

as to avoid any discontinuity¹⁵ in α and $d\alpha/dt$ within the range 40 to 50° where our results begin to depart from eq. 1. Table II contains our final smoothed values of d , α and $d\alpha/dt$, obtained in this manner. Both α and $d\alpha/dt$ are recorded to two more figures than are physically significant to allow exact interpolation and reproduction of our results.

TABLE III

PARAMETERS OF EQUATION 5					
Dilatometer	$A \times 10^6$	$B \times 10^9$	Dilatometer	$A \times 10^6$	$B \times 10^9$
9W	9.469	4.33	2S	9.755	3.59
2W	9.424	4.57	6S	9.714	3.92
10W	9.394	6.06	7S	9.668	4.89
6W	9.388	8.79	4S	9.668	3.01
7W	9.369	6.49	9S	9.666	5.85
5W	9.367	4.81	10S	9.606	8.13
4W	9.354	4.06	3S	9.597	4.26
8W	9.287	6.66	1S	9.596	5.08
1W	9.286	3.26	8S	9.578	5.47
3W	9.105	8.03	5S	9.564	3.97

The Expansion of Pyrex Vessels.—As a result of our measurements the volumes of the dilatometers can be represented by the equation

$$V_t = V_{25}[1 + A(t - 25) + B(t - 25)^2] \quad (5)$$

The parameters A and B , calculated from our final values of

(15) Discontinuities have sometimes been reported in density-temperature curves for pure liquids. See, for example, G. Antonoff and R. J. Conan, *Z. Naturforsch.*, **4a**, 156 (1949). The temperature intervals in the present measurements are too great to detect discontinuities if present, so continuity has been assumed as the only practical basis for estimating expansibilities from our results.

a and b (second approximation) of eq. (2), appear in Table III. In this table the dilatometers of each series are arranged in the order of decreasing values of A , the coefficient of expansion at 25°. Although the Pyrex used in constructing series W and series S was from different stock, dilatometers within a given series were made from common stock, and a particular piece of tubing served as the source of glass for two or three dilatometers. As expected, these group themselves into two's or three's with closely agreeing values of A , but it is surprising that the values of B should exhibit such wide variations between the individual dilatometers making up these groups. These differences in B point up what may be a serious weakness in the experimental method usually employed for precise measurement of the expansibilities of liquids. Customarily, the expansibility of the dilatometer is represented as a function of temperature by equating it to three times the linear coefficient of expansion of a cylindrical segment cut from the dilatometer or the tubing from which it was made. Our experience indicates that inaccuracies may result from this procedure, for Table III leaves no doubt that the act of fabrication introduces noteworthy variations into the volume coefficient of expansion. For example, among the five pairs of dilatometers, 7W-5W, 8W-1W, 7S-4S, 4S-9S and 3S-1S, the differential coefficients, $A(dV/dt)/V_{25}$, differ by only 0.02%, while the corresponding integral coefficients, $(V_{75} - V_{25})/70V_{25}$, differ by as much as 1%. This makes it probable that the discrepancies between our densities and those reported by Jones, Taylor and Vogel¹⁶ result from the use by those authors of a single parameter, $A = 9.66 \times 10^{-6}$, to describe the expansion of their two Pyrex dilatometers between 20 and 80°.

(16) G. Jones, E. F. Taylor and R. C. Vogel, *THIS JOURNAL*, **70**, 966 (1948).

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The Action of Dinitrogen Tetroxide on Hyponitrites, Nitrites and Oxides. The Induced Decomposition of Hyponitrites

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The action of dinitrogen tetroxide and nitrogen dioxide for 0.5 hr. on $\text{Ag}_2\text{N}_2\text{O}_2$, $\text{SrN}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$ and SrN_2O_2 , on AgNO_2 , $\text{Ca}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_2)_2$, approx. $\frac{1}{4}\text{H}_2\text{O}$ and on Ag_2O and CaO has been studied. The products of the reaction, both solid and gaseous, have been analyzed quantitatively. The results show that (i) the hyponitrites seem to suffer induced decomposition even at 0° according to equations (1) $\text{M}_2\text{N}_2\text{O}_2 = \text{M}_2\text{O} + \text{N}_2\text{O}$ and (2) $3\text{M}_2\text{N}_2\text{O}_2 = 2\text{M}_2\text{O} + 2\text{MNO}_2 + 2\text{N}_2$, which occur in their thermal decomposition,¹ (ii) hydrated nitrites and nitriles which decompose below 140° react and (iii) the primary product, nitrite, nitrate or both, of the action of N_2O_4 or NO_2 on oxides seems to be dependent on the nature of the oxide.

The action of dinitrogen tetroxide on hyponitrites of sodium and silver has been studied by Addison and the co-workers.² They identified in the products two oxyhyponitrites, which were oxidized ultimately to $\text{M}_2\text{N}_2\text{O}_6$; formation of $\text{M}_2\text{N}_2\text{O}_4$ and $\text{M}_2\text{N}_2\text{O}_5$ was also reported. The action of N_2O_4 and NO_2 on nitrites and oxides has been studied by many investigators. This has been reviewed by Addison and Lewis,³ who found that sodium nitrite underwent no change in contact with dinitrogen tetroxide and its thermal dissociation products up to 100°, while CaO and Na_2O_2 formed only nitrate below 124°. Ferraro and Gibson⁴

found formation of nitrates or addition compounds with oxides of Ag, Mg, Ca, Sr and Hg.

The present work was undertaken mainly to elucidate the effect of nitrogen dioxide on oxides, nitrites and hyponitrites, all of which are present in the system when the thermal decomposition of hyponitrites is studied. The complete system has been examined both before and after the reaction. The results show that (i) nitrogen of the hyponitrite molecule does not remain intact, (ii) water exercises a profound influence on the reactivity of nitrites, hydrated nitrites reacting even at 0° and silver nitrite, which is anhydrous, reacting only at 120°, (iii) in the case of CaO , which contains fixed oxygen, the primary product of the action of N_2O_4 or NO_2 is the nitrate, but in the case of Ag_2O , which has its oxygen not so firmly fixed, both ni-

(1) T. M. Oza and V. T. Oza, *J. Phys. Chem.*, **60**, 192 (1956).

(2) C. C. Addison, G. A. Gamlen and R. Thompson, *J. Chem. Soc.*, 346 (1952).

(3) C. C. Addison and J. Lewis, *ibid.*, 1874 (1953).

(4) J. R. Ferraro and G. Gibson, *THIS JOURNAL*, **75**, 5747 (1953).

trate and nitrite (and silver) seem to be the primary products. In either case nitric oxide is formed, but the amount of nitric oxide is almost half that of N_2O_4 consumed in the case of CaO and negligibly small in the case of Ag_2O .

Experimental

Materials.—Silver hyponitrite and strontium hyponitrite were the same pure materials reported earlier.^{5,6} Silver nitrite, dinitrogen tetroxide and silver oxide were the same as those used by Oza, Oza and Thaker.⁷ Calcium nitrite was prepared as follows (*vide* Oza and Dipali⁸; *cf.* Addison and Lewis⁹): $AgNO_2$ equivalent to 10 ml. of 1 *N* $CaCl_2$ was dissolved in ammonia (1:1), 10 ml. of 1 *N* $CaCl_2$ added, the mixture heated on a water-bath and filtered. The filtrate was boiled to expel ammonia, cooled, tested for absence of Ag^+ and Cl^- and evaporated on a water-bath to a sirupy consistency and then kept in an H_2SO_4 desiccator; crystals of $Ca(NO_2)_2 \cdot H_2O$ were obtained on the third day. These were washed with alcohol and dried with ether. Calcd. for $Ca(NO_2)_2 \cdot H_2O$: Ca, 26.66; NO_2 , 61.33. Found: Ca, 26.62; NO_2 , 61.35. Partial dehydration to $Ca(NO_2)_2$ approx. $\frac{1}{4}H_2O$ was effected as in Oza and Oza⁹ in the apparatus itself just before treatment with N_2O_4 . Calcium oxide was an ignited specimen of the pure substance; it contained 71.86% Ca (calcd. for CaO: Ca, 71.45).

The apparatus and procedure were essentially the same as in Oza, Oza and Thaker,⁷ with the difference that the 2-way tap b was replaced by a 3-way tap to facilitate admission of water into the system when required. To start an experiment, P_2O_5 in C was replaced by KOH-lye, which was placed also in D and E. The apparatus was evacuated, b closed, p surrounded by an intimate freezing mixture of ice and salt for 0.5 hr. and B, which contained a weighed quantity of the hyponitrite, nitrite or oxide, surrounded by a bath at the temperature of the experiment for 1 hr. The N_2O_4 tube was then broken and the released gas congealed in p. The tap b was then carefully opened partially, and N_2O_4 brought into contact with the substance in B or T; in the experiment at 0°, the N_2O_4 invariably was liquefied and wetted the whole of the substance in B (or T). At the end of the half hour, the gases present in the system were exposed to KOH in C, D. The tap C' was not opened until the system became colorless, then the unabsorbed gas was pumped off through KOH in E. Air was then introduced into the system by breaking the seal under A and the alkali solutions in C, D, E diluted to known volume for analysis. Fresh KOH-lye was then placed in C, A closed, the apparatus evacuated and B heated to 70–80° for 15 minutes to expel N_2O_4 or NO_2 adsorbed, if any, on the residue in B. The residue was then treated with water for analysis.

In the case of silver hyponitrite the residue at 130° showed a characteristic effervescence as observed previously by Addison and co-workers.² This effervescence was similar to that shown by the residue of the decomposed sodium hyponitrite on being treated with water. To be sure that this was not due to escape of any gas, P_2O_5 was placed in C and fresh KOH in E, the system evacuated and about 1 ml. of water admitted on to the residue. After allowing the water to be absorbed out by P_2O_5 , C was opened, but neither was the vacuum of the pump affected nor did the KOH solution show tests for nitrite or nitrate.

Results

The pumped gas was found to contain nitrous oxide and nitrogen. Oxygen was found absent. Nitrous oxide was absorbed out in cold alcohol. The alkali solution was analyzed for nitrite and for nitrate; the nitrite equivalent of nitrate found was subtracted from the nitrite found and the difference calculated to N_2O_3 according to the equation $2KOH + N_2O_3 = 2KNO_2 + H_2O$. N_2O_4 was calculated from nitrate found according to the equation

$2KOH + N_2O_4 = KNO_3 + KNO_2 + H_2O$. The residues, which in the case of hyponitrites and nitrites were not alkaline, were treated with water. For $Ag_2N_2O_2$ three solutions, A, B, C, were made as described by Oza and Thaker⁵ and analyzed in the same way for nitrite, nitrate (A) and for silver ion (A, B and C). Ag^+ found in A was completely accounted for by nitrite and nitrate, thus confirming the absence of free Ag_2O . In the case of strontium hyponitrite, the solution was examined for nitrite and nitrate after decomposing the residual hyponitrite by boiling; it is known¹⁰ that no nitrite or nitrate are formed on boiling the solution. The strontium in the hyponitrite taken less the total strontium in nitrate and nitrite found gave the strontium present as hyponitrite in the residue.

The results are given in Tables I, II and III. The most outstanding feature of the data of Table I is the indication of the presence of nitrous oxide and nitrogen in the gas. Other noteworthy features are as follows: (i) in the case of SrN_2O_2 the extent of the reaction is the greatest at 0°, while in the case of $Ag_2N_2O_2$ this is practically constant between 0 and 100° and increases thereafter; the silver salt produces nitrate (large) and nitrite; the hydrated strontium salt produces nitrate alone and the anhydrous strontium salt produces, like the silver salt, both nitrite and nitrate at 30° but only nitrate at 0°; (ii) the anhydrous strontium salt does not show the presence of nitrous oxide at 0°; (iii) nitric oxide is produced with all the three hyponitrites; (iv) the ratio of the mass of the product to the mass of $Ag_2N_2O_2$ taken is constant, the value (1.16) being somewhat less than that of Addison (1.20, 1.22). The important features of Table II are (i) $AgNO_2$ does not react up to 85° but reacts at 120° (9%) and more at 130° (15%); $Ca(NO_2)_2 \cdot H_2O$ shows considerable reaction but $Ca(NO_2)_2 \cdot \frac{1}{4}H_2O$ shows only slight reaction at 0°; at 130° the reaction with $Ca(NO_2)_2 \cdot H_2O$ diminishes (probably due to loss of water); nitric oxide is formed and its amount roughly equals that of N_2O_4 consumed. Table III shows that (i) the action is slow at 0°; Ag_2O forms almost equivalent amounts of nitrate and nitrite (and silver), the nitrate being always in small excess; CaO forms nitrate alone; the action increases with temperature and CaO forms nitrite alone at 140° when the reaction is about twenty times as great as at 30°; (ii) nitric oxide is formed with both the oxides, but while its amounts are almost half of those of N_2O_4 consumed in the case of CaO, these are triflingly small in the case of Ag_2O .

Discussion

The most outstanding observation of the present work is the formation of nitrous oxide and nitrogen in the action of dinitrogen tetroxide on the hyponitrites. The formation of these products cannot take place directly from N_2O_4 under the conditions of these experiments and must originate from the hyponitrites. In most of the experiments of this work the reactants were in contact with each other for 0.5 hr. only and the gas pumped thereafter through KOH-lye, before treating the residue with water, was found to contain the gaseous products identified. It is interesting to observe that there is

(5) T. M. Oza and R. H. Thaker, *THIS JOURNAL*, **77**, 4976 (1955).

(6) T. M. Oza and S. A. Patel, *J. Ind. Chem. Soc.*, **31**, 523 (1954).

(7) T. M. Oza, V. T. Oza and R. H. Thaker, *J. Chem. Soc.*, 2457 (1955).

(8) T. M. Oza and N. L. Dipali, *J. Ind. Chem. Soc.*, **27**, 290 (1950).

(9) T. M. Oza and V. T. Oza, *ibid.*, **32**, 596 (1955).

(10) T. M. Oza, V. T. Oza and N. L. Dipali, *ibid.*, **28**, 15 (1951).

TABLE I
 ACTION OF N_2O_4 AND NO_2 ON $Ag_2N_2O_2$, $SrN_2O_2 \cdot 5H_2O$ AND SrN_2O_2

Temp., °C.	Mass of substance taken (mmole)	Mass of N_2O_4 taken (mmole)	Mass of sub. consumed (mmole)	Nitrate formed (mmole)	Nitrite formed (mmole)	Metal formed (mmole)	N_2O_4 consumed (mmole)	N_2O_3 formed (mmole)	N_2 formed (mmole)	N_2O formed (mmole)
Substance: $Ag_2N_2O_2$										
0	0.3626	4.0650	0.2900	0.4400	0.1450	nil	0.583	0.3428	0.2455	0.0134
30	.4166	4.6560	.2900	.5300	.0500	nil	.6560	.4143	.2050	.0189
100	.3833	2.9330	.2900	.4700	.1200	nil	.5990	.5250	.1473	.0047
130	.4000	2.5800	.3800	.5900	.1200	0.0370	.7000	.4420	.2456	.02355
150	.3876	3.1330	.3900	.6200	.1100	0.0480	.5890	.3974	.2277	.0141
*0	.4094	4.1290	.2880	.4300	.1500	nil	.5580	.3482	.2545	.0141
*0	.3659	3.8190	.2970	.4400	.1500	nil	.4710	.3527	.2456	.0141
*130	.3949	2.6080	.3770	.5870	.1190	0.0300	.6780	.4287	.2233	.0094
Substance: $SrN_2O_2 \cdot 5H_2O$										
0	0.4797	3.4660	0.4800	0.4800	nil	nil	1.3910	0.8303	0.1428	0.5391
30	.4418	2.2660	.3700	.3700	nil	nil	1.0880	.6563	.1384	.3108
130	.4498	2.8590	.3300	.2400	0.0626	nil	0.5020	.1929	.1339	.2025
170	.4553	2.0750	.2300	.1500	0.0870	nil	0.3750	.0835	.0893	.2826
Substance: SrN_2O_2										
0	0.4539	2.7380	0.1460	0.1480	nil	nil	0.2740	0.1774	0.0938	...
170	0.4986	1.2380	0.1420	0.0820	0.0590	nil	0.1710	0.1554	0.1250	0.0565

 TABLE II
 Action of N_2O_4 and NO_2 on $AgNO_2$, $Ca(NO_2)_2 \cdot H_2O$ and $Ca(NO_2)_2 \cdot$ approx. $1/4H_2O$

Temp., °C.	Mass of substance taken (mmole)	Mass of N_2O_4 taken (mmole)	Mass of sub. consumed (mmole)	Nitrate formed (mmole)	Metal formed (mmole)	N_2O_4 consumed (mmole)	N_2O_3 formed (mmole)	NO (free) formed (mmole)
Substance: $AgNO_2$								
0	1.6420	7.986	nil	nil	nil	nil	nil	nil
30	1.5840	3.129	nil	nil	nil	nil	nil	nil
85	1.5770	2.370	nil	nil	nil	nil	nil	nil
120	0.6558	2.390	0.0560	0.0560	nil	0.06473	0.07142	nil
120 ^a	0.7909	1.728	0.1390	0.1380	nil	0.3000	0.2901	nil
130	1.7270	1.609	0.2630	0.2130	0.0400	0.3678	0.3937	nil
Substance: $Ca(NO_2)_2 \cdot H_2O$								
0	1.5860	4.1451	1.0700	1.100	nil	1.9190	1.5440	0.3660
30	1.9860	2.2670	1.3700	1.3700	nil	2.2670	1.8610	0.4241
150	1.4460	1.7090	0.5900	0.6100	nil	1.7100	1.5750	0.1205
Substance: $Ca(NO_2)_2 \cdot$ approx. $1/4H_2O$								
0	0.6981	3.4030	0.01700	0.0150	nil	0.0103	0.0098	nil
30	0.6857	2.4010	0.06750	0.0670	nil	0.1115	0.1071	nil
140	0.6820	2.6250	0.08700	0.08700	nil	0.2084	0.2071	nil
Substance: $Sr(NO_2)_2 \cdot H_2O$								
0	1.5250	3.4530	1.4300	1.4300	nil	2.7160	2.6420	...

^a This experiment was run for 1 hr.

 TABLE III
 Action of N_2O_4 and NO_2 on Ag_2O and on CaO

Temp., °C.	Mass of substance taken (mmole)	Mass of N_2O_4 taken (mmole)	Mass of sub. consumed (mmole)	Nitrate formed (mmole)	Nitrite formed (mmole)	Metal formed (mmole)	N_2O_4 consumed (mmole)	N_2O_3 formed (mmole)
Substance: Ag_2O								
0	0.4956	4.0580	0.0280	0.0200	0.0186	nil	0.01785	0.00536
0	.5301	4.1420	.0170	.0200	.0186	nil	.01785	.00536
30	.4870	3.1110	.0550	.0500	.0490	0.0010	.05355	.01110
110	.4482	2.8170	.1250	.0770	.0730	0.100	.07857	.0067
130	.4602	3.5000	.1300	.0840	.0800
130	1.1330	3.0440	.8900	.4300	.4000	0.9000	.4187	.0111
Substance: CaO								
0	1.8400	2.7070	0.0060	0.0060	nil	nil	0.02008	0.0103
30 ^a	1.8000	3.3270	0.0250	0.0250	nil	nil	0.03303	0.0134
140	1.8740	2.3340	0.4900	0.4200	0.0750	nil	1.0890	0.5312

^a This experiment was run for 2 hr.; no reaction could be observed in 0.5 hr.

no increase in the extent of the reaction up to 100° and that with SrN₂O₂ the extent actually diminishes with rise of temperature.

Experiments marked with an asterisk in Table I were done to determine whether a loose complex of the kind Ag₂N₂O₂·N₂O₄ was formed in the reaction. The product of the reaction at 0° was weighed, replaced in the system, the latter evacuated and then heated to 50° at first and to 100° next and the product was again weighed; the weight was found to remain unaltered. No gas was formed in the system or absorbed by KOH to form nitrite or nitrate. The ratio of the weight of the product to the weight of Ag₂N₂O₂ taken was found to be 1.16. The Ag₂N₂O₂ showed some change of color on being treated with N₂O₄ but became grey when treated with water. In the last of these experiments the product was treated with water without prior weighing to avoid exposure to air, but even then no gas was liberated and no change detected. It therefore appears that the evidence of Addison, based on the value of the ratio for the formation of peroxy acids of nitrogen, envisioned first by Angeli and Angellica¹¹ is not supported by the observations of the present work. We believe that they would not have drawn such a conclusion had they examined the whole system and found the presence of nitrous oxide and nitrogen, for they argue that "the number of nitrogen atoms does not change during the reaction."

As the relative amounts of nitrous oxide formed in the case of silver hyponitrite and strontium hyponitrite undergoing thermal decomposition^{5,12,13} are similar to those appearing in the present case and as the formation of these products must occur from the hyponitrites alone under the conditions of these experiments, it appears rational to argue that dinitrogen tetroxide and nitrogen dioxide exercise some sort of physical influence on the hyponitrites, inducing their decomposition. The thermal decomposition of hyponitrites has been shown to occur as (I) M₂N₂O₂ = M₂O + N₂O and (II) 3M₂N₂O₂ = 2M₂O + 2MNO₂ + 2N₂. Lack of appearance of oxide in the products and appearance of nitrate can be ascribed to secondary reactions of the oxide and nitrite formed in (I) and (II) with N₂O₄ and NO₂.

The nature of dinitrogen tetroxide has been considered, among others, by Addison.¹⁴ In the liquid state it consists of NO₂⁺·NO₂⁻. It is known that nitric oxide is usually a product of the reaction of dinitrogen tetroxide or nitrogen dioxide. It is also known that nitrate is formed when N₂O₄ or NO₂ acts on oxides.⁴ In the action of dinitrogen tetroxide or nitrogen dioxide on nitrites there seems to be no finality of views.³ N₂O₃ has been observed in the products in all the experiments of this work wherein reaction has occurred. The amounts of N₂O₃ in the reaction with CaO are almost half those of N₂O₄ consumed as required by the over-all reaction (i) M₂O + 2N₂O₄ = 2MNO₃ + N₂O₃.

(11) Angeli and Angellica, *Gazz. chim. ital.*, **30**, 593 (1900).

(12) J. R. Partington and C. C. Shah, *J. Chem. Soc.*, 2589 (1932).

(13) T. M. Oza and V. T. Oza, *ibid.*, 909 (1953).

(14) C. C. Addison and R. Thompson, *ibid.*, 5215 (1949), and following papers.

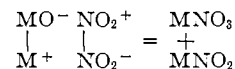
The peculiarities observed in the reaction with Ag₂O can be explained by the character of Ag₂O as compared with CaO; the oxygen in the former is much less firmly bound. Silver metal is also liberated. That N₂O₃ is formed, though in small amounts, in the case of Ag₂O too, shows that the ultimate mechanism of the reaction is probably the same and that in the case of Ag₂O further action probably ensues as (ii) Ag₂O + N₂O₃ = 2AgNO₂.

The above reactions occurring with the products of induced decomposition of silver hyponitrite should lead to over-all appearance of more nitrite than nitrate in the products, while actually the converse is found to be the case. This can happen only if a part of the nitrite formed underwent oxidation to nitrate. Our results (Table II) show that in the case of silver nitrite no reaction occurs at 85° and that at 120°, 9% of the nitrite is oxidized to nitrate in 0.5 hr. The action is therefore capable of taking place. The possibility that further action between AgNO₂ and N₂O₄ or NO₂ has occurred is indicated by the presence of N₂O₃ in the gas. The over-all effect of N₂O₄ on Ag₂N₂O₂ is given by the equation 3Ag₂N₂O₂ + 2N₂O₄ = 2AgNO₃ + 4AgNO₂ + 2N₂, which requires (i) N₂/Ag₂N₂O₂ = 0.66, as (roughly) found and (ii) AgNO₃/Ag₂N₂O₂ = 2.0 if all nitrite was oxidized to nitrate. Actually all nitrite is not oxidized, as expected, and the value found is 1.5 and the ratio of the total of nitrite and nitrate to hyponitrite is approximately 2.0.

In view of the work of the present authors on the nitrites,^{7,13} it does not seem unreasonable to conclude that the reactivity of nitrite with nitrogen dioxide or dinitrogen tetroxide may depend on the nature of the nitrite. Hydrated nitrites are found to react; the anhydrous nitrites decomposing at or below 140° may also seem to react because a product of their decomposition, the oxide, reacts. Silver nitrite is found to dissociate at 128°⁷ and is reported to decompose even earlier.¹⁵ It is found in this work to actually react at 120°; the finer state of division and the activated state of the substance at the instant of its formation might impart greater reactivity.

The absence of N₂O in the case of anhydrous strontium hyponitrite may be ascribed to the absence of the particular resonance form of the molecule.¹

The facts of this work (Tables II and III) show that the over-all reaction of N₂O₄ with nitrites is MNO₂ + N₂O₄ = MNO₃ + N₂O₃ and that with oxides may be M₂O + N₂O₄ = MNO₃ + MNO₂ or MO + 2N₂O₄ = M(NO₃)₂ + N₂O₃. Oxides of the type M₂O may react as



forming equivalent amounts of nitrite and nitrate. H₂O will form HNO₃ alone as HNO₂ decomposes. Oxides of the type MO will not react in this way and will form N₂O₃ as found.

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(15) Randall, Manov and Brown, *This Journal*, **60**, 694 (1938).