

Thermal decomposition of nitrogenous salts under vacuum

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Abstract

Thermal decomposition of a few nitrogenous salts, viz. ammonium sulphate, ammonium nitrate and barium nitrate in vacuum and ammonium chloride in the presence of UO_3 was studied over a temperature range 373–1273 K with an aim to understand their thermal decomposition behaviour. The relative amounts of various gaseous oxides of nitrogen formed were compared. Attempts were also made to explain the amounts of different gaseous oxides formed on the basis of the nature of the nitrogenous salts. (Int J Mass Spectrom 214 (2002) 375–381) © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thermal decomposition of nitrates leads to the formation of several gaseous oxides of nitrogen. The existence of seven oxides of nitrogen is reported in the literature [1,2]. Of these, nitrous oxide (N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2) are relatively stable and are predominantly formed. From a thermodynamic point of view, formation of these oxides from the constituting elements follows the order $\text{NO}_2 > \text{N}_2\text{O} > \text{NO}$ up to 800 K, and above this temperature the order changes to $\text{NO} > \text{NO}_2 > \text{N}_2\text{O}$ [3]. However, the extent of their formation from the decomposition of different nitrogenous salts could vary. Most of the previous studies on the decomposition behaviour of nitrates have been carried out either in air or argon atmosphere [4]. In the presence of an extraneous gas, the decomposition behaviour will be different. With this in view, Lippiatt et al. [5] have studied

the decomposition of nitrates by Knudsen effusion cell time-of-flight mass spectrometry. They observed that sodium, barium and strontium nitrates upon thermal decomposition give rise to NO, N_2 and O_2 and that the formation of NO increases up to about 873 K and then decreases. Szabo et al. [6] have investigated thermal decomposition of ammonium nitrate with and without the addition of other oxides, and observed that above 473 K and in a static atmosphere, pure ammonium nitrate gives essentially N_2O and considerable amounts of N_2 . These studies were carried out with an aim of investigating the conditions for quantitative evolution of N_2O . No studies were carried out on the evolution of other oxides of nitrogen. Formation of other major oxides of nitrogen have not been mentioned [5,6]. Most of the studies on high temperature inorganic mass spectrometry have been carried out on the inorganic vapours and these studies are limited to the gaseous metallic ion species [7,8]. Hoinkis and Matiske [9] have made detailed studies on thermal decomposition of silver and caesium nitrates by

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Knudsen cell mass spectrometry. However, their studies are mostly confined to the metallic ions and only a brief mentioning about the formation of NO^+ in the decomposition of AgNO_3 was made. The present paper deals with our experimental observation on the decomposition patterns of a few nitrogenous salts under vacuum and the relative amounts of various oxides of nitrogen formed.

2. Experimental

2.1. Instrument

The ultra high vacuum system used for the present studies has been described in detail elsewhere [10]. The system essentially consists of two parts, viz. (i) the sample decomposition and extraction part, and (ii) the gas analysis part, i.e., a quadrupole mass spectrometer. The sample decomposition component consists of a quartz reaction tube, a resistance furnace with a controller to heat the sample contained in the quartz reaction tube to the required temperature within ± 3 K and a McLeod gauge to monitor the pressure. The entire system is evacuated employing a mercury diffusion pump and a rotary backing pump. For the determination of the gas composition, a quadrupole mass spectrometer (Anglo Scientific Instruments, Spectramass DXM, Model Dataquad 200) has been employed. It consists of an 8 cm quadrupole mass filter, a constant energy electron impact ion source (70 eV produced by thorium-coated iridium filament), and a Faraday cup detector. The quadrupole mass analyser is evacuated with a turbomolecular pump and a rotary pump. The vacuum at the analyser is better than 10^{-7} mbar. The ionisation of the gases fed to the mass analyser is achieved by electron impact. The quadrupole mass analyser has unit mass resolution at 10% valley through out the mass range. The instrument has been provided with software by which the spectrum can be scanned in

(a) Bar graph mode: the spectrum can be obtained over a mass range of 10, 20, 50 or 100 with a provision to select the first mass. However, the spectrum is obtained at a single gain.

(b) Peak select mode: the peak intensities of various ions (up to 16 channels) can be obtained in this mode. The gain for each channel, i.e., each m/z , varies from E-05 to E-11 automatically, depending on the intensity of the ion being measured in that channel.

The selection of the above modes, the selection of the channels of particular m/z and the gains are carried out through a microprocessor control unit. The control unit is coupled to a personal computer for recording the spectra, both in bar graph and peak select mode. An off-line program retrieves the data and calculate the required parameters from the basic data. The salts used in the present studies are of Analar Reagent grade.

2.2. Method

About 2–50 mg of the salt was loaded into the quartz reaction tube and evacuated to better than 10^{-5} mbar. It was then degassed at room temperature for several hours under dynamic vacuum conditions. The reaction tube was then isolated under vacuum and heated at required temperature for 1–2 h. The non-condensable gases were then extracted and the gas composition was determined by feeding the gas to the quadrupole mass spectrometer, through a micro leak valve in such a way that the total pressure in the mass analyser is in 10^{-6} mbar range. A spectrum in bar graph mode

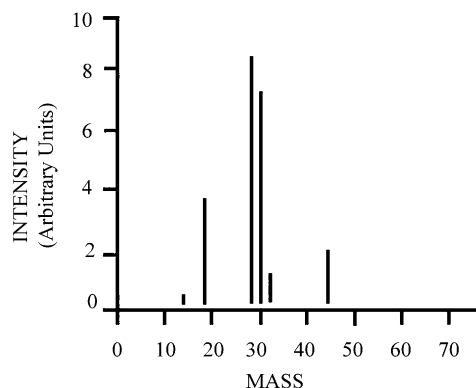


Fig. 1. Typical mass spectra of oxides of nitrogen (sample: $\text{Ba}(\text{NO}_3)_2$) gain = $1.0\text{E}-09$.

Table 1
Typical mass spectrum in peak select mode (decomposition of ammonium sulphate)

Channel	On/off	Mass	Torr
1	On	2	1.1E–08A
2	On	12	0.0E–11A
3	On	14	0.8E–09A
4	On	15	3.6E–10A
5	On	16	0.7E–09A
6	On	17	0.7E–08A
7	On	18	2.9E–08A
8	On	28	1.6E–07A
9	On	30	5.7E–07A
10	On	32	2.4E–07A
11	On	44	3.4E–07A
12	On	46	4.0E–10A
13	On	48	5.6E–10A
14	On	64	1.4E–08A
15	On	66	2.5E–11A
16	On	0	0.6E–06A

is first scanned to optimise the admittance of gases. Then, several spectra are recorded in peak select mode to get ionic intensities at various peaks. A typical mass spectrum is shown in Fig. 1 in a bar graph mode, and typical data obtained in the peak select mode are given in Table 1.

The bar graph spectrum shown in Fig. 1 has been for the decomposition of barium nitrate obtained at 973 K. Since the quantity of NO₂ formed is small, and the spectrum is taken at a gain E–09, a signal at m/z 46 could not be seen. However, in the peak select mode (Table 1: data for the decomposition of ammonium sulphate), the peak intensities of all peaks could be measured since the gain for each m/z was selected automatically.

3. Results and discussion

The salts are decomposed under static vacuum conditions and the gaseous products are directly fed to the quadrupole mass spectrometer for finding out the composition. Hence the composition of the gas can be taken as the one obtained at the temperature of decomposition. During our studies on thermal decomposition of nitrogenous salts containing oxygen,

oxides of nitrogen, viz. NO, N₂O and NO₂ were observed. However, in the studies with ammonium chloride, wherein no oxygen is present as a constituent in the compound, no such products were detected necessitating addition of ‘in situ’ oxygen generator like UO₃, KClO₃ or MnO₂ [11], which liberates oxygen on heating. KClO₃, being highly explosive at high temperature, has not been considered. We chose nuclear grade UO₃, which liberates oxygen easily when heated. The background peaks during the heating of UO₃ showed negligible peak intensities at m/z values corresponding to oxides of nitrogen. A salt to UO₃ ratio of about 1:10 was maintained.

It is a well-established fact that poly-atomic gases undergo fragmentation in addition to ionisation when bombarded by electrons with energy of ~70 eV. The fragmentation pattern is characteristic of the gas. Oxides of nitrogen are formed from the natural nitrogen and oxygen whose isotopic composition and abundance are ¹⁴N (99.64%), ¹⁵N (0.36%), ¹⁶O (99.756%), ¹⁷O (0.039%) and ¹⁸O (0.205%). Since ¹⁴N and ¹⁶O are more than 99.6% the oxides formed by these two isotopes only have been accounted for.

3.1. Calculation of partial pressures of NO, N₂O and NO₂ from measured intensities

The measured ion currents (intensities) in ampere for ions formed by electron impact from a neutral molecule is to be corrected for fragmentation [8]. All the intensities at different ion peaks are first corrected for the background. The corrected ion intensities at the mass numbers m/z : 30, 44 and 46 corresponding to the parent ions of NO, N₂O and NO₂ do not give directly the true intensities of these oxides because of fragmentation. With a view to calculating the true intensities of these oxides, the fragmentation pattern and fragment ion intensities are taken from the literature available in the fragmentation library supplied along with the equipment and the same are used [12]. Table 2 gives the fragment ion intensities for these three oxides.

It can be seen from Table 2 that for N₂O and NO₂, the parent peaks appearing at m/z 44 and 46

Table 2
Fragmentation coefficients [12] and ionisation cross sections [13] for oxides of nitrogen

Mass number of gaseous oxide	Mass of fragment ion and its intensity							Ionisation cross sections (σ , Å^2) at 70 eV
	46	44	30	28	16	15	14	
30 (NO)	–	–	90.82 ^a	–	0.92	1.83	6.42	2.807
44 (N ₂ O)	–	62.26 ^a	19.5	6.92	3.14	8.18	–	3.710
46 (NO ₂)	22.16 ^a	–	59.28	13.17	–	5.39	–	3.532

^a Denotes the parent ion intensity.

do not have any contributions from the fragment ions produced during the mass spectrometric analysis. The interference at m/z 44 due to CO₂ was found to be absent as the mass spectrum scanned did not indicate any peak at m/z 12 which is a characteristic peak in the fragmentation of CO₂. Carbon present in all these salts was also independently determined by combustion—gas chromatographic technique employing commercial determinator, and found to be less than hundred ppmw. By measuring the intensities at m/z 44 and 46 and taking fragment intensities at these mass numbers from Table 2, the expected pre-fragmentation intensities for m/z 44 and 46 were calculated. From these, the contributions of these two oxides at m/z 30 due to their fragmentation were calculated. The difference in the total intensity measured at m/z 30 and the value obtained due to the contribution of fragmentation of N₂O and NO₂, gives the net intensity at m/z 30 due to NO. This intensity was also converted into the expected pre-fragmentation intensity for NO. These computed parent peak intensities need to be further corrected for the ionisation cross sections [7] of these gases. The ionisation cross sections σ (Å^2) at 70 eV are taken from a data base [13] and are included in Table 2. The partial pressures of gases a and b can be expressed [7] as $p_a = kI_aT/\sigma_a$ and $p_b = kI_bT/\sigma_b$ where p_a and p_b are the partial pressures, I_a and I_b are the corrected peak intensities, σ_a and σ_b are the ionisation cross sections of gases a and b, respectively, T is temperature and k is pressure calibration factor. Ratio of partial pressures of gases a and b becomes $p_a/p_b = I_a\sigma_b/I_b\sigma_a$ which is independent of k and T . In the present work, all partial pressures are normalised with respect to one gas,

N₂O. These corrected pressures were used in comparing the ratios of the three oxides of nitrogen formed. At least five records constituting three spectra each in peak select mode were taken and the mean peak intensities were used in the above calculations. The comparison of the pressure ratios of the three oxides for different salts at various temperatures is given in Table 3. The following observations regarding the relative partial pressures of oxides of nitrogen could be made from the results:

(a) Nitrates



(b) (NH₄)₂SO₄



(c) NH₄Cl + UO₃



Figs. 2 and 3 show the plots of relative partial pressure ratios of NO:N₂O and NO₂:N₂O against the temperature. From Table 3 and Fig. 2, it can be observed that nitrates decompose to give mainly NO above 773 K. It can also be seen that the relative amounts of NO formed increase up to around 1073 K and then decreases, similar to the observations made by Lippiatt et al. [5] excepting that in the present work the reduction in intensity was observed at relatively higher temperature. In the thermal decomposition of

Table 3
The partial pressure ratios for N₂O:NO₂:NO

Temperature (K)	NH ₄ NO ₃	Ba(NO ₃) ₂	(NH ₄) ₂ SO ₄	NH ₄ Cl + UO ₃
373	–	–	–	1:0.008:0
473	1:0.006:0.45	1:0.006:0.44	1:0.026:1.85	1:0.009:0
573	–	–	–	1:0.017:0
673	1:0.011:0.85	–	1:0.016:0.48	1:0.011:0
773	1:0.011:3.04	1:0.012:3.17	–	1:0.014:0
873	–	–	1:0.013:0	–
923	–	–	1:0.013:0	1:0.014:0
973	1:0.011:5.75	1:0.011:5.82	–	–
1073	–	–	–	1:0.014:0
1123	1:0.011:4.76	–	–	–
1273	1:0.011:4.49 1:0.01:0 (in presence of UO ₃)	1:0.011:4.36 (0.00322 g) 1:0.011:4.36 (0.00216 g) 1:0.0008:0 (0.00242 g in air)	1:0.013:0	1:0.015:0
N:S:O	1:0:1.5 (in presence of UO ₃) it is 1:very high	1:0:3 (in presence of UO ₃) it is 1:very high	1:0.5:2	1:0:very high

Note: The ratios are evaluated from the mean of at least five records constituting of three spectra each in peak select mode.

AgNO₃, Hoinkis and Matiske [9] observed that NO formation became significant at 473 K, passes through a maxima at 693 K and then decreases. The decomposition patterns for barium nitrate with different amounts of the salts at the same temperature gave same ratios indicating that the comparison of ratios is independent of the amount of salt taken.

In presence of air or oxygen, NO completely decomposes to other oxides. At higher temperatures, depending upon the availability of oxygen/air, NO decomposes as follows:

(i) In the absence of oxygen

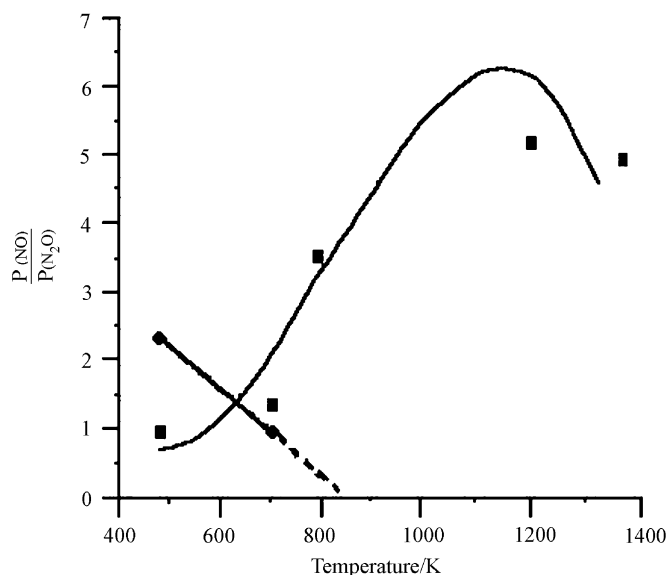


Fig. 2. Partial pressure ratios of NO and N₂O vs. temperature: (■) NH₄NO₃; (◆) (NH₄)₂SO₄.

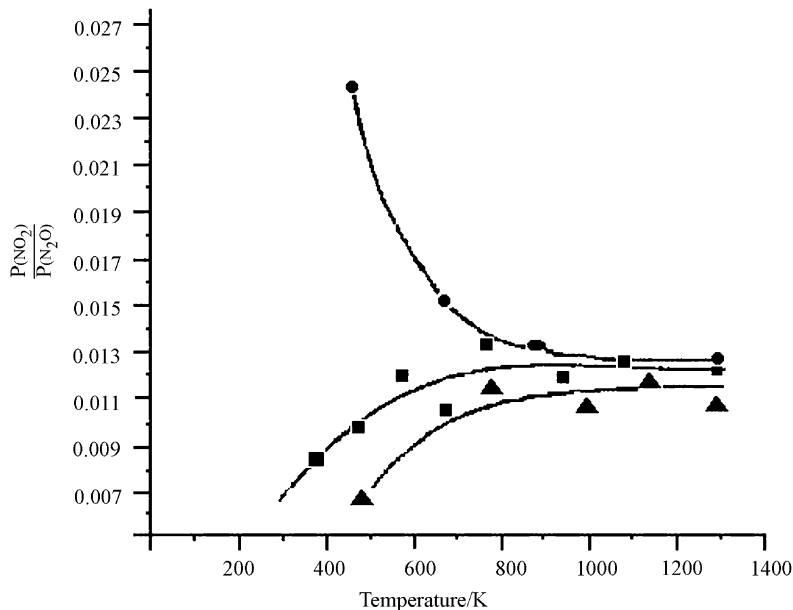


Fig. 3. Partial pressure ratios of NO_2 and N_2O vs. temperature: (●) $(\text{NH}_4)_2\text{SO}_4$; (■) $\text{NH}_4\text{Cl} + \text{UO}_3$; (▲) NH_4NO_3 .

(ii) In the presence of oxygen/air



In the case of ammonium sulphate, NO decreases with temperature and above 673 K it is completely decomposed to other oxides. In $\text{NH}_4\text{Cl} + \text{UO}_3$ mixture even at 373 K, NO is not observed due to the presence of large excess of oxygen. Similarly, the nitrates also do not show the presence of NO when the decomposition is carried out in presence of UO_3 or air. The reaction (ii) of oxygen with NO may be a kinetically fast reaction and hence even traces of NO are not observed.

The relative amounts of oxygen available for the formation of the oxides (both nitrogen and sulphur) is in the order $(\text{NH}_4)_2\text{SO}_4 < \text{NH}_4\text{NO}_3 < \text{Ba}(\text{NO}_3)_2 \ll \text{NH}_4\text{Cl} + \text{UO}_3$ and the amount of NO formed is in the reverse order. This could be due to the favourable formation of higher oxides.

The patterns of formation of NO_2 during the decomposition of NH_4NO_3 and $\text{NH}_4\text{Cl} + \text{UO}_3$ are similar and are shown in Fig. 3. Identical observation was made in the case of $\text{Ba}(\text{NO}_3)_2$ also. With increase in temperature the formation of NO_2 increases up to

773 K and then remains constant. However, in the case of $(\text{NH}_4)_2\text{SO}_4$, the formation of NO_2 decreases up to 773 K and above this temperature, it also reaches the same value as in the case of other gases. Even the formation of NO decreases above 673 K as can be seen from Table 3. This type of different behaviour could be due to the competition of sulphur and nitrogen for the available oxygen. Oxygen reacts with the available sulphur to form SO_2 . This can be seen from the mass spectra which shows peak at $m/z = 64$ corresponding to SO_2 (Table 1). The intensity of the peak at $m/z = 64$ increases with temperature as reported in our earlier paper [14] confirming the competition of S and N for the available oxygen. NO_2 formed further decomposes to N_2 , O_2 , N_2O and NO [3,15] at higher temperatures.

Above 773 K, the behaviour is similar with other salts. Higher amounts of N_2O formation at higher temperatures may be due to the decomposition of NO_2 to NO, N_2O , N_2 and O_2 . The decomposition product NO further decomposes to NO_2 and N_2O . This process proceeds till an equilibrium is established between NO_2 , N_2O and N_2 . Rodriguez and Hrbek [16],

in their studies on the decomposition studies on NO_2 , observed that at higher temperatures, above 500 K, NO and N_2 are formed. In our studies also we have observed peak at m/z 28, corresponding to N_2 , which is in line with the above published data. Near constancy in the intensity ratios of these oxides above 773 K, may possibly be due to the equilibrium among NO, N_2O and NO_2 .

4. Conclusions

- (i) Nitrates, on decomposition under vacuum give rise to mainly NO.
- (ii) At higher temperatures, above 1073 K, NO formation decreases.
- (iii) NO completely decomposes to other oxides of nitrogen when decomposition of nitrate salts is carried out in presence of excess of oxygen.
- (iv) All nitrogenous salts (even in the presence of in situ or external oxygen) on decomposition maintain same NO_2 and N_2O ratio above 773 K.
- (v) Nitrate salts on decomposition above 1273 K gives mainly NO and N_2O .

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