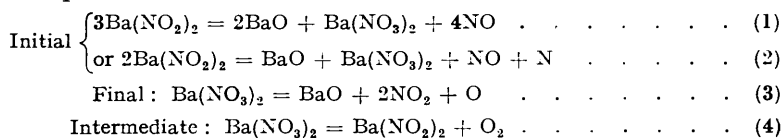## 187. The Thermal Decomposition of Calcium Nitrite.

By Trambaklal Mohanlal Oza and Vasantrai Trambaklal Oza.

This work has shown that two of the four reactions involved in the decomposition of nitrites are reversible. With progress of the decomposition, more nitrate is formed and progressively larger amounts of it decompose to produce NO_2. This oxide, in the system already containing NO, represses the equilibrium, $MNO_2 \rightleftarrows M_2O + NO_2 + NO$, explaining the tendency of the system to come to a standstill. Absence of nitrogen, in spite of the high temperature, is explained by (i) the reversible nature of the reaction, $MNO_2 + NO_2 \rightleftarrows MNO_3 + NO$ and (ii) the relative instability of nitrate in the atmosphere of nitric oxide.

THE action of heat on nitrites was studied by Ray (*J.*, 1905, **87**, 177). For barium nitrite, he represented the decomposition as :

$$\text{Initial} \begin{cases} 3Ba(NO_2)_2 = 2BaO + Ba(NO_3)_2 + 4NO & \quad . \quad . \quad . \quad . \quad . \quad . \quad (1) \\ \text{or } 2Ba(NO_2)_2 = BaO + Ba(NO_3)_2 + NO + N & \quad . \quad . \quad . \quad . \quad (2) \end{cases}$$

$$\text{Final}: Ba(NO_3)_2 = BaO + 2NO_2 + O \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\text{Intermediate}: Ba(NO_3)_2 = Ba(NO_2)_2 + O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

He noted that the calcium and the magnesium salt gave but little nitrogen, whereas the barium and the sodium salt gave considerable amounts. For magnesium nitrite, Ray and Ganguli (Ray, *loc. cit.*) found equivalent amounts of oxide and nitrite and 12—13% of nitrogen and accordingly regarded (2) as the primary process. Oza and Dipali (*J. Indian Chem. Soc.*, 1950, **27**, 305) showed that the gas never contained more than 3% of nitrogen and that the residue underwent well-defined changes during the decomposition and tended ultimately to attain the composition required by (1), but that reaction was complicated. Oza and his co-workers (Oza and Shah. *J. Univ. Bombay*, 1942, **11**, 70; Oza, *J. Indian Chem. Soc.*, 1945, **22**, 173; Oza and Walawalker, *ibid.*, p. 243) showed that the initial reaction is
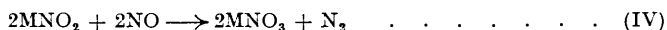
$$2MNO_2 \rightleftarrows M_2O + NO + NO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$
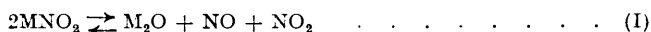
and more nitric oxide is then produced by the reaction

$$MNO_2 + NO_2 \longrightarrow MNO_3 + NO \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$
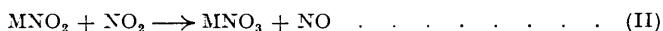
The nitrogen dioxide, produced in (I), reacts further :

$$M_2O + 2NO_2 \longrightarrow MNO_3 + MNO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (III)$$
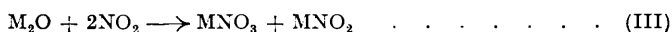
the last two reactions accounting for the preponderance of nitric oxide over the dioxide in the gas. The nitrogen-producing reaction has been shown to be

$$2MNO_2 + 2NO \longrightarrow 2MNO_3 + N_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (IV)$$

(cf. Oza and Shah, *loc. cit.*; Ostwald, *Annalen*, 1914, **403**, 32). Ray regarded the calcium and the magnesium salt as similar with regard to production of nitrogen, in spite of the fact that the respective decomposition temperatures are 400° and <150°. Sodium and potassium nitrite produced much more nitrogen at about 400°, as found by Oza (and also Ray).

The results of the present work on the decomposition of weighed amounts of calcium nitrite, *in vacuo*, show that the salt resembles magnesium nitrite. The work has also shown why calcium nitrite does not yield larger quantities of nitrogen in spite of higher temperature by tracing the distinctive behaviour to the reversible nature of reaction (II) (*Brit. Abs.*, 1942, I, 245), since the nitrate is unstable in the presence of nitric oxide (Divers, *J.*, 1871, **24**, 85).

Experimental

Calcium nitrite was prepared according to Oza and Dipali (*loc. cit.*, p. 290) [Found : Ca (as $CaSO_4$), 26·7; NO_2' (by $KMnO_4$ titration), 61·3. Calc. for $Ca(NO_2)_2, H_2O$: Ca, 26·7; NO_2', 61·3%].

Analyses. The gas always contained nitric oxide in excess. Hence, N_2O_3 (*i.e.*, NO_2) was assayed by determining nitrite in the alkali in bulb *B* (see below); the remaining gas contained the excess of nitric oxide and the nitrogen, and the former was absorbed in alkaline sodium sulphite solution. All volumes recorded are corrected to N.T.P. The residue was dissolved in boiled-out, hot, distilled water and calcium oxide was determined immediately by standard succinic acid solution. Nitrite was determined by standard permanganate in excess, addition of excess of tetroxalate, and back-titration. Nitrate was calculated by difference.

Apparatus and Procedure.—The all-glass apparatus (see Fig.) contained weighed $Ca(NO_2)_2,H_2O$ in a platinum crucible at *A*, connected to Sprengel and Hyvac pumps through ground-in glass joints, *J,J'*, and to bulb *B* through the internal seal *D*. The bulb contained

1—2 c.c. of saturated potassium hydroxide solution. The evacuated system was kept overnight before each experiment to test the vacuum, and the Sprengel pump then applied for $\frac{1}{2}$ hour. Heating was done electrically in a vertical furnace of nichrome wire, and temperature controlled by resistance mats to within 5—7°. Temperature was measured by a nitrogen-filled thermometer, the bulb of which was kept near the decomposing mass. Up to 350°, the rate of decomposition was slow and quick adjustment of temperature was necessary only above this.
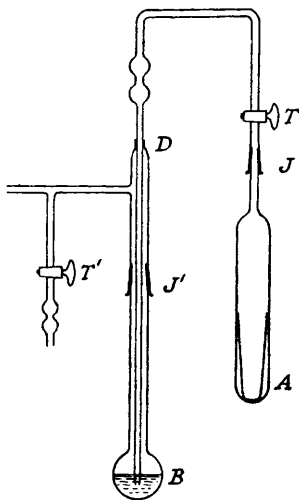
Bubbles (not affecting the vacuum, and presumably of water vapour) were formed in the bulb *B* at 100° but disappeared at 160°. At 240°, they again appeared and affected the vacuum.

In all experiments from 370° to 480°, N_2O_4, NO, N_2, CaO, $Ca(NO_2)_2$, and $Ca(NO_3)_2$ were present at the end. The table shows the results of 23 experiments: the first five were performed with a fixed weight of nitrite heated for 50 minutes at the temperatures stated, and the next five with a fixed weight at 420° for the periods stated. These ten experiments show that: (i) The amount of nitrogen is very small at 390°, and at higher temperatures does not exceed 3%; the proportion of NO_2 is high at the start, but the amount does not increase in proportion to the total gas; NO is the main gas (80%). (ii) The proportion of CaO is at first low (cf. magnesium nitrite) but increases later, while that of nitrate is higher at first and decreases later. (iii) The decomposition is most rapid in the first $1\frac{1}{2}$ hours, and later tends towards a limit. (iv) The proportion of nitrogen at first increases slowly with time, but later diminishes (Expts. 9 and 10) with decrease of nitrite in the residue.

In both these sets of experiments, CaO is low and $Ca(NO_3)_2$ relatively high at the start: this is a new observation and the explanation follows from the results of Expts. 11—14, in which nitrite is heated at 370° so that reaction is very slow and secondary reactions are least. The extent of decomposition in Expt. 14 is the same as that in Expt. 6 so that Expts. 11, 12, and 13 show the transitional residues: the proportion of oxide increases but that of nitrate diminishes slowly under these conditions. Expts. 15—19 show the results of heating various weights of nitrite at 360° for 50 minutes. Increase in weight accelerates the decomposition but retards production of nitrogen (cf. Expts. 4, 7, 8).

The observation that nitrogen production is low even at 480° contrasts with the corresponding observation with sodium and potassium nitrite. To determine the effect of time on production of nitrogen, Expts. 20—23 were performed. The nitrite was heated for about $\frac{1}{2}$ hour to produce nitric oxide, containing 2—3% of nitrogen, and the temperature lowered to 360° and kept thereat for 6 hours. Expts. 21, 22, and 23 yielded an unusually large proportion of nitrogen. Again, in Expt. 20, but little nitrogen was formed and the ratio in the last column is that usually found for experiments with magnesium nitrite. This shows that the ultimate residue is of the same type as in the latter salt. The cause of this may lie in both the increased relative stability (at the lower temperature) of calcium nitrate and the prevailing low pressure of nitric oxide in the system. In Expts. 21—23, in which the formation of nitrogen reached 6—8%, the ratios are 2 : 1 : 1.

The fact that the proportion of nitrogen increases with increase in the period of contact of nitric oxide over fused nitrite is significant, for it shows that temperature, by itself, is ineffective in producing nitrogen, but that the nature of the nitrite is important as it affects the stability of the nitrate in the atmosphere of nitric oxide. The experiments also show that nitrogen is produced by a heterogeneous reaction between the nitric oxide and the fused salt. The nitric

Results.

Expt. no.	Ca(NO$_2$)$_2$, H$_2$O, mg.*	Temp.	Gas evolved, c.c.	Composition, % :			Residue (mg.) :			Ca(NO$_2$)$_2$, decomp., mg.	Ratio (approx.) †
				NO$_2$	NO	N$_2$	Ca(NO$_2$)$_2$	Ca(NO$_3$)$_2$	CaO		
1	253·0	390°	5·2	21·1	78·8	0·1	193·0	25·2	3·9	29·5	3 : 2 : 1·1
2	255·0	410	6·4	10·9	87·5	1·6	191·4	28·7	42·0	33·0	3 : 2·1 : 0·7
3	250·0	430	—	—	—	—	165·0	40·6	9·5	40·6	3 : 1·7 : 1·2
4	256·7	450	15·8	13·9	83·5	2·7	146·8	57·2	14·0	79·1	3 : 1·7 : 1·2
5	251·0	480	29·0	8·3	88·6	3·1	62·7	105·5	31·1	158·2	3 : 1·6 : 1·4
		Time (hr.)									
6	251·2	½	6·6	17·9	80·3	1·8	178·1	36·9	5·6	42·9	3 : 2·1 : 0·9
7	254·0	1½	14·5	16·5	81·3	2·2	169·0	39·0	9·8	54·5	3 : 1·7 : 1·2
8	251·0	2	15·3	12·4	84·3	3·3	139·0	55·8	15·7	81·9	3 : 1·6 : 1·3
9	250·0	4	22·9	8·0	89·9	2·1	89·1	87·6	25·8	130·9	3 : 1·5 : 1·2
10	250·0	8	28·3	8·1	90·1	1·8	47·2	112·2	35·0	172·8	3 : 1·5 : 1·4
11	,,	1	1·4	7·1	92·8	0·1	190·0	33·2	1·4	30·0	3 : 2·7 : 0·33
12	,,	2	2·8	10·7	89·3	—	188·7	31·5	2·6	31·3	3 : 2·4 : 0·57
13	,,	4	4·1	9·9	90·0	0·1	179·8	37·6	4·2	40·2	3 : 2·3 : 0·74
14	,,	6	5·6	8·9	89·3	1·8	172·6	42·5	5·6	47·4	3 : 2·1 : 0·84
15	120·0	—	0·7	14·3	85·7	—	99·0	6·2	0·7	6·6	3 : 2·2 : 0·75
16	366·5	—	2·1	9·5	90·5	—	295·3	27·6	2·1	27·2	3 : 2·4 : 0·55
17	496·8	—	2·65	1·8	96·2	2·0	391·0	41·8	5·3	46·2	3 : 2·2 : 0·9
18	754·5	—	6·8	7·3	91·2	1·5	615·4	36·9	9·0	48·6	3 : 2·1 : 1·2
19	902·0	—	12·6	4·0	94·4	1·6	719·4	51·4	14·0	74·4	3 : 1·7 : 1·3
20	250·6	—	6·6	19·7	80·3	—	200·3	9·3	5·4	20·2	3 : 1 : 2
21	502·7	—	22·5	5·8	88·0	6·2	297·0	92·1	30·2	145·4	2 : 1 : 1
22	458·5	—	29·2	3·4	89·0	7·6	237·6	107·7	34·7	165·9	2 : 1 : 1
23	507·6	—	34·1	4·1	88·5	7·4	232·6	146·8	40·6	213·9	2 : 1 : 1

* The anhydrous salt is 88% of the monohydrate.
† This ratio is NO$_2$' used : NO$_3$' : oxide.

oxide induces the reaction, $MNO_3 + NO \longrightarrow MNO_2 + NO_2$, or the earlier decomposition, $2MNO_3 \longrightarrow 2MNO_2 + O_2$ (Divers, *loc. cit.*), thus disappearing from the system and arresting the reaction (IV) : diminution of nitrate with progress of the decomposition has been noticed in this work. The reaction (II) is thus reversible. This is under further investigation.

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