species. In the event of the kinetic

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parameters derived from two gas evolution peaks being different, it may be concluded that the two gases (even when evolved in the same temperature interval) are produced in two different thermal activation processes. Therefore, analysis of individual EGA peaks for kinetic parameters gives insight into the occurrence of multiple intermediates in a reaction equilibrium.

In EGA measurements using mass spectrometry, the time lag and hence the temperature lag involved in the evolution of a gas in the thermal analyser and its detection by the mass spectrometer is negligible. Hence the peak temperature of an EGA curve corresponds to the temperature of the maximum reaction rate,  $T_m$ . By analogy with the method suggested by Kissinger [1] for the analysis of DTA curves, the dependence of peak temperature of an EGA curve on heating rate may be expressed as

$$\ln\left(\frac{\beta}{T_m^2}\right) = C - \frac{E}{RT_m} \quad (1)$$

where  $\beta$  is the heating rate,  $E$  is the activation energy and  $C$  is a constant. Hence by reading  $T_m$  values from EGA curves recorded at different heating rates, the activation energy can be evaluated. The pre-exponential factor  $Z$  can be evaluated from the value of the constant  $C$ . When the EGA peaks are well-defined singlets, the analysis can be carried out more easily and thoroughly by assuming validity of the equation

$$\alpha = \frac{a}{A} \quad (2)$$

where  $\alpha$  is the fraction reacted,  $a$  is the area swept by the EGA peak up to time  $t$  and  $A$  is the total area under the EGA peak. Equation (2) may be used to generate  $\alpha$  versus temperature ( $T$ ) data in the entire temperature interval of the EGA peak. Such data are amenable to analysis for kinetic parameters [3–5]. The usefulness of the above approach in assessing the nature of thermal decomposition of thorium tetrapropyl ammonium nitrate (Th-TPAN) is examined in this paper.

## EXPERIMENTAL

Th-TPAN was precipitated from a 10% solution of tetrapropyl ammonium hydroxide in water (Eastman Organic Chemicals, USA) neutralised ( $\text{pH} \approx 5$ ) with 8 M nitric acid (Polypharm, Bombay, AR grade). 10 ml of tetrapropyl ammonium nitrate solution thus obtained was mixed with 10 ml concentrated nitric acid (overall  $\text{H}^+$  ion concentration 7–8 M). 6 ml of thorium standard solution in water ( $41.0 \text{ g l}^{-1}$ ) prepared by dissolving LR grade thorium nitrate (Indian Rare Earths, Bombay) was added to this mixture and stirred well. The precipitate was allowed to settle, filtered, washed with distilled alcohol, air dried and stored in a desiccator over anhydrous magnesium perchlorate. Analytical data for the precipitate

TABLE 1

Analytical data for thorium tetrapropyl ammonium nitrate

	Constituent				
	Th	C	H	N (inorg.)	N (tot.)
Observed (%)	23.52	29.00	5.45	7.98	11.88
Calculated (%)	23.77	29.51	5.73	8.61	11.48

agreed well with those for the composition,  $[(C_3H_7)_4N]_2Th(NO_3)_6$  (see Table 1). Carbon, hydrogen and nitrogen were analysed by using an elemental analyser (Carlo Erba, Model 1106).

The thermoanalytical studies were carried out using a simultaneous thermal analyser (Netzsch Geratebau, Model STA 409) coupled to a quadrupole mass spectrometer (Balzers, Model QMG 311) by a heated capillary and a frit valve (Balzers, Model GES 10). The mass spectrometer was maintained at a pressure of  $10^{-5}$  mbar under dynamic condition using an oil diffusion pump (Edwards High Vacuum, Model Diffstak 63). A quadrupole data processor (Balzers, Model QDP 101) facilitated simultaneous measurement of partial pressures of up to eight gases at different sensitivities as a function of time. Pt/Pt-10%Rh thermocouples were used as temperature and differential temperature sensors. The specimen holders were cups made from recrystallised alumina. Measurements were made on 10–30 mg samples at a heating rate of  $10\text{ K min}^{-1}$  in dynamic argon with a flow rate of  $40\text{ ml min}^{-1}$ .

## RESULTS AND DISCUSSION

The TG-DTA-EGA curves for thorium tetrapropyl ammonium nitrate in dynamic argon are presented in Figs. 1 and 2. The sample melts at a temperature of 430 K and the decomposition proceeds from the molten phase. The decomposition appears to be complicated, involving the formation of a number of products such as ammonia ( $m/z$  17), nitric oxide/ethane ( $m/z$  30), methylamine ( $m/z$  31), propylene ( $m/z$  42), nitrous oxide/propane/carbon dioxide ( $m/z$  44), ethylamine/dimethylamine ( $m/z$  45) and propylamine ( $m/z$  59). It was difficult to ascribe the ion current due to a particular mass to charge ratio to a specific species, because of the isobaric nature of many of the volatiles and the lack of a strictly quantitative measure of the evolved volatiles due to the dynamic nature of the sample injection into the mass spectrometer, and it was thus difficult to formulate a decomposition scheme. However, the TG measurements indicated the residue corresponding to the constant-mass plateau to be thorium oxide. A small mass loss (5%) step observed in the range 620–850 K, in addition to the main mass loss step, can arise for three possible reasons, (i) burning of carbonaceous residue in residual oxygen

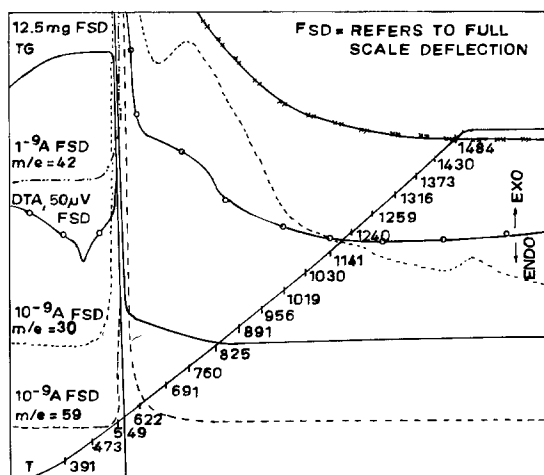


Fig. 1. Thermoanalytical curves for thorium tetrapropyl ammonium nitrate (Th-TPAN) in dynamic argon ( $40 \text{ ml min}^{-1}$ ). Initial sample mass, 29.0 mg; temperature in Kelvin.

present in argon, (ii) a second stage in the decomposition of Th-TPAN and (iii) slow desorption of a condensable vapour from the sample holder. Evolution peaks for gases with  $m/z$  44, 42 and 30 were prominent in this temperature range. The last two peaks would not have been observed if the mass-loss step were due to the burning of carbonaceous residue. Although, evolution peaks for gases with  $m/z$  30 and 44 could be observed even at 1500 K, these were unaccompanied by any mass-change step in the TG curve and hence must have been derived from a condensable volatile deposited on the cooler parts of the furnace. It is, therefore, probable that

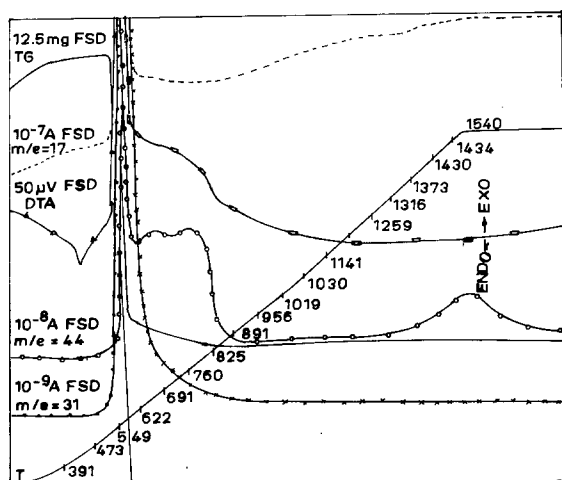


Fig. 2. Thermoanalytical curves for thorium tetrapropyl ammonium nitrate (Th-TPAN) in dynamic argon ( $40 \text{ ml min}^{-1}$ ). Initial sample mass, 29.0 mg; temperature in Kelvin.

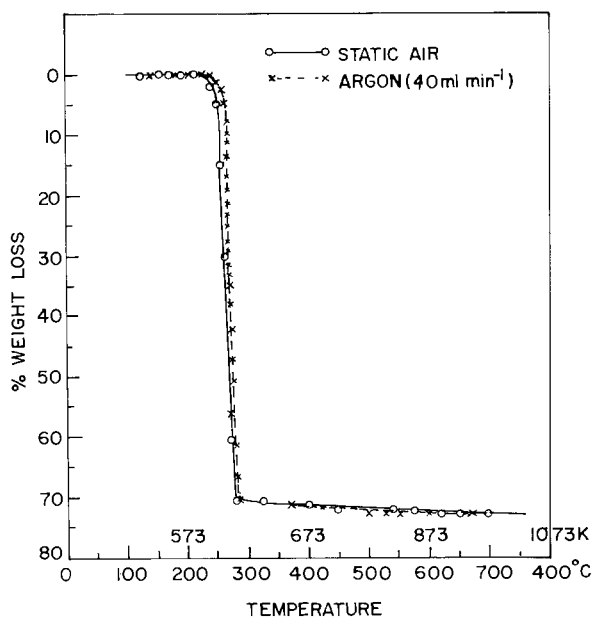
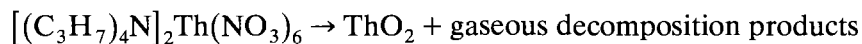


Fig. 3. Thermogravimetric curves for thorium tetrapropyl ammonium nitrate (Th-TPAN) in static air and dynamic argon atmospheres. Initial sample mass, 29.0 mg.

the second step on the TG curve is due to the slow evolution of condensable volatiles from the sample holder.

The presence of condensable vapours in the decomposition products indicates that no significant burning of organic matter takes place in the furnace during the decomposition in argon atmosphere. This is further evidenced by the nearly identical nature of the plots for percentage mass loss versus temperature (Fig. 3) observed in static air and dynamic argon. Mass loss due to carbon burn up in argon, if it takes place at all due to the presence of oxygen impurity, should have been at a significantly lower rate than in air. The present set of observations clearly indicates absence of carbonaceous residue in the decomposition products of Th-TPAN. Hence, the exothermicity observed in the DTA curve may be characteristic of the decomposition itself rather than the burning of carbonaceous matter. Thus the mass loss observed during the decomposition of Th-TPAN in argon is essentially due to the process



The decomposition is essentially a single-step process as apparent from the TG and EGA curves recorded with a sample of mass 14.5 mg (Fig. 4). The EGA peak for the gaseous species with  $m/z$  30 is a singlet in Fig. 4 unlike in Fig. 1. This observation substantiates the earlier conclusion that the multippeak nature of EGA curves for  $m/z$  30, 42 and 44 is due to the slow evolution of condensable volatiles from the sample holder. The

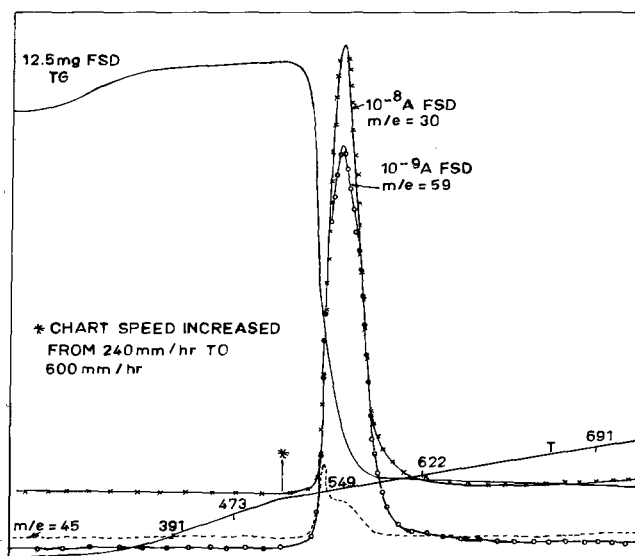


Fig. 4. Thermoanalytical curves for thorium tetrapropyl ammonium nitrate (Th-TPAN). Initial sample mass, 14.5 mg; temperature in Kelvin.

TABLE 2

Standard deviation of  $\ln g(\alpha) - \ln p(x)$  for evolved gas analysis curve for  $m/z$  30 (nitric oxide/ethane)

$g(\alpha)$	$E$ (kcal mol <sup>-1</sup> )			
	56.57	57.57	58.57	59.57
$\alpha^{1/4}$	0.7129	0.7275	0.7422	0.7569
$\alpha^{1/3}$	0.6635	0.6782	0.6928	0.7075
$\alpha^{1/2}$	0.5663	0.5868	0.5954	0.6099
$\alpha$	0.3017	0.3144	0.3273	0.3403
$\alpha^{3/2}$	0.2352	0.2330	0.2317	0.2314
$\alpha^2$	0.4621	0.4513	0.4407	0.4303
$1 - (1 - \alpha)^{1/3}$	0.1650	0.1732	0.1823	0.1921
$1 - (1 - \alpha)^{1/2}$	0.1978	0.2081	0.2189	0.2301
$[-\ln(1 - \alpha)]^{1/4}$	0.6442	0.6589	0.6735	0.6882
$[-\ln(1 - \alpha)]^{1/3}$	0.5719	0.5865	0.6012	0.6158
$[-\ln(1 - \alpha)]^{1/2}$	0.4289	0.4434	0.4579	0.4725
$[-\ln(1 - \alpha)]^{2/3}$	0.2905	0.3046	0.3187	0.3329
$-\ln(1 - \alpha)$	0.1272	0.1264 <sup>a</sup>	0.1272	0.1298
$\alpha + (1 - \alpha) \ln(1 - \alpha)$	0.5796	0.5671	0.5547	0.5424
$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}$	0.6311	0.6182	0.6053	0.5925
$[1 - (1 - \alpha)^{1/3}]^2$	0.7412	0.7276	0.7141	0.7006
$[(1 + \alpha)^{1/3} - 1]^2$	0.3622	0.3544	0.3464	0.3389
$1 - (1 - \alpha)^2$	0.4699	0.4838	0.4977	0.5117
$1 - (1 - \alpha)^3$	0.5820	0.5962	0.6105	0.6248
$1 - (1 - \alpha)^4$	0.6567	0.6712	0.6856	0.7001

<sup>a</sup> Minimum value of standard deviation.

evolution of volatiles takes place more easily and quickly when the sample layer thickness is halved and hence singlet peaks are observed in EGA curves recorded with 14.5 mg of sample. However, the peak due to evolution of gas with  $m/z$  45 shows a doublet even with a sample mass of 14.5 mg. It is possible that two different species contribute to the ion current observed for this mass to charge ratio. If these two gases are

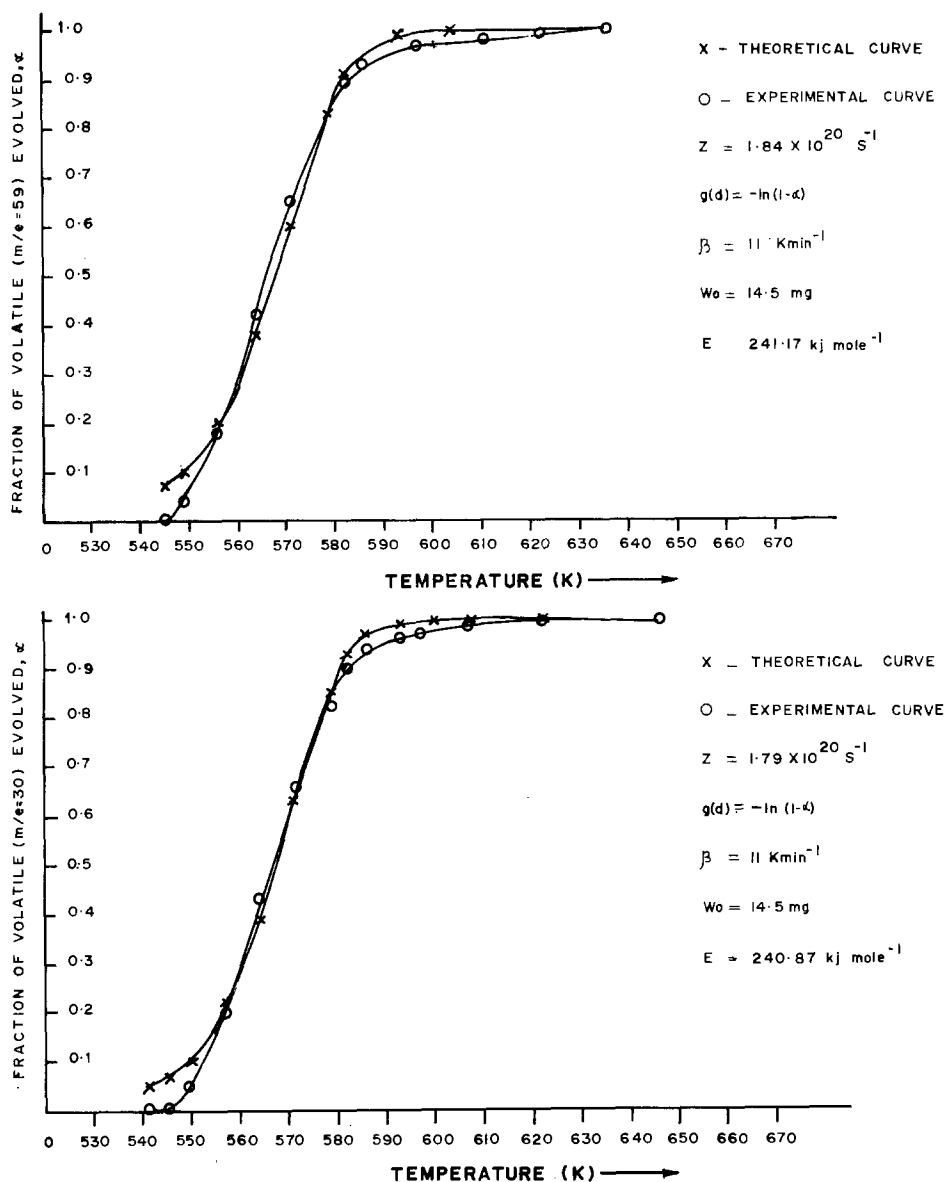


Fig. 5. Comparison between theoretical and experimental curves for the thermal decomposition of thorium tetrapropyl ammonium nitrate (Th-TPAN).

TABLE 3

Standard deviation of  $\ln g(\alpha) - \ln p(x)$  for evolved gas analysis curve for  $m/z$  59 (propylamine)

$g(\alpha)$	$E$ (kcal mol <sup>-1</sup> )			
	57.14	57.64	58.14	59.14
$\alpha^{1/4}$	0.8022	0.8103	0.8184	0.8345
$\alpha^{1/3}$	0.7505	0.7586	0.7666	0.7828
$\alpha^{1/2}$	0.6487	0.6568	0.6648	0.6808
$\alpha$	0.3735	0.3806	0.3877	0.4020
$\alpha^{3/2}$	0.2772	0.2775	0.2781	0.2799
$\alpha^2$	0.4826	0.4774	0.4723	0.4624
$1 - (1 - \alpha)^{1/3}$	0.2020	0.2069	0.2119	0.2226
$1 - (1 - \alpha)^{1/2}$	0.2456	0.2515	0.2575	0.2698
$[-\ln(1 - \alpha)]^{1/4}$	0.7184	0.7265	0.7346	0.7507
$[-\ln(1 - \alpha)]^{1/3}$	0.6386	0.6467	0.6547	0.6709
$[-\ln(1 - \alpha)]^{1/2}$	0.4808	0.4888	0.4968	0.5128
$[-\ln(1 - \alpha)]^{2/3}$	0.3283	0.3360	0.3438	0.3593
$-\ln(1 - \alpha)$	0.1440	0.1437 <sup>a</sup>	0.1439	0.1456
$\alpha + (1 - \alpha) \ln(1 - \alpha)$	0.6044	0.5979	0.5914	0.5786
$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}$	0.6625	0.6556	0.6488	0.6352
$[1 - (1 - \alpha)^{1/3}]^2$	0.7916	0.7842	0.7769	0.7622
$[(1 + \alpha)^{1/3} - 1]^2$	0.3908	0.3874	0.3840	0.3779
$1 - (1 - \alpha)^2$	0.5611	0.5688	0.5765	0.5918
$1 - (1 - \alpha)^3$	0.6761	0.6839	0.6918	0.7075
$1 - (1 - \alpha)^4$	0.7496	0.7576	0.7655	0.7815

<sup>a</sup> Minimum value of standard deviation.

evolved at different rates one would expect a doublet. Any interaction of the evolved volatiles with other gaseous species also may cause a decrease in the rates of their evolution. The rates of gas evolution may again increase as the decomposition rate increases, thus leading to the observation of a doublet or multiplet in the gas evolution pattern.

Further confirmation of single-step decomposition can be obtained from the analysis of individual EGA peaks for kinetic parameters. The method of Zsako modified previously [6,7] has been used in combination with eqn. (2) to determine kinetic parameters from the EGA curves for volatiles corresponding to  $m/z$  30 and 59. The results are presented in Fig. 5 and Tables 2 and 3 where the functions  $g(\alpha)$  and  $p(x)$  have the same significance as discussed elsewhere [6]. These results confirm that the evolution of both the volatiles is governed by the same rate equation. Mampel's random nucleation and growth law with one nucleus on each particle is applicable to both cases (Tables 2 and 3) and the values of activation energy and pre-exponential factor derived from the two EGA curves are in good agreement. The theoretical curves generated with the selected kinetic parameters are in good agreement with the experimental



curves over the range  $0.1 < \alpha < 0.9$ . These results clearly indicate that both gaseous species are evolved during the same rate-determining step. Hence it may be concluded that the nitrate and tetrapropyl ammonium moieties in the complex undergo simultaneous dissociation giving rise to nitric oxide ( $m/z$  30) and propylamine ( $m/z$  59).

## CONCLUSIONS

TG-DTA-EGA studies have shown that Th-TPAN decomposes in a single step. Although TG curves show the mass loss to take place in two steps, EGA curves recorded under different conditions of sample mass indicate the second step to be due to slow desorption of condensable volatiles from the sample holder. A doublet observed for the evolution peak for the gas corresponding to  $m/z$  45 may be due to the interaction of this species with other gaseous products since the kinetic parameters calculated from the evolution peaks for  $m/z$  30 and 59 indicate the dissociation of both nitrate and tetrapropyl ammonium moieties of the complex to be taking place in the same rate-determining step.

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