544. *The Thermal Decomposition of Mercurous and Mercuric Hyponitrite.*

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The gaseous and solid products formed by decomposition of mercurous and mercuric hyponitrite when heated for various times at temperatures from 100° to 200° are reported. The effect of oxygen on the decomposition of the mercuric salt is also reported.

RAY and GANGULI[1] found that mercurous hyponitrite decomposed slowly at 80°, rapidly at 150°, giving nitric and nitrous oxides, nitrogen dioxide, nitrogen, mercury, mercuric oxide, and mercurous nitrate. They assumed a tautomeric change between its "oxylic" and "imidic" forms and represented the reactions as $(HgNO)_2 = 2Hg + 2NO$ (1), $HgO{\cdot}N{:}NO{\cdot}Hg = (Hg_2O)\ Hg + HgO + N_2O$ (2) and $4(HgNO)_2 = 2HgNO_3 + 6Hg + N_2 + N_2O$ (3). Divers,[2] in preparing mercuric hyponitrite, found that, on drying in air, it evolved nitric oxide copiously, forming mercurous nitrate. He represented the reactions as $HgN_2O_2 = HgO + N_2O$ (4) and $HgN_2O_2 = Hg + 2NO$ (5). Neither Divers nor Ray[3] isolated the pure salt.

We prepared pure mercuric hyponitrite, and decomposed weighed quantities of both the hyponitrites, *in vacuo*, at various temperatures up to 200° and for various times. Mixtures of the mercurous salt with mercuric oxide were similarly decomposed, and the mercuric salt was decomposed also in an atmosphere of oxygen. The products were examined quantitatively as far as possible.

Between 100° and 180° both hyponitrites give mercurous and mercuric oxide, mercurous nitrite, mercury, nitrous and nitric oxide, nitrogen dioxide, and nitrogen. Mercurous nitrate is formed only at 180° and above. Admixture of mercuric oxide with either hyponitrite increases the production of mercurous nitrite. In oxygen, decomposition of mercuric hyponitrite is accelerated and more mercurous nitrite is produced, together with mercurous nitrate. Mercuric hyponitrite seems to decompose *via* the mercurous salt: $2HgN_2O_2 = Hg_2N_2O_2 + 2NO$; $Hg_2N_2O_2 = Hg_2O + N_2O$.

EXPERIMENTAL

Materials.—Both the salts were prepared, in small quantities at a time, by double decomposition in the dark[2,4] between pure sodium hyponitrite pentahydrate and cold solutions of mercurous or mercuric nitrate (cf. refs. 5, 6). The precipitate formed was washed 6—8 times with a little water, then successively with alcohol and ether, and dried over sulphuric acid and phosphorus pentoxide in a darkened vacuum-desiccator (Found: Hg, 87·1; N, 6·2. Calc. for $Hg_2O_2N_2$: Hg, 87·0; N, 6·1%. Found: Hg, 76·9; N, 10·8. Calc. for HgO_2N_2: Hg, 77·0; N, 10·7%). The mercurous salt was bright yellow, and the mercuric cream-coloured. Both were affected by light. The former started to decompose at 80—82°, and the latter suffered visible change on storage and decomposed at about 95°, but exploded if suddenly heated at 160°. Mercuric oxide was prepared from solutions of potassium hydroxide and mercuric nitrate.

The solubility in water of mercurous hyponitrite was 0·1058 g./l., of mercuric hyponitrite 0·13225 g./l., and of yellow mercuric oxide $2{\cdot}33 \times 10^{-4}$ g./l.[7] Mercurous oxide was only negligibly soluble. 1N-Nitric acid had but slight effect on mercury and 0·5N-acid had none.

Procedure.—A weighed amount of hyponitrite was placed in an all-glass system which was then evacuated and heated in an oil-bath at the required temperature (±2°). Gaseous

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[1] Ray and Ganguli, *J.*, 1907, **91**, 1399.
[2] Divers, *J.*, 1899, **75**, 90, 119.
[3] Ray, *J.*, 1897, **71**, 348.
[4] Ray, *J.*, 1897, **71**, 95.
[5] Thum, Dissertn., Prague, 1893.
[6] Ray, *J.*, 1907, **91**, 1904.
[7] Carret and Herschler, *J. Amer. Chem. Soc.*, 1938, **60**, 299.

products were passed by means of a Sprengel pump through caustic alkali solution, which was titrated, before and after passage of the gas, to give the amount of dinitrogen trioxide.

The residue from a decomposition was shaken with water till the filtrate gave no test for nitrite or nitrate or for mercurous mercury. The filtrate (A) contained nitrite, nitrate, and hyponitrite. The insoluble portion was treated with 0·5N-nitric acid, and the residual mercury collected on a sintered-glass funnel and weighed. The solution was treated with a very slight excess of 1% sodium chloride solution and filtered, and mercuric sulphide precipitated from the filtrate. In (A) the total mercury was determined as mercuric sulphide after oxidation of mercurous ion; and in an aliquot part, heated at 60° sufficiently to decompose the hyponitrite [8] and oxidise the mercurous ion, nitrite was determined with permanganate. If nitrate was present, the total nitrate was also determined (ferrous sulphate method) after oxidation of nitrite. From the nitrite content the mercurous nitrite was calculated, and from the total nitrate less that equivalent to the nitrite, the amount of mercurous nitrate was deduced, mercurous ion being absent in (A). Unconsumed mercurous hyponitrite was calculated from the difference of total mercurous mercury and that as nitrite (and nitrate). In the products from mercuric hyponitrite, the mercurous mercury in (A) was almost equivalent to the nitrite, showing the presence of very little mercurous hyponitrite in the residue.

Decomposition of mercurous hyponitrite. The product was yellow, interspersed with grey. Below 180°, nitrite but no nitrate was present; as mercuric nitrite is unstable at and above 80° (unpublished work), this nitrite must have been the mercurous salt, stabilized by the free mercury present.

The results are shown in Table 1, from which the effects of (*a*) temperature and (*b*) time are clear and do not need detailed discussion. Another series of experiments at 120° for 1 hr. on weights of 0·06—0·60 g. of mercurous hyponitrite showed a slight tendency for the nitric oxide and nitrogen dioxide to increase, and nitrous oxide to decrease, with increasing mass. A series of experiments at 100° for ½, 1, or 2 hr. with 0·25 g. of hyponitrite (*a*) alone and (*b*) with addition of 0·1 g. of mercuric oxide showed that the latter caused a 5—7 fold increase in the weight of hyponitrite decomposed and in the proportion of mercurous nitrite formed.

TABLE 1. *Effect of temperature and time on the decomposition of mercurous hyponitrite.*

	$Hg_2N_2O_2$		Gas evolved (ml.)					Products (mole per mole decomp.)			
Temp.	taken (g.)	decomp. (g.)	Total	NO	NO_2	N_2O	N_2	Hg	Hg_2O	HgO	$HgNO_2$
(*a*) *Effect of temperature* (1 hr.)											
100°	0·2520	0·0152	0·91	0·50	0·06	0·35	*	0·785	0·342	0·181	0·198
120	,,	0·1658	10·15	5·2	0·9	3·6	0·45	0·678	0·242	0·580	0·208
140	0·2518	0·1842	11·20	5·69	1·02	4·0	0·51	0·817	0·183	0·575	0·214
160	0·2524	0·2124	12·5	6·1	1·15	4·7	0·6	0·914	0·092	0·675	0·249
180	0·2512	0·2512	14·2	6·65	1·35	5·5	0·7	0·906	0·031	0·760	0·266 †
200	0·2516	0·2516	15·4	7·1	2·0	5·5	0·8	1·0	—	0·661	0·233 ‡
(b) *Effect of time* (120°)											
Min.											
15	0·2508	0·0329	1·75	1·25	0·1	0·3	0·1	0·028	0·485	0·492	0·440
30	,,	0·0617	4·20	2·65	0·45	1·0	0·2	0·331	0·338	0·566	0·266
45	0·2516	0·1160	7·58	4·05	0·8	2·5	0·3	0·635	0·273	0·544	0·228
60	0·2520	0·1658	10·15	5·2	0·9	3·6	0·45	0·678	0·242	0·580	0·208
120	0·2510	0·1821	11·0	5·55	1·05	4·0	0·45	0·689	0·219	0·590	0·226
180	0·2506	0·1966	12·2	6·15	1·3	4·25	0·55	0·815	0·162	0·602	0·229

* Trace. † Trace of $HgNO_3$. ‡ 0·06 mol. of $HgNO_3$.

The above results would show that the initial change is presumably $Hg_2N_2O_2 = Hg_2O + N_2O$, mercury and mercuric oxide being formed from the mercurous oxide,[9] and that the formation of mercurous nitrite is due to the presence of mercuric oxide. Formation of oxyhyponitrite has been postulated by Addison, Gamlen, and Thompson,[10] and the existence of two forms of hyponitrite also by Ray and Ganguli [1] and by Oza and Oza.[11] One of these forms might

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[8] Oza, Oza, and Dipali, *J. Indian Chem. Soc.*, 1951, **28**, 75.

[9] Bruns and Pfordten, *Ber.*, 1888, **21**, 2010.

[10] Addison, Gamlen, and Thompson, *J.*, 1952, 338.

[11] Oza and Oza, *J. Phys. Chem.*, 1956, **60**, 192.

produce nitrous oxide and mercurous oxide, and the other would yield oxyhyponitrite, producing mercurous nitrite and nitric oxide: $Hg_2N_2O_2 + HgO = 2Hg + HgN_2O_3$ and $HgN_2O_3 = HgNO_2 + NO$.

TABLE 2. *Effect of temperature and time on the decomposition of mercuric hyponitrite.*

	HgN_2O_2		Gas evolved (ml.)					Products (mole per mole decomp.) *			
Temp.	taken (g.)	decomp. (g.)	Total	NO_2	NO	N_2O	N_2	$HgNO_2$	Hg_2O	HgO	Hg
(a) *Effect of temperature* (1 hr.)											
100°	0·2526	0·0192	1·31	0·12	0·75	0·35	0·1	0·142	0·0993	0·0771	0·567
120	0·2514	0·1001	13·85	0·74	7·93	4·3	0·9	0·162	0·157	0·200	0·333
140	0·2518	0·1094	16·9	1·05	9·15	5·65	1·1	0·164	0·125	0·221	0·257
160	0·2508	0·2443	26·15	2·25	12·0	10·5	1·45	0·142	0·0431	0·453	0·318
180	0·2510	0·2510	26·85	2·4	12·1	10·75	1·6	0·146	0·147	0·473	0·350
200	0·2508	0·2508	27·1	2·6	12·1	10·75	1·6	0·127	0·0058	0·475	0·358
(b) *Effect of time* (100°)											
Min.											
15	0·2528	0·0553	6·26	0·37	3·2	2·4	0·3	0·129	0·116	0·235	0·244
30	0·2504	0·0773	9·3	0·5	5·0	3·3	0·5	0·113	0·149	0·196	0·312
45	0·2502	0·0960	12·45	0·7	7·0	4·1	0·6	0·121	0·144	0·192	0·314
60	0·2514	0·1001	13·85	0·75	7·9	4·3	0·9	0·173	0·157	0·200	0·333
120	0·2512	0·1615	19·1	1·4	10·1	6·5	1·1	0·150	0·145	0·221	0·348
180	0·2514	0·2431	25·8	2·0	12·3	9·9	1·6	0·132	0·066	0·485	0·250

* The mixtures seemed to contain some mercurous hyponitrite.

Decomposition of mercuric hyponitrite. The effects of temperature during 1 hr. and of time at 100° are shown in sections (a) and (b), respectively, of Table 2. The products are similar to those from the decomposition of the mercurous salt.

A 10-fold increase in the weight of salt heated produced only a 4—5-fold increase in the products, the proportion of mercurous oxide increasing and that of mercuric oxide decreasing, and, as with the mercurous salt, the latter oxide is probably consumed by the mercuric hyponitrite.

TABLE 3. *Effect of time on the decomposition of mercuric hyponitrite at* 100°.

	HgN_2O_2		Gas evolved (ml.)				Surplus	Solid products (g.)			
Time (min.)	taken (g.)	used (g.)	NO_2	NO	N_2O	N_2	O_2 (ml.)	$HgNO_2$	Hg_2O	HgO	Hg
(a) In vacuo *											
30	0·2510	0·0008	—	0·27	—	—	—	Nil	Trace	Nil	Nil
60	0·2524	0·0190	0·22	0·36	0·36	0·1	—	0·0026	0·0030	0·0012	0·008
120	0·2502	0·0408	0·32	0·81	0·90	0·2	—	0·0046	0·0091	0·0077	0·011
240	0·2512	0·0836	0·64	2·1	2·3	0·35	—	0·0119	0·0220	0·0174	0·0152
(b) *In oxygen* †											
30	0·2522	0·0104	0·18	—	0·27	Trace	12·3	0·0098	Trace	Nil	Nil
60	0·2510	0·0509	0·66	—	1·00	0·3	12·1	0·0192	,,	0·0022	0·0086
120	0·2516	0·0509	1·1	—	1·8	0·45	12·0	0·0255	,,	0·0088	0·0102
240	0·2502	0·0832	2·2	—	2·9	0·5	10·9	0·0410	,,	0·0132	0·0184

* No $HgNO_3$ formed. † Traces of $HgNO_3$ formed.

Table **3** contains results of experiments at 100° *in vacuo* and in oxygen. Under the former conditions, nitric oxide, and under the latter, mercurous nitrite predominate in the early stages among the gases and solids respectively.

These facts can be explained in terms of the two equations given on p. 2727. Nitrogen dioxide can, in either case, arise from mercurous nitrite, and nitrogen, nitrogen dioxide, and mercurous nitrite by the action of nitric oxide on mercuric oxide.[12,13]

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[12] Schoch, *Amer. Chem. J.*, 1903, **29**, 319.

[13] Oza, *Nature*, 1955, **175**, 385.