188. *The Thermal Decomposition of Calcium Hyponitrite Tetrahydrate.*

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Calcium hyponitrate tetrahydrate is found to behave, in its decomposition by heat, like the sodium salt pentahydrate, but small differences are ascribed to (i) undetachable H_2O in the former and the readily detachable H_2O in the latter; (ii) the instability of $Ca(NO_2)_2$ and relatively great stability of $NaNO_2$, formed in the decomposition. Further, it has been found possible to decompose $CaN_2O_2,4H_2O$, which ordinarily decomposes *in vacuo* at 330°, at as low a temperature as 125—140°, and the products of the decomposition at the two temperatures are similar. The results are discussed.

PURE alkaline-earth hyponitrites were decomposed, and equations assigned, by Partington and Shah (*J.*, 1932, 2589). Divers (*J.*, 1899, **75**, 117); *Proc. Roy. Soc.*, 1871, **19**, 425; *Chem. News*, 1871, **23**, 206), Ray and Ganguli (*J.*, 1907, **91**, 1399, 1866) and others (Kirschner, *Z. anorg. Chem.*, 1898, **16**, 424; Thum, *Monatsh.*, 1893, **14**, 294; *Sitzungsber. Akad. Wien*, 1893, **102**, 284; Partington and Shah, *J.*, 1931, 2071) studied the decomposition of hyponitrites and of hyponitrous acid. The reactions were found to be complex, and different products were formed by different hyponitrites : *e.g.*, the sodium salt decomposed according to $3Na_2N_2O_2 = 2Na_2O + 2NaNO_2 + 2N_2$ (1); the lead and the copper salt

$MN_2O_2 = MO + N_2O$ (2), and the calcium, barium, and strontium according to (2) and also $5MN_2O_2 = M(NO_3)_2 + 4MO + 4N_2$ (3) and $2MN_2O_2 = 2MO + 2NO + N_2$ (4).

In the present investigation, weighed quantities of sodium and calcium hyponitrites were decomposed under various conditions, and the products examined quantitatively. The two salts behave similarly except for differences due to (1) the more stable H_2O molecules in the calcium salt and (2) the instability of calcium nitrite at the decomposition temperature. Further, the calcium salt decomposes even at 125°, and the proportion of the decomposition products then formed is different from that at higher temperatures.

EXPERIMENTAL

Calcium hyponitrite was prepared by double decomposition (Partington and Shah, *loc. cit.*, 1932) (Found: Ca, 23·3; N, 16·0. Calc. for $CaN_2O_2,4H_2O$; Ca, 23·3; N, 16·3%). It could not be dehydrated without decomposition.

Analyses.—(i) The gas contained traces of N_2O_4 and appreciable amounts of NO, N_2O, and N_2: the dinitrogen tetroxide was indicated by slight trailing of mercury in the Sprengel pump in *all* experiments. Nitric oxide was absorbed in alkaline sodium sulphite saturated with nitrous oxide, and the latter then determined by absorption in cold alcohol, the absorbent being freely replaced and the gas stored over it for 2 hours after contraction had ceased. The residual gas was nitrogen. Recorded volumes are all corrected to N.T.P. (ii) The solid residue was kept under vacuum until it dissolved; it contained oxide, nitrite, nitrate, and only traces of hyponitrite (in some experiments). Calcium oxide was titrated with standard succinic acid immediately after dissolution, the solution having been boiled to decompose traces of hyponitrite (Oza, Oza, and Dipali, *J. Indian Chem. Soc.*, 1950, **27**, 305); nitrite was estimated as described in the preceding paper. Nitrate was calculated if required.

Apparatus and Procedure.—These were the same as described in the preceding paper. The bulb under the internal seal contained phosphoric oxide when anhydrous conditions were desired.

Table 1 gives results of decomposition of (i) two different masses at a constant temperature (Expts. 1 and 2), (ii) the same mass at two different temperatures (300°, 360°). They show that CaO, $Ca(NO_2)_2$, N_2O, NO, and N_2 are present in all the experiments and their proportions vary with both mass and temperature and that, in general, increase in mass and lowering of temperature produce similar effects. In Table 2 are given results of two experiments in which the gaseous products were pumped off as quickly as possible by keeping the system under vacuum. The three sets, collectively, show normal features (Table 1) but in both Expts. 5 and 6 the first stage is different from the third and the second is of transitional type. The residue contains more CaO as N_2O increases, whereas NO and N_2 run parallel. The experiments also show that N_2 and NO are formed in larger proportions in the initial stages.

In these experiments a tendency for decomposition to occur at lower temperatures was noted, and this had not hitherto been reported. In Expt. 7 the temperature was kept at 100° for a time and then for 15 minutes at every step of 25° above. Some gas was liberated at 150° and more again between 175° and 200°. Complete decomposition occurred only at 340—360°. The analyses show all the gaseous components to be present at each stage, but the proportion of NO and N_2 is low at low temperatures and large at higher ones, and the contrary is the case with N_2O.

Partington and Shah (*loc. cit.*, 1931) found sodium hyponitrite to decompose quantitatively according to (1). Oza (*J. Indian Chem. Soc.*, 1944, **21**, 75) found traces of nitric oxide and ascribed them to secondary decomposition of the nitrite formed as above. Partington and Shah did not find appreciable calcium nitrite in the decomposition of the hyponitrite. Calcium nitrite is more unstable at 350° than the sodium salt and is likely to give more NO. In Expt. 8, $Ca(NO_2)_2,H_2O$ was added to the hyponitrite, and the mixture decomposed: the gas formed at 330° contained an increased proportion of nitric oxide. Hence the hyponitrite seems to decompose like the sodium salt to produce nitrite as intermediate unstable product.

The formation of nitrous oxide from calcium hyponitrite may be formulated as in (2) and no such reaction seems to occur with sodium hyponitrite. It is, however, known that $Na_2N_2O_2,5H_2O$ produces N_2O if suddenly decomposed in vacuum. The latter salt is known to become dehydrated readily in a vacuum, and the dehydration will be quicker at high temperatures; but $CaN_2O_2,4H_2O$ is not dehydrated. In Table 3 are given results of sudden decomposition, at 330° in a vacuum, in a platinum crucible, of weighed amounts of $Na_2N_2O_2$

TABLE 1. *Effect of* (*i*) *mass* (*Expts.* 1, 1*a*, and 2) *and temperature* (*Expts.* 3 *and* 4) *on the decomposition of* $CaN_2O_2,4H_2O$.

			Gas evolved, c.c.				Gas : compn. %				Residue, mg.	
Expt. no.	Mass, mg.*	Temp.	Total	NO	N_2O	N_2	NO	N_2O	N_2	Ratio, $N_2O : N_2$	CaO	$Ca(NO_2)_2$
1	53·8	320°	5·9	0·7	3·2	2·0	11·3	55·5	33·3	62·5 : 37·5	10	1·65
	(312)										(180)	(12·5)
1*a*	101·4	,,	13·2	2·0	7·5	3·7	14·7	56·7	28·3	66·5 : 33·5	22	2·5
	(588)										(396)	(18·8)
2	202·0	,,	25·1	3·5	14·8	6·8	13·7	59·1	27·1	68·5 : 31·4	61·6	0·5
	(1170)										(1068)	—
3	151·6	300	19·2	1·7	12·5	5·0	9·0	65·2	26·1	71·5 : 28·5	45·2	1·82
	(879)										(831)	(13·8)
4	144·5	350—360	18·9	2·7	10·2	6·0	14·3	54·0	31·8	63·0 : 37·0	33·6	0·9
	(840)										(600)	—

* Numbers in parentheses show μg.-mols.

TABLE 2. *Decomposition of different amounts of* $CaN_2O_2,4H_2O$, *at a constant temperature* (320—330°), *the evolved gas being collected in three successive portions.*

		Vol. (c.c.) (1)				Vol. (c.c.) (2)				Vol. (c.c.) (3)				Totals (c.c.)				Residue, g. :	
Expt. no.	Wt., g.	Total	NO	N_2O	N_2	Total	NO	N_2O	N_2	Total	NO	N_2O	N_2	Total	NO	N_2O	N_2	CaO	$Ca(NO_2)_2$
5	0·1999	5·2	0·9	2·6	1·7	5·4	0·7	3·0	1·7	16·6	1·5	11·1	4·0	27·2	3·1	16·7	7·4	0·0532	0·0099
			17·3	50·0	32·7		13·0	55·5	31·5		9·0	66·8	24·2		11·5	61·0	27·4		
6	0·2570	14·4	2·4	7·8	4·2	9·2	0·65	6·45	2·1	12·1	0·8	8·3	2·9	35·7	3·85	22·5	9·2	0·0851	0·00495
			16·6	54·1	29·2		7·0	70·0	23·0		6·8	68·6	23·5		10·8	63·3	25·5		

* Numbers in the second line in each case show percentage of the gas in the mixture.

Expt. No. 7. *Decomposition of the same* $CaN_2O_2,4H_2O$ (0·1000 g.) *first at* 125—140°, *then at* 175—200°, *and lastly at* 340—360°.

Composition (c.c.) * of gas released at :																	
125—140°				175—200°				340—360°				Totals (c.c.) :				Residue, g.	
Total	NO	N_2O	N_2	Total	NO	N_2O	N_2	Total	NO	N_2O	N_2	Total	NO	N_2O	N_2	CaO	$Ca(NO_2)_2$
1·6	0·2	1·0	0·4	8·1	0·5	6·0	1·6	2·8	0·85	1·0	0·9	12·5	1·55	8·0	2·9	0·0266	0·0099
	12·5	62·5	25·0		6·1	74·0	19·9		30·3	35·7	31·1		12·4	64·0	23·2		

Expt. No. 8. *Decomposition at* 330° *of* $CaN_2O_2,4H_2O$ *after admixture with* 25% *of* $Ca(NO_2)_2,H_2O$.

Mass, g.		Composition (c.c.) * of gas released				Residue, g.	
$CaN_2O_2,4H_2O$	$Ca(NO_2)_2,H_2O$	Total	NO	N_2O	N_2	CaO	$Ca(NO_2)_2$
0·1236	0·0300	16·7	3·3	9·0	4·4	0·035	0·02145
			19·8	53·9	26·3		

* Numbers in the second line in each case give the percentage composition.

TABLE 3. *Decomposition, on a platinum surface of* (i) $Na_2N_2O_2$ *and* (ii) $Na_2N_2O_2,5H_2O$ *at about* 330°.

Expt. no.	Substance	Mass, g.*	Gas evolved (c.c.)			Residue, g. : *	
			Total	N_2	N_2O	Na_2O	$NaNO_3$
9	$Na_2N_2O_2$	0·1048 (0·99)	11·2	11·2	0·00	0·03534 (0·55)	0·03807 (0·54)
10	,,	0·1330 (1·25)	17·3	17·3	0·00	0·04774 (0·77)	—
11	$Na_2N_2O_2,5H_2O$	0·1250 (0·64)	10·9	9·75	1·15	0·0279 (0·45)	0·03145 (0·46)
12	,,	0·2060 (1·05)	18·2	15·8	2·4	0·04585 (0·74)	0·04933 (0·72)

* Numbers in parentheses are in mg.-mols.

TABLE 4. *Decomposition of* $CaN_2O_2,4H_2O$ *after initial heating at different temperatures for various periods over* P_2O_5 *in evacuated system.*

Expt. no.	Mass, g.‡	Temp.*	P †	Remarks	Gas evolved (c.c.) in successive portions §				Totals (c.c.) §				Residue, g. : ‡	
					Total	NO	N_2O	N_2	Total	NO	N_2O	N_2	CaO	$Ca(NO_2)_2$
13	0·1000 (0·58)	90—100°	6	No decomp. Decomp. occurred at 260° on rise of temp. after the 6 days, gas = 11·7 c.c.	—	—	—	—	11·7	1·5 12·7	5·9 50·0	4·3 37·3	0·0224 (0·40)	0·00165
14	0·1025 (0·59)	125—140	1	(i) Gas given off during this period : 1st release = 3·8 c.c.	(i) 3·8	0·2 4·9	2·0 53·6	1·6 41·7	12·3	1·5 12·2	7·4 60·1	3·4 27·6	0·0266	0·0050
				(ii) On rise of temp. after the day, decomp. occurred at 300° : 2nd release = 8·5 c.c.	(ii) 8·5	1·3 15·4	5·4 64·3	1·8 21·4	—	—	—	—	—	—
15	0·0732 (0·42)	210—225	½	No decomp. Decomp. occurred at 330° on raising the temp. after the 12 hrs. : gas = 9·54 c.c.	—	—	—	—	9·54	1·6 17·0	2·8 29·2	5·1 54·0	0·015	0·00025
16	0·1026	,,	3	Gas given off : (i) 1st release at 125—140°, = 2·8 c.c.	(i) 2·8	0·2 7·1	1·85 66·0	0·75 26·9	12·7	1·0 7·9	6·1 48·0	5·75 44·1	0·0238	0·0165
				(ii) 2nd release at 210°, = 2·1 c.c.	(ii) 2·1	0·2 9·5	1·45 66·0	0·45 24·5						
				(iii) On raising temp. after the 72 hrs., 3rd release at 320°, = 7·8 c.c.	(iii) 7·8	0·6 7·0	2·6 33·0	4·6 59·0						

* Initial temperature of heating.

† Period of (continuous) exposure, in days, of $CaN_2O_2,4H_2O$ to P_2O_5 at the initial temperature.

‡ Numbers in parentheses indicate mg.-mols.

§ Numbers in the second line in each case indicate percentages of the gas.

(Expts. 9 and 10) and $Na_2N_2O_2,5H_2O$ (Expts. 11 and 12). Expt. 9 shows remarkable regularity in the proportions of Na_2O and $NaNO_2$ (all the hyponitrite has not decomposed); nitrogen alone is formed in Expts. 9 and 10, but nitrous oxide is also formed in Expts. 11 and 12. Again, the proportion of N_2O increases with the weight of $Na_2N_2O_2,5H_2O$, as with $CaN_2O_2,4H_2O$.

To understand further the role of H_2O in the tetrahydrate in forming N_2O, it would be necessary to study the dehydrated salt, but as it is impossible to effect this dehydration without decomposition, phosphoric oxide was kept in the evacuated system containing the tetrahydrate, and the latter was kept at and above 100° and ultimately decomposed, by appropriately raising the temperature. Gas evolved in the initial period of heating was collected separately and analysed. Table 4 shows the results: even N_2 and NO do not vary concurrently; the gas evolved initially in Expt. 14 shows a large proportion of nitrogen and yet a low proportion of nitric oxide, but the gas subsequently evolved contains so much nitric oxide as to make the total normal. This shows that nitrogen and nitric oxide are not formed in the same reaction, *i.e.*, calcium nitrite is probably formed first, and nitric oxide last. The usual proportions of N_2O and N_2 have become reversed in Expt. 15. This supports the probability that dehydrated $CaN_2O_2,4H_2O$ might produce more nitrogen, for Expt. 16 shows a normal ratio (cf. Table 1) for N_2 and N_2O in the first release and a reversal of it in the last release. In the last, the dehydrating influence of phosphoric oxide has prevailed for a time at 210°. The residue shows higher nitrite content, whereas the proportion of nitric oxide in the gas is small.

Discussion.—The facts that (i) evolution of nitrous oxide becomes very low under dehydrating conditions when H_2O of $CaN_2O_2,4H_2O$ is in a state of strain, and (ii) dehydration of this tetrahydrate under ordinary conditions is impossible, suggest, by analogy with behaviour of $Na_2N_2O_2,5H_2O$, that production of nitrous oxide is connected with H_2O of $CaN_2O_2,4H_2O$. The observation that low temperature and greater weight produce more nitrous oxide is consistent with this view.

The decomposition of $CaN_2O_2,4H_2O$ at 125—140° to form all the normal products of the decomposition renders it probable that the reactions may be

$$\text{(I)}\quad CaN_2O_2 + H_2O \text{ (from } 4H_2O \text{ of hyponitrite)} = CaO + H_2N_2O_2$$

the other products being then formed as (Ray and Ganguli, *loc. cit.*)

$$\text{(II)}\quad \text{(i) } H_2N_2O_2 = H_2O + N_2O;\quad \text{(ii) } 3H_2N_2O_2 = 2H_2O + 2HNO_2 + 2N_2 \rightarrow \tfrac{2}{3}H_2O + \tfrac{2}{3}HNO_3 + \tfrac{4}{3}NO$$

(II, ii) will interfere with the unimolecular reaction (II, i), as found by Hantzsch and Kaufmann (*Annalen*, 1896, **292**, 317). The results of Table 4 also make it likely that anhydrous calcium hyponitrite, if it could be prepared, would react thus:

$$3CaN_2O_2 = 2CaO + Ca(NO_2)_2 + 2N_2 \quad \ldots\ldots\ldots \quad \text{(i)}$$

the nitrite produced decomposing, in part, thus:

$$3Ca(NO_2)_2 = 2CaO + Ca(NO_3)_2 + 4NO \quad \ldots\ldots\ldots \quad \text{(ii)}$$

This hypothesis is supported by the facts that (*a*) nitric oxide always accompanies nitrogen but has never been found alone, (*b*) the proportion of nitric oxide never exceeds that of nitrogen, (*c*) the residue contains much nitrite when the nitric oxide content of the gas is small, and (*d*) a stage of evolution of much nitrogen and little nitric oxide is followed by one of larger nitric oxide evolution (Expt. 14).

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