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The Thermal Decomposition of Sodium Nitrate and the Effects of Several Oxides on the Decomposition

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The thermal decomposition of sodium nitrate and the effects of several oxides, such as silica, titania, zirconia, alumina, and magnesia, on the decomposition were studied up to 900 °C by means of the thermal analysis, gas analysis, and chemical analysis of the reaction products. The reaction of sodium nitrate and silica was especially investigated in some detail over a wide composition range. The thermal decomposition of sodium nitrate started at about 450 °C. The gases formed were O_2, NO, and N_2, the formation of N_2 being detected above 680 °C. The thermal decomposition of sodium nitrate was supposed to consist of the following three successive or concurrent reaction processes, according to the degree of the reaction: (I) the decomposition of sodium nitrate to nitrite and oxygen, (II) the first-order liquid-phase reaction, with some kind of quantitative relationship between nitrate and nitrite, and (III) the formation reaction of sodium oxide, expressed by the Avrami-Erofe'ef equation. The (II) and (III) reaction processes can be reasonably interpreted if the existence of the peroxide ion is assumed. Acidic oxides, such as silica and titania, were supposed to lower the activation energy of the (III) reaction process by forming stable salts with sodium nitrate and/or its intermediate reaction products. The effects of these oxides on the thermal decomposition of sodium nitrate could be interpreted by the relative scale of the acidity of oxides.

Sodium nitrate is one of the most important components used in the chemical industry. In recent years, it has been used as the source of the sodium used in multi-component glass fibers for optical waveguides.[1)] This is because sodium nitrate has some advantages, such as oxidation and clarification effects, a low melting point, and a low decomposition temperature. However, few studies have been made of the reaction of sodium nitrate and several oxides. Furthermore, in the studies of the thermal decomposition of sodium nitrate,[2–6)] there are some disagreement concerning the decomposition temperature and/or the kind of gas formed.

In the previous paper,[7)] the following results were obtained with regard to the reaction of sodium nitrate and silica: (1) the formed gases in this system up to 800 °C were O_2 and NO; (2) 3 to 7 wt% sodium nitrite was present in the reaction system just before the formation of gas ceased; (3) the reaction products were sodium metasilicate (Na_2SiO_3) and disodium disilicate ($Na_2Si_2O_5$), depending on the silica content in the sample mixtures, and (4) the history of preparation and the relative surface area of the silica scarcely affect this reaction. However, the mechanism of the thermal decomposition of pure sodium nitrate was not investigated, since this decomposition appeared to be difficult to investigate in view of the creep-out of the melt of sodium nitrate from a platinum reaction vessel. In relation to the decomposition of sodium nitrate, disagreements among the other workers' paper[2–6)] seem to be caused by not taking account of the possibility of the effect of the experimental conditions, such as the measuring atmosphere and the material of the reaction vessel, on the decomposition, and by not setting up precise conditions of gas analysis.

In this study, the thermal decomposition of sodium nitrate and the effects of silica, titania, zirconia, alumina, and magnesia on the decomposition were investigated by a simultaneous measurement of thermogravimetry (TG), differential thermal analysis (DTA), differential thermogravimetry (DTG), and gas chromatograpy (GC), by which the gas formed could be analysed directly in a short time. Furthermore, the effect of silica addition was investigated over a relatively wide range of silica compositions.

Experimental

Samples. Reagent-grade sodium nitrate, titania, zirconia, and magnesia from the Wako Chemical Industries, Ltd., and alumina from the Nishio Industries, Co., Ltd., were ground under 100 mesh in an agate mortar and dried in an oven at 100 °C. Commercially available α-quartz was also ground under 100 mesh by means of a ball mill, washed with acid and distilled water, and dried in the oven. Sodium nitrate was mixed with one of these oxides by dry-blending at each run. The composition of sample is indicated by the atomic ratio, X_i (=i/Na; i=Si, Ti, Zr, Al, or Mg), in each sample mixture.

Apparatus and Procedure. The TG-DTA measurement was carried out with a high-temperature thermobalance from the Rigaku Denki Co., Ltd. The DTG was carried out with a differentiator from the Rikadenki Kogyo Co., Ltd., in order to differetiate the TG curve. A GC-2C-type gas chromatograph from the Shimadzu Seisakusho, Ltd., was used for quantitative gas analysis, in which silica-gel and molecular-sieve 5A were used as the column-packing reagents after treatment by the method descrived by Sakaida *et al.*[8)]

The simultaneous measurement of TG-DTA, DTG, and GC was carried out as follows. At first ,the sample mixture (less than 80 mg) was weighed in a reaction vessel (5 mm in diameter, 5 mm in depth), and this vessel was placed on a sample holder in the thermobalance; then, the ambient gas was introduced into the measuring system and adjusted to the desired flow rate (50 cm³ min⁻¹). Secondly, the sample was heated at 20 °C min⁻¹ and then held at 250 °C for about one hour. By this procedure, a trace amount of adsorbed water could be removed. The sample was then heated up to the desired temperature at the rate of 5 °C or 20 °C per min. In gas chromatography, argon was used as the carrier gas, and the gas formed from the sample was introduced into the gas chromatograph every 2 min

It took less than one minute from gas formation to gas sampling.

On the other hand, the reaction products were identified by X-ray powder diffractometry with Cu $K\alpha$ radiation. These reaction products were also used for quatitative analysis. About 100 mg of the reaction products were dissolved in water for one hour and then filtered. The unreacted silica was determined from the amount of dissolution residue. The silicates and total sodium were determined by atomic absorption spectrometry and flame emission spectrometry respectively. The sodium nitrate and sodium nitrite were determined by using a nitrate-ion electrode from the Toa Electronics, Ltd., and by UV spectrometry with sulfanilic acid respectively.

Results and Discussion

Effect of Experimental Condition on the Thermal Decomposition of Sodium Nitrate. In order to investigate the thermal decomposition of sodium nitrate and the effects of several oxides on the reaction, various factors which seemed to affect the reaction were investigated. They are, for example, the amount of the sample mixture, the heating rate, the ambient gas and its flow rate, and the material of the reaction vessel. The use of a small amount of the sample would result in a better thermal response. Taking the accuracy of the measurement into consideration, a sample mixture containing 8.5, 10.0 or 17.0 mg of sodium nitrate was used. In the binary system of sodium nitrate and silica, the similar shapes of the TG and DTG curves, and also the similar behavior of gas formation, were shown for the sample with the same value of X_{Si} in the ranges from 14.5 mg to 58.0 mg ($X_{\mathrm{Si}}=1.0$) and from 38.0 mg to 77.0 mg ($X_{\mathrm{Si}}=5.0$). The heating rate and the flow rate of the ambient gas scarecely affected the decomposition in the range investigated here; therefore, they were not important experimental factors. It is well known that a quartz or Pyrex-glass reaction vessel affects the decomposition. The reason for this is that sodium nitrate reacts with these vessels to form stable salts. On the other hand, platinum and stainless steel vessels seldom affect the decomposition; however, a creep-out of the fused sample from the vessel sometimes occurs. The reactivity of the vessels and the creep-out of the sample were investigated with platinum, gold, and two kinds of sintered magnesia vessels (MgO-A vessel: pressed at 9.3×10^{3} kg cm^{-2} and heated at 1000 °C for one day; MgO-B vessel: pressed at 1.85×10^{4} kg cm^{-2} and heated at 1000 °C for two days). There are no appreciable difference among these reaction vessels. Figure 1 shows the DTG curves and the behavior of the gas formation when a platinum or MgO-B vessel was used. The rate of weight loss, $d\alpha/dt$, is the differential of the fraction of weight loss, α, with respect to the reaction time, t. $R_{\mathrm{O_2}}$, R_{NO}, and $R_{\mathrm{N_2}}$ are the formation rates of O_2, NO, and N_2, respectively per mole of sodium nitrate. These results resemble each other below 700 °C. If the MgO-B vessel affected the decomposition, this behavior when a MgO-B vessel is used would be similar to that in the reaction of sodium nitrate and magnesia, which will be described later. When the sodium nitrate was held at a constant temperature, the MgO-B vessel, where no creep-out of the melt occurred, was used because it required a long time for measurement (for example, it took 260 min at 592 °C).

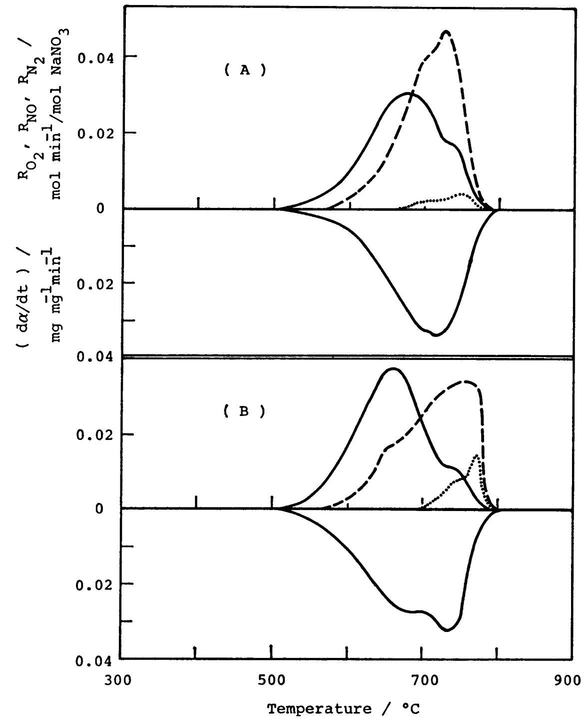

Fig. 1. DTG curves and the behavior of gas formation for the thermal decomposition of sodium nitrate with platinum (A) or MgO-B (B) reaction vessel in argon atmosphere. The solid line, the interrupted line and the dotted line indicate the formation rate of O_2 ($R_{\mathrm{O_2}}$), NO (R_{NO}), and N_2 ($R_{\mathrm{N_2}}$), respectively.

Then, the effect of the heating atmosphere, such as argon, nitrogen, oxygen and air on the reaction of the binary system of sodium nitrate and silica was investigated at the flow rate of 50 cm^3 min^{-1}. Figure 2 shows the TG curves and DTG curves for the reaction in argon (a) and oxygen (b). The TG and DTG curves for the reaction in nitrogen showed a shape similar to those obtained in argon. In air, they showed an intermediate shape between (a) and (b). The DTG curve of (b) showed peaks at 730 °C and 755 °C and shifted to a higher temperature than that of (a). From these results, it is evident that the partial pressure of oxygen (perhaps also nitrogen monoxide) affects the decomposition.

Thermal Decomposition of Sodium Nitrate. Figure 3 shows the results of the simultaneous measurement of TG-DTA, DTG, and GC on the thermal decomposition after heating at 5 °C min^{-1}. The DTA curves show the endothermic peaks at 278 °C and 308 °C which correspond to the transformation and melting. The TG and DTG curves indicate that the decomposition finished at 800 °C. It is found from the behavior of gas formation that, at first, sodium nitrate generates O_2, secondly, O_2 and NO, and then, over 680 °C, O_2 NO, and N_2. On the decomposition of sodium nitrite, the formation of N_2 was scarecely detected, so the formation must be caused by the reaction pro-

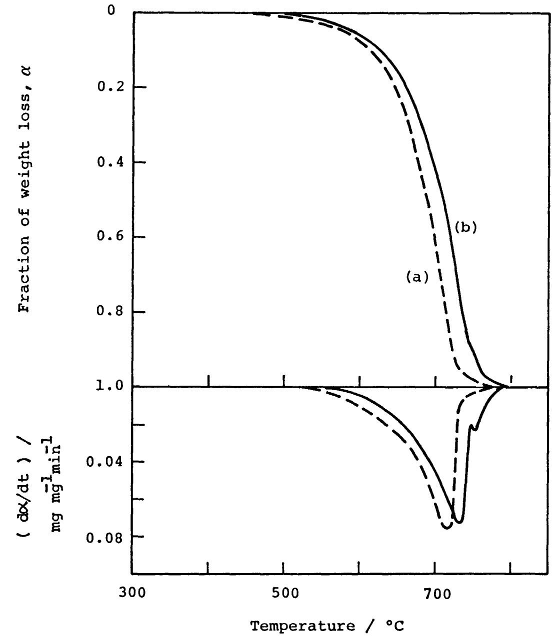

Fig. 2. TG and DTG curves for the reaction of sodium nitrate and silica ($X_{Si}=1.0$) in argon (a) or in oxygen (b).

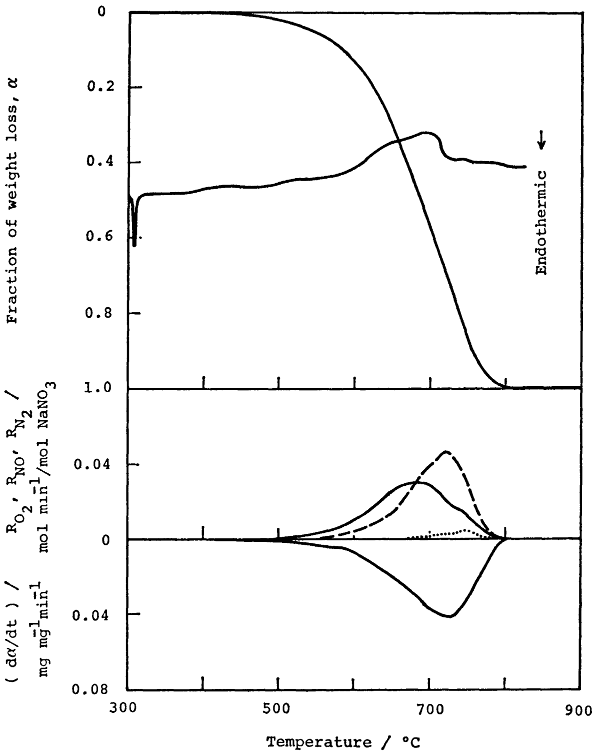

Fig. 3. TG, DTA, and DTG curves, and the behavior of gas formation for the thermal decomposition of sodium nitrate in argon atmosphere. The solid line, the interrupted line and the dotted line indicate R_{O_2}, R_{NO}, and R_{N_2}, respectively.

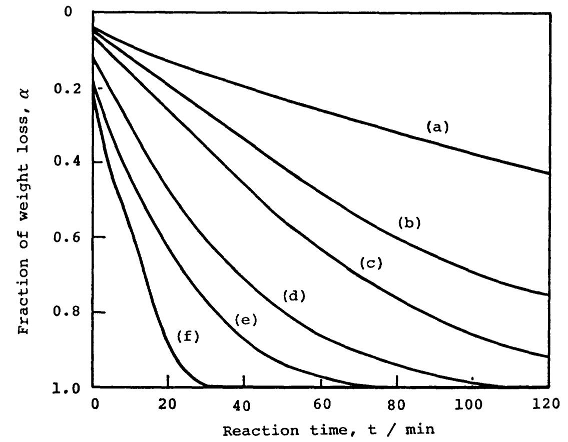

Fig. 4. TG curves for the thermal decomposition of sodium nitrate in argon.
(a): 592 °C, (b): 611 °C, (c): 625 °C, (d): 648 °C, (e): 672 °C, (f): 703 °C.

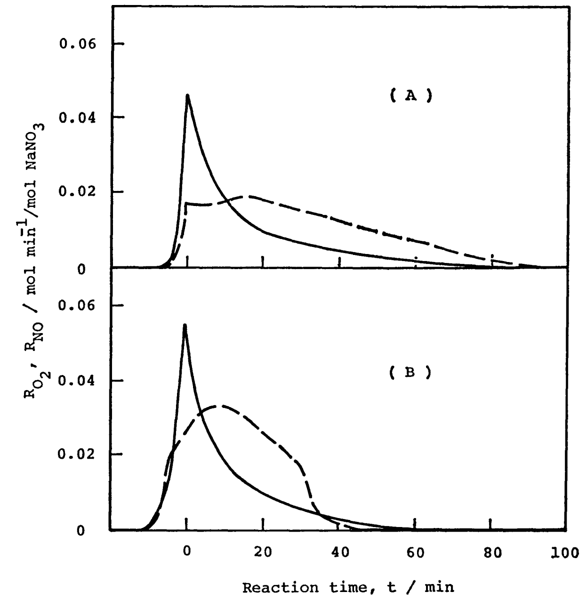

Fig. 5. The behavior of gas formation for the thermal decomposition of sodium nitrate at 648 °C (A) and 672 °C (B). The solid line and interrupted line indicate R_{O_2} and R_{NO}, respectively.

cess that sodium nitrate directly decomposes or reacts with its reaction products.

Furthermore, the decomposition was investigated at various constant temperatures in the range from 592 °C to 703 °C. Figure 4 and 5 show the TG curves and the behavior of gas formation respectively.

The TG curves in Fig. 4 were analysed by the method described by Hancock and Sharp.[9] This method is based on the Avrami-Erofe'ef equation (Eq. 1):

$$(-\ln(1-\alpha))^{1/n} = kt, \qquad (1)$$

where α is the fraction reacted, k is the kinetic constant, and t is the reaction time. The n value is a constant peculiar to this type of reaction; usually, it is an integer larger than 2. Hancock showed that, when ln (−ln (1−α)) is plotted against (ln t), an approximately linear relation is observed for many kinds of solid-state reactions and the first-order and zeroth-order reactions. For the first- and zeroth-order reactions, the n slopes equal unity and 1.24 respectively. Figure

6 illustrates the ln $(-\ln(1-\alpha))$ *vs.* (ln t) plots for the decomposition of sodium nitrate. Figure 6 shows the ranges in which the kinetic equation of the first-order reaction is valied ($\alpha \leqq 0.85$) and in which the Avrami-Erofe'ef equation with $n=3$ is valid ($\alpha \geqq 0.85$). In the α ranges mentioned above, the TG curves being estimated with the kinetic equation of the first-order reaction and the Avrami-Erofe'ef equation, Fig. 7 obtained. They give approximately linear plot. The kinetic constants were obtained from these slopes. From their Arrhenius plot, the apparent activation energy was calculated to be 223 kJ mol^{-1} for the first-order reaction below 648 °C and 243 kJ mol^{-1} for the $n=3$ range above 672 °C.

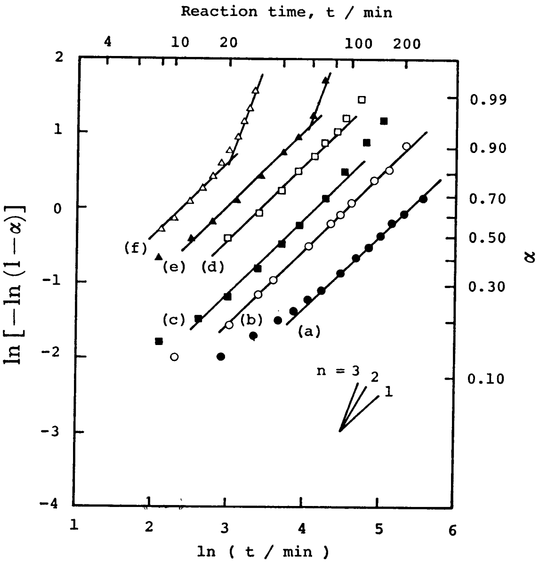

Fig. 6. $\ln(-\ln(1-\alpha))$ versus ($\ln t$) plot for the thermal decomposition of sodium nitrate.
(a): 592 °C, (b): 611 °C, (c): 625 °C, (d): 672 °C, (d): 703 °C.

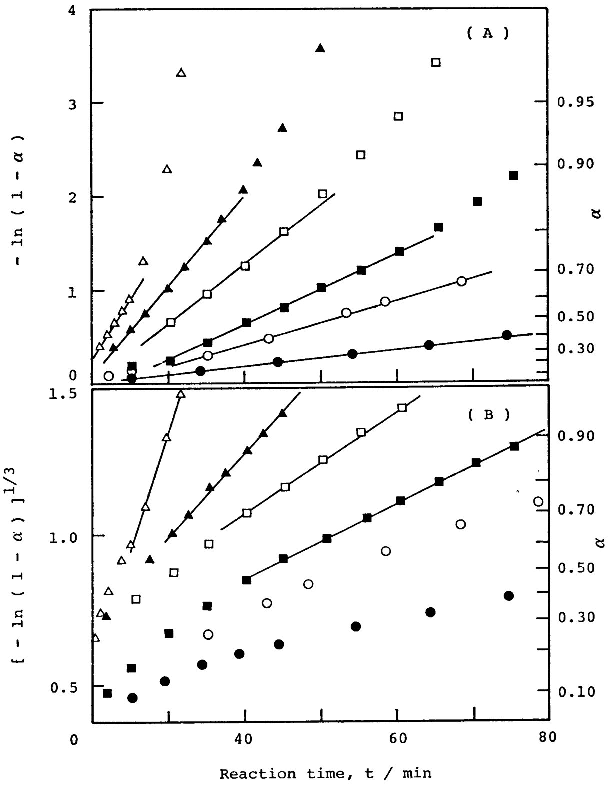

Fig. 7. Estimation of TG curves with the kinetic equation of the first order reaction (A) and Avrami-Erofe'ef equation with $n=3$ (B) for the thermal decomposition of sodium nitrate.

The behavior of gas formation was analysed by the method of plotting the formation ratio of O_2 to NO *versus* α. They are illustrated in Fig. 8, which shows that the formation of O_2 is remarkable at the initial and final stages of the reaction. In the middle stage of the reaction, the R_{O_2}/R_{NO} value is nearly constant in the α range from 0.25 to 0.75. This strongly suggests that it is reasonable to divide the thermal decomposition of sodium nitrate into three successive or concurrent reaction processes. From the analysis of the solid-state reaction products, it was found that the amount of sodium nitrite in the melt increased at the initial stage of the reaction and decreased at the middle and final stages. The three predominant reaction processes in the initial, middle and final stages of the reaction may be summalized as follows:

Process I (predominant in the initial stage); the thermal decomposition of sodium nitrate to nitrite and oxygen (Eq. 2)

$$NaNO_3 = NaNO_2 + 1/2O_2. \tag{2}$$

This reaction process has been studied by several workers.[2-6)]

Process II (predominant in the middle stage); the first-order liquid-phase reaction with some kind of quantitative relationship between nitrate and nitrite in the melt; the reverse reaction of sodium nitrite to form nitrate also occured. This can reasonably be interpreted if the existence of sodium peroxide or

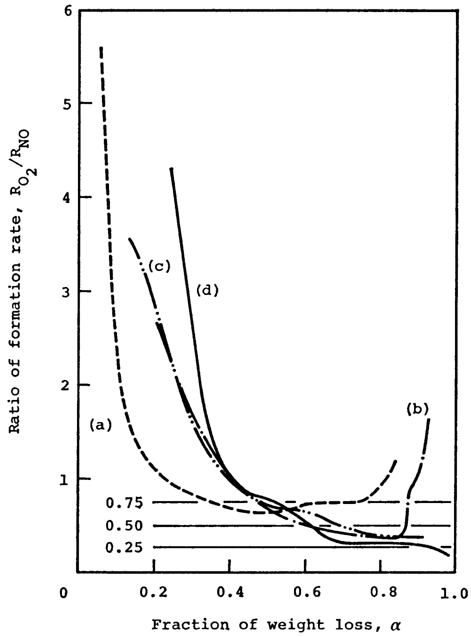

Fig. 8. The ratio of the formation rate of O_2 to NO, R_{O_2}/R_{NO} at various constant temperatures.
(a): 611 °C, (b): 648 °C, (c): 672 °C, (d): 703 °C.

hyperoxide as an intermediate during the decomposition of sodium nitrate is assumed. Paniccia *et al.*[10] reported that sodium peroxide was the main basic species in (sodium–potassium) nitrate eutectic *in vacuo*. Under the argon flow, peroxide is also considered to be the main basic species. This reaction process is expressed by the following equations:

$$NaNO_2 = 1/2Na_2O_2 + NO \tag{3}$$

$$Na_2O_2 = Na_2O + O \tag{4}$$

$$NaNO_2 + O = NaNO_3 \tag{5}$$

$$Na_2O_2 + O = NaO + O_2. \tag{6}$$

As the equilibrium constant of the I reaction process (Eq. 2) increases with an increase in the temperature, the R_{O_2}/R_{NO} value of the II precess will be close to 0.25, which is the formation ratio of O_2 to NO in Eq. 7:

$$NaNO_2 = 1/2Na_2O + NO + 1/4O_2 \tag{7}$$

Precess III (predominant in the final stage); the reaction process to form sodium oxide. Eq. 1 was applied to the solid-state reaction by taking account of the nucleation at various places in a crystal and the gradual piling up of these nuclei with the progress of the reaction. However, in the III process, it is reasonable to conclude that the reaction proceeds by means of a mechanism by which oxide precipitates are formed from the melt and the precipitate becomes the nuclei of the subsequent reaction. This process was remarkable at higher temperatures.

Effects of Several Oxides on the Decomposition. From the viewpoint of the Lux-Flood acid-base theory, sodium nitrate is considered to act as a base in the reaction with acidic oxides. Therefore, the effects of oxides with different acidities on the thermal decomposition of sodium nitrate was investigated at a constant heating rate. The results obtained are shown in Figs. 9 and 10.

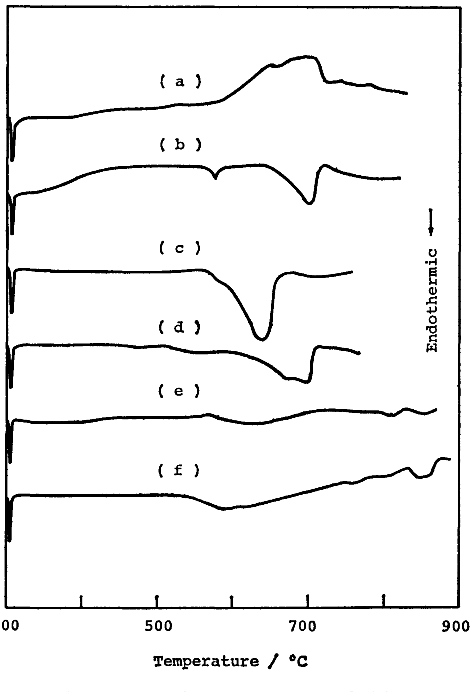

Fig. 9. DTA curves for mixtures of binary system including sodium nitrate (0.2 mmol) with X_i=2.0. (a): Sodium nitrate, (b): $NaNO_3$+SiO_2, (c): $NaNO_3$+TiO_2, (d): $NaNO_3$+ZrO_2, (e): $NaNO_3$+Al_2O_3, (f): $NaNO_3$+MgO.

The DTA curves in Fig. 9 show the relatively large endothermic peaks for the reactions at about 700 °C, 640 °C, and 690 °C in the systems containing silica (b), titania (c), and zirconia (d) respectively. In the (b) system, the endothermic peak at 575 °C indicates the transformation of α- to β-quartz.

To understand the effects of oxides in detail, the $2Z_i/r$ values were calculated as one of the scale of the acidity of oxides: here, Z_i is the charge of the metal ion, M^{Z_i+}, and r is the interatomic distance. The values of r were calculated from the data of Pauling.[11] The $2Z_i/r$ values express the relative bond strength between M^{Z_i+} and O^{2-}, the larger value indicating the stronger acidity. These values for several oxides are shown in Table 1. In Fig. 10, the behavior of the gas formation in the reaction of binary systems

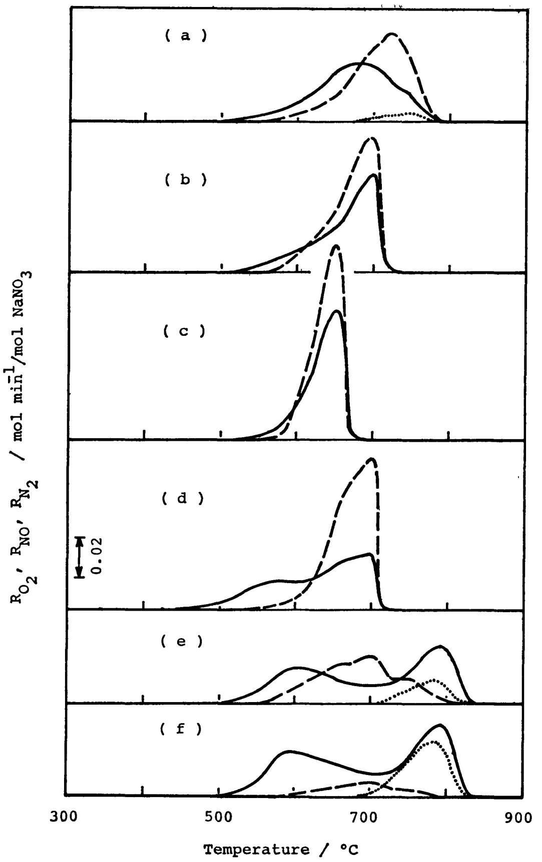

Fig. 10. The behavior of gas formation by the reaction in binary system containing sodium nitrate (0.2 mmol) with X_i=2.0.
(a): Sodium nitrate, (b): $NaNO_3$+SiO_2, (c): $NaNO_3$+TiO_2, (d): $NaNO_3$+ZrO_2, (e): $NaNO_3$+Al_2O_3, (f): $NaNO_3$+MgO.

Table 1. $2Z_i/r$ values for several oxides

Na_2O	MgO	Al_2O_3	ZrO_2	TiO_2	SiO_2
0.83	1.95	3.26	3.54	3.81	4.71
weak ←		acidity		→	strong

containing silica (b), titania (c), zirconia (d), alumina (e), and magnesia (f), arranged in the order of acidity, is shown. The thermal decomposition of pure sodium nitrate (a) is also presented for the sake of comparison. Strong acidic oxides, such as silica and titania, remarkably accelerate the thermal decomposition of sodium nitrate ((b) and (c)). In the reaction of sodium nitrate and such basic oxides as magnesia (f), the formation of O_2 in the temperature range from 500 °C to 600 °C is characteristic. When the basic oxides are characterised by the formation rate of O_2 at 600 °C, this decreases in the order of: (f), (e), (d), and (c)$\approx$(b). This trend agrees well with the order of acidities in Table 1. From the values in Table 1, the behavior of gas formation in the (c) system would be expected to show an appearance intermediate between (b) and (c), but Fig. 10 shows that the reaction in (c) is more accelerated than in (b). The reason for this is that the titania used in this experiment was very fine (the volume avarage particle size: 4 μm).

Reaction of Sodium Nitrate and Silica. Silica is an important material in the glass industry. Therefore, the reaction in the binary system of sodium nitrate (0.1 or 0.2 mmol) and silica was investigated at various constant temperatures from 570 °C to 700 °C and over a relatively wide range of silica composition. The results of the analysis of the reaction products ($X_{Si}=0.5$ to 5.0) were similar to those in the previous report.7) Figure 11 shows the behavior of gas formation at 650 °C. When the X_{Si} value is 1.0, the range in which the R_{O_2} and R_{NO} values are both constant exists at the reaction times from 12 to 38 minutes. Even if the X_{Si} value is 0.5, the reaction is accelerated by silica, and when X_{Si} is 3.0 and 5.0, the reaction is more accelerated than the reaction with $X_{Si}=1.0$. In all cases, a range of nearly constant R_{NO} values was observed. Figure 12 shows the DTG curves of these systems. They also indicate the increase of the rate of weight loss with the increase in the X_{Si} value. The characteristic acceleration of the reaction was found at the final stage of the reaction. The peak based on this acceleration shifted to the shorter-reaction-time side with the increase in X_{Si} value, until it could not be detected at all at $X_{Si}=5.0$. When the $(d\alpha/dt)_{\alpha=0.25}$ values, which is the rate of weight loss at $\alpha=0.25$, were plotted versus X_{Si} as a scale of the effect of silica, Fig. 13 was obtained. The larger X_{Si} value gives the larger $(d\alpha/dt)_{\alpha=0.25}$ value. Nearly constant $(d\alpha/dt)_{\alpha=0.25}$ values were obtained at $X_{Si}\geqq5.0$ and $X_{Si}\leqq1.0$. These results indicate that, at $X_{Si}\leqq1.0$, the acceleration of the decomposition reaction of sodium nitrate by the addition of silica is scarcely observed in the first stage of the reaction ($\alpha\leqq0.25$), but it becomes evident with the increase in the X_{Si} value, while at $X_{Si}\geqq5.0$ the degree of acceleration is almost constant.

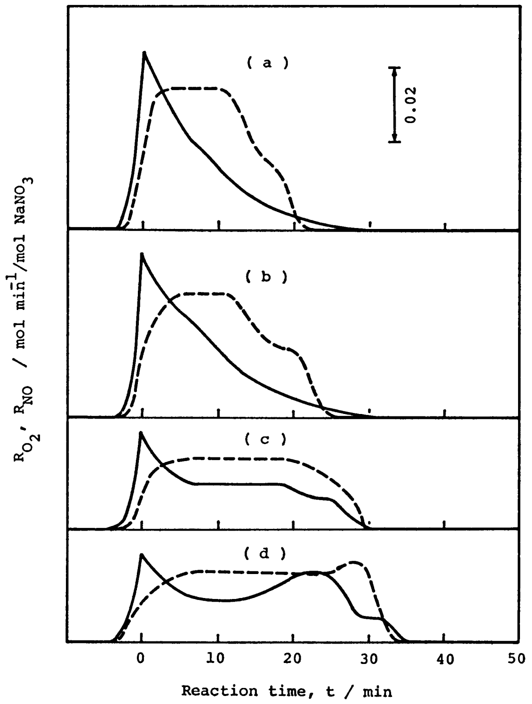

Fig. 11. Effect of silica on the behavior of gas formation at 650 °C.
(a): $X_{Si}=5.0$, (b): $X_{Si}=3.0$, (c): $X_{Si}=1.0$, (d): $X_{Si}=0.5$. The solid line and interrupted line indicate R_{O_2} and R_{NO}, respectively.

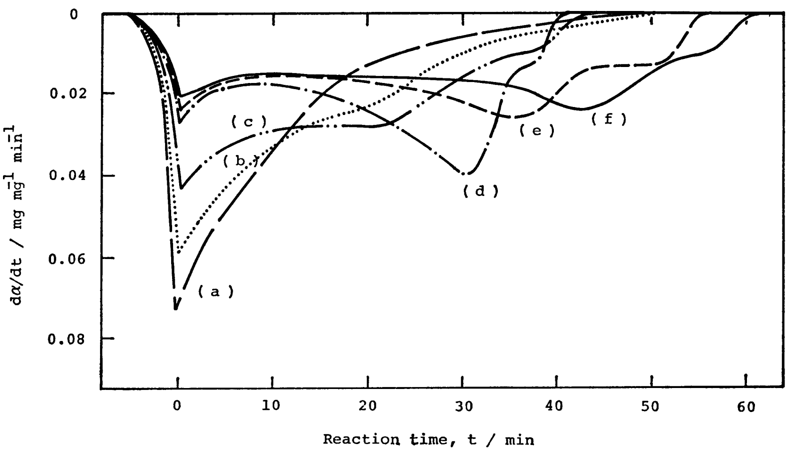

Fig. 12. Effect of silica on DTG curves at 650 °C. (a): $X_{Si}=5.0$, (b): $X_{Si}=4.0$, (c): $X_{Si}=3.0$, (d): $X_{Si}=2.0$, (e): $X_{Si}=1.0$, (f): $X_{Si}=0.5$.

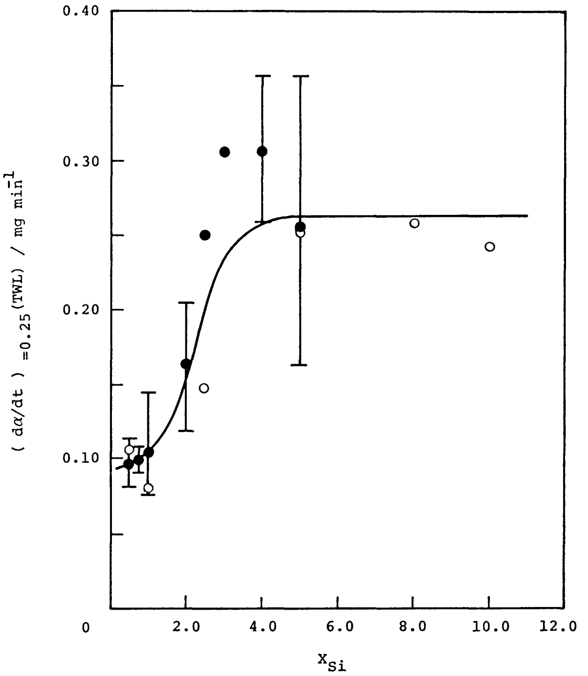

Fig. 13. $(d\alpha/dt)_{\alpha=0.25}$ (TWL) values for various X_{Si} values at 650 °C. (TWL) means the total amount of weight loss.
Open circle: 0.1 mmol $NaNO_3$, closed circle: 0.2 mmol $NaNO_3$.

By analysing TG curves by means of Hancock and Sharp's method, the n value was obtained as close to 3 at $\alpha \geqq 0.25$. This indicates that the reaction of sodium nitrate and silica is expressed by Avrami-Erofe'ef equation with $n=3$ and that the diffusion of Na^+ into silica ($n=0.54$ to 0.62) or the phase-boundary reaction ($n=1.07$, 1.11) is not a rate-determining step. Thus the mechanism of the reaction of this system is considered to be one in which the main basic species, sodium peroxide, reacts with a strong acidic oxide, silica, and forms the precipitate of silicate, and that they then grow in the melt. The apparent activation energy, ΔE, and the frequency factor, k_0, are shown in Table 2 for various X_{Si} values. The increase in k_0 supports the above-mentioned mechanism. ΔE is lower at $X_{Si}=1.0$ and 3.0 compared to that of the thermal decomposition of pure sodium nitrate. The reason for this is probably that silica, which is a strong acidic oxide, reacts with the basic species, such as sodium peroxide, and so lowers the activation energy of the reaction. Sodium metasilicate and disodium disilicate were identified as the reaction products. It is easily supporrted that these reaction products also affect the decomposition of sodium nitrate. At $X_{Si}=4.0$ and 5.0, a large amount of silicates would be formed and precipitated in the melt and at the boundary in the early stage on the reaction. These silicates are considered to cover a part of the surface of silica and to interfere with the effective contact of melt and silica. The increase in activation energy at X =4.0 and 5.0 might thus be caused. If so, about the same value of $(d\alpha/dt)_{\alpha=0.25}$ at $X_{Si} \geqq 5.0$ is considered to result from the competitive effects of covering and acceleration.

TABLE 2. APPARENT ACTIVATION ENERGY, ΔE, AND FREQUENCY FACTOR, k_0, FOR THE REACTION OF SODIUM NITRATE AND SILICA

X_{Si}		ΔE/kJ mol^{-1}		$\ln(k_0/\text{min}^{-1})$	
		a	b	a	b
0	$n=1$	—	223	—	25.5
	$n=3$	243	—	26.7	—
1.0		179	179	20.5	20.5
3.0		204	179	22.9	19.9
4.0		226	198	25.2	22.3
5.0		229	177	25.8	19.8

a: $\alpha \geqq 0.85$.
b: $0.25 \leqq \alpha \leqq 0.85$.

Sodium nitrate in this system may be supposed to decompose through the reactions expressed in Eqs. 2 to 6, but silica would react with sodium peroxide to form sodium metasilicate *via* disodium disilicate.

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