Sodium Hyponitrite *

By CONST. N. POLYDOROPOULOS **

The solubilities of sodium hyponitrite in alkali are reported. Thus a better understanding of the conditions of its preparation is provided. Besides two crystalline hydrates of sodium hyponitrite not previously reported are identified. Finally the two dissociation constants of hyponitrous acid determined at various concentrations are calculated by extrapolation to zero.

In the course of an investigation of the structure of the hyponitrite anion by means of its Raman and Infrared spectra (7) we had inevitably to deal with the methods of preparation and some properties of a few hyponitrites. The purpose of this paper is to present the results of our experience, as far as it is interesting, in the hope that this would facilitate the work of future investigators.

A. Solubility of sodium hyponitrite

Sodium hyponitrite has always been known to be very soluble in water and considerably less soluble in strongly alkaline solution (1). Nothing more has been reported about its solubility.

Since it is almost impossible to have solutions of sodium hyponitrite free from hydroxide we determined its solubilities in sodium hydroxide solutions. The value of this curve of solubilities for the recrystallizations of sodium hyponitrite is apparent.

The samples were analyzed as follows. Solutions of sodium hyponitrite and hydroxide were left in a desiccator at 20° C to separate some crystals. For strongly alkaline solutions vac - H_2SO_4 desiccator was used. Then some of the liquid was weighed out in a small bottle and diluted to a fixed volume.

An aliquot part of this solution was immediately neutralized (phenolphth.) with dilute acetic acid, and an excess of 0.1 n silver nitrate solution added, filtered and in the filtrate the excess of silver was titrated with potassium thiocyanate. Thus $N_2O_2^{--}$ was estimated (9).

In another part the total alkali was titrated (methyl - orange) with hydrochloric acid. From this the equivalent of the hyponitrite was subtracted.

The difference of the sum of the two percentages ($Na_2N_2O_2 + NaOH$) from 100 was taken as water.

The results are shown in Table 1. From these figures a triangular diagram can be drawn.

TABLE 1. Solubility of sodium hyponitrite in solutions of sodium hydroxide.

NaOH	$Na_2N_2O_2$	H_2O
18.8	17.8	63.4
29.0	6.15	64.8
36.9	4.17	58.9
45.2	1.20	53.6
46.5	0.96	52.5
46.4	0.97	52.4

Grams of components per 100g of solution.

As it would be seen from this diagram, the best solvent for a recrystallization of sodium hyponitrite is 20% sodium hydroxide. Concentration of a solution like this reduces the solubility of hyponitrite rapidly. In less alkaline solutions saturated with sodium hyponitrite its decomposition produces alkali enough to make the solution supersaturated with respect to the hyponitrite left.

B. The hydrates of sodium hyponitrite

Crystals of sodium hyponitrite obtaized under various conditions have been analyzed by previous workers. They were always washed with alcohol and ether and dried before the analysis.

We observed that single, well formed and glasslike transparent crystals of sodium hyponitrite dehydrate quickly in absolute or 95% alcohol.

Therefore we did not trust washing them with alcohol not only because of the danger of dehydration but also because we would have to dry them afterwards to remove the alcohol and ether, and we would not know for how long, since they lose their water of crystallization very easily.

Instead we let them grow in their mother solutions sufficiently large (1-2 mm thick and 3-5 mm long) so that we were able to pick up some of them apparently perfect and well formed and dry them mechanically with soft paper.

The $N_2O_2^{--}$ was determined by precipitation and back titration of the excess of silver. Another sample was left in $CaCl_2$ - desiccator (in a

preweighed crucible) for 4 - 6 days until its weight remained constant. The loss was taken as water. To the dehydrated sample ammonium sulphate was added with one or two drops of water. It was left in the cold first for 24 hours to avoid spitting by vigorous decomposition of the hyponitrite and then it was carefully dried burnt and weighed as Na_2SO_4. The sum of the three percentages (Na^+, $N_2O_2^{--}$ and H_2O) was always around 99, which proves that the crystals lose all of their water over calcium chloride within five days.

The results of the analyses were always near to either $Na_2N_2O_2.4H_2O$ or $Na_2N_2O_2$ $6H_2O$.

TABLE 2. Examples of results of analyses of sodium hyponitrite hydrates.

Found	Na^+	$N_2O_2^{--}$	H_2O	*Sum*
a	25.7	31.9	41.2	98.8
b	21.8	27.9	49.1	98.8
Calculated for				
$Na_2N_2O_2 \cdot 4H_2O$	25.8	33.7	40.5	100.0
$Na_2N_2O_2 \cdot 5H_2O$	23.5	30.6	45.9	100.0
$Na_2N_2O_2 \cdot 6H_2O$	21.5	28.0	50.5	100.0

Assigned formula :
$a = Na_2N_2O_2 \cdot 4H_2O$
$b = Na_2N_2O_2 \cdot 6H_2O$

The hexa - hydrate was formed in solutions concentrating from 20 to 30 % NaOH. The tetra-hydrate was found in solutions approaching 40 % NaOH. The solutions from which Partington (2) reports to have obtained the octa-hydrate seem to have been not strongly alkaline. On the other hand Oza's (3) analyses on crystals obtained from very concentrated NaOH agree with the composition of a tri - hydrate. Therefore, as anticipated, the more alkaline the mother solution the less hydrated the crystals.

Neither the hexa - nor the tetra - hydrate has been previously reported in the literature. The penta - hydrate has been reported instead (1,2).

Perhaps the best criterion to settle any doubts whether our analyses were correct would be a crystallographic study. No crystallographic work is found in the literature on any hyponitrite. However an X - ray test (8) on a crystal for which our analysis showed the composition $Na_2N_2O_2 \cdot 6H_2O$, carried out in the Crystallography Department of University College London, verified this formula.

C. Divers'–Partington's method of preparation

For the preparation of sodium hyponitrite we used Divers' method involving sodium amalgam (1).

Several other methods of preparing sodium hyponitrite have been reported in the litera-

ture. Since none of them seems to exceed in merits Divers' method on account of simplicity and purity of products which therefore remains the standard method, we are presenting the results of our experience on the best way of carrying it out, in some detail.

Reducing sodium nitrite in comparatively small proportions (25 g.) with sodium amalgam is rather inconvenient. Since the sodium hyponitrite obtained never exceeds the $^1/_7$ of the nitrite used, larger quantities are needed anyway.

We reduced sodium nitrite in batches of 250-350 g in a large, strong separating funnel, of about 2 litres capacity provided with a short outlet underneath and a wide neck. Its rubber stopper was bearing : (a) a thermometer, (b) a mercury sealed stirrer, (c) a glass tube serving as an exit of the gases evolved and (d) another small separating funnel through which liquid amalgam could be introduced.

Precautions must be taken to avoid contamination by CO_2.
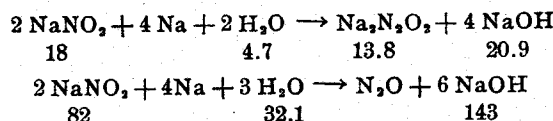
The amalgam is introduced in a thin stream to the solution of sodium nitrite under good stirring and cooling with tap water running outside (the whole apparatus is placed into the sink). After some amalgam has been added (about 20 % of that required for the whole reduction) cooling is not necessary any more since heat is no longer evolved in appreciable amount.

When the effervescence stops the mercury is removed from underneath, some more sodium is dissolved in it and the reduction carried on until the solution does not evolve any gas in contact with the amalgam. Usually a little more than the theoretical amount of sodium is required (70 - 80 g of sodium per 100 g of sodium nitrite). Thus the sodium can be used in parts of 20 g dissolved in about 300 ml of mercury.

The yield is 18 % referred to the nitrite.

As far as the concentration of the original sodium nitrite solution is concerned one has to take into account the yield of the reaction and the solubilities of the final products.

The reaction can be represented by two equations. About 18 g of nitrite (out of 100) is reduced to hyponitrite and the rest is reduced and decomposed :

$$2NaNO_2 + 4Na + 2H_2O \longrightarrow Na_2N_2O_2 + 4NaOH$$
$$\quad 18 \qquad\qquad 4.7 \qquad 13.8 \qquad\quad 20.9$$

$$2NaNO_2 + 4Na + 3H_2O \longrightarrow N_2O + 6NaOH$$
$$\quad 82 \qquad\qquad 32.1 \qquad\qquad 143$$

The numbers underneath the formulae represent equivalent quantities. Therefore by reduction of 100 g of sodium nitrite, 36.8 g of water are consumed and 13.8 g of sodium hyponitrite and 163.9 g of hydroxide are formed.

If 300 g of water had been used the final solution will contain 263 g of water, 164 g of so-

dium hydroxide and 14 g of sodium hyponitrite, i.e. it will be about 37 °/₀ in hydroxide and 4 °/₀ in hyponitrite. That means (according to Table 1) that it will be just saturated with sodium hyponitrite. The use of a 1 : 3 solution of sodium nitrite was recommended by Divers.

If on the other hand one uses only 200 g of water, the final solution will contain 163 g of water and 164 g of sodium hydroxide, i.e. it will be about 50°/₀ in hydroxide, in which sodium hyponitrite is almost insoluble and will separate. This is Partington's modification (2).

The choice of either method depends upon whether silver or sodium hyponitrite is desirable.

If sodium hyponitrite is needed, Partington's method is advisable. After the end of the reduction one leaves the mixture still for 24 hours, when the hyponitrite separates as a sort of scum on top of the strongly alkaline solution and partly as a sediment. One filters through a coarse sintered glass filter (while protecting from the air), dissolves the solid part in a little water and adds some more amalgam to destroy any hydroxylamine present and reduce any traces of nitrite left. Then the solution may be filtered and concentrated in a vac - H₂SO₄ desiccator. Some silver hyponitrite can be obtained by precipitation from the first, strongly alkaline filtrate.

Concentration of the mother solution obtained after Divers (37 °/₀ NaOH and 4 °/₀ Na₂N₂O₂) is rather difficult (because of its low vapour pressure) and it does not reduce the solubility of hyponitrite considerably. This solution is best precipitated with 10°/₀ silver nitrate after a mere dilution. In view of the large quantity of alkali it contains, neutralization before precipitation is undesirable, nor is it necessary. Silver nitrate forms silver oxide first but by good stirring the brown oxide turns to yellow hyponitrite (1). The brown colour of the oxide serves as an indicator of the end of the precipitation. The precipitate separates quickly and it can be washed by two or three decantations to remove the alkali. It can be rid of silver oxide by a little acetic acid. For further purification it is dissolved in dilute nitric acid and reprecipitated as reported in the literature.

D. *Sodium hyponitrite from silver hyponitrite*

We obtained very good crystals of sodium hyponitrite starting from the silver salt. This method has been used by a number of previous workers but only for preparations of dilute solutions of sodium hyponitrite.

Silver hyponitrite was purified as usual and filtered through a glass filter. The wet paste was then introduced in small portions to a concentrated solution of pure sodium iodide containing some hydroxide, under agitation with a glass rod, until the yellow colour of silver hy-

ponitrite did not disappear any more and filtered. The filtrate contains some silver hyponitrite which is slightly soluble in concentrated sodium hyponitrite solutions. A few drops of sodium iodide were then added until no more precipitate was formed, and the solution was filtered again and concentrated in vac - H₂SO₄. Crystals of Na₂N₂O₂ · 6 H₂O separate in a few days usually very well formed.

Any small excess of iodide in the solution does not contaminate the crystals of hyponitrite.

E. *The two ionization constants of hyponitrous acid*

As it is known, during the titration of a solution of sodium hyponitrite with a strong acid, phenolphthalein decolourizes at about the half of the acid needed to turn methyl-orange red (4,5). However the actual titration curve is not found in the literature.

In view of the importance of the consequences of this experimental datum we carried out the experiments somehow more extensively and precisely than previously reported.

Freshly prepared solutions of sodium hyponitrite of various concentrations were titrated with 0,1 n - or n - HCl. The pH was measured with a pH - meter provided with glass - and calomel electrodes. A temperature compensator gave the pH at 25° C.

The solutions were prepared by dissolving crystals of pure sodium hyponitrite in distilled water previously boiled. The actual concentration of the solutions was determined independently (but at the same time with the pH-titration) by precipitation with silver nitrate and back titration of the excess.

Figure 1 shows the titration curve of a 0.090 m solution of sodium hyponitrite. It closely resembles the curve obtained from the titration of sodium carbonate and therefore there is no doubt that hyponitrous acid dissociates according to two different dissociation constants, i. e. the formulae H₂N₂O₂ and Na₂N₂O₂ are correct.
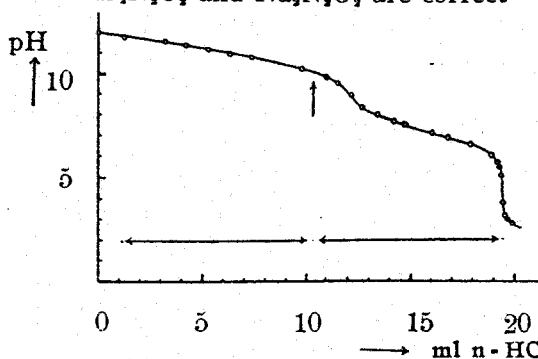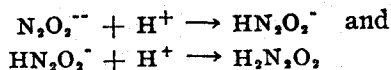

Fig. 1. Change of pH during the titration of sodium hyponitrite.

The arrows underneath the curve, calculated on the basis of the silver determination of the

concentration, show the points where the reactions

$$N_2O_2^{--} + H^+ \longrightarrow HN_2O_2^- \quad \text{and}$$
$$HN_2O_2^- + H^+ \longrightarrow H_2N_2O_2$$

start and end.

Similar curves although displaced towards lower pH values are obtained from more dilute solutions of sodium hyponitrite.

The quantity A was estimated by precipitation with silver. Since the addition of the reagent (HCl) during the titration increases the volume of the solution, M was calculated at every point of measurement of the pH.

Table 3 shows the calculation of K_2 from the titration curve (Fig. 1), where A was found 9.18 ml.

The mean value is $K_2 = 8.2 \times 10^{-12}$. For

TABLE 3. Calculation of K_2 from pH measurements

| C	M	$\frac{C}{A}M$	pH	[H+]	[OH-]	[HN₂O₂-]	[N₂O₂--]	K₂
	$\times 10^{-2}$	$\times 10^{-2}$		$\times 10^{-12}$	$\times 10^{-3}$	$\times 10^{-2}$	$\times 10^{-2}$	$\times 10^{-12}$
2.06	8.90	2.00	11.54	2.88	3.47	2.35	6.55	8.03
3.07	8.82	2.94	11.34	4.57	2.19	3.16	5.66	8.18
4.12	8.74	3.90	11.14	7.25	1.38	4.04	4.70	8.43
5.17	8.65	4.84	10.94	11.5	0.87	4.93	3.72	8.67
6.22	8.57	5.75	10.80	15.9	0.63	5.81	2.76	7.55

The point of decolouration of phenolphthalein never coincides with the calculated one shown by the arrows. This is probably due to some decomposition of the hyponitrite taking place during the titration. The difference is smaller in more dilute solutions.

Therefore titration of sodium hyponitrite solutions for analytical determination with acid and the two indicators will give too low results, unless the solution is very dilute and the titration is carried out quickly. Still the phenolphthalein point will be uncertain within a few tenths of a ml.

Another point of interest available from these curves is the calculation of the dissociation constants:

$$K_1 = \frac{[H^+][HN_2O_2^-]}{[H_2N_2O_2]} \quad , \quad K_2 = \frac{[H^+][N_2O_2^{--}]}{[HN_2O_2^-]}$$

In order to calculate K_2 at a point where C mls of acid have been added we may assume that the whole of the acid has neutralized a part of the $N_2O_2^{--}$ according to

$$N_2O_2^{--} + H^+ \longrightarrow HN_2O_2^-$$
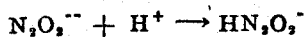
and some more of the $N_2O_2^{--}$ has been hydrolyzed to create sufficient [OH⁻] according to

$$N_2O_2^{--} + H_2O \longrightarrow HN_2O_2^- + OH^-$$
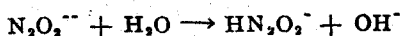
If M is the imaginary concentration of $N_2O_2^{--}$ before the above two reactions took place, and A is the equivalent (in mls) of acid to transform the whole of $N_2O_2^{--}$, into $HN_2O_2^-$ then the concentration of $HN_2O_2^-$ created by the first reaction will be $\frac{C}{A} \times M$ and its total concentration :

$$[HN_2O_2^-] = \frac{C}{A} \times M + [OH^-]$$

The concentration of $N_2O_2^{--}$ will be :

$$[N_2O_2^{--}] = M - [HN_2O_2^-]$$

other concentrations the following values of K_2 were obtained :

M = 87.0, 41.2, 19.2, 13.6, 6.74, 2.35 × 10⁻³
K₂ = 8.2, 6.2, 6.0, 13.4, 9.2, 12.2 × 10⁻¹²

Extrapolation to zero (against the square root of M) gives

$$K_2 = 1.46 \pm 0.26 \times 10^{-11}$$
at infinite dilution

Latimer (6) from the pH = 11.4 of a 9.52×10^{-3}M solution of hyponitrous acid neutralized with alkali calculates $K_2 = 1.00 \pm 0.25 \times 10^{-11}$.

For the calculation of K_1 the analytically determined concentration of hyponitrite (precipitation by Ag⁺) has no value, since part of it is decomposed during the first step of the titration. The difference between the points of rapid change of pH must be taken as measuring the concentration. At the middle between these two points the concentrations of $HN_2O_2^-$ and $H_2N_2O_2$ are equal and therefore $pK_1 = pH$ [Latimer (6)].

Thus we obtained for the various concentrations

M = 5.92, 3.72, 0.86, 0.66, 0.51, 0.24 × 10⁻²
K₁ = 7.08, 5.01, 16.2, 8.91, 10.00, 12.6 × 10⁻⁸

Extrapolation to zero gives a probable value of

$$K_1 = 1.12 \pm 0.27 \times 10^{-7}$$
at infinite dilution

as compared with $9 \pm 2 \times 10^{-8}$ of Latimer's (6).

To make sure that K_1 does remain constant along the part of the curve coresponding to it, an experiment was carried out as follows : A 0.01 M solution of sodium hyponitrite (crystals) was titrated quickly and immediately after its preparation. Measurements were not taken until the pH dropped to 7. From this point on a few more measurements were taken as shown in Table 4. Thus the most important measurements

TABLE 4. Calculation of K_1 from pH measurements

C ml	pH	K_1
		$\times 10^{-7}$
13.80	7.00	1.68
15.70	6.75	1.43
17.15	6.43	1.64
18.20	6.18	1.71
18.60	6.10	1.60
18.85	6.00	1.68
20.30	4.20	
21.20	3.00	

were obtained within less than five minutes from the preparation of the solution and therefore the analytically determined concentration must be valid. It was equivalent to 10.45 ml. From the data of Table 4, K_1 can easily be calculated. It remains well constant.

Our values for both K_1 and K_2 are therefore a little higher than Latimer's. This may be due either to the fact that Latimer does not mention any extrapolation to zero concentration or to slightly different technique used. To calculate K_1 Latimer titrates a solution of hyponitrous acid with alkali, and for K_2 he is satisfied with measuring the pH of a solution of hyponitrous acid neutralized to $Na_2N_2O_2$. It seems preferable to titrate $Na_2N_2O_2$ with acid, rather than $H_2N_2O_2$ with alkali as the former method will tend to reduce errors due to decomposition which occurs in acid solution.

ΠΕΡΙΛΗΨΙΣ

Ὑπονιτρῶδες νάτριον

Ὑπὸ ΚΩΝΣΤ. Ν. ΠΟΛΥΔΩΡΟΠΟΥΛΟΥ

Ἀναφέρονται αἱ διαλυτότητες τοῦ ὑπονιτρώδους νατρίου εἰς διαλύματα NaOH διαφόρων περιεκτικοτήτων (Πίν. 1). Ὡς προκύπτει, περίπου 20% NaOH διαλύει εἰς σημαντικὴν ποσότητα τὸ $Na_2N_2O_2$, ἐνῶ τὸ τελευταῖον τοῦτο εἶναι σχεδὸν ἀδιάλυτον εἰς NaOH 50%. Ὅθεν ὁ καλύτερος διαλύτης δι' ἀνακρυσταλλώσεις $Na_2N_2O_2$ (ἐντὸς ξηραντῆρος κενοῦ — H_2SO_4) εἶναι ~ 20% NaOH, δεδομένου ὅτι εἰς ὀλιγώτερον ἀλκαλικὰ διαλύματα ἡ ταχυτάτη διάσπασις τοῦ $Na_2N_2O_2$ καθιστᾶ τὴν ἀνακρυστάλλωσίν του ἀδύνατον.

Πιστοποιεῖται ἡ ὕπαρξις δύο ὑδριτῶν $Na_2N_2O_2 \cdot 4H_2O$ καὶ $Na_2N_2O_2 \cdot 6H_2O$ μὴ ἀναφερομένων εἰς τὸ παρελθόν.

Διὰ τὴν παρασκευὴν ὑπονιτρώδους νατρίου ἐχρησιμοποιήθη ἡ μέθοδος Divers ἤτοι ἀναγωγὴ $NaNO_2$ δι' ἀμαλγάματος νατρίου. Ἡ ἀπόδοσις ἀνέρχεται εἰς 18%. Δίδονται λεπτομερεῖς ὁδηγίαι.

Κρύσταλλοι ὑπονιτρώδους νατρίου ἐλήφθησαν καὶ διὰ συμπυκνώσεως εἰς ξηραντῆρα τοῦ διαλύματος τοῦ προκύπτοντος ἐκ τῆς ἐπιδράσεως καθαροῦ $Ag_2N_2O_2$ ἐπὶ πυκνοῦ διαλύματος NaJ.

Παρηκολουθήθη ἡ πορεία τοῦ pH κατὰ τὴν ὀγκομέτρησιν δι' HCl διαλυμάτων ὑπονιτρώδους νατρίου διαφόρων συγκεντρώσεων. Ἐκ τῆς προκυπτούσης καμπύλης (Σχ. 1) εἶναι φανερὸν ὅτι τὸ ὑπονιτρῶδες ὀξὺ ἔχει δύο σταθερὰς διαστάσεως K_1 καὶ K_2 ὡς τὸ ἀνθρακικόν. Ὑπελογίσθησαν αἱ τιμαὶ τῶν K_1 καὶ K_2 δι' ἑκάστην συγκέντρωσιν M ὑπονιτρώδους νατρίου. Διὰ προεκβολῆς τούτων εἰς ἄπειρον ἀραίωσιν εὑρίσκεται $K_1 = 1.12 \pm 0.27 \times 10^{-7}$ καὶ $K_2 = 1.46 \pm 0.26 \times 10^{-11}$.

REFFRENCES

1. Divers E : *J. Chem. Soc.* **75**, 95 (1899).
2. Partington J. R., Shah C. C. : *J. Chem. Soc.* 2071 (1931).
3. Oza T. M. : *J. Ind. Chem. Soc.* **22**, 225 (1945).
4. Raschig F. : «*Schwefel—u. Stickstoff—Studien*» Verlag Chemie G. m. b. H. Leipzig—Berlin, 1924.
5. Abel E., Proisl J. : *Wien. Monatsh.* **72**, 1 (1938).
6. Latimer W. M., Zimmerman H. W. : *J. Am. Chem. Soc.* **61**, 1550 (1939).
7. Millen D. J., Polydoropoulos C., Watson D. : «*Normal Co-ordinate Analysis for trans centro-symmetric X_2Y_2 Molecules. Application to the Hyponitrite Ion*». To be published in the J. Chem. Soc.
8. To be published.
9. Polydoropoulos C. : *This Journal* **24A**, 89 (1959).

(Εἰσήχθη τῇ 20ῇ Αὐγούστου 1959)