The Reaction of Sodium Nitrite with Silica

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The reaction of sodium nitrite with silica has been investigated over the relatively wide composition range (Na/Si=0 to 10.0) below 800 °C. In an argon atmosphere, sodium nitrite reacts with oxygen to form sodium nitrate above 400 °C and decomposes to sodium oxide via other oxide species above 500 °C, irrespective of the coexistence of silica. The reaction of sodium nitrite with silica in an argon atmosphere consists of two stages. In the early stage (<600 °C), the main gaseous product is NO, while in the later stage nearly equimolar amounts of NO and O_2 are formed. The early stage is further divided into two reaction processes: Process I, in which peroxide is considered to be formed in the melt by generating NO, and Process II, in which nitrate and silicates are formed by generating NO and a trace amount of O_2. Peroxide is supposed to be stabilized at the solid-liquid interface, even if no silicates have been formed at relatively low temperatures. In the later stage, the reaction process or mechanism can be regarded as similar to that of sodium nitrate with silica, as the concentration of nitrite in the melt is very low.

The high-temperature behavior of alkali-metal nitrates, especially sodium nitrate, accompanying thermal decomposition is of interest in the manufacture of multicomponent glass fibers for optical wave guides, the vitrification of radioactive wastes from nuclear reactors, the surface treatment of metals and alloys, etc. In the previous papers,[1,2] it has been revealed that several wt% of sodium nitrite is formed as an intermediate during the decomposition of sodium nitrate, irrespective of the coexistence of silica. The investigation of the thermal decomposition of sodium nitrite should give some useful information on the high-temperature behavior of the nitrates.

With respect to the thermal decomposition of sodium nitrite, only a few studies have been made. Reactions 1 and 2 have been investigated by Freeman[3] and Bond et al.[4] respectively:

$$NaNO_2 + 1/2 O_2 \rightleftarrows NaNO_3 \qquad (1)$$

$$NaNO_2 = 1/2 Na_2O + \text{Gaseous Products (in Ar)} \qquad (2)$$

Freeman[3] has calculated the changes in the free energy of Reaction 1 to be -14.8, -7.4, and -2.8 kJ mol^{-1} at 600, 650, and 700 °C respectively, and the apparent activation energy to be 86.6 kJ mol^{-1} for the forward reaction and 187 kJ mol^{-1} for the backward reaction. The apparent activation energy of 179 kJ mol^{-1} has been obtained for Reaction 2 by analyzing the thermograms with the Avrami-Erofe'ef equation.[4] There is, however, not enough data with respect to the gaseous and solid reaction products in the paper by Bond et al.[4]

According to the acid-base theory by Lux and Flood, both sodium nitrate and nitrite behave as bases, namely oxide-ion donors, during the decomposition process. Therefore, in the binary system containing an acidic oxide, the reaction process to form oxide species, such as O^{2-}, O_2^{2-}, and O_2^-, is supposed to be predominant. This may be a clue to the clarification of the reaction mechanism. In the present study, the reaction of sodium nitrite with silica has been mainly investigated by a simultaneous measurement of thermogravimetry (TG), differential thermal analysis (DTA), differential thermogravimetry (DTG), and gas chromatography (GC), and the analysis of the solid reaction products.

The decomposition mechanism of sodium nitrite is also discussed.

Experimental

Materials. Reagent-grade sodium nitrite (Wako Pure Chemical Industries, Ltd.) was ground under 100 mesh in an agate mortar and dried in an oven at 100 °C. Commercially available α-quartz was ground by means of a ball mill, washed with nitric acid and distilled water, and dried in the oven. The sodium nitrite and silica were mixed by dry-blending for each run. The compositions of the sample mixtures will be represented by the atomic ratio of silicon to sodium (Si/Na= Y_{Si}).

Apparatus and Procedure. For the TG-DTA measurement, a high-temperature thermobalance (Rigaku Denki Co., Ltd.) was used. DTG was carried out with a differentiator (Rikadenki Kogyo Co., Ltd.) in order to differentiate thermograms. A GC-2C-type gas chromatograph (Simadzu Seisakusyo, Ltd.) was used for quantitative gas analysis, in which silica gel and molecular sieve 5A were used as column-packing reagents after treatment by the method described by Sakaida et al.[5]

A weighed sample mixture (6.9—66.9 mg) containing 0.1 or 0.2 mmol of sodium nitrite in a platinum vessel was placed on a sample holder in the thermobalance; the ambient gas (Ar or O_2) was then introduced and adjusted to the desired flow rate (50 cm³ min⁻¹). Then the sample was heated at the rate of 5.0 or 20 °C min⁻¹ after holding it at 250 °C for an hour to remove a trace amount of adsorbed water. The gas formed from the sample was introduced into the gas chromatograph every two minutes by using Ar as the carrier gas.
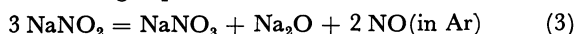
On the other hand, the solid reaction products were identified by means of X-ray diffractometry with Cu $K\alpha$ radiation, followed by chemical analysis. The heat-treated samples were kept in a desiccator with magnesium perchlorate as a desiccant. For the quantitative analysis, 100 mg portions of the reaction products were dissolved in water and then filtered with a membrane filter. Unreacted silica was determined by gravimetry. The amounts of sodium and silicon in the filtrate were determined by means of flame spectrophotometry and atomic absorption spectrometry respectively. The sodium nitrate and nitrite were determined by means of ion-exchange chromatography (with Dionex model 10).

The details of the experimental procedures and various factors which seem to affect the reaction have been discussed in the previous papers.[1,2]

Results and Discussion

Reaction Products. Figures 1 and 2 show the gaseous and solid reaction products respectively. The gases formed up to 720 °C were O_2 and NO on the thermal decomposition of sodium nitrite, irrespective of the presence of silica. A trace amount of N_2 was generated above 680 °C. The final solid reaction product was sodium metasilicate and/or disodium disilicate. It is evident from Figs. 1 and 2 that sodium nitrite decomposes above 400 °C generating only NO, and above 500 °C generating NO and O_2 to form sodium nitrate, sodium metasilicate, and disodium disilicate. It is also evident from Fig. 1 that the sample weight scarcely affects the reaction.

Figure 3 show the distribution of the sodium ion among the solid reaction products. In Fig. 3 (A) and (B), analytical values can be obtained below 600 °C, for sodium nitrite reacts with the platinum vessel above 600 °C, in the absence of silica.[6] In an argon atmosphere, sodium nitrite decomposed above 450 °C to form almost equimolar sodium nitrate and sodium oxide by generating NO [Fig. 3 (A)]. In an oxygen atmosphere, sodium nitrite reacted with O_2 above 400 °C to form nitrate, while above 500 °C it decomposed to form oxide [Fig. 3 (B)]. Under a high partial pressure of atmospheric oxygen, such highly oxidized compounds as peroxide might be formed. The reactions are expressed by the following equations:

$$3\,NaNO_2 = NaNO_3 + Na_2O + 2\,NO(\text{in Ar}) \qquad (3)$$

$$2\,NaNO_2 + O_2 = 2\,NaNO_3(\text{in } O_2) \qquad (4)$$

The reaction of sodium nitrite with silica in an argon

Fig. 2. Solid reaction products in sodium nitrite–silica system $(Y_{Si}=1.0)$.
Atmosphere: Ar, heating rate: 5.0 °C min^{-1}. ●: SiO_2 (20.8°), ▲: $NaNO_2$ (44.5°), ○: $NaNO_3$ (47.9°), □: $\alpha\text{-}Na_2Si_2O_5$ (23.6°), ■: Na_2SiO_3 (16.8° in 2θ).
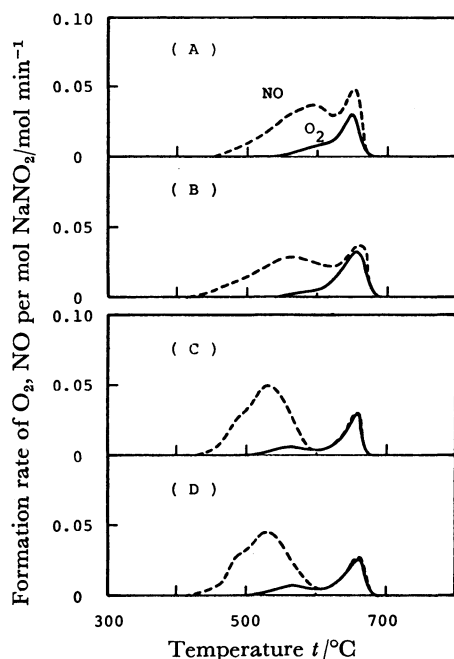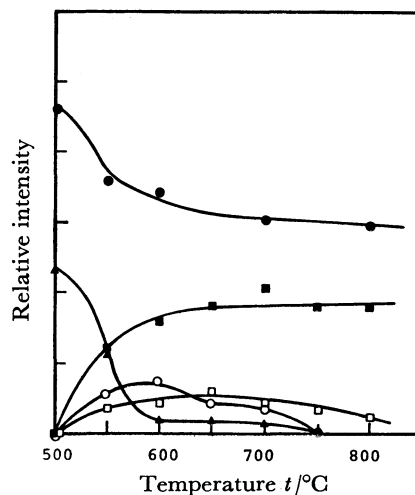

Fig. 1. Behavior of gas formation in the reaction of sodium nitrite with silica.
Atmosphere : Ar, heating rate : 5.0 °C min^{-1}. (A): $Y_{Si}=1.0$ (0.1 mmol $NaNO_2$), (B): $Y_{Si}=1.0$ (0.2 mmol $NaNO_2$), (C): $Y_{Si}=2.0$ (0.1 mmol $NaNO_2$), (D): $Y_{Si}=2.0$ (0.2 mmol $NaNO_2$).
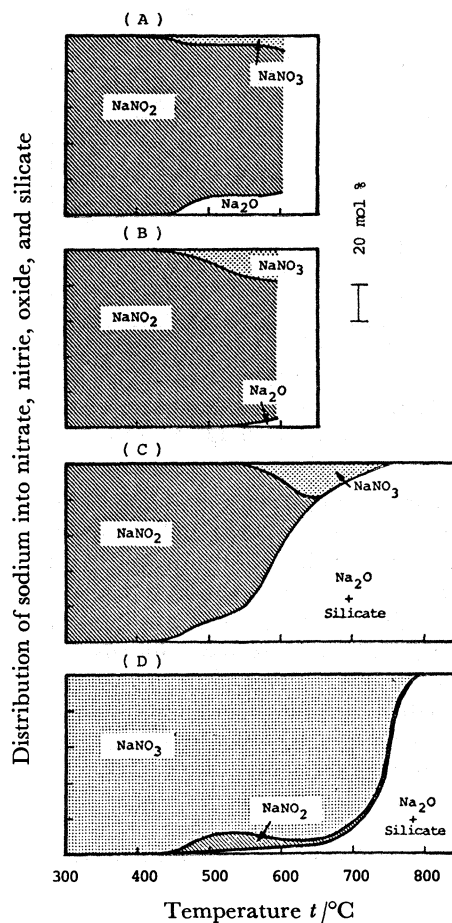

Fig. 3. Fraction of sodium compounds in reaction products.
Heating rate: 5.0 °C min^{-1}. (A): $NaNO_2$ in argon atmosphere, (B): $NaNO_2$ in oxygen atmosphere, (C): $NaNO_2\text{-}SiO_2$ in argon atmosphere $(Y_{Si}=1.0)$, (D): $NaNO_3\text{-}SiO_2$ in argon atmosphere $(Y_{Si}=1.0)$.
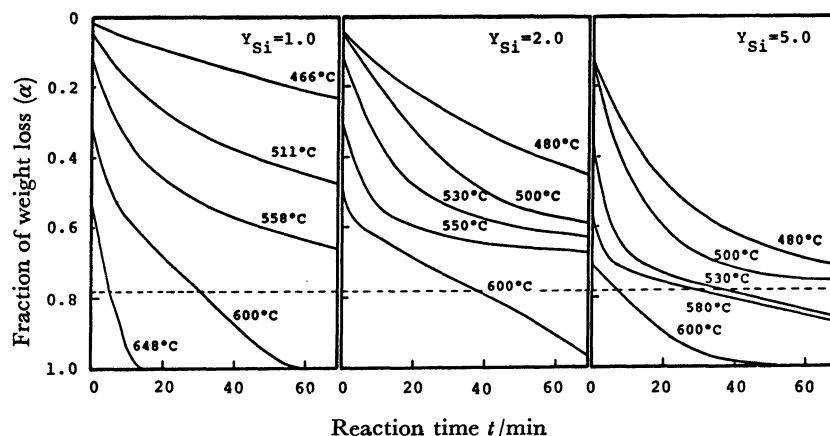
Fig. 4.   Isothermal thermograms of sodium nitrite–silica system in argon atmosphere.
The dashed line at $a=0.789$ indicates the fraction of weight loss when all of
sodium nitrite in sample decomposed to form peroxide according to Eq. 5.

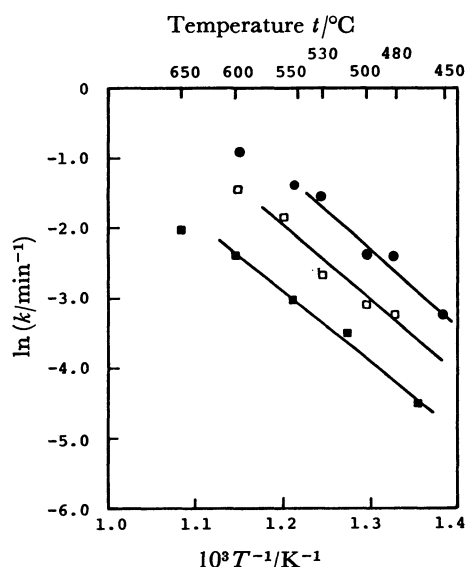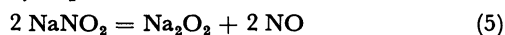Fig. 5.   Arrhenius plots for NO formation reaction.
■ : $Y_{si}=1.0$, □ : $Y_{si}=2.0$, ● : $Y_{si}=5.0$.

Table 1.   ACTIVATION ENERGY AND FREQUENCY
FACTOR FOR THE NO-FORMATION REACTION
OBTAINED FROM Fig. 5

Composition Y_{si}	Apparent activation energy, $\Delta E/kJ\ mol^{-1}$	Frequency factor, $\ln(k^\circ/min^{-1})$
1.0	81.2	8.8
2.0	98.3	12.3
5.0	97.1	12.9

atmosphere can be roughly classified into two stages.   In
the early stage (<600 °C), especially below 530 °C, the
main anion species in the melt is nitrite.   In Fig. 3 (C),
the mol percent of sodium compounds other than nitrate
and nitrite is about 20% at 530 °C.   However, it was
found by chemical analysis that silicates are scarcely
formed below 530 °C.   This indicates that some oxide
species, probably including peroxide,[7] can exist stably
in an argon atmosphere.   The reaction below 530 °C
is expressed by Eq. 5:

$$2\ NaNO_2 = Na_2O_2 + 2\ NO \qquad (5)$$

Sodium nitrate and silicates were formed in the temper-
ature range from 530 to 600 °C.   In the later stage (>600
°C), the reaction is almost identical with that of sodium
nitrate with silica, as the main anion species in the melt
is nitrate.   In the present paper, the early stage of the
reaction is mainly discussed.

Isothermal Reaction of Sodium Nitrite with Silica.
Figure 4 shows thermograms obtained when samples
containing 0.1 mmol of sodium nitrite were heated at

various temperatures in an argon atmosphere.   Ther-
mograms have a trend to approach gradually the dashed
line below 550 °C at 1.0 and 2.0 in Y_{si}, or below 500 °C
at 5.0 in Y_{si}.   After a reaction time of 3 h, a indicates
a value from 0.789 to 1.000 in all cases.   This suggests
that the reaction of sodium nitrite with silica consists of
two stages: the rapid formation of sodium peroxide, and
the sluggish reaction of peroxide with silica.   These two
reaction stages correspond to the early and later stages
described above.   The apparent activation energy (ΔE)
and the frequency factor ($\ln k^\circ$) for the rapid reaction
were obtained by extrapolating DTG curves to 0 in the
fraction of weight loss (a) and by plotting the $(da/dt)_{a=0}$
values versus the reciprocal temperatures.   The plot is
shown in Fig. 5.   The values of ΔE and $\ln k^\circ$ are listed
in Table 1.   The fact that the apparent activation
energies at both 2.0 and 5.0 in Y_{si} are almost the same,
irrespective of the composition, strongly indicates that
the early-stage reaction is characteristic of the decompo-
sition of sodium nitrite to form peroxide in the melt.   In
the later stage, the thermograms for the sample with 1.0
in Y_{si} were analyzed by the Avrami-Erofe'ef equation
as was described in a previous paper.[2]   The Arrhenius
plot showed a good linearity, and the value of 181 kJ
mol^{-1} was obtained for the apparent activation enrgy.
This value is quite close to that obtained for the final
stage of the reaction of sodium nitrate with silica, 179 kJ
mol^{-1}, and to that obtained by Bond *et al.*[4]

*Reaction of Sodium Nitrite with Silica at a Constant Heating
Rate.*   It is difficult to obtain data to discuss the
elementary reactions in the early stage isothermally,
because the nitrite considerably decomposes before
reaching the desired temperatures.   Therefore, the

reaction of sodium nitrite with silica was investigated at a constant heating rate.

Zambonin et al.[8-10] reported that oxide species such as O_2^-, O_2^{2-}, O^-, and O^{2-} act as bases in the nirate melt. For the early reaction stage of sodium nitrite with silica, the following assumptions are appropriate judging from the results of various analyses of reaction products, etc:
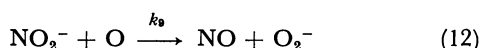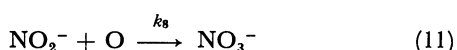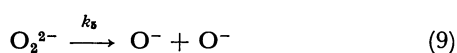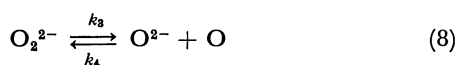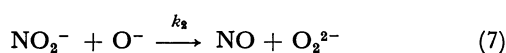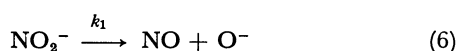
(i) The formation and the dissociation of O_2 are neglected.

(ii) The formed nitrate does not decompose.

(iii) Approximately spherical ions with an identical charge, for example O_2^- and O_2^{2-}, do not react with each other.

(iv) The gas formed (NO) is carried away from the system by the carrier gas.

If these assumptions are valid, the following equations may be considered for the reaction mechanism:

$$NO_2^- \xrightarrow{k_1} NO + O^- \tag{6}$$

$$NO_2^- + O^- \xrightarrow{k_2} NO + O_2^{2-} \tag{7}$$

$$O_2^{2-} \underset{k_4}{\overset{k_3}{\rightleftarrows}} O^{2-} + O \tag{8}$$

$$O_2^{2-} \xrightarrow{k_5} O^- + O^- \tag{9}$$

$$O_2^- \underset{k_7}{\overset{k_6}{\rightleftarrows}} O^- + O \tag{10}$$

$$NO_2^- + O \xrightarrow{k_8} NO_3^- \tag{11}$$

$$NO_2^- + O \xrightarrow{k_9} NO + O_2^- \tag{12}$$

For the thermal decomposition of sodium nitrite, the concentration of O, O^-, O_2^-, and O_2^{2-} is supposed to be very low.[8-10] If the stationary state is assumed to the formation of these species, Eq. 13 is obtained:

$$-\frac{d[NO_2^-]}{dt} = 3 k_8[O][NO_2^-] \tag{13}$$

As [O] is considered to be almost constant in a relatively narrow temperature range, Eq. 13 can be rearranged, thus:

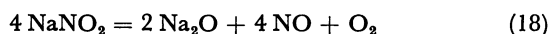$$- \ln [NO_2^-] = 3 k_8 [O] t \tag{14}$$

The concentration of nitrite, the reaction time (t), and the kinetic constant (k_8) are expressed by Eqs. 15 to 17:

$$[NO_2^-] = \frac{3(1-1.9\alpha)}{3-1.9\alpha} \tag{15}$$

$$t = \frac{T-T_0}{v} \tag{16}$$

$$k_8 = k_8^{\circ} \exp\left(-\frac{\Delta E_8}{RT}\right) \tag{17}$$

where the constant value of 1.9 in Eq. 17 is the ratio of the final weight loss of Reaction 18 to that of Reaction 3 per mol of sodium nitrite:

$$4 NaNO_2 = 2 Na_2O + 4 NO + O_2 \tag{18}$$

T, T_0, and v are the sample temperature, the temperature when the reaction starts, and the heating rate respectively. By substituting Eqs. 15, 16, and 17 into Eq. 14, Eq. 19 can be obtained:

$$y = \ln\left[-\ln\frac{3(1-1.9\alpha)}{3-1.9\alpha}\right] - \ln\frac{3(T-T_0)}{v}$$

$$= \ln k_8^{\circ} [O] - \frac{\Delta E_8}{RT} \tag{19}$$

For the reaction of sodium nitrite with silica, Reaction 5 consists of the elementary reactions of (6) and (7). Assuming the stationary state with respect to the formation rate of O^-, Eqs. 20 and 21 are obtained:

$$-\frac{d[NO_2^-]}{dt} = 2k_1[NO_2^-] \tag{20}$$

$$y = \ln\left[-\ln\frac{2(1-1.27\alpha)}{2-1.27\alpha}\right] - \ln\frac{2(T-T_0)}{v}$$

$$= \ln k_1^{\circ} - \frac{\Delta E_1}{RT} \tag{21}$$

where the constant value of 1.27 in Eq. 21 is the ratio of the final weight loss of Reaction 18 to that of Reaction 5 per mol of sodium nitrite.

Thermograms obtained for the samples heated at a constant rate of 5 °C min^{-1} are analyzed by means of Eq. 19 for the decomposition of sodium nitrite and by means of Eq. 21 for the reaction of sodium nitrite with silica. The heating rate from 1.25 to 10.0 °C min^{-1} scarcely affected the y versus T^{-1} plot.

Figures 6 and 7 show the thermograms and the DTG curves for the samples containing 0.1 mmol of sodium nitrite. The DTG curve with 1.0 in Y_{Si} has three peaks (550, 600, and 640 °C). The two peaks at lower temperatures belong to the early stage of the reaction.

Figures 8 and 9 show the y versus T^{-1} plots for the thermal decomposition of sodium nitrite and for the reaction of sodium nitrite with silica respectively. In Figs. 8 and 9, the y versus T^{-1} plots consist of two straight lines, irrespective of the coexistence of silica, and the early stage of the reaction is further divided into two reaction processes; Process I at lower temperatures and Process II at higher temperatures.

In Process I, the value of ΔE_8 for the thermal decomposition of sodium nitrite was 111 kJ mol^{-1}. The value of ΔE_1 in Process I for the reaction of sodium nitrite with silica were almost constant; their average value was 69
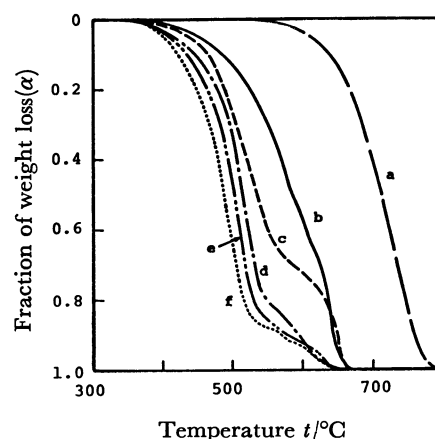

Temperature $t/$°C

Fig. 6. Thermograms in sodium nitrite–silica system at constant heating rate in argon atmosphere.
a: $Y_{Si}=0$, b: $Y_{Si}=1.0$, c: $Y_{Si}=2.0$, d: $Y_{Si}=5.0$, e: $Y_{Si}=7.5$, f: $Y_{Si}=10.0$.
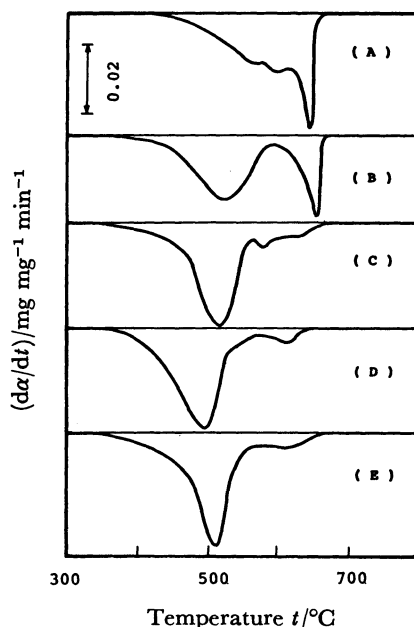
Fig. 7. DTG curves in sodium nitrite–silica system at constant heating rate in argon atmosphere.
(A): $Y_{Si}=1.0$, (B): $Y_{Si}=2.0$, (C): $Y_{Si}=5.0$, (D): $Y_{Si}=7.5$, (E): $Y_{Si}=10.0$.

Fig. 8. [$\ln(k_8{}^\circ[O])-\Delta E_8/RT$)] vs. T^{-1} plot for the thermal decomposition of sodium nitrite in argon atmosphere.
$T_0=278$ °C, $v=5.0$ °C min^{-1}. The arrow indicates the point where oxygen was detected by gas chromatography.

kJ mol^{-1} (S. D.: 8 kJ mol^{-1}), which was considerably smaller than the value of 111 kJ mol^{-1} for ΔE_8. It is clear from this result that silica acts an acid and lowers the activation energy of the formation of peroxide by stabilizing the peroxide at the solid-liquid interface on the melt and silica.

In Process II, the value of 187 kJ mol^{-1} was obtained for the activation energy of the thermal decomposition of sodium nitrite. For the system of sodium nitrite and silica, the activation energies in Process II are listed in
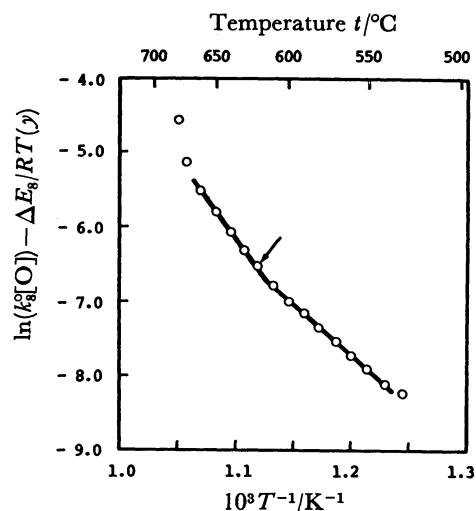
Table 2. These values depend upon the composition and tend to increase with an increase in Y_{Si} below 5.0. Above 5.0 in Y_{Si}, however, they are almost constant, and the average value is 211 kJ mol^{-1} (S. D.: 10 kJ mol^{-1}). This large value of activation energy compared to that for Process I may be caused by the formation of disilicate on the solid-liquid interface because of the existence of a considerable quantity of silica compared to that of the melt above 5.0 in Y_{Si}.

In Process II, the reactions accompanying a trace amount of O_2 generation might be caused by the increase in the amount of atomic oxygen in the melt. These
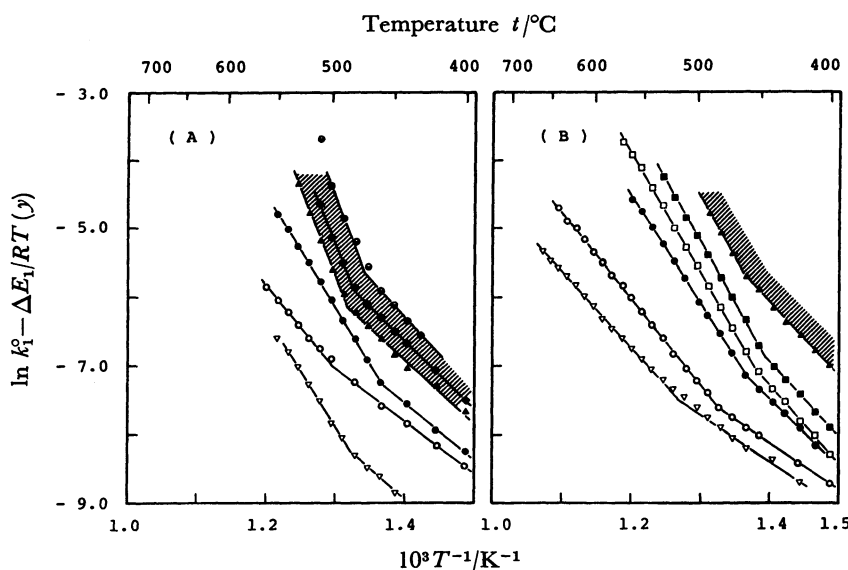

Fig. 9. [ln $k_1{}^\circ-\Delta E_1/RT$] vs. T^{-1} plots for the reaction of sodium nitrite with silica in argon atmosphere.
$T_0=278$ °C, $v=5.0$ °C min^{-1}. (A): 0.1 mmol NaNO$_2$, (B): 0.2 mmol NaNO$_2$, ∇: $Y_{Si}=0.5$, $\bigcirc$: $Y_{Si}=1.0$, $\bullet$: $Y_{Si}=2.0$, $\square$: $Y_{Si}=3.0$, $\blacksquare$: $Y_{Si}=4.0$, $\blacktriangle$: $Y_{Si}=5.0$, $\ominus$: $Y_{Si}=7.5$, $\blacklozenge$: $Y_{Si}=10.0$.
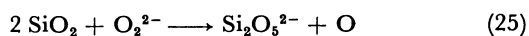Above 5.0 in Y_{Si} (Shadows), the effect of silica addition on the reaction is not evident.

TABLE 2. ACTIVATION ENERGY FOR PROCESS II
OBTAINED BY THE USE OF THE y vs. T^{-1} PLOT

Composition Y_{Si}	Apparent activation energy/kJ mol^{-1}	
	0.1 mmol NaNO$_2$	0.2 mmol NaNO$_2$
0.25	97.7	—
0.50	127	89.4
1.00	94.2	103
2.00	137	131
3.00	—	148
4.00	—	159
5.00	209	213
7.50	203	—
10.00	217	—

reactions are expressed by Eqs. 22 and 23:

$$O + O_2{}^{2-} \longrightarrow O_2 + O^{2-} \qquad (22)$$

$$O + O \longrightarrow O_2 \qquad (23)$$
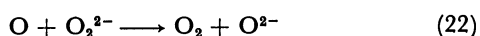
Atomic oxygen would be supplied by the following reactions:

$$NO_3{}^- \longrightarrow NO_2{}^- + O \qquad (24)$$

$$2\,SiO_2 + O_2{}^{2-} \longrightarrow Si_2O_5{}^{2-} + O \qquad (25)$$

$$Si_2O_5{}^{2-} + O_2{}^{2-} \longrightarrow 2\,SiO_3{}^{2-} + O \qquad (26)$$

$$O_2{}^{2-} \longrightarrow O^{2-} + O \qquad (8)$$

$$O_2{}^- \longrightarrow O^- + O \qquad (9)$$

Below 1.0 in Y_{Si}, the activation energy in Process II is quite close to that for the decomposition of sodium nitrite in Process I, and the rate-determining step of these processes seems to be Reaction 11. This is supported by the facts that the amount of oxygen generated

in these processes is quite small and that both processes are nitrate-formation reactions. The apparent activation energy obtained by analyzing the thermograms at 1.0 in Y_{Si} with Eq. 19 agrees with the activation energy for the decomposition of sodium nitrite in Process I better than the average value of the activation energies for the system of sodium nitrite and silica below 1.0 in Y_{Si}, 102 kJ mol^{-1}.

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