The Thermal Decomposition of Silver Nitrite.

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Examination of the results of decomposition of silver nitrite alone, under different conditions, and with the addition of silver oxide has shown that the reaction $AgNO_2 = Ag + NO_2$ proceeds through the intermediate fast reaction $2AgNO_2 \rightleftharpoons Ag_2O + N_2O_3 (= NO + NO_2)$. Silver oxide has been isolated by carrying out the decomposition in oxygen. Experiments were also carried out on the mutual effect of the substances present (or formed) in the system; *e.g.*, the effect of (*a*) nitric oxide and (*b*) nitrogen dioxide on (i) silver oxide and (ii) silver nitrite and of nitric oxide on silver nitrate. The equilibrium $AgNO_3 + NO \rightleftharpoons AgNO_2 + NO_2$ was isolated; this reaction replenishes the nitrite and is fairly rapid under the experimental conditions so that it arrests the formation of nitrogen as $AgNO_2 + NO = AgNO_3 + \frac{1}{2}N_2$ by preventing the access of nitric oxide to nitrite. Formation of silver nitrate seems to occur by $AgNO_2 + O = AgNO_3$ though some of it is formed also by $Ag_2O + NO_2 = AgNO_3 + Ag$: the oxygen comes, at 130°, when the dissociation of nitrogen dioxide is absent, from silver oxide. No evidence is found for the reaction $Ag_2O + 2NO_2 = AgNO_3 + AgNO_2$ which is characteristic of wet systems.

Divers (*J.*, 1871, **24**, 85) found that silver nitrite fused at 134° in air and evolved a reddish gas at 150°. He thought the reaction (1) $3AgNO_2 = 2Ag + AgNO_3 + N_2O_3$ occurred below 134° and represented the ultimate changes as (2) $2AgNO_2 = Ag + AgNO_3 + NO$, as he found neither silver oxide nor nitrogen in the decomposition products. Divers and Schimidzu (*J.*, 1885, **47**, 630) found that silver nitrate, unmixed with nitrite, was formed by the action of nitrogen dioxide on reduced spongy silver. They also heated silver

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* Unpublished work on *iso*butyl bromide in which P-radicals are produced by attack on a tertiary group suggests that such an attack is still readier, leading apparently to very long chains.

nitrite with nitrogen dioxide at 125° for 15 hr. and found that half the nitrite was oxidized to nitrate; however, they believed that silver nitrate was formed by the action of nitrogen dioxide on silver (5, below) and not on silver nitrite. Oswald, on the other hand (*Compt. rend.*, 1911, **152**, 381), supposed that nitrate was formed as (3) $AgNO_2 + NO_2 = AgNO_3 + NO$. Ray and Ganguli (*Proc.*, 1905, **21**, 279) found their two varieties of silver nitrite to decompose differently according to (4) $\alpha\text{-}AgNO_2 = Ag + NO_2$ with a side reaction (5) $Ag + N_2O_4 = AgNO_3 + NO$, and (6) $\beta\text{-}AgNO_2 = Ag + O + NO$. Tzentnershver and Checinski (*Bull. Intern. Acad. Polonaise, Classe Sci. math. nat.*, 1935, *A*, 156) studied the thermal dissociation of silver nitrite, and Blumenthal and Checinski (*ibid.*, p. 165) studied the kinetics of the dissociation. The former found that the dissociation occurred as (7) $AgNO_2 = Ag + NO_2 - 18{,}900$ cal. and (8) $2AgNO_2 = Ag + AgNO_3 + NO - 15{,}500$ cal., and regarded formation of nitrate as the primary change; the latter found that (7) was complete at 195°/2 mm. but (8) was incomplete at 195°/753 mm.; further that (7) was reversible at room temperature and that (8) went almost to completion. Checinski and his co-workers thought that the reactions in the decomposition occurred as in (4) and (5) and that they were of first order at low pressures and of second order under atmospheric pressure. Randall, Manov, and Brown (*J. Amer. Chem. Soc.*, 1938, **60**, 694) used the equation $2AgNO_2(s) = Ag(s) + AgNO_3(s) + NO(g)$ to compute the heat capacities of the substances concerned: their silver nitrite decomposed at 101·6°.

We now describe experiments on the decomposition of pure silver nitrite, *in vacuo*, under different conditions, alone and with the addition of silver oxide. The products of the reaction were quantitatively examined at various stages with a view to collect evidence for the transitory formation of silver oxide. Experiments were then done to examine the mutual effect of the substances present (or formed) in the system: *e.g.*, the action of (*a*) nitric oxide and (*b*) nitrogen dioxide on silver oxide and on silver nitrite; and of nitric oxide on silver nitrate. Finally silver oxide was isolated by conducting the decomposition at 130° in an atmosphere of oxygen (11 cm. pressure).

EXPERIMENTAL

Materials.—Silver nitrite was prepared from pure sodium nitrite and silver nitrate, recrystallized, dried in a desiccator (H_2SO_4), pulverized, and kept in a desiccator in the dark (Found: Ag, 70·1; NO_2', 29·9. Calc. for $AgNO_2$: Ag, 70·1; NO_2', 29·9%). Silver oxide was prepared from very dilute solutions of the nitrate and potassium hydroxide, and the dark grey precipitate washed freely with water, and dried in vacuum desiccator (H_2SO_4) (Found: Ag, 93·2. Calc. for Ag_2O: Ag, 93·1%). Nitric oxide was obtained by heating pure silver nitrite and absorbing the gases in alkali: it was all absorbed in alkaline sulphite. Pure dinitrogen tetroxide was prepared according to Addison, Gamlen, and Thompson (*J.*, 1953, 338); after fractionation it was collected in tubes of 4—6 mm. diameter, drawn out to a capillary at one end, and sealed: it was completely absorbed in concentrated potassium hydroxide solution producing equivalent amounts of nitrite and nitrate. Silver metal was obtained from silver nitrate solution by displacement with pure copper, washed, pulverized, analysed (found pure), and stored. Oxygen was prepared from potassium chlorate in a T system closed by a tap.

The apparatus used for studying decomposition was as described by Oza and Oza (*J.*, 1953, 908), a T-piece carrying the tube containing potassium chlorate plugged by glass wool and provided with a tap being attached in experiments in oxygen (Table 8). The experiments with dinitrogen tetroxide were done in the apparatus shown in Fig. 1: *d* is the tetroxide tube, previously weighed, and inserted with its capillary elongation inside the bore of key of the stopcock, *A*. The substance (oxide or nitrite) was weighed and placed in *T*, and *B* was heated in a bath for ½ hr. at the temperature of the experiment before the tetroxide tube was broken. *P* (or *Q*) was cooled in an ice-bath, and nitrogen dioxide was passed over the substance in *T* by alternately cooling and warming *P* and *Q*. Phosphoric acid was placed in *C* before the start of each experiment and the apparatus evacuated and allowed to stand for 1 hr.; *b'* was then turned off, phosphoric oxide removed, and potassium hydroxide solution placed in *C*, *D*, and *E*. By turning *A*, the capillary of tetroxide tube *d* was broken, and gas released: the glass was collected at the end of the experiment and weighed to get the weight of tetroxide taken at the start. The apparatus used for studying the effect of nitric oxide is shown in Fig. 2; *B* is a bulb

(100 c.c.) to contain (weighed) silver oxide, nitrite, or nitrate between taps T_1 and T_2. The pressure of the pure nitric oxide, produced on the left of T_1, is noted on the Sprengel pump through the upper branch of T_2; T_1 and T_2 are closed, gas to the right of T_2 pumped out, and heating of B started. At the end, the gas is collected in aqueous potassium hydroxide (lower branch of T_2), and nitrogen dioxide determined by analysing the alkali for nitrite.

Analyses.—The residue, examined for nitrite, nitrate, silver, and silver oxide, showed the absence of the last in all experiments except those of Table 8 : it was extracted with hot water till no silver ions passed into solution and made up to a known volume (A) : the solution was alkaline in those experiments of Table 8 which show the presence of silver oxide. The insoluble portion (Ag) was dissolved in hot dilute (1 : 1) nitric acid, boiled till no nitrous fumes were evolved, and diluted to a known volume (B). A and B were analysed for silver by Volhard's method, and A also for nitrite and nitrate (Oza and Oza, *loc. cit.*); the silver in A less that equivalent to nitrite and nitrate found gave that equivalent to Ag_2O. The gas pumped off was analysed for nitric oxide and nitrogen, nitrogen dioxide being absorbed with its equivalent nitric oxide in alkali (in the apparatus) and determined as nitrite ($2KOH + N_2O_3 = 2KNO_2 + H_2O$). When nitric oxide was absent, the gas was tested for oxygen and, if this was present, absorbed in alkaline pyrogallol. Nitric oxide was absorbed in alkaline sulphite. All recorded volumes are at N.T.P.

FIG. 1.

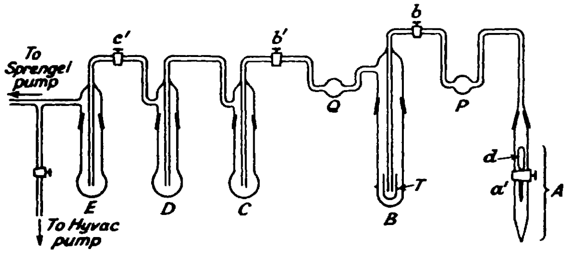
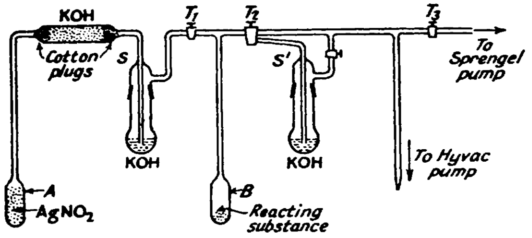


FIG. 2.



Results.—To find the initial temperature of decomposition of silver nitrite 0·35 g. of it was kept *in vacuo* surrounded by an oil-bath and heated for ½ hr. at 50°; the temperature was then raised by 10°/10 min. to 100°; it was kept at 102—103° for 1 hr. (Randall, Manov, and Brown, *loc. cit.*) and then raised by 5°/10 min. Decomposition occurred at 128°.

For experiments at 480° heating was done electrically and the temperature was constant to within ±5°; for others, in an oil-bath, the temperature was controlled mechanically to within ±1°.

Table 1 contains results of experiments on the effect of time, mass, and temperature on the decomposition. They show the presence of nitric oxide and nitrogen dioxide in the gaseous and of silver and silver nitrate in the solid products; no nitrogen or oxide was present in any case. Expts. 1—8 were done with 0·35 g. of nitrite, at 130°, for varying times and show a greater rate of decomposition during the first 2 hr. in which the proportion of nitrogen dioxide increases and that of nitric oxide diminishes slowly; after 2 hr. the proportions are reversed. The ratio Ag : $AgNO_2$(consumed) is fairly constant, while the trends of the ratios Ag : $AgNO_3$ and $AgNO_2$(consumed) : $AgNO_3$, which are similar (low at first, sudden increase to maximum at 2 hr., steady fall), are dissimilar to those of Ag : $AgNO_2$(consumed). This shows that per unit of silver nitrite decomposed, formation of silver is steady but that of silver nitrate is not, *i.e.*,

TABLE 1. *Effect of time, mass, and temperature upon the decomposition of silver nitrite.*

(a) Effect of time at 130° on 0·35 g. of silver nitrite.

Expt. No.	Duration (hr.)	Gas evolved (c.c. at N.T.P.) * Total	NO	NO_2	Solid products : Ag †	$AgNO_3$ †	$AgNO_2$ used †	$\frac{Ag}{AgNO_3}$	$\frac{Ag}{AgNO_2}$	$\frac{AgNO_2}{AgNO_3}$
1	½	2·83	1·66 (59·3)	1·15 (40·6)	0·0094 (0·087)	0·00307 (0·018)	0·0151 (0·098)	4·81	0·887	5·43
2	1	6·90	4·03 (58·4)	2·87 (41·6)	0·0267 (0·247)	0·0041 (0·024)	0·0457 (0·297)	10·25	0·832	12·32
3	2	14·02	8·12 (57·9)	5·9 (42·1)	0·0632 (0·58)	0·0081 (0·048)	0·0973 (0·63)	12·29	0·926	13·26
4	4	17·28	10·58 (61·2)	6·7 (38·8)	0·0788 (0·73)	0·0142 (0·083)	0·1256 (0·82)	8·76	0·895	9·76
5	6	18·98	11·57 (60·9)	7·4 (39·1)	0·0858 (0·79)	0·0210 (0·124)	0·1414 (0·92)	6·4	0·865	7·4
6	8	20·5	12·5 (61·0)	8·00 (39·0)	0·0945 (0·87)	0·0260 (0·15)	0·1572 (1·0)	5·72	0·858	6·67
7	10	23·00	14·1 (61·3)	8·9 (38·7)	0·1067 (0·9)	0·0315 (0·18)	0·1808 (1·2)	5·34	0·837	6·38
8	12	25·8	16·5 (64·0)	9·3 (36·0)	0·1183 (1·1)	0·0486 (0·29)	0·2125 (1·4)	3·86	0·797	4·83

(*b*) Effect of mass at 130° in 2 hr.

Expt. No.	Mass (g.)	Total	NO	NO_2	Ag †	$AgNO_3$ †	$AgNO_2$ used †	$\frac{Ag}{AgNO_3}$	$\frac{Ag}{AgNO_2}$	$\frac{AgNO_2}{AgNO_3}$
9	0·1098	4·03	2·04 (50·6)	1·99 (49·4)	0·0192 (0·18)	0·00242 (0·014)	0·0296 (0·19)	12·4	0·927	13·4
10	0·2405	9·9	5·6 (56·2)	4·3 (43·8)	0·0451 (0·42)	0·0055 (0·032)	0·0693 (0·45)	12·9	0·929	13·9
11	0·3526	14·02	8·12 (57·9)	5·9 (42·1)	0·0632 (0·58)	0·0081 (0·048)	0·0973 (0·63)	12·3	0·926	13·3
12	0·4814	22·22	13·1 (58·8)	9·1 (41·2)	0·1075 (0·99)	0·0110 (0·065)	0·1639 (1·1)	15·35	0·930	16·5
13	0·6006	26·12	16·0 (61·3)	10·1 (38·7)	0·1247 (1·1)	0·0138 (0·081)	0·1901 (1·2)	14·2	0·927	15·3
14	0·7210	30·03	18·1 (60·4)	11·9 (40·6)	0·1349 (1·2)	0·0166 (0·097)	0·2073 (1·3)	12·8	0·926	14·0

(*c*) Effect of time at 230° on 0·26 g. of silver nitrite.

Expt. No.	Duration (min.)	Total	NO	NO_2	Ag †	$AgNO_3$ †	$AgNO_2$ used †	$\frac{Ag}{AgNO_3}$	$\frac{Ag}{AgNO_2}$	$\frac{AgNO_2}{AgNO_3}$
15	8	20·3	10·1 (50·0)	10·1 (50·0)	0·0972 (0·90)	0·0393 (0·23)	0·1742 (1·1)	3·88	0·796	4·87
16	15	27·5	12·8 (46·5)	14·7 (53·4)	0·1293 (1·2)	0·0501 (0·29)	0·2362 (1·5)	4·1	0·779	5·2
17	45	30·9	14·1 (45·4)	16·8 (54·6)	0·1477 (1·4)	0·0516 (0·30)	0·2574 (1·7)	4·5	0·820	5·5
18	165	30·8	14·0 (45·4)	16·8 (54·6)	0·1474 (1·4)	0·0510 (0·30)	0·2570 (1·7)	4·5	0·814	5·6
19	285	,,	,,	,,	,,	,,	,,	,,	,,	,,
20	405	,,	,,	,,	,,	,,	,,	,,	,,	,,

(*d*) Effect of temperature on 0·35 g. of silver nitrite in 2 hr.

Expt. No.	Temp.	Total	NO	NO_2	Ag †	$AgNO_3$ †	$AgNO_2$ used †	$\frac{Ag}{AgNO_3}$	$\frac{Ag}{AgNO_2}$	$\frac{AgNO_2}{AgNO_3}$
21	130°	14·02	8·1 (57·9)	5·9 (42·1)	0·0632 (0·58)	0·0081 (0·048)	0·0973 (0·63)	12·3	0·926	13·3
22	170	26·7	17·3 (64·7)	9·4 (35·3)	0·1012 (0·94)	0·0337 (0·20)	0·1746 (1·1)	4·7	0·822	5·8
23	200	35·2	17·9 (50·9)	17·3 (49)	0·1628 (1·5)	0·0430 (0·25)	0·2723 (1·8)	6·0	0·853	7·00
24	220	39·1	19·6 (50·2)	19·5 (49·8)	0·1778 (1·6)	0·0527 (0·31)	0·3011 (2·0)	5·3	0·842	6·3
25	240	42·5	19·5 (45·9)	23·0 (54·1)	0·2052 (1·9)	0·0603 (0·35)	0·3471 (2·3)	5·4	0·841	6·4
26	480	52·7	21·6 Plus O_2 = 3·0 c.c.	28·1	0·2416 (2·2)	0·0085 (0·050)	0·3516 (2·3)	4·5	0·978	45·8

* Composition (%) is given in parentheses.

† Parentheses contain m moles or mg.-atoms.

silver nitrate is not a product of primary change as required by eqns. (1), (2), and (5). Expts. 9—15 show the effect of mass on the formation of the products: increase of mass diminishes the proportion of nitrogen dioxide but increases that of nitric oxide as when the latter is produced from the former. The ratio Ag : $AgNO_2$(consumed) is again constant, the value being comparable with that in expts. 1—8; the other two ratios, which amongst themselves show similar trends, have values similar to the value in the 2-hr. expt. (No. 3) when the mass is less than 0·35 g., but with a larger mass the value increases; it seems that the net silver nitrate production is greater in expts. 9—11 than in 12—14, and since in the latter expts. the amounts of nitric oxide and nitrogen dioxide are higher, it appears that silver nitrate is effectively reduced by nitric oxide: $AgNO_3 + NO = AgNO_2 + NO_2$ (Oza and Oza, *loc. cit.*). Expts. 15—20 show the effect of time at a higher temperature (230°) on a constant mass (cf. expts. 1—8): at 130° the decomposition was incomplete in 12 hr., but at 230° it is complete in 15 min. Expts. 17—20 show static conditions in the system although some nitrite is present even after 6¾ hr.; the rate of formation of nitrate is higher, as before, at first. At 480° (expt. 26) no nitrite is left. This shows that at 500—550°, the temperature used by Mehta (*Brit. Abs.*, 1942, I, 245), the rate of decomposition must be very great and the silver oxide, found by him, may have been formed by the interaction of silver in the system with atmospheric oxygen. The higher proportions of nitrogen dioxide in expts. 15—20 and smaller values of Ag : $AgNO_3$ and $AgNO_2 : AgNO_3$, indicating enhanced nitrate formation, show formation of nitrate by nitrogen dioxide. Expts. 21—26 show the effect of temperature in 2 hr.: at 480°, when no nitrite is left, the system contains free oxygen and silver nitrate (which was steadily increasing in expts. 21—25) diminishes, showing that oxygen was formed from it: the system was exposed to alkali throughout, so that nitrous fumes were all absorbed and only surplus nitric oxide left. At 130° and 170° nitric oxide exceeds nitrogen dioxide; at 200—220°, the two are identical and at 240° and 480° nitrogen dioxide exceeds nitric oxide. The ratio Ag : $AgNO_2$(consumed) is of practically the same order as in the preceding experiment, but Ag : $AgNO_3$ and $AgNO_2 : AgNO_3$, which are large at 130°, become small at 170°, increase, and remain fairly steady up to 240°: this shows that a nitrate-forming reaction becomes prominent after 130°; but expt. 1 has shown that it is prominent also at 130° in the first stages of the decomposition. The prominence at 130° is not likely to be due to nitrogen dioxide because its proportion is low in expt. 1 and higher in expt. 2—in the latter, nitrate formation has abated. Thus it appears that the cause of nitrate formation is different at 130° from that above 130°. In the latter case it may be due to dissociation of nitrogen dioxide (Richardson, *J.*, 1887, **51**, 397; Bodenstein and Kotayama, *Z. Electrochem.*, 1909, **15**, 244), producing oxygen as $NO_2 \rightleftharpoons NO + \frac{1}{2}O_2$. At and below 130°, however, it may be due to oxidation by silver oxide: $2AgNO_2 \rightleftharpoons Ag_2O + NO + NO_2$ (T. M. Oza and Shah, *J. Univ. Bombay*, 1942, 70; T. M. Oza, *J. Indian Chem. Soc.*, 1945, **22**, 173; cf. Ostwald, *Annalen*, 1914, **403**, 32). The results show somewhat larger production of silver up to 2 hr. (expts. 1—3). With progress of the reaction and accumulation of nitrogen dioxide, silver may be used up as in (5) (Divers and Schimidzu, *loc. cit.*).

The above study makes it probable that nitrate formation occurs as $AgNO_2 + O = AgNO_3$, oxygen coming from silver oxide, $Ag_2O \rightleftharpoons 2Ag + O$ (Lewis, *Z. physikal. Chem.*, 1905, **52**, 310; *J. Amer. Chem. Soc.*, 1906, **28**, 139), at 130° and from dissociation of nitrogen dioxide above 130°. Silver oxide is known to decompose more readily in presence of nitric oxide (Auden and Fowler, *Chem. News*, 1895, **72**, 163; Sabatier and Senderens, *Compt. rend.*, 1892, **114**, 1429, 1476; **115**, 236). Silver nitrate is also reduced to nitrite by nitric oxide present in the system.

Decomposition of Mixtures of Silver Nitrite and Silver Oxide.—The results of decomposition of mixtures of silver nitrite (0·35 g.) with silver oxide (0·05 g.) are given in Table 2. Expts. 27—29 show the effect of time at 130° (cf. expts. 1—3, Table 1), and expts. 29—34 the effect of temperature in 2 hr. (cf. expts. 21—26, Table 1). At 130° the decomposition is retarded in the early stages, but this is not so at higher temperatures: some nitrogen is formed, more silver is formed, and yet neither the amount nor the proportion of nitrogen dioxide increases up to 1 hr. and silver nitrite consumed and nitrate formed are greater. In the later stages, the position is different: in 2 hr. nitrite consumed is less in expt. 29 than in expt. 3, though silver and silver nitrate formed continue to be greater in the former. As the temperature is 130° ($<$140°), increased formation of nitrate is probably not due to oxygen from nitrogen dioxide, and as a larger amount of silver is present, more silver oxide has decomposed; hence some silver nitrate in the 2-hr. experiment seems to have been formed from silver oxide as in (*a*) $Ag_2O + NO_2 = AgNO_3 + Ag$. In the earlier experiment, at 130°, however, the above data show that some nitrate may have been formed as in (*b*) $AgNO_2 + Ag_2O = AgNO_3 + 2Ag$.

TABLE 2. *Effect of time at* 130° *and of temperature on the decomposition of mixtures of silver nitrite* (0·35 *g.*) *with silver oxide* (0·05 *g.*) *for* 2 *hr.**

Expt. No.	Time (hr.)	Gas evolved (c.c. at N.T.P.)				Solid products :		$AgNO_2$ used	Ag_2O left (g.)	$\frac{Ag}{AgNO_3}$	$\frac{Ag}{AgNO_2}$	$\frac{AgNO_2}{AgNO_3}$
		Total	NO	NO_2	N_2	Ag	$AgNO_3$					
27	½	2·58	1·54 (59·7)	1·04 (40·3)	nil	0·0167 (0·15)	0·0074 (0·044)	0·0242 (0·16)	0·0466	3·56	0·987	3·6
28	1	5·72	3·5 (60·8)	2·2 (39·1)	bubble	0·0362 (0·33)	0·0133 (0·078)	0·0464 (0·30)	0·0360	4·3	1·1	4·0
29	2	15·8	9·4 (59·4)	6·2 (39·5)	0·2 (1·1)	0·0692 (0·64)	0·0241 (0·14)	0·0857 (0·56)	0·0255	4·5	1·15	4·0
	Temp.											
30	170°	25·4	12·7 (49·8)	12·5 (49·1)	0·3 (1·1)	0·1256 (1·2)	0·0351 (0·21)	0·1619 (1·0)	0·0128	5·6	1·1	5·1
31	200	44·0	21·8 (49·6)	21·8 (49·6)	0·4 (0·8)	0·2091 (1·9)	0·0472 (0·28)	0·2714 (1·8)	nil	7·0	1·1	6·3
32	220	47·9	23·8 (49·6)	23·8 (49·6)	0·4 (0·8)	0·2254 (2·1)	0·0544 (0·32)	0·3013 (2·0)	nil	6·5	1·1	6·1
33	240	49·0	24·3 (49·6)	24·3 (49·6)	0·4 (0·8)	0·2408 (2·2)	0·0802 (0·47)	0·3458 (2·2)	nil	4·7	0·99	4·8
34	480	69·8	32·5	32·5	0·9	0·2916 (2·7)	0·0033 (0·019)	0·3518 (2·3)	nil	139·2	1·2	120·5
			Plus O_2 = 3·9 c.c. (46·6)	(46·6) (5·5)	(1·3)							

* Parentheses are used as in Table 1.

The increased formation of nitrate in spite of the low nitrite consumption can arise also by the prevalence of the reaction (*c*) $Ag_2O + 2NO_2 = AgNO_2 + AgNO_3$, whereby nitrite may be replenished in the system. The behaviour of nitrogen dioxide towards silver oxide at 130° clarifies this point (see p. 2459).

At higher temperatures, the amount of nitrogen dioxide in the experiments of Table 2 is greater than in those of Table 1; that of silver formed is also greater, as expected; that of silver nitrate formed is also greater but those of silver nitrite consumed are identical. The last fact shows that either silver nitrite is replenished, as in eqn. (*c*), or silver nitrite is not consumed in making nitrate, as when nitrate is formed as in eqn. (*a*).

TABLE 3. *Effect of nitric oxide* (40 *cm. press.*) *on* Ag_2O (0·1 *g.*) *for different times at* 130° (*expts.* 35—37) *and at* 115° (38—43).*

Expt. No.	Duration (hr.)	Gas evolved (c.c. at N.T.P.)			Solid products :			Ag_2O used	$\frac{\frac{1}{2}Ag}{Ag_2O}$	$\frac{AgNO_3}{AgNO_2}$
		Total	NO_2	N_2	Ag	$AgNO_2$	$AgNO_3$			
35	½	0·76	0·59 (77·6)	0·17 (22·4)	0·0060 (0·055)	0·0039 (0·025)	0·0013 (0·0076)	0·0102 (0·044)	0·65	0·3
36	2	1·8	1·4 (80·3)	0·35 (19·6)	0·0159 (0·15)	0·0095 (0·062)	0·0032 (0·019)	0·0264 (0·11)	,,	,,
37	5	3·8	3·15 (83·8)	0·6 (16·2)	0·041 (0·38)	0·0219 (0·14)	0·0083 (0·049)	0·0662 (0·28)	,,	,,
38	½	0·4	0·25 (60·5)	0·15 (39·5)	0·0010 (0·0094)	nil —	test + —	0·0011 (0·0047)	1·0	—
39	2	1·2	0·7 (61·2)	0·5 (38·8)	0·0032 (0·030)	test + —	0·0021 (0·012)	0·0049 (0·021)	0·7	large
40	5	1·9	1·3 (67·5)	0·6 (32·5)	0·0051 (0·047)	0·0010 (0·0067)	0·0041 (0·024)	0·0092 (0·040)	0·6	3·6
41	10	3·9	2·8 (71·2)	1·1 (28·8)	0·0223 (0·21)	0·0104 (0·067)	0·00094 (0·055)	0·0383 (0·16)	0·6	0·8
42	15	6·0	4·2 (69·9)	1·8 (30·1)	0·0328 (0·30)	0·0219 (0·14)	0·0167 (0·098)	0·0633 (0·27)	0·5	0·7
43	20	7·3	5·1 (69·9)	2·2 (30·4)	0·0516 (0·48)	0·0388 (0·25)	0·0239 (0·14)	0·1010 (0·43)	0·5	0·56

* Parentheses are used as in Table 1.

Reaction of Silver Oxide and Nitric Oxide.—Experiments on the action of nitric oxide (under 40 cm.) on silver oxide (0·1 g.) are given in Table 3. Expts. 1—3 were done at 130° and 4—9 at 115°. The results show the presence of nitrogen dioxide, nitrogen, silver, silver nitrite, and silver nitrate. Nitrogen dioxide increases and nitrogen diminishes slowly with time. In expts. 1—3 the quantities of nitrite are greater than those of nitrate; the ratios ½Ag : Ag_2O(consumed) and $AgNO_3 : AgNO_2$ are both constant with time, showing the steady progress of the reaction with time: this shows that the reactions may be fairly rapid at 130°. Expts. 4—9 were therefore performed at 115°, and show that ½Ag : Ag_2O is about unity at the start and both this ratio and the ratio $AgNO_3 : AgNO_2$ diminish with progress of the reaction. No nitrite is present, and a test for nitrate (phenolsulphonic acid) is obtained after ½ hr.; after 2 hr. nitrate is measurable but not nitrite; the quantities of both are measurable at the subsequent stages and the ratio $AgNO_3 : AgNO_2$ diminishes, showing that formation of silver nitrite increases with time more rapidly than that of the nitrate.

Since ½Ag : $Ag_2O = 1$ at ½ hr., the probable initial reaction is $Ag_2O = 2Ag + O$: this reaction is evidently induced by nitric oxide, for pure silver oxide scarcely began to decompose at 310°. The diminution in the value of this ratio with the progress of the experiment shows that this initial reaction is followed by reactions in which the oxide is so used as to liberate less silver metal, *i.e.*, by $Ag_2O + NO_2 = AgNO_3 + Ag$ or $Ag_2O_2 + 2NO_2 = 2AgNO_3$.

The fact that no nitrite is present in the initial stages when nitrate is indicated, shows that reactions like $Ag_2O + NO = AgNO_2 + Ag$ or $Ag_2O_2 + 2NO = 2AgNO_2$ may not occur and the formation of nitrite occurs as $AgNO_3 + NO = AgNO_2 + NO_2$ (Oza and Oza, *loc. cit.*).

Reaction of Nitric Oxide and Silver Nitrate at 128°.—Experiments on the action of nitric oxide (under 50 cm.) on silver nitrate (0·1 g.) at 115°, 120°, and 125° are given in Table 4. These experiments were not performed at 130° since silver nitrite, an expected product of reaction, begins to decompose at 128° (see p. 2459). No silver is formed in these experiments; nitrogen dioxide is formed and its quantity remains unchanged after the equilibrium stage which, as the results show, is established in about 6 hr. These results therefore show that nitrite found in the experiments with silver oxide and nitric oxide is likely to have been formed by reduction of the nitrate by nitric oxide.

TABLE 4. *Effect of nitric oxide* (50 *cm. press.*) *on a fixed mass* (*ca.* 0·1 *g.*) *of silver nitrate at* 115—125° *for different times.*

Expt. No.	Temp.	Time (hr.)	$AgNO_3$ taken (g.)	Composition of gas (c.c.): Total	NO	NO_2	Residue (mg.) * $AgNO_2$	$AgNO_3$	$AgNO_3$ used
44	115—117°	6	0·1004	104·83	104·42	0·41	3·182	96·9	3·5
45	,,	12	0·1006	105·65	105·24	0·41	3·18	97·1	3·5
46	120—122	3	0·1026	111·23	110·24	1·09	7·4	94·4	8·2
47	,,	6	0·1024	106·78	105·15	1·63	11·15	90·1	12·3
48	,,	30	0·1006	107·09	105·46	1·63	11·15	88·3	12·3
49	125—127	3	0·1012	106·53	105·12	1·41	9·085	91·2	10·01
50	,,	6	0·1020	105·79	104·91	1·88	12·07	89·0	13·00
51	,,	12	0·1020	106·87	104·99	1·88	12·07	89·0	13·00

* No residue of Ag.

Reaction of Silver Oxide and Nitrogen Dioxide at 110°, 130°, *and* 250°. This reaction under our conditions has been studied in order to find out if the reaction $Ag_2O + 2NO_2 = AgNO_2 + AgNO_3$ occurs. The results of these experiments, each of which was done for ½ hr., are given in Table 5 and show that the reaction produces both nitrite and nitrate but in a manner that produces silver also. Little nitric oxide is liberated in the reaction, though there are indications that it is probably involved therein. The reactions may therefore be $Ag_2O + NO_2 = Ag_2O_2 + NO$ and $Ag_2O_2 + 2NO = 2AgNO_2$ (Addison and Lewis, *J.*, 1953, 1874) simultaneously with $Ag_2O + NO_2 = AgNO_3 + Ag$.

TABLE 5. *Action of nitrogen dioxide on silver oxide at* 110—250°.

Expt. No.	Temp.	Ag_2O taken (g.)	N_2O_4 taken (g.) *	$AgNO_2$ formed (g.) †	$AgNO_3$ formed (g.) †	Ag formed (g.) †	Ag_2O left (g.) †	N_2O_3 formed (c.c.)	N_2O_4 left (c.c.)
52	110°	0·1040	0·2590 (63·0)	0·0114 (0·072)	0·0132 (0·078)	0·0110 (0·10)	0·0292 (0·125)	0·15	61·3
53	130	0·2630	0·2800 (68·2)	0·0616 (0·40)	0·0736 (0·434)	0·0972 (0·89)	0·201 (0·86)	nil	58·8
54	130	0·1086	0·3224 (78·5)	0·0123 (0·080)	0·01444 (0·085)	0·0117 (0·108)	0·0317 (0·13)	nil	—
55	250	0·1000	0·2912	0·00204	0·0559	0·05544	nil	0·25	67·1

* Parentheses give c.c.
† Moles or g.-atoms in parentheses.

Reaction of Silver Nitrate with (a) *Nitrogen Dioxide and* (b) *Nitric Oxide.*—The course of reaction (*a*) at 120°, 130°, and 200° for ½ hr. is shown in Table 6. There is slight oxidation at 120° and at 130°, and a more distinct one at 200°; at 130° and 200°, silver is present, showing that nitrite has decomposed. The slight oxidation at 120° may be attributed to very slight dissociation of nitrogen dioxide below 140°, and presumably there is no oxidation by nitrogen dioxide (Addison and Lewis, *loc. cit.*) : the reaction is therefore $AgNO_2 + O = AgNO_3$. The reaction (*b*) for 2 hr. is shown in Table 7. There is slight production of nitrogen as may be expected (Oza, *loc. cit.*; Oza and Walawalker, *J. Indian Chem. Soc.*, 1945, **22**, 243) because of absence of nitrate which permits the reaction $AgNO_2 + NO = AgNO_3 + \frac{1}{2}N_2$; the production of nitrate then represses this reaction as $AgNO_3 + NO \rightleftharpoons AgNO_2 + NO_2$ is conspicuous as already observed.

TABLE 6. *Action of nitrogen dioxide on silver nitrite at* 120°, 130°, *and* 200°

Expt. No.	Temp.	$AgNO_2$ taken (g.)	N_2O_4 taken (g.)	$AgNO_3$ formed (g.)	Ag formed (g.)	$AgNO_2$ left (g.)	N_2O_3 formed (c.c.)	N_2O_4 left (c.c.)
56	120°	0·1010	0·2200	0·00894	nil	0·0929	1·6	52·1
57	130	0·2660	0·1480	0·0326	0·00432	0·2250	8·82	27·8
58	200	0·2060	0·2650	0·0916	0·0423	0·0625	12·00	56·88

TABLE 7. *Action of nitric oxide* (*press.* 50 *cm.*) *on* $AgNO_2$ (*fixed mass*) *for* 2 *hr. at* 130°, 150°, 170°, *and* 200°.

Expt. No.	Temp.	$AgNO_2$ taken (g.)	Gas in system at end (c.c.) : Total	NO_2	NO	N_2	Residue (g.) : * $AgNO_3$	Ag (g.)	$AgNO_2$ (g.)	$AgNO_2$ used (g.) *
59	130°	0·3546	114·9	3·6	111·15	0·2	0·0349 (0·205)	0·0265 (0·245)	0·2834	0·07124 (0·463)
60	150	0·3534	120·4	5·4	114·45	0·5	0·0434 (0·255)	0·0530 (0·49)	0·2387	0·1147 (0·745)
61	170	0·3528	130·3	8·1	121·3	0·9	0·0514 (0·30)	0·0819 (0·76)	0·1893	0·1635 (1·06)
62	200	0·3500	142·6	12·2	129·3	1·1	0·0647 (0·38)	0·1018 (0·94)	0·1463	0·2037 (1·3)

* Parentheses used as in Table 1.

The above study has shown that under the conditions used in this work, of the possible solid products of the decomposition, *viz.*, silver and its nitrate and oxide, silver is likely to be slowly acted upon by nitrogen dioxide especially when the pressure in the system increases; nitrate is produced; silver nitrate reacts effectively with nitric oxide to replenish some of the consumed nitrite, and silver oxide reacts very effectively with nitric oxide even when the pressure of the gas is very small. An experiment showed that at 110—115° reaction occurred even when the pressure of nitric oxide was 5 cm. It thus became obvious that the cause of destruction of silver oxide lay probably in the simultaneous production of nitric oxide. If therefore nitric oxide

TABLE 8. *Decomposition of* $AgNO_2$ (*fixed mass*) *at* 130° *in oxygen* (11 *cm. press.*) *for varying periods* (a) *without addition of silver* (*expts.* 63—70) *and* (b) *with addition of finely divided silver* (*expts.* 71—74).*

Expt. No.	Time (hr.)	$AgNO_2$ taken (g.)	Gas in system at end (c.c.) : Total	NO_2	N_2	O_2	Residue : Ag_2O (mg.)	Ag (mg.)	$AgNO_2$ (mg.)	$AgNO_3$ (mg.)	$AgNO_2$ used (g.)
63	½	0·3510	110·1	1·1	nil	109·0	nil	1·62	328·0	23·0	23·0
64	1	0·3522	111·14	2·4	trace	108·7	nil	2·16	302·8	52·2	49·4
65	2	0·3522	108·4	3·00	0·11	105·3	nil	2·7	289·3	65·1	62·9
66	4	0·3506	108·3	4·2	0·15	104·0	1·32	3·2	269·8	82·2	80·8
67	6	0·3507	107·3	5·5	0·2	101·65	1·66	5·2	255·2	92·4	95·5
68	8	0·3546	107·3	6·0	0·22	101·0	1·5	6·7	241·9	111·2	112·7
69	10	0·3536	107·3	7·2	0·27	99·8	1·2	8·1	232·1	119·8	121·5
70	12	0·3538	105·9	9·2	0·20	96·6	1·2	10·8	216·7	122·1	137·1
71	1	0·3512	106·4	1·1	trace	105·3	nil	36·7	328·0	23·2	23·2
72	2	0·3504	106·7	2·8	0·14	103·8	nil	37·2	287·2	67·2	63·2
73	4	0·3522	107·4	4·2	0·18	103·0	1·28	38·4	270·5	83·7	81·7
74	8	0·3518	109·2	6·1	0·21	102·9	1·44	41·8	238·1	113·3	113·7

* Finely divided silver added in expts. 71—74 was, respectively, 0·0350, 0·0352, 0·0356, and 0·0352 g.

could be destroyed before it completely reacted with silver oxide, the latter might be isolated, at least in part.

Decomposition of Silver Nitrite in Oxygen at 130°.—The results of experiments with 0·35 g. of the nitrite decomposed for varying periods of time at 130° in an atmosphere of oxygen (11 cm. press.) are given in Table 8; they show the presence of silver oxide in the solid products after 4 hr. or more. Silver nitrite is present throughout along with its products of decomposition. It may be argued that the oxide may have been produced by the action of oxygen on finely divided silver produced in the system, but it must be remembered that silver nitrite is continuously decomposing and producing oxides of nitrogen so that the silver metal is in contact *not with oxygen* but with a mixture of nitrogen dioxide and oxygen: comparison with the results of time expts. (1—8, Table 1) shows that more nitrate is present in the experiments now described. Expts. 71—74 were done under the same conditions as expts. 1—8, but under oxygen and with the previous addition of 0·035 g. of silver to the 0·35 g. of nitrite: the results show larger formation of nitrate and no increased formation of silver oxide.

Conclusion.—The present study shows that the primary change in the decomposition of silver nitrite is

$$2AgNO_2 \rightleftharpoons Ag_2O + N_2O_3\ (= NO + NO_2) \qquad (1)$$

This brings silver nitrite into line with the other nitrites already studied by Oza and his co-workers. The dissociation (1) is followed by reactions of silver oxide with nitric oxide (and also, to a certain extent, with nitrogen dioxide) to destroy the former. In the meanwhile some oxygen from silver oxide reacts with nitrite to form nitrate:

$$AgNO_2 + O = AgNO_3 \qquad (2)$$

Nitrate, produced at higher temperatures, is produced from nitrite, and oxygen from nitrogen dioxide.

Silver oxide reacts vigorously with nitric oxide to produce nitrate as the primary product: nitrite is produced subsequently from the nitrate, thus replenishing nitrite:

$$AgNO_3 + NO \rightleftharpoons AgNO_2 + NO_2 \qquad (3)$$

Silver oxide reacts with nitrogen dioxide to liberate silver and but little nitric oxide; the reaction may proceed by intermediate formation of silver peroxide:

$$Ag_2O + NO_2 = Ag_2O_2 + NO \qquad (4)$$

followed by the action of nitrogen oxide and dioxide on silver peroxide to produce nitrite and nitrate. Production of silver can be ascribed to the reaction

$$Ag_2O + NO_2 = AgNO_3 + Ag \qquad (5)$$

Nitrogen is never produced in the decomposition of silver nitrite, as nitrate is produced in the system almost from the start of the decomposition so that access of nitric oxide to nitrite is prevented by reaction (3).

Ultimately silver, silver nitrate, silver nitrite, nitric oxide, and nitrogen dioxide are left in the system except when the heating is intense (480°), in which case no nitrite is left. Neither silver nor silver nitrate appears to be the primary product of the reaction.

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