# THE INTERACTION OF NO<sub>2</sub>-N<sub>2</sub>O<sub>4</sub> AND BARIUM, SODIUM AND SILVER NITRITES\*

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Abstract—The interaction of  $NO_2-N_2O_4$  and barium nitrite, sodium nitrite, and silver nitrite respectively was followed as a function of the temperature and time of interaction. It was found that in limited ranges the nitrite ion was oxidized to the nitrate ion at approximately an exponential rate. The region of oxidation was limited by the thermal stability of the co-existing nitrite-nitrate phases. For the barium salt this was in the region of 400°C, for the silver salt  $\sim$ 300°C, and for the sodium salt some temperature in excess of 450°C.

The interaction of  $NO_2-N_2O_4$  and barium nitrite, sodium nitrite, and silver nitrite has been studied as a part of a program to elucidate the oxidation chemistry of  $NO_2$  in the presence of metallic oxides. The initiation of this study on these metallic nitrites arose as a result of the appearance of ionic nitrite in the interaction of  $NO_2$ and certain metallic oxides. It was desired to further investigate the oxidative step of nitrite ion to nitrate ion, which seemed the evident step in this type of interaction. $^{(1,2)}$ 

#### **EXPERIMENTAL**

THE sodium and silver nitrite used in this study were obtained from the Baker Chemical Company and were of reagent grade with a purity of  $\sim$ 99 per cent. The barium nitrite was obtained from the Fielding Chemical Company and had a stated purity of about 96 to 99 per cent. The nitrogen dioxide was obtained from the Matheson Chemical Company. The gas was purified by transferring it under vacuum through a magnesium perchlorate tube to the storage trap. The nitrogen dioxide was further purified by repeated fractionation until the solid condensate was snow white.<sup>(3)</sup>

The interaction of NO<sub>2</sub>-N<sub>2</sub>O<sub>4</sub> and barium, sodium and silver nitrite was studied as a function of the temperature of interaction at a pressure of 65.5 cm/Hg. The samples were reacted for an appropriate time, and the excess nitrogen dioxide removed by evacuation. During evacuation a moderate quantity of physically adsorbed nitrogen dioxide was removed. The infrared spectra of the samples were then taken in Nujol R mull. A model 221 Perkin-Elmer double-beam spectrometer was used. The samples were also analysed for total nitrogen content, only for the silver and sodium salts. A modified micro-Dumas method was used which employs a coppercopper oxide mixture in the decomposition tube.<sup>(4)</sup> In each case the samples were standardized with similar salts of known purity.

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- (2b) P. GRAY and A. D. YOTTE, Quart. Rev. IX No. 4, 367 (1955).
  (3c) E. S. FREEMAN, J. Phys. Chem., 60, 1437 (1956).
- <sup>(3)</sup> W. F. GIAQUE and J. D. KEMP, J. Chem. Phys., 6, 40 (1938).

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<sup>&</sup>lt;sup>(4a)</sup> H. H. WILLARD and H. DIEHL, Advanced Quantitative Analysis, 5th Ed. p. 338, D. Van Nostrand, N.Y. <sup>(4b)</sup> F. EMICH, Monatsh. 13, 90 (1892).

## **RESULTS-BARIUM NITRITE**

The interaction between  $NO_2-N_2O_4$  and  $Ba(NO_2)_2$  was followed as a function of the temperature of interaction in the range from 100° to 500°C. Although it was not immediately possible to obtain analytical data for the nitrogen composition, it was possible to obtain from the infra-red data a number of important features.



Ordinate: % transmission Abscissa: microns

The infra-red spectra of the reacted products are reproduced in Fig. 1. Bands which are observed at about 3.5, 6.8, and 7.3 microns are due to uncompensated Nujol. The bands observed at about 7.5, 12.0 and 12.2 microns<sup>(5)</sup> are due to ionic nitrate while bands at about 8.05, 12.1 and 12.25 microns are due to ionic nitrite.<sup>(6a)</sup> One may see that in general both nitrate and nitrite are found together simultaneously and that the presence of nitrate becomes more prominent with increasing temperatures up to about  $300^{\circ}$ C. Above this temperature the intensity for both nitrate and nitrite tends to decrease.

This is seen more clearly in Fig. 2 in which the relative amount of nitrite is plotted as a function of the temperatures of interaction, i.e.:

$$I_{\lambda 8 \cdot 05} / I_{\lambda 8 \cdot 05} + I_{\lambda 12 \cdot 2}$$
$$I_{NO_2} / I_{NO_2} + I_{NO_3}$$

or:

The relative amount of nitrite decreases with increasing temperature up to  $400^{\circ}$ C. The relative amount of nitrite then increases slightly. It should be noted that in the <sup>(5)</sup> F. VRATNY, *Appl. Spectros.* **13**, 59 (1959).

(6a) F. VRATNY, M. TSAI and F. GUGLIOTTA, Nature, Lond. 188, No. 4749, 484 (1960).



FIG. 2.-Relative amount of nitrite as a function of the temperature of interaction.



FIG. 3.—Spectra for the interaction of  $NO_2-N_2O_4$  and  $Ba(NO_2)_2$  for various lengths of time  $P_{NO_2} = 65.5$  cm/Hg at 100 and 200°C. Ordinate: % transmission Abscissa: microns

temperature region 400-500°C, barium nitrate-nitrite begins to significantly decompose. Although there is a slight increase in the relative amount of nitrite, there is a general decrease in overall nitrogen.

The interaction was followed as a function of time. It was found that above 200°C the kinetics were increasingly complicated by the associated reaction of decomposition. However, at or below 200°C it was possible to follow the transition of nitrite to

nitrate. In both cases, the oxidation proceeded at approximately an exponential rate. The spectra of the samples for this general progression may be seen in Fig. 3. It may be noted that the band at about 8.05 microns increases in intensity while the bands at 7.5 and 12.0 microns increase in intensity with time.

To reiterate, the oxidation of nitrite to nitrate proceeds at all temperatures studied at approximately an exponential rate. The oxidation process is complicated by the thermal instability of the solid phase at elevated temperatures (above 400°C) which then increases with rise in temperature.

# **RESULTS-SODIUM NITRITE**

The interaction between  $NO_2-N_2O_4$  and  $NaNO_2$  was followed as a function of the temperature of interaction. The amount of nitrogen was found to vary from about 21 per cent for interaction at room temperature to about 15.5 per cent for interaction at 400°C to 500°C. The results are shown in Fig. 4.

One may see that the nitrogen content suggests the presence of nitrite at temperatures up to about 100°C. Above this temperature oxidation of nitrite to nitrate occurs up to about 250°C. Above this temperature it is apparent that nitrogen is being lost as a result of thermal decomposition.

The spectra of the interacted samples clarify the simultaneous processes of decomposition and oxidation. The spectra of the interacted products are reproduced in Fig. 5. The bands observed at about 3.5, 6.8 and 7.3 microns are due to uncompensated Nujol mull. The bands at about 7.7 and 12.0 microns are due to ionic nitrate,<sup>(6)</sup> while the bands at about 8.0 and 12.1 microns are due to ionic nitrite.<sup>(6a,b)</sup> The occurrence of nitrate appears at the expense of nitrite. One may see that for temperatures above  $100^{\circ}$ C, nitrate coexists with the nitrite ion. Even for the lower temperatures (below  $100^{\circ}$ C) it is possible to see the appearance of a slight amount of oxidation (see the band at 7.7 microns). As the temperature increases the presence of nitrate becomes more prominent. This is further exhibited in Fig. 6, where the relative amount of nitrate in the sample is plotted as a function of the temperature of interaction, i.e.,

or:

$$I_{\lambda 12 \cdot 0}/I_{\lambda 12 \cdot 0} + I_{\lambda 12 \cdot 1}$$

$$I_{NO_{\bar{2}}}/I_{NO_{\bar{2}}}+I_{NO_{\bar{2}}}$$

A signoidal rate pattern is observed as a function of the temperature of interaction. It may be noted in this regard that at a given temperature the growth of nitrate and decay of nitrite appear to be an exponential function of the time of interaction.

It is evident that at lower temperatures, oxidation of nitrite to nitrate is a slow process. As the temperature of interaction increases the oxidation process is facilitated. Thermal decomposition accompanies oxidation at more elevated temperatures above 300°C. The slope of the curve in Fig. 6 in the temperature range of  $100^{\circ}-200^{\circ}C$  would suggest that the oxidation of nitrite to nitrate has a moderately high activation energy. However, it should be noted that in this same temperature range, the predominant specie in the gas phase is NO<sub>2</sub> and evidently is the precursor to oxidation rather than the dimer N<sub>2</sub>O<sub>4</sub>. A possible mode of oxidation may occur via the production of nitric oxide, an oxide ion, and a positive lattice defect.

$$NO_2(ADS.) \rightarrow NO + O^= + 2(\Box^+)$$

<sup>(6b)</sup> D. WILLIAMS, J. Amer. Chem. Soc. 61, 2987 (1939).



FIG. 4.—Percent nitrogen vs. the temperature of interaction of NO<sub>2</sub> and NaNO<sub>2</sub> for  $P_{NO_2} := 65.5$  cm/Hg.



FIG. 5.—Spectra of the interaction product of NO<sub>2</sub> and NaNO<sub>2</sub> for  $P_{NO_2} = 65.5$  cm/Hg and t = 17 hours at the indicated temperatures. Ordinate: % transmission Abscissa: microns



FIG. 6.—Relative nitrate as a function of the temperature of interaction  $I_{12:0}/I_{12:0} \leftarrow I_{12:1} = I_{NO_3} - I_{NO_3} - I_{NO_2} -$ 

This could be followed by oxidation and defect consumption via:

 $O^- + NO_2^- \rightarrow NO_3^- + 2(\square^-).$ 

### **RESULTS-SILVER NITRITE**

The interaction between  $NO_2-N_2O_4$  and  $AgNO_2$  was followed as a function of the temperature of interaction. The amount of nitrogen varied from about 8.6 per cent for interaction at 100°C to zero percent at 400°C. The results are shown in Fig. 7. One may see that the percentage of nitrogen would indicate a composition between  $AgNO_2$  and  $AgNO_3$  for the temperature range up to about 200°C. For higher temperatures the nitrogen content drops to that of  $AgNO_3$ , and finally drops to zero at 400°C. It is immediately evident that the solid phase— $AgNO_2$  or  $AgNO_3$  is thermally unstable above 300°C.

The spectra of the interacted samples clarify the path of interaction in the oxidation process of nitrite to nitrate. The spectra are reproduced in Fig. 8. The bands observed



FIG. 7.—Percent nitrogen as a function of the temperature of interaction.  $P_{NO_2} = 65.5 \text{ cm/Hg}, t = 17 \text{ hours}.$ 





at about 3.5, 6.8 and 7.3 microns are due to uncompensated Nujol. The bands at about 7.7 and 12.5  $\mu$  are due to ionic nitrate,<sup>(5)</sup> while the bands at 8.3 and 11.9  $\mu$  are due to silver nitrite.<sup>(6a,b)</sup> It may be seen that the presence of nitrate increases with the temperature of interaction up to 300°C. This extends somewhat the range studied by



FIG. 9.—Relative amount of nitrate as a function of the temperature of interaction.  $P_{NO_2} = 65.5 \text{ cm/Hg}, t = 17 \text{ hours.}$ ordinate:  $I_{\lambda_{12}\cdot 5}/I_{\lambda_{12}\cdot 5} + I_{\lambda_{11}\cdot 9}$ i.e.  $I_{NO_3} - I_{NO_3} - I_{NO_2} - Abscissa:$  temperature of interaction

 $Oza^{(7)}$ , while the presence of nitrite decreases up to 300°C and then makes a slight increase at 300°C. Neither nitrite nor nitrate was found in the sample which was reacted at 400°C. This point is further illustrated in Fig. 9 in which the relative amount of nitrate is plotted as a function of the temperature of interaction. The intensity of

<sup>(7)</sup> V. T. OZA, J. Ind. Chem. Soc. 35, 411 (1958).

the band at  $12.5 \mu$ , divided by the intensity sum of the bands at 11.9 and  $12.5 \mu$ , is given as a function of the temperature of interaction. It is evident that nitrate becomes more prominent up to a temperature of 200°C. The relative amount then decreases in the higher temperature region in which AgNO<sub>3</sub> becomes thermally unstable.

In the temperature region  $100^{\circ}$ -200°C it was observed that the decrease in nitrite ion or increase in nitrate ion are approximately exponential functions of time. Above 200°C the kinetics of interaction are complicated by thermal decomposition.

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