385. *The Liquid Dinitrogen Tetroxide Solvent System. Part XIV.* Reactions of Sodium, Calcium, and Zinc Oxides with Dinitrogen Tetroxide and its Thermal Dissociation Products.*

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The following reactions have been studied: (*a*) The reactions of calcium and zinc oxides, and of sodium peroxide, with liquid dinitrogen tetroxide; the metal nitrate is the only salt produced in each reaction, and nitrites are not formed as intermediates. (*b*) The reaction of the three oxides with nitrogen dioxide gas at temperatures up to 140° and for various periods of contact; the products are the same as with the liquid tetroxide. (*c*) Corresponding reactions at temperatures above 140° are more rapid, and produce nitrite as well as nitrate. The quantity of nitrite decreases with increase in temperature; at constant temperature the quantity of nitrate increases, at the expense of nitrite, with duration of contact. (*d*) The effects observed in (*c*) have been explained on the basis of the ready reaction between the oxides and nitric oxide to produce nitrites, and by the oxidation of these to nitrates, which occurs in the high-temperature range only.

These experiments were initiated in order to determine the conditions under which metal oxides react with dinitrogen tetroxide, since oxides have been postulated (Part VIII, *J.*, 1951, 2833) as intermediates in the metal–dinitrogen tetroxide reaction mechanism which predominates at higher temperatures. It was soon established that reaction does occur to give products in agreement with the postulated mechanism. However, much of the evidence in the literature on reactions between metal oxides and dinitrogen tetroxide is contradictory, especially where the thermal dissociation products of the tetroxide are not taken into account. A detailed investigation has therefore been carried out into these reactions.

Calcium oxide has been stated to give a mixture of nitrate and nitrite with nitrogen dioxide gas at room temperature (Oswald, *Ann. Chim.*, 1914, **1**, 44), at 180° (Partington and Williams, *J.*, 1924, **125**, 947), and over the temperature range 15—300° (Briner,

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* Part XIII, preceding paper.

Lugrin, and Monnier, *Helv. Chim. Acta*, 1930, **13**, 64). Anhydrous uranium oxides give uranyl nitrate on reaction with nitrogen dioxide for some hours at 90° under 14 atm. pressure (Gibson and Katz, *J. Amer. Chem. Soc.*, 1951, **73**, 5437). Reaction between barium oxide and nitrogen dioxide (Dulong, *Ann. Chim. Phys.*, 1816, **2**, 317) was found to give a mixture of nitrate and nitrite. Muller (*Annalen*, 1862, **122**, 1) states that oxides react to give nitrate uncontaminated with nitrite, whereas Briner *et al.* (*loc. cit.*) claim that oxides give nitrite as well as nitrate in liquid dinitrogen tetroxide.

The experiments described below leave no doubt that, in these reactions, nitrite does not occur in the product so long as the N_2O_4 and NO_2 molecules are the only species present, and is only formed at temperatures where the dissociation $NO_2 \longrightarrow NO + \frac{1}{2}O_2$ is appreciable; the nitrite does not therefore result from primary attack by nitrogen dioxide. Harcourt (*J.*, 1861, 267) found the oxides of the alkali metals to react with nitric oxide to give the nitrites. Reactions of liquid dinitrogen tetroxide may therefore be compared with reactions in the gaseous state provided that the latter are carried out at temperatures not exceeding about 140°. The upper temperature limit at which reactions have been studied is determined by the decomposition temperature of the products; some relevant values are given below:

Compound	$Zn(NO_3)_2$	$Ca(NO_3)_2$	$Ca(NO_2)_2$	$NaNO_3$	$NaNO_2$
Decomposition detectable at	160°	450°	230°	380°	320°
Decomposition rapid at	240	500	360	—	—

Lack of correlation with decomposition temperatures is responsible for apparently contradictory reports on reaction products; *e.g.*, Gmelin (see Mellor, "Treatise, etc.," Vol. II, p. 486) claimed that sodium burns in nitrogen dioxide to give sodium monoxide, whereas Holt and Sims (*J.*, 1894, **65**, 432) found the product to be a mixture of nitrite and nitrate.

Reactions with Liquid Dinitrogen Tetroxide.—(a) *Calcium oxide.* On addition of the liquid, no apparent reaction occurred. After about 10 hours' contact at a temperature near the boiling point (21·3°), the liquid had become brown. On evaporation, the free-flowing powder remaining was pale green, owing to adsorbed dinitrogen tetroxide. The last traces of adsorbed tetroxide were difficult to remove; in these experiments the powder was heated at 100° for 24 hours, the colour reverting to white but change in weight being negligible. The product was then analysed (*a*) by ultra-violet spectrophotometer, and (*b*) by use of Devarda's alloy for total nitrogen content, and potassium permanganate to detect nitrite. In no case was nitrite found in the product; the reaction may be represented as $CaO + 2N_2O_4 = Ca(NO_3)_2 + N_2O_3$ (see Table 1).

TABLE 1. *Reaction of calcium oxide with liquid dinitrogen tetroxide.*

Expt. No.	1	2	3	4	5	6	7
Period of contact (hours)	16	16	30	40	40	44	44
% Conversion of oxide into nitrate...	22·4	27·4	35·1	44·0	44·4	23·0	54·0

In all experiments (except No. 6) it was necessary to replenish the dinitrogen tetroxide at intervals of about 8 hours. In Expt. 6 the liquid was kept at +10° and no replenishment was necessary. The smaller degree of conversion into nitrate in this case indicates that the reaction is temperature-dependent, although not to the extent suggested by the values in Table 1, since the addition of fresh tetroxide in the other experiments agitates the solid and may expose fresh oxide surfaces to attack by the tetroxide. The incomplete conversion of oxide into nitrate even on long contact is attributed to the cohesive nature of the calcium nitrate formed as a coating round each oxide particle. The rate of reaction of calcium metal with dinitrogen tetroxide diminishes rapidly for the same reason. It appears that the physical nature of those nitrates (*e.g.*, calcium and sodium) which do not form complex salts with dinitrogen tetroxide differs from those nitrates (*e.g.*, zinc) which form such complexes. The former are sufficiently cohesive to decrease (and even inhibit) reaction, whereas the latter have little cohesive character.

In the reactions of calcium metal and of calcium oxide, no intermediate formation of nitrite can occur, since calcium nitrite is stable in liquid dinitrogen tetroxide. A sample immersed in the tetroxide at 20° for 7 days was recovered.

(b) *Zinc oxide.* Dry zinc oxide reacted on contact with liquid dinitrogen tetroxide; nitric oxide was evolved and the colour of the liquid changed through brown to green within a few minutes. The reaction continued for some hours at a slower rate, and may be represented as $ZnO + 4N_2O_4 = Zn(NO_3)_2,2N_2O_4 + N_2O_3$. At 20°, reaction is about 80% complete after 10 hours, and about 95% after 20 hours.

(c) *Sodium peroxide.* When sodium peroxide was added to liquid dinitrogen tetroxide, no discoloration of the liquid took place, even on long standing. The product was found to contain nitrate, but no trace of nitrite. The sodium peroxide used contained small amounts of carbonate and hydroxide as impurities. A separate study of the reaction of these compounds with liquid dinitrogen tetroxide showed that these impurities involve no complication of the sodium peroxide reaction, since sodium nitrate is the only salt produced. The extent of reaction of sodium peroxide at 20° for periods of contact up to 48 hours did not exceed 20%. The reaction is $Na_2O_2 + 2NO_2 = 2NaNO_3$.

Reactions with Gaseous Nitrogen Dioxide and its Dissociation Products.—(a) *Sodium peroxide.* Experimental results are given in Table 2. Below 140° reaction was slow, but the rate of conversion into nitrate increased with increasing temperature. Above 140°, reaction became more rapid and the results in Table 2 show three pronounced effects: (1) appreciable quantities of nitrite are produced above 140°: (2) at a constant temperature above 140°, the quantity of nitrite produced decreases (and the nitrate increases) with time; (3) the quantity of nitrite produced decreases with increase in temperature.

TABLE 2. *Reaction of sodium peroxide with gaseous nitrogen dioxide.*

Temp.	Period of contact (hours)	Conversion, %: into nitrate	into nitrite	Temp.	Period of contact (hours)	Conversion, %: into nitrate	into nitrite
40°	12	7·1	0·0	190°	1·5	49·0	33·5
100	6	12·5	0·0	200	1·75	53·3	27·3
134	44	28·4	0·0	200	2·75	81·5	10·2
170	5	22·7	23·9	250	5	77·8	7·2

Since nitrite is first produced at the temperature at which nitrogen dioxide dissociates into nitric oxide and oxygen, nitrite production may be attributed to the presence of nitric oxide (Table 3). In the range 100—140° there was no visible change in the appearance of the solid. Above 150° reaction was rapid; the solid fused in the gas stream and resolidified as the formation of nitrite carried the composition of the mixture past the sodium peroxide–sodium nitrite eutectic. The reaction may be represented as $Na_2O_2 + 2NO = 2NaNO_2$, and the small amount of nitrate in the product is attributed to oxidation of nitrite by peroxide in the liquid melt. An important observation in these experiments is the considerable increase in rate and extent of reaction which takes place at about 140°: the fact that this takes place at the same temperature as that at which nitrogen dioxide dissociates may not be entirely coincidental, although there appears to be no physical property of the nitric oxide molecule which undergoes change at about this temperature. Again, the general behaviour of sodium peroxide in other systems does not show evidence of sharp changes in reactivity at this temperature. The appearance of nitrite in the reaction product above 140° (col. 4, Table 2) may be attributed to the dissociation of nitrogen dioxide at this temperature, but the large amounts of nitrite observed are due to the high rate of this reaction, which begins at the same temperature.

TABLE 3. *Reaction of sodium peroxide with nitric oxide.*

Temp.	Period of contact (hours)	Conversion, %: into nitrate	into nitrite	Temp.	Period of contact (hours)	Conversion, %: into nitrate	into nitrite
120°	1	0·0	3·5	200°	2	4·0	77·5
150	1	2·3	69·0	210	1	5·0	66·7

The decrease in nitrite content with time at a constant temperature above 140° (Table 2) is explained satisfactorily by the oxidation of nitrite to nitrate at these temperatures by nitrogen dioxide (Table 4). In order to determine the mechanism of this high-temperature oxidation, the reactions of sodium nitrite with nitric oxide and with oxygen were examined. Oxygen was found to have no effect upon sodium nitrite over periods of 7 hours at 150°, and 9 hours at 270°. Nitric oxide did not react with sodium nitrite at temperatures between 150° and 270° for periods up to 5 hours. The oxidising powers of nitrogen dioxide are not therefore due to nitric oxide or oxygen molecules produced by dissociation. Since the reaction is so largely dependent upon temperature, it may be considered to arise from oxidation by atomic oxygen produced by impact at the solid surface of NO_2 molecules possessing the necessary thermal energy, thus: $NO_2 \longrightarrow NO + O$, followed by $NaNO_2 + O \longrightarrow NaNO_3$. Katz and Gruen (*J. Amer. Chem. Soc.*, 1949, **71**, 2106) suggest that atomic oxygen is the active species in the oxidation of the oxides U_3O_8 and UO_2 to UO_3 by nitrogen dioxide at 250—300°.

TABLE 4. *Reaction of sodium nitrite with nitrogen dioxide.*

Temp.	Period of contact (hours)	$NaNO_2$, %, oxidised to $NaNO_3$	Temp.	Period of contact (hours)	$NaNO_2$, %, oxidised to $NaNO_3$
100°	7	0·0	170°	3·25	17·0
122	43	5·4	200	3	49·5
150	4	2·9	250	9	57·0
160	3	10·8	260	6	23·7

(b) *Calcium oxide.* Experimental results are given in Table 5. The trace of nitrite sometimes observed below 140° is probably due to adsorbed nitrogen dioxide. In these experiments a stream of nitrogen dioxide was passed over the calcium oxide, so the nitric oxide produced was removed continually from the system. In Briner, Lugrin, and Monnier's experiments (*loc. cit.*) the nitric oxide produced was retained in the system by the use of sealed tubes, and appreciable nitrite formation was observed. The experimental conditions are clearly important here, since we could not detect reaction between calcium oxide and nitric oxide below 140° at atmospheric pressure even in 3 hours.

TABLE 5. *Reaction of calcium oxide with nitrogen dioxide.*

		Conversion, %				Conversion, %	
Temp.	Period of contact (hours)	into nitrate	into nitrite	Temp.	Period of contact (hours)	into nitrate	into nitrite
124°	24	5·9	0·0	200°	1·5	39·3	7·4
124	45	8·3	0·2	230	1·5	44·0	3·0
134	24	9·0	0·4	260	1·5	52·3	1·2
134	46	19·3	0·2	260	4·25	54·2	0·6
170	3·25	35·7	10·3				

Above 140°, absorption of nitrogen dioxide by calcium oxide was relatively rapid, with the production of nitrite as well as nitrate, but the quantity of nitrite produced was much less than in the case of sodium peroxide. The nitrite content decreased with time and with increasing temperature; this is readily explained by the oxidation of calcium nitrite to nitrate by nitrogen dioxide, which Partington and Williams (*loc. cit.*) have found to occur slowly at 180° but rapidly at 280°. The low nitrite contents of the product will also be due partly to the fact that calcium oxide reacts only slightly with nitric oxide; the nitrite produced in this reaction is small compared with that produced by sodium peroxide (Table 3). The nitrite values given for experiments above 150° (Table 5) are minimum values, and the quantity of nitrite produced originally in the reaction will exceed these values. The concentration of nitric oxide in the gas stream in these experiments was much less than that employed in the calcium oxide–nitric oxide experiments, so over this higher temperature range the formation of nitrite cannot be attributed (as in the case of sodium peroxide) entirely to the presence of nitric oxide in the gas stream. The ready reaction of nitric oxide with peroxides suggests an additional process for the production of calcium nitrite; atomic oxygen formed by decomposition of nitrogen dioxide at high temperatures may oxidise calcium oxide to calcium peroxide, which then reacts directly with nitric oxide, *i.e.*, $CaO + O \longrightarrow CaO_2$, followed by $CaO_2 + 2NO \longrightarrow Ca(NO_2)_2$.

(c) *Zinc oxide.* Zinc oxide reacts readily with nitrogen dioxide. Below 100° the product was a viscous liquid identical with that produced on warming the complex $Zn(NO_3)_2,2N_2O_4$. When this was heated in a current of dry air at 100°, nitrogen dioxide was evolved, leaving a mixture of zinc oxide and zinc nitrate. Reactions carried out above 100° gave a product free from combined nitrogen dioxide. In these reactions it was essential to remove all nitrogen dioxide from the atmosphere before allowing the temperature of the reaction mixture to fall below 100°, as the dioxide was rapidly absorbed by the zinc nitrate present. Over the available temperature range the reaction $ZnO + 3NO_2 = Zn(NO_3)_2 + NO$ is not greatly temperature-dependent, and is about 70% complete after 8 hours at 160°.

EXPERIMENTAL

Metal Oxide–Gas Reactions.—The solid reactant was contained in a silica boat, which was placed in a 25 cm. × 2·5 cm. Pyrex-glass combustion tube. The tube terminated in B19 ground joints, and was closed by a 2-way glass tap on the inlet end, and a straight tap on the outlet. For reaction temperatures below 140°, the combustion tube was contained in an electrically-controlled thermostatic oven. For higher temperatures the combustion tube was passed through a hole (1—2 mm. clearance) in a heated aluminium block, 15 × 10 × 10 cm. Two thermometers were placed in holes drilled to the centre of the block. The combustion tube was guarded by phosphoric oxide traps at each end. The solid was weighed in the pre-weighed boat enclosed in a stoppered weighing tube, then transferred directly to the combustion tube. Transfers were carried out in a dry-box. For reactions involving nitrogen dioxide, the combustion tube was evacuated, closed, and connected to a vessel containing liquid dinitrogen tetroxide. It was then heated to the required temperature, opened, and a steady current of nitrogen dioxide drawn over the boat. The stream of gas could be controlled more readily by application of a slight vacuum than by warming the liquid tetroxide. The tube was then closed at the inlet, evacuated, and allowed to cool. Dry air was admitted to the combustion tube, and the boat and contents were immediately transferred to a stoppered weighing tube. For reactions involving nitric oxide, the oxygen was removed from the apparatus by successively passing in dry nitrogen, and evacuating the vessel. The nitric oxide was passed through the combustion tube in a stream of dry nitrogen.

Materials. Calcium and zinc oxides were dried immediately before use by heating them at 600° for 1 hour, and cooling them in a vacuum desiccator. The zinc oxide was of A.R. quality; the calcium oxide was prepared by heating A.R. calcium carbonate in a silica boat at 1000° to constant weight.

The peroxide content of A.R. sodium peroxide was determined by hydrolysis in cold boric acid solution, and titration with potassium permanganate. A sample of the peroxide was hydrolysed, the hydrogen peroxide decomposed by boiling the solution in a flask fitted with a Bunsen valve, and the alkalinity determined by titration before and after precipitation of the carbonate. The sample used contained 6·2% of sodium carbonate and 0·7% of sodium hydroxide.

Anhydrous calcium nitrite was prepared as follows. About 1 g. of freshly precipitated silver nitrite was added to a suspension of a slight excess of calcium oxide in boiling water. The silver oxide was filtered off, and excess of calcium ions removed from the solution by treatment with carbon dioxide and boiling. The liquid was concentrated, and finally evaporated in a vacuum desiccator. On prolonged standing the yellowish-white hydrate of calcium nitrite was obtained. This was crushed and heated at 160° to remove water of crystallisation (Partington and Williams, *loc. cit.*); ultra-violet spectrophotometric analysis showed the product to be at least 97% pure.

Nitric oxide was prepared by reaction of 4N-sulphuric acid and solid sodium nitrite (Part IX, *J.*, **1951**, 2838). The nitrogen dioxide was removed from the gas stream by passage through towers packed with activated alumina and with sodium hydroxide pellets, and the nitric oxide finally dried (P_2O_5).

Analysis of products. (a) ZnO–N_2O_4 Reaction. On warming, the product evolved dinitrogen tetroxide, giving a yellow viscous liquid which changed (after 3 hours' heating at 100°) into a white crystalline powder. This powder was partly soluble in water; the insoluble portion was identified as zinc oxide, and the solution contained zinc nitrate free from nitrite. Analysis of the powder gave Zn, 36·1; NO_3^-, 63·2% (Calc. for conversion of 92% of zinc oxide into zinc nitrate: Zn, 36·15; NO_3^-, 63·1%). Analysis of the original product (Part IX, *loc. cit.*) gave Zn, 19·1; NO_2^-, 24·0% [Calc. for 89·1% conversion of zinc oxide into $Zn(NO_3)_2,2N_2O_4$: Zn, 19·1; NO_2^-, 24·05%].

(b) Na_2O_2–NO_2 Reactions above 140°, and Na_2O_2–NO reactions. These reactions are considered together, since both give rise to solid products which are mixtures of sodium peroxide, nitrite, and nitrate. The product was hydrolysed in water, and hydrogen peroxide decomposed by boiling the solution. The solution was then analysed for nitrate and nitrite content by ultra-violet spectrograph. Removal of hydrogen peroxide was essential since it absorbs strongly in the range 280—370 mμ. For accurate analysis of the nitrite content it was therefore necessary to confirm the stability of the nitrite ion in alkaline solution of hydrogen peroxide. A mixture of known quantities of sodium peroxide and sodium nitrite (with the latter about 5% of the mixture) was therefore dissolved in water, and the ultra-violet absorption spectrum of the solution determined immediately. In separate portions of the solution the hydrogen peroxide was then decomposed (i) by boiling the solution and (ii) by keeping it for a week. In each case the absorption spectrum of the resulting solution confirmed that there was no change in its nitrite content.

In all the above reactions the increase in weight of the solid was determined accurately, and was found to correspond to the nitrate and nitrite produced in the reaction. This excludes the possibility of the formation of salts of other nitrogen oxy-acids.

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