Production of *cis*-Na$_2$N$_2$O$_2$ and NaNO$_3$ by Ball Milling Na$_2$O and N$_2$O in Alkali Metal Halide Salts

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ABSTRACT: Ball milling of sodium oxides and alkali metal halide salts under a pressure of 2 atm nitrous oxide at temperatures of 38 ± 4 °C is reported. After 2.5 h of ball milling, FTIR data for both ^{14}N$_2$O and ^{15}N$_2$O additions show conclusively that *cis*-Na$_2$N$_2$O$_2$ is formed based on excellent agreement with data reported earlier by Jansen and Feldmann who prepared pure crystalline *cis*-Na$_2$N$_2$O$_2$ by reaction of sodium oxide and nitrous oxide for 2 h at 360 °C in a tube furnace. Continued ball milling under nitrous oxide leads to slow buildup of NaNO$_3$ with yields on the order of 24% achieved in 20 h. Production of nitrate only occurs during active ball milling. Studies over the first 10 h reveal a trend among potassium halide salts: KBr ≅ KCl > KI ≫ KF. Ball milling of sodium oxide alone under an atmosphere of N$_2$O gives much lower yields than ball milling in the presence of added alkali metal halide salt. Ball milling of sodium oxide and nitrous oxide in fluorocarbon oil, silicone oil, calcium fluoride, clinoptilolite, molecular sieves, and silica gel does not lead to significant yields of either *cis*-Na$_2$N$_2$O$_2$ or NaNO$_3$.

■ INTRODUCTION

Abatement of •NO, •NO$_2$, and N$_2$O from industrial exhaust gases is an important transformation, particularly for the high-volume Ostwald process which combusts ammonia to produce nitric acid.[1] The two radicals •NO and •NO$_2$ are much more reactive than N$_2$O. In the BASF DeNOx process,[2] they are reduced to dinitrogen and water, as shown in eqs 1 and 2.

$$4 \bullet NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{1}$$

$$6 \bullet NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \tag{2}$$
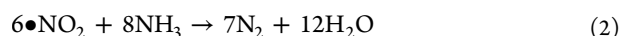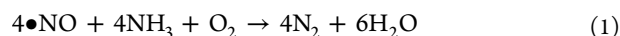
The harsh pollution arising from •NO, •NO$_2$, and their reaction products with air has been apparent for more than a century. The need to also remove waste N$_2$O has increased after it became recognized as a significant atmospheric greenhouse gas three hundred times more harmful than carbon dioxide.[3] The BASF DeNOx process destroys it by high-temperature thermal decomposition of ceria-based catalysts covered with platinum gauze,[2] as shown in eq 3.[4]

$$2N_2O \rightarrow 2N_2 + O_2 \qquad \Delta G_{298}^{0} = -52 \text{ kcal/mol} \tag{3}$$

In addition to destruction of valuable NH$_3$ in the DeNOx process, it also wastes the chemical potential present of a set of reactive species {•NO, •NO$_2$, N$_2$O} which could be further oxidized rather than reduced. Nearly a hundred years ago, Lewis and Randall[5] concluded that oxidation of dinitrogen to nitric acid had a free energy change near zero and that at ambient conditions an equilibrium solution of 0.1 M HNO$_3$ could be produced
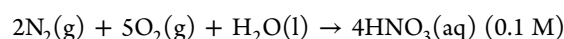
$$2N_2(g) + 5O_2(g) + H_2O(l) \rightarrow 4HNO_3(aq) \ (0.1 \ M)$$
$$\Delta G_{298}^{0} = 0 \text{ kcal/mol} \tag{4}$$

A catalytic process for eq 4 could result in elimination of the Ostwald process entirely. It presents a formidable challenge. For that reason, we have begun investigation of reactivity of nitrous oxide with metal oxides, as shown in eq 5
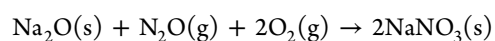
$$Na_2O(s) + N_2O(g) + 2O_2(g) \rightarrow 2NaNO_3(s)$$
$$\Delta G_{298}^{0} = -110 \text{ kcal/mol} \tag{5}$$

To the best of the authors' knowledge, direct conversion of nitrous oxide to nitrate has not been reported. A path to reaction 5 might proceed through addition of nitrous oxide to a metal oxide to form a hyponitrite complex. The reverse of this reaction has been extensively studied due to its importance in enzymatic reduction of nitric oxide.[6] There are surprisingly few reports of addition of nitrous oxide directly to a metal oxo compound to form a hyponitrite.[7] A notable exception is the report of Jansen and Feldmann[8] that N$_2$O and Na$_2$O react in a tube furnace to produce *cis*-Na$_2$N$_2$O$_2$, as shown in eq 6.

$$Na_2O(s) + N_2O(g) \rightarrow \textit{cis-}Na_2N_2O_2(s)$$

$$(360\,°C,\ 2\,h) \tag{6}$$
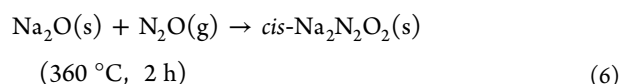
The other reported preparation[8] of *cis*-$Na_2N_2O_2$ is indirect and involves reaction of •NO with Na in liquid NH_3. The structurally characterized complex of Jansen and Feldmann was found to have greater stability than amorphous *cis*-$Na_2N_2O_2$ and began decomposition to sodium orthonitrite[9] (which may be viewed as $NaNO_2$ trapped in a matrix of Na_2O) at temperatures above 360 °C.

■ RESULTS AND DISCUSSION

The current work reports ball milling[10] studies of sodium oxide and nitrous oxide. Initial attempts at ball milling Na_2O and N_2O met with limited success. FTIR spectra recorded through air exclusion ATR measurements revealed the characteristic bands of *cis*-$Na_2N_2O_2$ in moderate yields. The very moisture sensitive nature of the mixture of unreacted sodium oxide and *cis*-$Na_2N_2O_2$ always led to slow hydration and decomposition releasing N_2O gas. Pellet spectra taken in KBr left no doubt that *cis*-$Na_2N_2O_2$ was formed, matching very closely with bands reported by Jansen and Feldmann.[8] Production of nitrate was not observed.

In attempts to increase yield, the ball milling reactions were repeated with additional reagents such as silica gel, zeolites, fluorocarbon oil, silicone oil, CaO, and CaF_2 which were added to the mixer cells. The reactions did not occur at room temperature. Heating to 80 and then 140 °C also failed to yield any detectable product. At temperatures of 140 °C, the fluorocarbon oil under these conditions was found to react with the sodium oxide forming a cross-linked polymer.[11] In all exploratory reactions, the authors have used small quantities of active ingredients and exercised prudent safety measures which are essential in the high energy ball milling of reactive materials.[12] Eventually, it was decided to mill a mixture of anhydrous KBr (1.5 g) and Na_2O (0.5 g). This resulted in a large increase in *cis*-$Na_2N_2O_2$ yield and with further milling resulting in the steady production of sodium nitrate ($NaNO_3$). Representative spectra are shown in Figure 1.
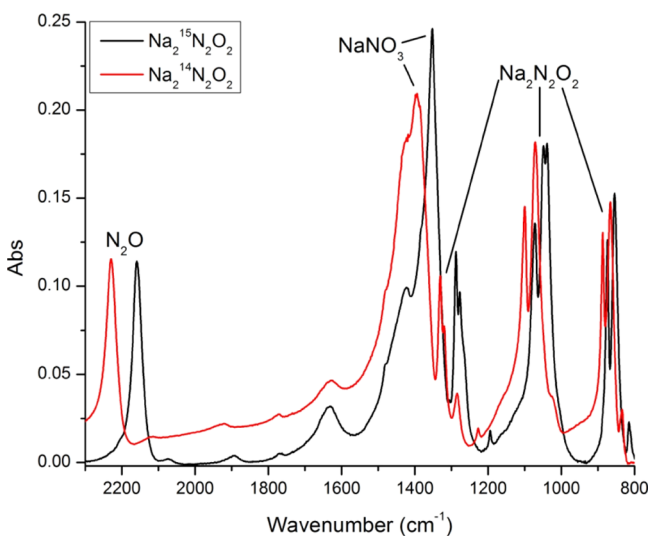
Figure 1. Comparison of FTIR data for ball milling results of Na_2O/KBr under 3 atm $^{14}N_2O$ (red) and $^{15}N_2O$ (black). The spectra shown were obtained after ≈6 h time ball milling.

Production of nitrate was proven by direct addition methods to the KBr pellet spectra and quantified by dissolution of the samples in distilled water, as discussed in Supporting Information. Ball milling of the KBr/Na_2O sample matrix under $^{15}N_2O$ resulted in isotopic shifts in excellent agreement with literature values for $Na_2N_2O_2$ and $NaNO_3$ and is summarized in Table 1.

Table 1. Tabulated Peak Assignments for Balling Milling Reactions of Na_2O and $^{14}N_2O$ or $^{15}N_2O$

| peak assignment	$Na_2^{14}N_2O_2$ (cm^{-1})	$Na_2^{15}N_2O_2$ (cm^{-1})
N_2O	2229.9	2158.4
$NaNO_3$	1384.6	1352.4
$Na_2N_2O_2$ N−O	1330.4, 1319.9	1287.9, 1277.2
$Na_2N_2O_2$ N=N	1099.8, 1071.5	1072.0, 1043.7
$Na_2N_2O_2$ N=N−O	886.8, 855.0	873.8, 854.5

See Supporting Information for additional details regarding assignments and comparison to literature data.[8] Note that in all FTIR data in KBr, it is not possible to assign the counterion. Note that this and other salts could be referred to as {Na, K}N_2O_2 but this is not done for simplicity.

FTIR spectroscopic data for the initial rate of reaction are shown in Figure 2 for Na_2O/KBr pellet spectra and for Na_2O/
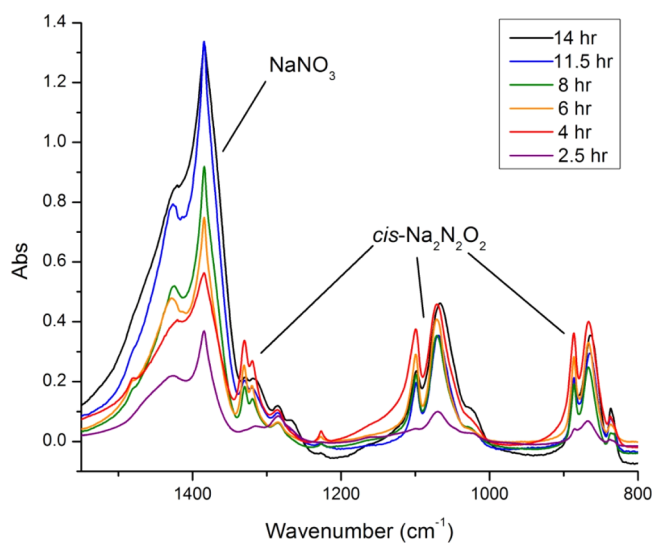
Figure 2. KBr pellet FTIR spectra as a function of time for ball milling of Na_2O (0.5 g) in KBr (1.5 g) under 30 psi, 2.0 ATM N_2O.

KCl in Supporting Information. There is a steady growth in the peak assigned to nitrate. The only source of oxygen in these reactions was nitrous oxide. The net stoichiometry of nitrate formation under these conditions corresponds to reaction 7.[13] The average temperature of 38 ± 4 °C for the reaction refers to the measured temperature of the mixing jar. It is known that local temperatures at the collision site may be considerably higher for short periods of time.[10]

$$Na_2O + 5N_2O \rightarrow 2NaNO_3 + 4N_2$$
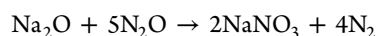
$$\Delta G_{298}{}^0 = -210\ kcal/mol \tag{7}$$

The KBr pellet data give a picture of the relative ratios of the product and how they change with time. More quantitative data were obtained by studies of hydrolysis reactions of

weighed solid samples. The initial rate of nitrate production derived from aqueous ATR spectra of hydrolyzed samples as a function of time are shown for KF, KCl, KBr, and KI in Figure 3.
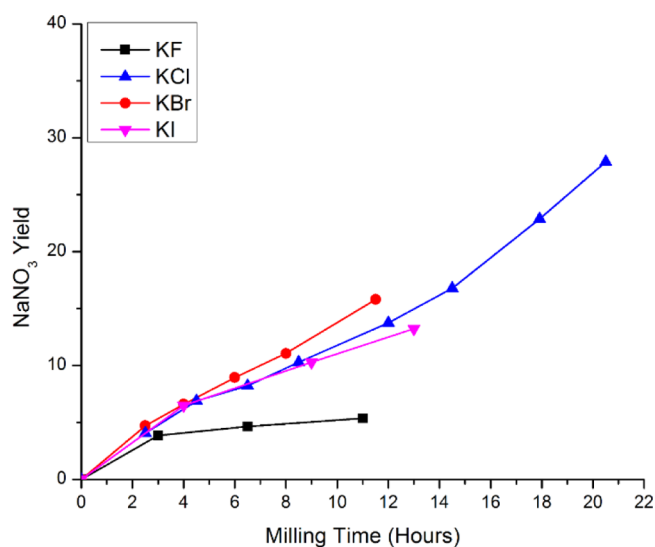

Figure 3. Initial rates of production of nitrate as a function of time (h) for KF, KBr, KCl, and KI.

The rates of reaction appear to be roughly in the order KBr ≅ KCl ≅ KI > KF. The spectra for the KF reaction also appear to show lower amounts of cis-$Na_2N_2O_2$ than the other alkali metal halides. Ball milling the reaction and then stopping it under gas pressure does not lead to continued product buildup in our experience to date. It is only under active ball milling conditions that nitrate is produced. The process of removing a sample in the glovebox results in inevitable contact with water which produces NaOH which does not react with N_2O under these conditions.

The extinction coefficient for cis-$Na_2N_2O_2$ is not known, and due to its extreme moisture sensitivity, only estimates can be made. Hydrolysis in acid solution releases all bound N_2O, including that which is encapsulated in the matrix. Bands due to encapsulated N_2O may be seen inFigure 1for both $^{14}N_2O$ and $^{15}N_2O$. It should be noted that even in the absence of added Na_2O, KBr alone under milling conditions was shown to lead to pellets with encapsulated N_2O as well. Grassian and Miller[14] have reported infrared data for surface-bound N_2O on higher valent oxides as have others.[15] As described in Supporting Information, we have briefly studied this in our system and find no evidence of detectable complex formation at room temperature on the surface of a pristine KBr pellet. Encapsulated carbon dioxide has also been detected in KBr pellets[16] and may also arise from in $situ$ chemical generation of carbon dioxide. Our results on ball milling of only KBr and N_2O and getting a small signal of encapsulated N_2O are attributed to a minor trapping which may occur as part of the ball milling procedure. A long-term study of pellets containing cis-$Na_2N_2O_2$, as discussed in Supporting Information, show that there is a parallel decrease in bands due to hyponitrite together with an increase in bands of encapsulated nitrous oxide suggesting that slow migration of trace water through the pellet matrix is responsible.

In basic solution, it is known that the cis-$Na_2N_2O_2$ rapidly loses N_2O but that the $trans$ isomer does this only in acidic

solution.[17] A study of both basic and acidic hydrolysis and the volume of N_2O evolved as detected by gas-phase FTIR studies has allowed us to piece together, as described in Supporting Information in more detail, a rough reaction profile showing the time evolution of products in this reaction. A first picture of these results is shown in Figure 4.
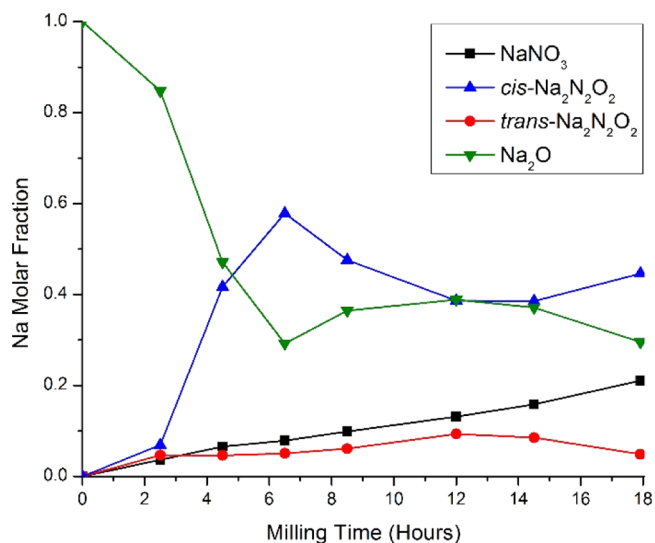
Figure 4. Mole fraction in total Na distribution for the first 20.5 h of ball milling 0.5 g Na_2O in 1.5 g KBr in standard conditions.

As shown in Figure 4, there is a slow production of $NaNO_3$ that occurs throughout the reaction. Surprisingly, the N_2O evolution studies showed that after an induction period of about 2 h, there is a fairly rapid rise in concentration of cis $Na_2N_2O_2$ to nearly 0.6 mole fraction of all distributed sodium oxide starting material. This then decreases and remains roughly constant. To our surprise, the basic hydrolysis product showed consistent low levels of $trans$-$Na_2N_2O_2$ < 0.1 mole fraction present in solution. An exact match was obtained by comparison of an authentic sample. There is no evidence in the pellet FTIR data for formation in the pellet itself of $trans$-$Na_2N_2O_2$. It is possible that this arises from the cis isomer hydrolysis but it seems more likely to the authors that it may arise from hydrolysis of an unidentified intermediate material. It should also be added that iodometric titration for the presence of peroxide in the solution shows levels less than ≈2% in these reactions. In most cases, there are no signs of significant Fe concentration in the salt matrix or corrosion of the mixing chamber. In the presence of not sufficiently dry material, the presence of moisture has led to some corrosion and detection of Fe in the salt matrix. The role of trace Fe catalysis of the oxidation cannot be excluded, but provided all materials are rigorously dry, there is no significant evidence for that.

The crude kinetic data shown in Figure 4 are also complicated due to the fact that this is not a simple reaction in solution. The apparent slow rise in the initial formation of cis-$Na_2N_2O_2$ may be due to the fact that it requires several hours to reduce the size of the salt matrix down to the micron or nanometer scale. Once the near nano-meter scale is reached and the surface area and activity are higher, the true rate of binding of N_2O to activated Na_2O may be faster than apparent. The tentative conclusion can be made at this point that formation of cis-$Na_2N_2O_2$ is faster than its oxidation. Extended

ball milling for time periods of 50 h results in yields of approximately 50 percent. Improvement of the oxidation step may serve to shorten that time and work is currently underway to study these reactions in the presence of added oxidation catalysts and oxidants. Scanning electron microscopic studies as well as computational investigation of the solids formed are in progress.[18]

In spite of a relatively slow rate of conversion and only moderate yields, this represents the first conversion of nitrous oxide to nitrate at low temperatures and pressures of N_2O. In addition, there is now more ready access to investigations of the reactivity of cis-$Na_2N_2O_2$ which may be prepared in situ at ≈ 38 °C and possibly lower temperatures. The RETSCH mm500 is equipped to study such low-temperature reactions and such work is planned. Work in progress[18] is aimed at understanding the current mechanism and designing an improved one with increased rate and product yield from the full set of gases N_2O, •NO, •NO_2, and O_2. The fact that nitrous oxide can be converted at ambient conditions to nitrate, as demonstrated in this work, makes the search for conditions to produce nitrate from dinitrogen proposed by Lewis and Randall a century ago[5] seem less impossible.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02119.

    Experimental section and reaction details (PDF)

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https://pubs.acs.org/10.1021/acsomega.1c02119

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.
At this time, a patent pending has been filed for the underlying process technology (Filed on 04/15/2021).

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(12) Caution is indicated in all ball milling experiments, particularly with a potentially powerful oxidant such as nitrous oxide. Care must be taken that no readily combustible material is available to nitrous oxide under these conditions. Examination of the cell itself following each experiment is also called for, since oxidation or nitridation may also occur, particularly under active milling conditions at higher temperatures.

(13) This is the net reaction, it is possible that N_2O converts to O_2 or a peroxide, but the ultimate source of O_2 comes from N_2O itself. Work under mixed N_2O/O_2 atmosphere is in progress.

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■ NOTE ADDED AFTER ASAP PUBLICATION

The version of this paper that was published ASAP July 8,
2021, contained minor errors in eqs 1 and 2. The corrected
version was reposted July 8, 2021.