SIMULTANEOUS DYNAMIC THERMOGRAVIMETRY AND MASS SPECTROMETRY OF THE EVAPORATION OF ALKALI METAL NITRATES AND NITRITES

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Six alkali metal nitrates and nitrites were evaporated in vacuum at a constant heating rate in a combined mass spectrometric and thermogravimetric apparatus. Time resolved profiles of decomposition gases and kinetics were obtained for $LiNO_3$, $NaNO_3$, KNO_3, Na/KNO_3, $NaNO_2$ and KNO_2. Activation energies for the evaporation of these salts were calculated and compared to previous results of isothermal experiments. In the temperature range 650–850 K, the decomposing nitrates released NO, N_2 and O_2 while the nitrites released only NO and N_2.

Recent interest in the thermal stabilities of the alkali metal nitrates and nitrites has arisen largely from potential uses of these salts as electrolytes in high temperature batteries [1], as latent [2] and sensible [3] heat storage media, and as heat transfer fluids in solar thermal-electric power systems [4]. In these applications the high temperature stability is a focal point in selecting a salt. Although there are numerous reports in the literature [5–10] concerning the thermal stability of the nitrates and nitrites of the alkali metals, they are contradictory in their conclusions regarding the complex mechanism of decomposition of these materials [10, 11]. All agree, however, that nitrates decompose to nitrites:

$$MNO_3 \rightarrow MNO_2 + 1/2 \, O_2 \tag{1}$$

where *M* refers to Na, K or Li. The nitrites, in turn, can decompose as follows [5–9]

$$2 \, MNO_2 \rightarrow M_2O_2 + 2 \, NO, \tag{2}$$

$$2 \, MNO_2 \rightarrow 2 \, MO_2 + N_2 \tag{3}$$
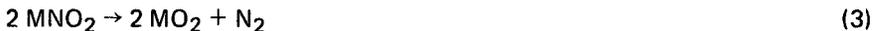
Although N_2 and O_2 are thermodynamically more stable [5] than N_xO_y molecules above 500 K, N_xO_y molecules have been identified in the decomposition products of nitrates and nitrites [5–7, 12].

In addition to decomposition, the nitrates and nitrites of sodium, potassium and lithium may vaporize congruently [13, 14]. Monomers and dimers of the nitrates and nitrites have been observed beginning about 50 K above their respective melting

points [14]. In the temperature range 650—850 K both decomposition and vaporization of the nitrates and nitrites occur.

In this work the relative thermal stabilities of molten $NaNO_3$, KNO_3, $LiNO_3$, $NaNO_2$, KNO_2 and equimolar sodium-potassium nitrate (Na/KNO_3) were investigated using simultaneous dynamic thermogravimetry and mass spectrometry. The combined rates of decomposition and vaporization in vacuum were measured and the decomposition gases were identified.

Experimental

Dynamic (constant heating rate, CHR) experiments were performed with $LiNO_3$, $NaNO_3$, KNO_3, $NaNO_2$, KNO_2 and Na/KNO_3 in a combined thermogravimetry/mass spectrometry (TG/MS) apparatus. The salts were heated in vacuum from 330 K to 1000 K at 25 K min^{-1}. A microprocessor-based data acquisition system was used to collect sample weight and temperature data at 30-second intervals. The data were subsequently analyzed and plotted by a separate computer program. The mass range of the evolved gases was swept every 30 seconds.

The salt samples were precipitated onto a gold coupon (1.49 cm^2 surface area) from saturated aqueous solutions. Samples were dried in air and then in vacuum at 330 K for 3 hr. Ultrapure $NaNO_3$, KNO_3 and Na/KNO_3 (Spex Industries), and reagent grade $NaNO_2$, KNO_2 and $LiNO_3$ were used. The sample sizes ranged from 4.3 to 11.8 mg. No dependence on sample weight was observed.

The TG/MS system was a combination of a Cahn R–H microbalance and an Extranuclear mass spectrometer. The microbalance had a sensitivity of 10^{-5} g. The mass spectrometer had an axial ionizer and 100 eV ionizing energy. The coupons were suspended vertically in a furnace 2 mm above a temperature recording thermocouple. When the samples were melted, the salts covered the gold coupons uniformly and completely. The mass spectrometer was connected to the furnace by a 6 mm diameter tube at the level of the sample. The circuitous path between the furnace and the mass spectrometer excluded the possibility of detecting high temperature condensible species such as $NaNO_3$ (g). Therefore, only gases such as N_2, O_2 and N_xO_y species could be recorded.

Results and discussion

The rate of weight loss over each 30-second interval was calculated and assigned to the average temperature of that time interval. The minimum detectable rate was 0.008 mg cm^{-2} min^{-1} and the highest rate measured was about 1 mg cm^{-2} min^{-1} for all salts investigated. These specific rates are plotted vs $1/T$ for $LiNO_3$, $NaNO_3$, KNO_3, Na/KNO_3, $NaNO_2$ and KNO_2 in Figs 1 through 6, respectively. All samples completely evaporated by 900 K. In each figure, two runs are plotted and the re-
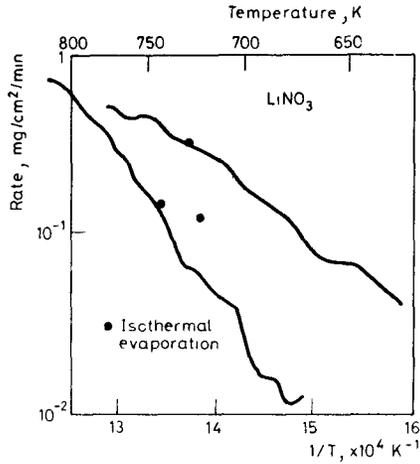
Fig. 1 The temperature dependence of the evaporation rate of $LiNO_3$
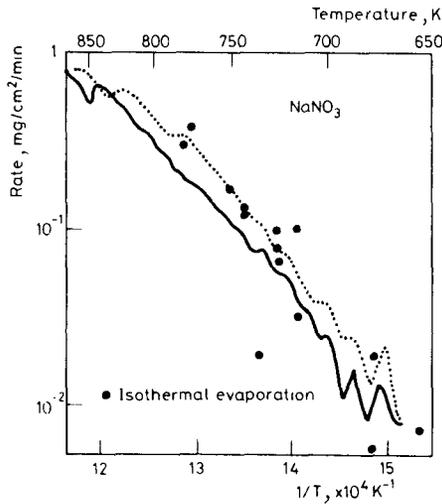
Fig. 2 The temperature dependence of the evaporation rate of $NaNO_3$

producibility of the results is good for the data of $NaNO_3$, KNO_3 and Na/KNO_3, and reasonable for $NaNO_2$ and KNO_2. The data for $LiNO_3$, however, showed the largest difference between runs. Also plotted in Figs 1—5 are individual data points obtained under isothermal evaporation conditions in a previous study [15, 16]. No similar data are available for KNO_2, however. The isothermal and dynamic rates are in reasonable

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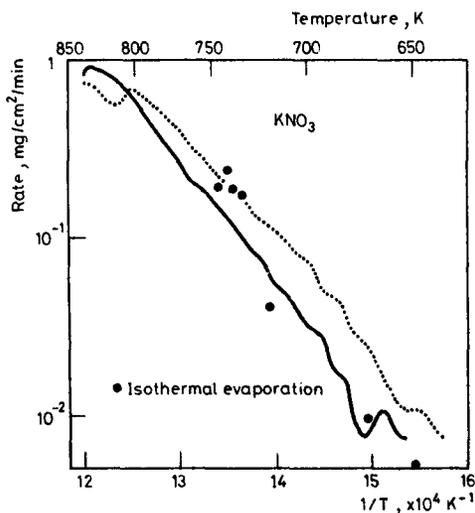
Fig. 3 The temperature dependence of the evaporation rate of KNO_3
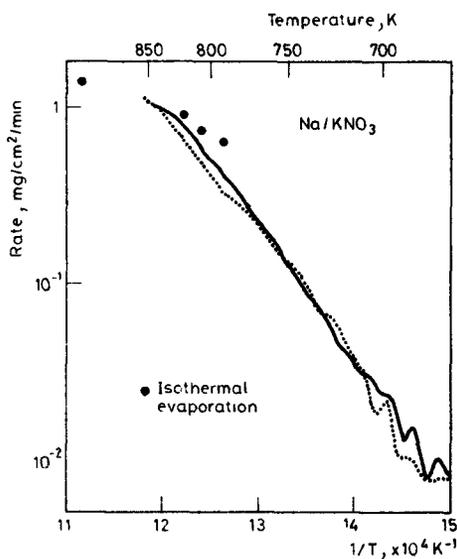
Fig. 4 The temperature dependence of the evaporation rate of Na/KNO_3

agreement, a similar observation was made in a previous study of decomposing sulfates [17].

The evaporation rates were highest on the average for $LiNO_3$. The evaporation rates for the other salts were very similar: approximately 0.008 mg cm^{-2} min^{-1} at 650 K and 0.5 mg cm^{-2} min^{-1} at 800 K. Recent isothermal TG studies in vacuum
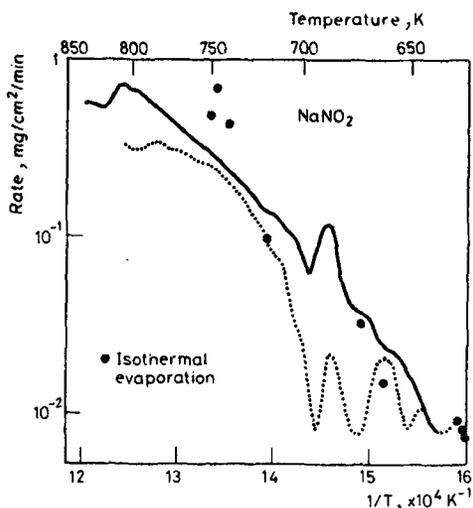
Fig. 5 The temperature dependence of the evaporation of $NaNO_2$
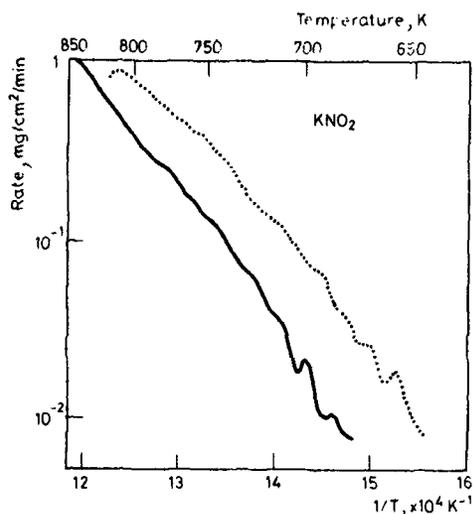
Fig. 6 The temperature dependence of the evaporation of KNO_2

[15, 16] had shown that the evaporation rates decreased in this order: $LiNO_3 \cong$ $\cong NaNO_2 > KNO_3 > NaNO_3$. The same trend in decomposition was observed in differential scanning calorimetry (DSC) analysis [19] (except that $LiNO_3$ was not tested). The differences in stability between KNO_3 and $NaNO_3$ was slight, and statistically insignificant. Sweeny [18] using DTA and TG in air, concluded that $NaNO_3$ was

Table 1 Apparent activation energies for evaporation

| Material | E_a, kJ mol^{-1} | |
	Dynamic	Isothermal[a]
LiNO$_3$	122	—
NaNO$_3$	137	153
KNO$_3$	143	146
Na/KNO$_3$	151	127
NaNO$_2$	122	134
KNO$_2$	139	—

[a] The isothermal E_a are reported in References 15 and 16; however, no data are available for the E_a of KNO$_2$ or LiNO$_3$.

less stable than KNO$_3$, although the reported range of decomposition temperatures for both nitrates overlap.

The thermal stabilities of the salts were compared by calculating the apparent activation energies of the dynamic weight loss tests. Because previous studies [15, 16] had shown that the rate of evaporation rapidly decreased as decomposition proceeded above 740 K (that is, the rates decreased with time during isothermal experiments), the high temperature ends of the curves of Figs 1—6 were not included in the activation energy analyses. The activation energies, E_a, are listed in Table 1 and compared to the corresponding values obtained in other isothermal studies [15, 16]. The differences between the apparent activation energies, as determined from isothermal vs. dynamic tests, ranged from 2 to 19 percent. However, the reported E_a values are precise to 20.5 kJmol^{-1} for a 90 percent confidence level, and thus the differences in the activation energies are statistically insignificant.

Nitrate decomposition resulted in the evolution of NO, N$_2$ and O$_2$ gases. Nitrite decomposition resulted in the release of NO and N$_2$ only. In order to compare the results we defined T_e as the temperature at which the rate of evaporation is 0.1 mg cm^{-2} min^{-1}, and T_a as the temperature at which the decomposition gases N$_2$ and NO were detected in the mass spectrometer. The latter temperature corresponds to a weight loss rate of about three orders of magnitude lower than that used to establish T_e. Table 2 lists the average values for T_e and T_a and the melting points for the materials investigated. The values of T_e range from 674 to 746 K and the appearance temperature, T_a, ranged from 534 to 736 K for all experiments. The average value of T_e for Na/KNO$_3$ was the highest (745 K) while those of NaNO$_2$ and LiNO$_3$ were the lowest, 703 and 704 K, respectively. In all cases, decomposition gases were detected at temperatures as much as 177 K lower than the corresponding T_e. Generally, T_a for NO (g) was less than the related value for N$_2$ (g), by as much as 72 K in the case of LiNO$_3$. The evolution of N$_2$ and O$_2$ may be independent such as by reactions (2) and (3). The appearance temperatures of the decomposition of nitrites

Table 2 Values of T_e and T_a for the alkali metal nitrates and nitrites

Material	T_{mp}, K	T_e, K	$T_{a_{N_2}}$, K	$T_{a_{NO}}$, K
$LiNO_3$	537	704	650	598
$NaNO_3$	580	738	714	688
KNO_3	607	723	710	706
Na/KNO_3	498	745	706	692
$NaNO_2$	544	703	538	539
KNO_2	713	724	616	612

T_e temperature at which evaporation rate is 0.1 mg cm^{-2} min^{-1};
T_a temperature at which the indicated gaseous species was first observed mass spectrometrically.

in vacuum were lower than their corresponding values in air [5—7], and the T_e for nitrates and the corresponding nitrites were similar, signifying that the evaporation processes (vaporization and decomposition) are roughly equivalent for the corresponding nitrates and nitrites.

Conclusions

Dynamic thermogravimetry and mass spectroscopy experiments were performed in vacuum on six alkali metal salts: $LiNO_3$, $NaNO_3$, KNO_3, Na/KNO_3, $NaNO_2$ and KNO_2. The nitrates decomposed and released N_2, NO and N_2, while the nitrites released N_2 and O_2 only. The apparent activation energies of evaporation ranged from 122 kJmol^{-1} ($NaNO_2$, $LiNO_3$) to 151 kJmol^{-1} (Na/KNO_3). The rates of evaporation and the activation energies of the dynamic experiments agreed well with previous results of isothermal determinations.

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Zusammenfassung — Sechs Alkalimetallnitrate und -nitrite wurden in Vakuum, bei konstanter Erwärmungsgeschwindigkeit in einer kombinierten massenspektroskopischen und thermogravimetrischen Vorrichtung verdampft. Für $LiNO_3$, $NaNO_3$, KNO_3, Na/KNO_3, $NaNO_2$ und KNO_2 wurden die zeitzerlegten Profile der Zersetzungsgase, sowie die Kinetik erhalten. Für die Verdampfung dieser Salze wurden die Aktivationsenergien berechnet, und mit früheren Ergebnissen der isothermischen Versuche verglichen. In dem Temperaturbereich 650 bis 850 K wird von den zerfallenden Nitraten NO, N_2 und O_2 befreit, die Nitrite entwickeln dagegen nur NO und N_2.

Резюме — Шесть нитратов и нитритов щелочных металлов были испарены в вакууме в обьединенном совмещенном МС-ТГ приборе при постоянной скорости нагрева. Временно-разрешенные профили разложения газов и кинетика реакции были получены для $LiNO_3$, $NaNO_3$, KNO_3, Na/KNO_3, $NaNO_2$ и KNO_2. Вычислены энергии активации реакции испарения этих солей и сопоставлены с предыдущими результатами изотермических измерений. Разложение нитратов в температурной области 650—850 К происходит с выделением моноокиси азота, азота и кислорода, а нитритов — моноокиси азота и азота.