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The Thermal Decomposition of Silver Hyponitrite

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RECEIVED FEBRUARY 14, 1955

Of the solid products, only silver oxide is produced in the primary change $Ag_2N_2O_2 = Ag_2O + N_2O$, which is immediately followed by reaction or reactions in which silver nitrite is produced. Silver, silver nitrite and silver nitrate are all products of secondary changes. The complex nature of the decomposition is due to the reactions which follow the formation of silver nitrite. No such reaction as $Ag_2N_2O_2 = 2Ag + 2NO$ seems to occur. Silver nitrate is not directly formed from silver hyponitrite. Apparently silver hyponitrite is not oxidized by nitrogen dioxide at or below 150°.

The thermal decomposition of silver hyponitrite has been studied by a number of investigators.[1-6] Divers and Haga[1] reported that the decomposition is similar to that of nitrite as they found nitric oxide, silver and silver nitrate. Divers[5] later detected nitrogen dioxide, nitrogen and traces of nitrite. Thum[3] found nitrous oxide but no nitrite. Divers obtained silver nitrate as required by

$$3(AgNO)_2 = 4Ag + 2AgNO_3 + 2N_2 \quad (1)$$

and assumed the primary change to be

$$2(AgNO)_2 = 4Ag + N_2 + 2NO_2 \quad (1a)$$

which was followed by

$$(AgNO)_2 + 4NO_2 = 2AgNO_3 + 4NO \quad (1b)$$

Kirschner[4] supposed that nitrous anhydride was formed in the primary stage. Ray and Ganguli[6] suggested, on the other hand, that the primary changes are

$$2(AgNO)_2 = 2N_2O + (2Ag_2O = 4Ag + O_2) \quad (2a)$$

$$(AgNO)_2 = 2Ag + 2NO \quad (2b)$$

$$5(AgNO)_2 = AgNO_3 + 2N_2 + (2Ag_2O = 4Ag + O_2) \quad (2c)$$

thus, according to them nitrate is formed from silver hyponitrite. Both Ray and Divers ascribed nitrogen production to the primary change, but Divers' equations differ for low (1a) and for high (1) temperatures. Ray and Ganguli's results do not conform to the requirements of (1) supposed by Divers to explain quantitatively the reaction at higher temperatures. Ray and Ganguli assumed the formation of silver oxide but found none in the residue.

We have studied the decomposition, *in vacuo*, of silver hyponitrite and mixtures of the hyponitrite with silver oxide and silver nitrite. Silver oxide was isolated; temperature was found to have little influence on the nature of the products; and nitrogen, nitrous oxide, nitric oxide, nitrogen dioxide, silver, silver oxide, silver nitrite and silver nitrate were *all* produced in the decomposition as long as hyponitrite was present. The primary change is $Ag_2N_2O_2 = Ag_2O + N_2O$; the secondary changes arise from silver oxide and the formation of silver nitrite in the system. The secondary changes mask the primary change altogether.

(1) E. Divers and T. Haga, *J. Chem. Soc.*, **45**, 78 (1884).
(2) Vanderplaats, *Ber.*, **10**, 1507 (1887).
(3) A. Thum, "Biatrige Zur Kentnis der untersalpetrigensaure," Prag. 1893; *Sietzber Akad. Vien.*, **102**, 284 (1893); *Monatsh.*, **14**, 294 (1893).
(4) A. Kirschner, *Z. anorg. Chem.*, **16**, 424 (1898).
(5) E. Divers, *J. Chem. Soc.*, **75**, 108 (1899); *Ber.*, **36**, 2878 (1903).
(6) P. C. Ray and A. C. Ganguli, *J. Chem. Soc.*, **91**, 1399 (1907).

Experimental

Materials.—**Silver hyponitrite** was prepared by dissolving analytically pure $Na_2N_2O_2 \cdot 5H_2O$ in the minimum amount of water and adding 8% silver nitrate dropwise with constant stirring to a darkened beaker; no brown precipitate should be formed. The canary yellow precipitate, which had been washed with water, was treated with alcohol and ether, and dried in the dark in a desiccator. The salt retained its bright yellow color. *Anal.* Calcd. for $Ag_2N_2O_2$: Ag, 78.26; N, 10.14. Found: Ag, 78.3; N, 10.71. Silver oxide was prepared from silver nitrate and dilute potassium hydroxide, and silver nitrite from silver nitrate and sodium nitrite; both were analytically pure.

Analyses. Gas.—Nitrous anhydride and nitrogen dioxide were absorbed by alkali which was analyzed for nitrite (or for nitrite and nitrate, if nitric oxide was not present in the gas) and calculated according to the equation $N_2O_3 + 2KOH = 2KNO_2 + H_2O$ or $2NO_2 + 2KOH = KNO_3 + KNO_2 + H_2O$. The pumped gas contained nitrous oxide, nitric oxide and nitrogen. Nitrous oxide was absorbed in cold alcohol and the gas stored over the alcohol for two hours after contraction had ceased. Nitric oxide was absorbed in alkali sulfite saturated with nitrous oxide and nitrogen. Residual gas was taken as nitrogen. All recorded volumes are at N.T.P. **Residue.**—The residue which contained Ag, Ag_2O, $Ag_2N_2O_2$, $AgNO_2$ and $AgNO_3$ was treated with hot water until the filtrate did not test for nitrite or for alkalinity. The solubilities of Ag_2O and $Ag_2N_2O_2$ at 80° were 0.06804 and 0.00024 (g./liter), respectively; filtrate (A) therefore contained Ag_2O, $AgNO_2$ and $AgNO_3$ while the insoluble portion (B) contained $Ag_2N_2O_2$ and Ag. (B) was treated with 0.08–0.1 *N* nitric acid which dissolved $Ag_2N_2O_2$ but did not attack Ag; the latter was dissolved in nitric acid (1:1). (A) was analyzed for total Ag, nitrite and nitrate[7]; if the amount of nitrate was small, 0.01 *N* potassium nitrate was added as a carrier. The total Ag minus the Ag equivalent of the nitrite and nitrate gave the Ag present as Ag_2O.

Apparatus and Procedure.[8]—The oil-bath was controlled to ±1°. For higher temperatures, a cylindrical nichrome furnace was used which was controlled by a rheostat to ±5°. To find the decomposition temperature of hyponitrite, 0.2 g. was heated at 100° for 30 minutes, then the temperature was raised 10° in 15 minutes, maintained constant for another 15 minutes and so forth. The salt retained its bright yellow color and decomposed without explosion at 158°.[9] Divers[5] reported that the decomposition occurs between 140 and 160°; Thum[3] observed dense fumes at 100° and the brisk evolution of gas at 140° and denied the explosive character of the decomposition reported by Vanderplaats.[2]

The influence of some variables on the decomposition of silver hyponitrite is shown in Table I. Experiments 1–6 show that the volume of free gas (unabsorbed by potassium hydroxide) contracts above 170°, even in the half-hour experiments; this indicates the conversion of nitric oxide to nitrogen dioxide.

Experiments 7–12 show the effect of temperature on hyponitrite heated for one hour: (a) the residue contains no $Ag_2N_2O_2$ or Ag_2O, while the gas contains all the products of the decomposition, N_2, N_2O, NO and NO_2, in *all* the experiments; (b) Ag increases and $AgNO_2$ diminishes with rising

(7) M. S. Shah and T. M. Oza, *ibid.*, 725 (1931).
(8) T. M. Oza and V. T. Oza, *ibid.*, 907 (1953).
(9) A. E. Menke, *ibid.*, **33**, 401 (1878); W. Zorn, *Ber.*, **10**, 1306 (1878).

TABLE I

EFFECTS OF TEMPERATURE, MASS AND TIME ON THE DECOMPOSITION OF SILVER HYPONITRITE[a]

1 Expt. no.	2 $Ag_2N_2O_2$, g.	3 Temp., °C.	4 Time, hr.	5 Total gas ml.	6 Composition of gas, % NO	NO_2	N_2O	N_2	7 Solid products formed per unit $Ag_2N_2O_2$ consumed Ag	Ag_2O	$AgNO_3$	$AgNO_2$	8 $Ag_2N_2O_2$ consumed,[a] g.	9 Ratios $\frac{Ag_2O}{Ag}$	$\frac{AgNO_2}{AgNO_3}$	10 Solid products, g. Ag[a]	Ag_2O	$AgNO_2$	$AgNO_3$
1	0.2526	160	0.5	5.6	88.75		8.00	3.2											
2	.2512	170	.5	27.6	85.9		9.5	4.5											
3	.2545	180	.5	27.2	81.3		12.9	5.9											
4	.2542	160	2	26.8	85.8		9.8	4.4											
5	.2516	180	2	25.5	88.3		7.1	4.6											
6	.2534	200	2	23.5	84.3		8.1	7.7											
7	.1018	160	1	14.7	67.2	16.5	7.2	9.1	1.8	Nil	0.025	0.021	All consumed		1.28	0.0764 (7.1×10^{-4})		0.0025 (1.6×10^{-5})	0.0022 (1.3×10^{-5})
8	.1020	180	1	14.9	69.7	16.5	5.4	8.3	1.9	Nil	.016	.023	All consumed		0.77	0.0773 (7.2×10^{-4})		0.0017 (1.1×10^{-5})	0.0024 (1.4×10^{-5})
9	.1018	200	1	14.3	65.8	21.9	4.9	7.4	1.9	Nil	.010	.014	All consumed		.74	0.0761? (7.1×10^{-4})		0.0009 (6.4×10^{-6})	0.0015 (8.6×10^{-6})
10	.1016	220	1	15.2	64.9	24.7	3.5	6.9	1.9	Nil	.007	.012	All consumed		.66	0.0783 (7.2×10^{-4})		0.0007 (4.8×10^{-6})	0.0012 (7.3×10^{-6})
11	.1016	240	1	15.3	65.4	26.3	1.8	6.5	2.0	Nil	.005	.011	All consumed		.48	0.0799 (7.4×10^{-4})		0.0005 (3.2×10^{-6})	0.0011 (6.7×10^{-6})
12	.1036	480	1	16.1	69.4	23.4	3.9	3.3	2.0	Nil	...	.016	All consumed		..	0.0799 (7.4×10^{-4})		Nil	0.0017 (1.0×10^{-5})
13	.1504	160	1	17.9	74.2	15.6	7.0	3.1	1.8	0.06	.007	.011	0.1473 (5.3×10^{-4})	0.33	.73	0.1054 (9.8×10^{-4})	0.0094 (3.9×10^{-5})	0.0011 (7.0×10^{-6})	0.0016 (9.6×10^{-6})
14	.1836	160	1	23.5	78.3	13.4	5.7	2.6	1.7	.06	.007	.010	0.1750 (6.3×10^{-4})	.035	.77	0.1251 (1.2×10^{-3})	0.0107 (4.6×10^{-5})	0.0012 (7.7×10^{-6})	0.0017 (1.0×10^{-5})
15	.2445	160	1	32.0	78.8	12.6	4.4	4.1	1.7	.05	.006	.009	0.2307 (8.4×10^{-4})	.03	.73?	0.1784 (1.6×10^{-3})	0.0115 (4.9×10^{-5})	0.0014 (9.0×10^{-6})	0.0021 (1.2×10^{-5})
16	.3018	160	1	41.3	78.6	10.8	5.3	5.2	1.9	.04	.005	.007	0.2845 (1.0×10^{-3})	.02	.80	0.2095 (1.9×10^{-3})	0.0119 (5.1×10^{-5})	0.0015 (1.0×10^{-5})	0.0021 (1.2×10^{-5})
17	.3498	160	1	47.7	78.3	12.2	4.9	4.6	1.9	.04	.005	.007	0.3308 (1.2×10^{-3})	.02	.82	0.2429 (2.2×10^{-3})	0.0146 (6.3×10^{-5})	0.0016 (1.1×10^{-5})	0.0022 (1.3×10^{-5})
18	.3996	160	1	55.2	78.2	13.0	4.4	4.4	1.9	.04	.005	.006	0.3772 (1.4×10^{-3})	.02	.81	0.2765 (2.6×10^{-3})	0.0173 (7.5×10^{-5})	0.0018 (1.2×10^{-5})	0.0024 (1.4×10^{-5})
19	.1801	160	0.25	1.4	*50.0*	*43.4*	*6.6*	Nil	*1.3*	*.28*	...	...	0.0187 (6.8×10^{-5})	.23	..	0.0097 (9.0×10^{-5})	0.0053 (2.3×10^{-5})	Test only	Test only
20	.1868	160	0.5	11.3	76.9	15.2	2.4	5.4	1.8	.09	...	.005	0.0875 (3.2×10^{-4})	.06	..	0.0612 (5.7×10^{-4})	0.0075 (3.2×10^{-5})	Test only	0.0004 (2.5×10^{-6})
21	.1867	160	0.75	13.3	71.8	19.0	4.6	4.6	1.8	.10	.008	.009	0.0967 (3.5×10^{-4})	.06	.99	0.0661 (6.1×10^{-4})	0.0093 (4.0×10^{-5})	0.0007 (4.8×10^{-6})	0.0008 (4.9×10^{-6})
22	.1836	160	1	23.5	78.3	13.4	5.7	2.6	1.8	.06	.006	.010	0.1750 (6.3×10^{-4})	.04	.70	0.1251 (1.2×10^{-3})	0.0108 (4.6×10^{-5})	0.0011 (7.0×10^{-6})	0.0017 (1.0×10^{-5})
23	.1843	160	1.25	27.7	77.8	13.5	5.1	3.6	1.8	.09	.007	.015	0.1765 (6.4×10^{-4})	.04	.53	0.1261 (1.2×10^{-3})	0.0103 (4.4×10^{-5})	0.0013 (8.2×10^{-6})	0.0026 (1.5×10^{-5})
24	.1871	160	1.5	31.2	77.7	13.8	5.1	3.4	1.8	.05	.014	.039	0.1803 (6.5×10^{-4})	.03	.41	0.1272 (1.2×10^{-3})	0.0089 (3.8×10^{-5})	0.0026 (1.7×10^{-5})	0.0070 (4.1×10^{-5})

[a] Numbers in parentheses give g. atoms or g. moles.

TABLE II

THE COMPOSITION OF GAS AND SOLID PRODUCTS FORMED AT VARIOUS STAGES IN THE DECOMPOSITION OF $Ag_2N_2O_2$ (0.3 g.) AT 160°

1	2	3	4 Gas evolved,[a] ml.					5 Solid products, g.				6 Solid products formed per unit $Ag_2N_2O_2$ consumed, g.			
Expt. no.	Stage no.	$Ag_2N_2O_2$ consumed	Total	NO	NO_2	N_2O	N_2	Ag	Ag_2O	$AgNO_2$	$AgNO_3$	Ag	Ag_2O	$AgNO_2$	$AgNO_3$
25	1	0.0748	7.2	4.9	1.6	0.36	0.36	0.0501	0.0070	Test	0.00037	0.67	0.09	Trace only	0.005
				(68)	(22)	(5)	(5)								
26	2	.0502	7.8	5.7	1.2	0.47	0.47	.0368	.00001	.00104	.00084	.74	.0002	0.02	.017
				(73)	(15)	(6)	(6)								
27	3	.0561	8.5	6.75	0.95	0.46	0.36	.0416	.00075	.00024	.00118	.74	.013	.004	.021
				(79)	(11)	(5)	(5)								
28	4	.0845	12.4	9.9	1.9	0.27	0.27	.0655	.0029	.00015	0018	.77	034	0018	021
				(80)	(15)	(2.5)	(2.5)								
29	5	.0372	7.9	5.0	1.6	0.7	0.65	.0413	None (all used up)	.0012	0034	1 1	Nil	032	092
				(63)	(20)	(9)	(8)								

[a] Values in parentheses are percentages of gas evolved.

temperature; the latter disappears at 480° while $AgNO_3$ increases from 160 to 180°, falls off and then increases again at 480°; the ratio $AgNO_2/AgNO_3$ decreases with increasing temperature; (c) the volume of gas steadily increases (*cf.* expts. 1–6) with rising temperature; (d) there is little change in the proportion of nitric oxide, but the proportion of nitrogen dioxide increases above 180°, while that of nitrous oxide and nitrogen diminishes with rising temperature (up to 240° for nitrous oxide).

Experiments 13–18 show the effect of the mass of salt decomposed. (a) Both Ag_2O and hyponitrite are present in the residue, the amount of Ag_2O increasing with the increasing mass of hyponitrite; per unit $Ag_2N_2O_2$ consumed Ag is fairly constant, but Ag_2O is not and Ag_2O/Ag diminishes with increasing mass. (b) $AgNO_2/AgNO_3$ tends to increase. (c) The percentage of nitrogen and nitrous oxide are, as before, low.

Experiments 19–24 show the effect of heating time. (a) In the 15 minute experiment (19) nitrogen is absent; this indicates that it is not a product of the primary change. The proportion of nitrous oxide is highest in this experiment. (b) Nitrate appears earlier than nitrite. (c) Ag_2O increases up to 1 hour and then diminishes, but Ag, $AgNO_2$ and $AgNO_3$ increase with time. (d) The proportion of nitric oxide is the lowest and that of nitrogen dioxide the highest at the start. (e) Per unit hyponitrite consumed, Ag_2O produced is very high in 15 minutes (*cf.* N_2O), falls rapidly in the next 15 minutes, and remains low from then on. (f) As Ag_2O/Ag is very high in expt. 19, as compared with expts. 20–24, Ag_2O is probably formed first and Ag produced from it afterwards. (g) The amounts of $AgNO_3$ and $AgNO_2/AgNO_3$ show that the formation of nitrate increases with time. The results of expt. 19 have been reproduced.

$Ag_2N_2O_2$ (0.3 g.) was heated at 160° until the decomposition, as seen by the release of gas, ceased; the pump was kept working and the gas collected as formed in five consecutive lots. The proportion of N_2O was highest in the first lot. The residue contained some nitrite even though decomposition had ceased. Table II contains the results of five experiments on heating $Ag_2N_2O_2$ in this way; the decomposition was allowed to proceed to a different extent in each experiment. The quantities given for a stage are the differences between the amount at that stage and the amount found in the preceding stage or stages.

On the basis of the amount found and the amount produced per unit $Ag_2N_2O_2$ consumed, Ag_2O is high and $AgNO_2$ and $AgNO_3$ are low in the first stage. In the second stage Ag_2O falls off markedly while $AgNO_3$ and $AgNO_2$ increase. This indicates that Ag_2O is formed initially and the latter substances are formed later on. If the relatively low percentage of nitrous oxide in the first stage is attributed to its adsorption on the glass walls,[10] these results suggest that the primary change is $Ag_2N_2O_2 = Ag_2O + N_2O$. The reaction $Ag_2N_2O_2 = 2Ag + 2NO$ is probably not a primary change, since $Ag_2O/Ag_2N_2O_2$ and Ag_2O/Ag are both high in the initial stage; the presence of considerable Ag early in the decomposition does not necessarily indicate that this reaction occurs since Ag is more stable than Ag_2O. In the second stage the nitrite, which has been formed at the expense of Ag_2O, may be a product of the reaction of (a) Ag_2O with $Ag_2N_2O_2$ or (b) Ag_2O with NO (and/or NO_2). That more nitrate than nitrite appears in the first stage does not mean that the former is produced earlier in the decomposition, since under the experimental conditions $AgNO_3$ is more stable than $AgNO_2$ which reacts to give $AgNO_3$ and the oxides of nitrogen.[11]

In the third stage the amount of nitrite decreases with an increase in nitrate. In the fourth stage, the amount of gas evolved is proportional to the large amount of hyponitrite consumed, but the percentage of N_2O is relatively low; the amounts of Ag_2O and $AgNO_3$ and the proportion of NO and NO_2 become greater. In the last stage $Ag_2N_2O_2$ and Ag_2O disappear, NO falls, NO_2 increases and nitrite and nitrate increase considerably.

In the first and fourth stages, the hyponitrite consumed is relatively large, while the proportion of N_2O produced is not; in the fifth stage the hyponitrite consumed is small and the percentage of N_2O is high. Thus, the N_2O produced is not directly related to the hyponitrite consumed and silver hyponitrite is probably consumed in more than one way.

Decomposition of Mixtures of Ag_2O and $Ag_2N_2O_2$.—Since less nitrous oxide is formed than would be expected from the reaction $Ag_2N_2O_2 = Ag_2O + N_2O$, some of the hyponitrite is probably oxidized to nitrite and/or nitrate. As Ag_2O is always present when hyponitrite is present, $Ag_2N_2O_2$ and Ag_2O may react. This hypothesis was tested by decomposing mixtures of $Ag_2N_2O_2$ and Ag_2O. The results are given in Table III. On the whole the proportion of N_2O is lower than that found in the decomposition of hyponitrite alone. At 150 and 160° more nitrite is formed than nitrate; $AgNO_2/AgNO_3$ is highest in 15 minutes at 160° and decreases with time; and this ratio falls with rising temperature. This shows that nitrate is produced from the nitrite.

It is surprising that at 150°, at which $AgNO_2$ is unstable, *only a trace of nitrate is found although nitrite is present.* The presence in the system of the dissociation products of $AgNO_2$ (Ag_2O, NO and NO_2)[11] probably retards the decomposition of the nitrite.

These results indicate that $Ag_2N_2O_2$ reacts with Ag_2O to produce nitrite and *not* nitrate: $Ag_2N_2O_2 + 2Ag_2O = 2AgNO_2 + 4Ag$. The low production of nitrous oxide in the decomposition of $Ag_2N_2O_2$ is therefore due to this reaction. Furthermore, the large amount of silver found can be accounted for in this way and by the decomposition of $AgNO_2$ which is known to produce Ag. The reaction $Ag_2O + NO_2 = AgNO_3 + Ag$ may also contribute to the production of nitrate.[12]

The fact that nitrate is present in larger proportions than nitrite in the initial stage of the decomposition at 160° is another evidence for the absence of the reaction $Ag_2N_2O_2 = 2Ag + 2NO$ in the primary stage. If NO were produced in large amounts it would not only have affected the stability of Ag_2O but also reduced the proportion of nitrate by the reaction[8] $AgNO_3 + NO = AgNO_2 + NO_2$ which we have found[11] to be quite prominent at such temperatures. The fact that at a higher temperature a larger percentage of nitrous oxide is produced *in one-half hour* (expts. 1–6) also supports the view that nitric oxide is not produced in the primary stage.

Decomposition of Mixtures of $AgNO_2$ and $Ag_2N_2O_2$.—To determine whether the reaction $Ag_2N_2O_2 = 2Ag + 2NO$ ac-

(10) D. H. Bengham and F. P. Burt, *J. Phys. Chem.*, **24**, 540 (1925).

(11) T. M. Oza, V. T. Oza and R. H. Thaker, *J. Chem. Soc.*, 2457 (1955).

(12) P. Sabatier and J. B. Senderens, *Bull. soc. chim.*, [3] **9**, 668 (1892); *Compt. rend.*, **115**, 236 (1893); **114**, 1429 (1892).

TABLE III

THE DECOMPOSITION OF MIXTURES OF $Ag_2N_2O_2$ AND Ag_2O

1 Expt. no.	2 $Ag_2N_2O_2$, g.	3 Ag_2O, g.	4 Temp., °C.	5 Time, hr.	6 Gas evolved, ml.	7 Compn. of gas in % NO	NO_2	N_2O	N_2	8 $Ag_2N_2O_2$ consumed, g.	9 Solid products,[a] g. Ag	Ag_2O	$AgNO_2$	$AgNO_3$	10 $AgNO_2/AgNO_3$	11 Ag_2O consumed, g.
30	0.1012	0.0274	150	1	0.52	50.0	50.0	..	..	0.0081	0.0054 (5.0×10^{-5})	0.0257 (1.1×10^{-4})	0.0015 (9.9×10^{-6})	Test only	Large	0.0017
31	.1000	.0211	160	0.25	1.55	46.5	40.0	6.5	7.0	.0187	0.0126 (1.2×10^{-4})	0.0188 (8.1×10^{-5})	0.0054 (3.5×10^{-5})	0.0011 (6.3×10^{-6})	14	.0023
32	.1002	.0212	160	0.5	6.1	76.4	15.4	3.5	4.8	.0298	0.0272 (2.5×10^{-4})	0.0123 (5.3×10^{-5})	0.0068 (4.4×10^{-5})	0.0014 (8.1×10^{-6})	5.5	.0089
33	.1000	.0210	160	0.75	10.4	74.1	16.9	4.2	4.8	.0602	0.0504 (4.7×10^{-4})	0.0108 (4.7×10^{-5})	0.0076 (4.9×10^{-5})	0.0019 (9.9×10^{-6})	4.9	.0102
34	.1004	.0206	160	1	13.7	74.2	17.2	4.0	4.6	.1004	0.0850 (7.9×10^{-4})	0.0076 (3.3×10^{-5})	0.0063 (4.1×10^{-5})	0.0028 (1.7×10^{-5})	2.5	.1004
35	.1000	.0202	180	1	14.3	72.2	19.0	4.4	4.4	All consumed	0.0890 (8.2×10^{-4})	Nil	0.0059 (3.8×10^{-5})	0.0030 (1.8×10^{-5})	2.1	.018
36	.1004	.0200	200	1	14.7	68.1	21.0	4.9	5.9	All consumed	0.0915 (8.5×10^{-4})	Nil	0.0055 (3.6×10^{-5})	0.0035 (2.1×10^{-5})	1.7	All consumed
37	.1000	.0208	220	1	13.0	52.1	30.6	5.5	11.8	All consumed	0.0923 (8.5×10^{-4})	Nil	0.0028 (1.8×10^{-5})	0.0052 (3.1×10^{-5})	0.6	All consumed
38	.1012	.0214	240	1	13.0	51.7	31.0	5.5	11.8	All consumed	0.0923 (8.5×10^{-4})	Nil	0.0027 (1.8×10^{-5})	0.0053 (3.1×10^{-5})	0.5	All consumed
39	.1000	.0206	480	1	13.3	51.0	32.1	5.4	11.5	All consumed	0.0939 (8.7×10^{-4})	Nil	....	0.0055 (3.3×10^{-5})	...	All consumed

[a] Values in parentheses are gram atoms or gram moles.

TABLE IV

THE DECOMPOSITION OF MIXTURES OF $Ag_2N_2O_2$ AND $AgNO_2$

1 Expt. no.	2 $Ag_2N_2O_2$, g.	3 $AgNO_2$ added, g.	4 Temp., °C.	5 Time, hr.	6 Total gas, ml.	7 Composition of gas in % NO	NO_2	N_2O	N_2	8 Solid products, g. Ag	Ag_2O	$AgNO_2$	$AgNO_3$	9 $Ag_2N_2O_2$ consumed, g.
40	0.1016	0.0256	120	1	0.84	66.7	33.3	..	..	Nil	Nil	0.0256	Nil	Nil
41	.1020	.0244	130	1	0.84	66.7	33.3	..		0.0041	Nil	.0190	0.0010	Nil
42	.1020	.0264	140	1	3.1	61.2	38.8	..		.0097	Nil	.0095	.0031	Nil
43	.1020	.0256	150	1	4.1	67.9	32.1	..		.134	Nil	.0047	.0033	Nil
44	.1000	.0050	160	1	4.8	62.1	28.5	5.7	3.8	.0359	0.00945	.0036	.0015	0.0574
45	.1000	.0050	160	4	15.6	71.1	18.4	6.4	4.1	.0780	Nil	.0025	.0031	.1000
46	.1000	.0100	160	4	15.5	20.0	5.4	5.4	4.1	.0810	Nil	.0025	.0040	.1000
47	.1000	.0154	160	4	16.4	20.9	5.1	5.1	3.9	.0840	Nil	.0025	.0052	.1000

companies $Ag_2N_2O_2 = Ag_2O + N_2O$ in the primary stage, the decomposition of mixtures of silver hyponitrite and silver nitrite was studied (Table IV). $AgNO_2$ decomposes at 128°[11] and $Ag_2N_2O_2$ at 158°; the decomposition of the nitrite, therefore, would expose the Ag_2O, produced by the decomposition of $Ag_2N_2O_2$, to nitrous gases. Although $AgNO_2$ produces more nitrogen dioxide than nitric oxide, the effect would be noticeable. The hyponitrite remains unchanged up to 150° although nitrite has decomposed; this indicates that hyponitrite, like nitrite, is not oxidized by nitrogen dioxide at 150°. The reaction at 160° is very slow; 0.1 g. of $Ag_2N_2O_2$ which decomposes completely in 1 hour in the absence of added nitrite (expt. 7, Table I), took 4 hours to decompose. The amount of Ag_2O after 1 hour at 160° was 0.0094 g. (expt. 44) as compared with 0.06 g. formed from 0.15 g. of $Ag_2N_2O_2$ under the same conditions (Table I, expt. 13); this shows that oxides of nitrogen react with Ag_2O. Therefore, in a system in which nitrous gases are generated, Ag_2O is consumed more effectively to produce nitrite and nitrate. As neither nitrite nor nitrate is present in appreciable amounts at the start of the decomposition (Table I, expt. 19) when Ag_2O and nitrous gases are present, the reaction $Ag_2N_2O_2 = 2Ag + 2NO$, which would introduce large additionala mounts of nitric oxide *in the system, containing* Ag_2O, *probably does not occur.*

Conclusion

The primary change in the decomposition of silver hyponitrite appears to be

$$Ag_2N_2O_2 = Ag_2O + N_2O \quad (I)$$

Apparently this reaction is not accompanied by any other change, such as $Ag_2N_2O_2 = 2Ag + 2NO$. Reaction I is instantly followed by

$$Ag_2N_2O_2 + 2Ag_2O = 2AgNO_2 + 4Ag \quad (II)$$

The formation of $AgNO_2$ in this way, at 160° and above, is followed by its decomposition (above 128°) producing, ultimately, $AgNO_3$, Ag and oxides of nitrogen. Nitrate is formed from nitrite and not directly; it may be produced, to some extent, by $Ag_2O + NO_2 = AgNO_3 + Ag$. As nitric oxide is formed it reacts with nitrate to regenerate nitrite to some extent, $AgNO_3 + NO \rightleftarrows AgNO_2 + NO_2$.

The decomposition of silver nitrite, which follows reactions I and II, retards the decomposition of silver hyponitrite by reaction I. The formation of nitrite from the hyponitrite also reduces the amount of hyponitrite decomposing by I and explains low percentage of nitrous oxide in the gas; although I is the primary change, the reaction apparently stops as soon as Ag_2O and $AgNO_2$ (optimum) are present and starts again when these approach a limiting concentration. Thus, the decomposition of silver hyponitrite seems to proceed by the propelling action of silver oxide formed, at intervals, during the decomposition.

That I is not accompanied by $Ag_2N_2O_2 = 2Ag + 2NO$ is supported by the following observations: (a) nitric oxide destroys Ag_2O rapidly with the formation of nitrogen dioxide, nitrite and nitrate; (b) silver oxide oxidizes silver hyponitrite even at 150° while the oxides of nitrogen do not do so; and (c) when large quantities of silver nitrite are present in the system containing silver hyponitrite, silver oxide is not found.

The formation of nitrogen is not explained. It is found whenever silver oxide is present or produced in contact with nitric oxide or oxides of nitrogen. As nitric oxide and nitrogen dioxide are both present in the system, it is not likely that the reaction[8] $AgNO_2 + NO = AgNO_3 + {}^1/_2N_2$ occurs to any appreciable extent.

Thanks are due to Dr. V. T. Oza for help in blowing the systems and for gas analyses.

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Measurement of the Amount of Bound Water by Ultrasonic Interferometer

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RECEIVED DECEMBER 13, 1954

A general theory which enables us to evaluate the amount of the bound water of non-electrolyte and of high polymer in solution from ultrasonic velocity measurements has been introduced, and applied for glucose, maltose and dextrin solutions. The ultrasonic velocity was measured by an interferometer making use of X-cut crystal of resonance frequency 1 mc. The measurements were made at 20.0°. The amount of bound water was found to be 0.43, 0.23, 0.40 cc./g. of glucose, maltose and dextrin, respectively.

Introduction

It is a well-known fact that, in solutions of electrolytes, the water molecules bound to an electrolyte ion are compressed owing to the strong electric field of the ion to form a very hard structure. Passinski,[1] Wada[2] and Sasaki[3] evaluated the degree of hydration of ions from adiabatic compressibility measurements. They assumed the compressibility of bound water and of the ion itself to be both negligibly small. But the applicability of this method for the evaluation of non-electrolytes or high polymers in aqueous solutions is questionable, the bound water of non-electrolytes or the molecules of high polymers being reasonably supposed to be of appreciable compressibility. We have deduced a more general formula taking account of the compressibilities of bound water and of the solute particle, and have applied it to the solutions of sugars as well as high polymers and estimated the amount of bound water.

Theoretical

If M grams of solute is dissolved in V_0' cc. of solvent, some of the solvent, say v_0' cc., will be attached to the solute and compressed to be v_2' cc., and, consequently, there will result a solution of volume V' cc. Accordingly it follows that

$$V' = V_0' + V_1' + v_2' - v_0' \quad (1)$$

in which

$V_1' = M/d_1$ = volume of solute in V' cc. soln.
d_1 = true density of solute in soln. (solvation effect being not taken into account)

Differentiating (1) with respect to the pressure, P

$$\frac{dV'}{dP} = \frac{dV_0'}{dP} + \frac{dV_1'}{dP} + \frac{dv_2'}{dP} - \frac{dv_0'}{dP}$$

Let β, β_0, β_1 and β_2 represent the adiabatic compressibility of solution, solvent, solute and bound water, respectively.

From definition these β's are given by

$$\beta = -\frac{1}{V}\frac{dV}{dP}$$

therefore we obtain the relation

$$V'\beta = V_0'\beta_0 + V_1'\beta_1 + v_2'\beta_2 - v_0'\beta_0$$

For 1 cc. solution, this can be written in the form

$$\beta = V_0\beta_0 + V_1\beta_1 + v_2\beta_2 - v_0\beta_0 \quad (2)$$

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