

Heavy metal hyponitrites

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The best pH range for the precipitation of insoluble hyponitrites of several heavy metals is found by comparison of titration curves. Mixtures of a soluble metallic salt and hyponitrous acid are gradually neutralized with alkali and the course of the pH is followed. The hyponitrites of Ag, Cu, Pb, Cd, Co (II), Zn, and Ni precipitate as neutral salts at pH 2-3, 3.5-4.5, 4.5-5, 5-6, 6-7, 6-7, and 6.5-7.5 respectively. Solutions of Al, Cr (III), Fe (III), Sn (II) and Sn (IV) do not form hyponitrites under the same conditions; hydroxides are precipitated instead. A brown FeN_2O_2 is probably formed at pH 6.5-7 but it is too unstable. Mercury forms HgN_2O_2 and $\text{Hg}_2\text{N}_2\text{O}_2$ in extremely acid media.

Formation of insoluble hyponitrites of several heavy metals has been reported by a number of investigators (1-12). However disagreements concerning the composition of the precipitates formed are not rare. As a rule these were obtained by precipitating sodium hyponitrite with a solution of a soluble salt of the metal studied, or vice versa. The influence of the pH of the solution during the precipitation has not been considered*. Thus occasional coprecipitation of insoluble metal hydroxide may have occurred in many cases and, consequently, substances described as basic metal hyponitrites may have been in fact mixtures of neutral salt and hydroxide.

An investigation of the ability of the ion $\text{N}_2\text{O}_2^{2-}$ to be a ligand in coordination compounds has started in this Laboratory (14), with silver ion being tried as a center of coordination. Extension of this investigation to other metals requires a knowledge of the influence of the pH as outlined above. This work was undertaken with a view of establishing at what pH each hyponitrite can be precipitated in a single phase of definite composition.

The method employed is simple and conclusive. A solution of a soluble salt of the metal studied containing free hyponitrous acid was neutralized slowly with NaOH and the pH of the mixture was plotted against the amount of the alkali added. The curve obtained was compared with that of the titration of the same amount of metallic salt under the same conditions (concentration etc.) but without hyponitrous acid present.

Experimental

Sodium hyponitrite was prepared by reduction of a NaNO_2 solution with sodium amalgam, the latter

* This is not surprising, since the most of the work available has been done as early as before 1930.

being obtained electrolytically. The soluble hyponitrite was transformed to $\text{Ag}_2\text{N}_2\text{O}_2$ (by precipitation with AgNO_3) which was kept under water often renewed.

When pure $\text{Ag}_2\text{N}_2\text{O}_2$ was needed a part of the stock substance was dissolved in dilute HNO_3 (about 0.1N), filtered, reprecipitated with alkali up to a pH about 5 and washed thoroughly.

Hyponitrous acid was prepared by treating a solution of HCl of suitable concentration with excess $\text{Ag}_2\text{N}_2\text{O}_2$ freshly purified but not dried. The filtrate (solution of pure $\text{H}_2\text{N}_2\text{O}_2$) was always used without undue delay.

The solutions of NaOH were prepared by dilution of clear saturated NaOH, with all necessary precautions to avoid contamination by CO_2 .

The pH of the solutions was measured with a Cambridge Portable Type pH Meter provided with glass and calomel electrodes. A series of salt bridges ending with 1N KNO_3 was interposed between the calomel electrode and the solution tested. The pH response of the set, checked over the range of pH 1 to 13, was found to be quite satisfactory. The average deviation was 0.0035 per pH unit.

Results and Discussion.

Fig. 1 illustrates an example of comparison of the two titration curves. Nickel hyponitrite is a voluminous precipitate resembling the hydroxide of the same metal even in colour. This, as well as the comparatively small difference, between the pH of precipitation of the two substances, is perhaps the reason why formation of nickel hyponitrite is not mentioned by previous investigators. The other hyponitrites referred to in Fig. 3 differ from the corresponding hydroxides in colour or the appearance or both.

If the concentration of hyponitrous acid is less than that of the metal, the formation of MN_2O_2 is followed by the subsequent precipitation of M(OH)_2 , as shown by Fig. 2. The hy-

ponitrite content of the total precipitate (determined afterwards by dissolution in HNO_3 and

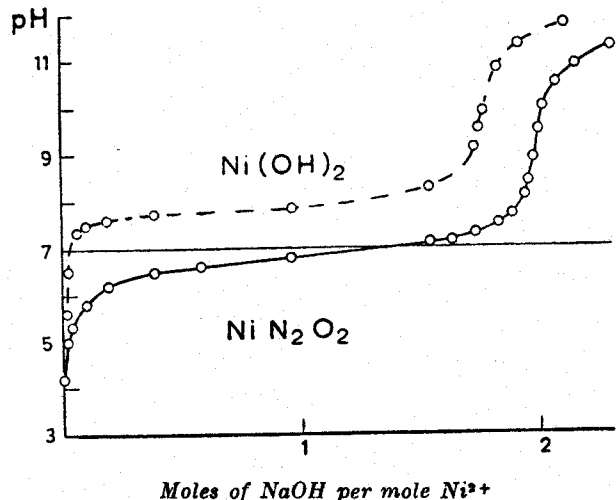


Fig. 1. Titration of $\text{Ni}(\text{NO}_3)_2$ (upper line) and of the same solution in presence of $\text{H}_2\text{N}_2\text{O}_2$ (lower line) with alkali.

precipitation with AgNO_3) is equal to that indicated by the arrow underneath the titration curve.

No evidence of formation of basic salts was obtained. The hyponitrites of the bivalent metals included in Fig. 3 precipitate as MN_2O_2 , at a narrow pH range lower than that of the corresponding hydroxide.

The points of measurements are not marked in Fig. 3 because (a) they lie well on the curves drawn, with only a few exceptions where the deviations are still less than 0.1 pH unit, and

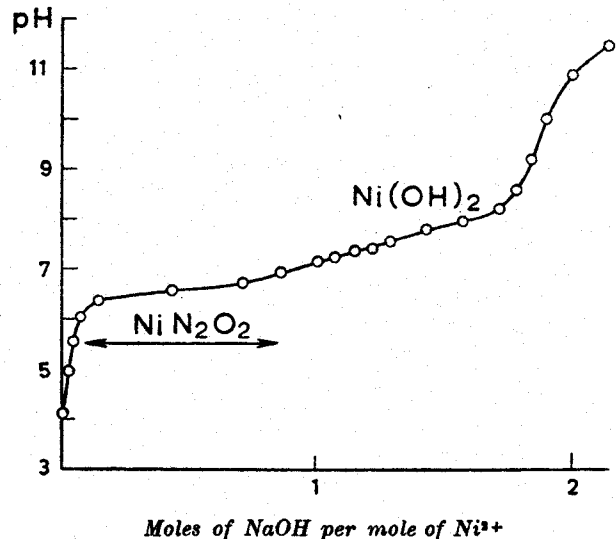


Fig. 2. Separation of nickel hyponitrite on neutralization of a mixture of hyponitrous acid and excess $\text{Ni}(\text{NO}_3)_2$.

(b) the curves can represent true equilibrium states only with an approximation of a few tenths of pH. The latter was inevitable because waiting after each addition of reagent for the equilibrium to be established too long, would have resulted in serious decrease of the concentration of hyponitrous acid (by decomposition), which was intended to be nearly equal to that of the metal. Thus the titrations had to be comple-

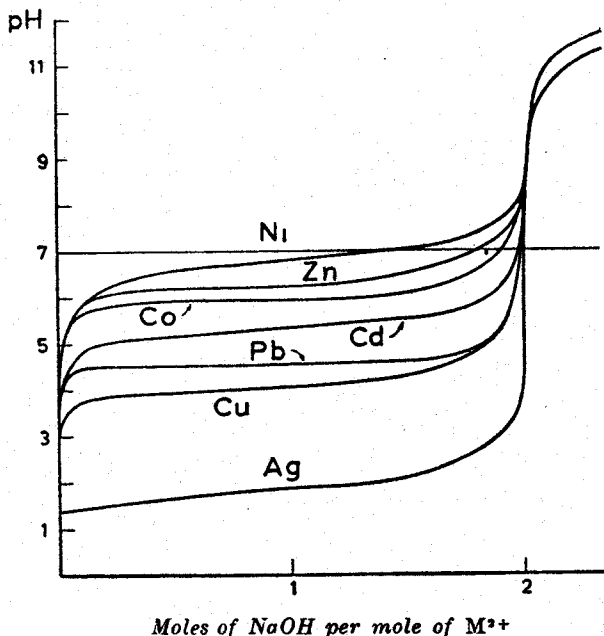


Fig. 3. pH of precipitation of metal hyponitrites. For $\text{Ag}_2\text{N}_2\text{O}_2$, the rapid rise of pH corresponds to addition of 1 equiv. OH^- per Ag^+ .

ted within about 30 minutes. The concentrations were around 0.03M and the reagent 1.0 N NaOH.

Fig. 4 illustrates one example of not formation of insoluble hyponitrite. By raising the pH, Al^{3+} precipitate as hydroxide irrespectively of whether hyponitrous acid is present or not. Neutralization of the latter occurs at pH higher

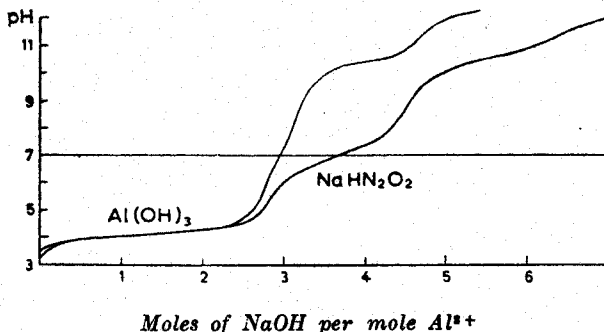


Fig. 4. Precipitation of $\text{Al}(\text{OH})_3$ from $\text{Al}_2(\text{SO}_4)_3$ (upper line) and from a mixture of the same solution and hyponitrous acid (lower line).

than 4.5, after the precipitation of the metal as hydroxide has been completed.

Similar behaviour show solutions of Cr (III), Fe (III), Sn (II) and Sn (IV). Their precipitation takes place at low pH, to be followed by a subsequent neutralization of hyponitrous acid.

Ferrous hyponitrite. Bivalent iron (fresh solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 6\text{H}_2\text{O}$) in presence of hyponitrous acid forms a brown precipitate at pH 6.5-7. Under the same conditions (but without hyponitrous acid) blue-green $\text{Fe}(\text{OH})_2$ precipitates at a pH about 8. By the shape of the titration curves (which closely resemble those of Fig. 1) the composition of the brown substance is likely to be FeN_2O_2 . A verification of this by analysis is unfortunately impossible because the substance is too unstable. As soon as it is formed it starts decomposing gas bubbles being evolved. The decomposition can not be stopped by making the solution highly alkaline or by washing the precipitate.

Mercury. Mercuric hyponitrite has been prepared in the past by mixing solutions of soluble mercuric salts with a solution of $\text{Na}_2\text{N}_2\text{O}_2$. The precipitate formed was reported to be a basic salt of the composition $\text{HgN}_2\text{O}_2 \cdot 3\text{Hg}(\text{OH})_2$ (4,5). Probably it was a mixture, because when the alkaline $\text{Na}_2\text{N}_2\text{O}_2$ solution was neutralized first and then added to a mercuric nitrate solution the normal salt HgN_2O_2 was obtained (3).

However a more acid medium seems to be preferable. If a 0.03 M solution of $\text{Hg}(\text{NO}_3)_2$ (acidified by a little HNO_3 to prevent hydrolysis) is slowly neutralized by NaOH , mercury starts precipitating as soon as the pH is raised above 2.1, and the precipitation is almost complete at pH 3. This constitutes a serious danger of coprecipitation of HgO or $\text{Hg}(\text{OH})_2$, or a basic nitrate together with the HgN_2O_2 , if the latter is precipitated from solutions not acid enough. Indeed mercuric hyponitrite is now proved to be insoluble enough at pH even below 2, to allow for a better method for its preparation in pure condition.

When 0.1 M $\text{Hg}(\text{NO}_3)_2$ (acidified) is mixed with pure 0.05 M $\text{H}_2\text{N}_2\text{O}_2$, a crystalline pale yellow powder precipitates immediately, although the liberated HNO_3 lowers the pH down to 1.5. If the amount of hyponitrous acid is by some 50% more than required, almost the whole of mercury is precipitated. It makes no difference which way the two solutions are mixed.

Similar is the case of mercurous hyponitrite. It has been described (3) as a yellow precipitate obtainable by dropping a solution of sodium hyponitrite into mercurous nitrate. This reminds one of the well known yellow basic mercurous nitrate which is easily precipitated at pH 2-3, particularly as mercurous hyponitrite of an orange colour can be obtained at lower pH, as

follows.

An acid solution of mercurous nitrate containing 0.5 mole of $\text{Hg}_2(\text{NO}_3)_2$ and 0.5 mole of HNO_3 per litre was used as stock solution. Five ml of this diluted to 200 ml (pH=1.8) and neutralized dropwise with NaOH do not form any precipitate up to 1.5 ml of 1.0 N alkali (pH=2.2). Further addition of NaOH precipitates yellow basic mercurous nitrate. But if 5 ml of the same stock mercurous solution are treated with 200 ml of hyponitrous acid (about 0.04 molar) an orange crystalline powder separates at once. Again some 80% of Hg_2^{2+} is precipitated and the HNO_3 set free lowers the pH to 1.5. The same substance is formed if the mercurous solution is dropped into the solution of hyponitrous acid.

Thus pale yellow mercuric and orange mercurous hyponitrites can be formed in dilute nitric acid solutions at a pH about 1.5 where hydrolysis of Hg^{2+} or Hg_2^{2+} to hydroxides or basic salts is excluded. Both substances can easily be washed by decantation and dried even in the ordinary atmosphere. They are decomposed by NaOH , being converted to the orange mercuric or the black mercurous oxides respectively. An equivalent amount of $\text{Na}_2\text{N}_2\text{O}_2$ is then found in the alkaline solution. A quantitative determination of the latter shows that the two substances are neutral salts i.e. HgN_2O_2 and $\text{Hg}_2\text{N}_2\text{O}_2$.

Table I summarizes the results.

Table I. Optimum pH of precipitation of hyponitrites.

	Colour	pH
NiN_2O_2	Light green	6.5-7.5
FeN_2O_2 ?	Brown (unstable)	6.5-7
ZnN_2O_2	White	6-7
CoN_2O_2	Light brown	6-7
CdN_2O_2	Yellowish white	5-6
PbN_2O_2	Yellow	4.5-5
CuN_2O_2	Green	3.5-4.5
$\text{Ag}_2\text{N}_2\text{O}_2$	Bright yellow	2-3
HgN_2O_2	Pale yellow	1.5-2
$\text{Hg}_2\text{N}_2\text{O}_2$	Orange	1.5-2

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Π Ε Ρ Ι Λ Η Ψ Ι Σ

Υπονιτρώδη άλατα βαρέων μετάλλων

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Αναζητείται ή πλέον εύνοική περιοχή pH διά την κατακρήμνισιν δυσδιαλύτων υπονιτρωδών άλάτων διαφόρων μετάλλων εις καθαράν κατάστασιν. Διάλυμα άλατος του υπό μελέτην μετάλλου, περιέχον και ελεύθερον υπονιτρώδες όξύ, έξουδετερούται βαθμιαίως δι' άλκάλεις υπό παρακολούθησιν του pH. Η έπιτυγχανομένη καμπύλη συγκρίνεται με την της κατακρήμνίσεως του αύτου διαλύματος, άλλ' άνευ υπονιτρώδους όξέος (Σχ. 1). Σχηματισμός βασικών άλάτων, συχνάκις άναφερομένων υπό παλαιότερων έρευνητών, εις ούδεμίαν περίπτωσιν διεπιστώθη. Ούτως άποδεικνύεται ότι ή έν χρήσει μέθοδος, ήτοι της κατακρήμνίσεως μεταλλικών άλάτων διά διαλύματος υπονιτρώδους νατρίου (λίαν άλκαλικού λόγω ύδρολύσεως) άνευ προσεκτικού έλέγχου του pH, δυνατών να οδηγήση εις μίγματα άκαθορίστου συστάσεως. Χαρακτηριστικόν τούτου παράδειγμα άποτελεί ή περίπτωσης των άλάτων ύδραργύρου και ύφωδραργύρου. Μία περίπτωσης διαδοχικής κατακρήμνίσεως ούδετέρου υπονιτρώδους άλατος και έν συνεχεία ύδροξειδίου φαίνεται εις τó σχήμα 2. Τó σχήμα 3 και ó πίναξ 1 παρέχουν την περιοχήν pH, έντός της όποιας έκαστον υπονιτρώδες κατακρήμνίζεται ως ούδέτερον έλας (Έκ του Έργαστηρίου Φυσικοχημείας Πανεπιστημίου Άθηνών)

ΕΠΙΣΤΟΛΑΙ ΠΡΟΣ ΤΗΝ ΣΥΝΤΑΞΙΝ

Τό πινένιον ως άδρανές μέσον ήλεκτροφορήσεως

Υπό ΑΝΑΣΤΑΣΙΟΥ Α. ΧΡΗΣΤΟΜΑΝΟΥ

Είναι γνωστόν ότι ή ήλεκτροφόρησις πρωτεϊνών, πεπτιδών ή και άμινοξέων επί διηθητικού χάρτου υπό ύψηλοτέρας τάσεις των 500 V, προκαλεί διά θερμάνσεως του χάρτου έλαττωματικήν ήλεκτροφόρησιν ή και άπανθράκωσιν του χάρτου ένεκα έξατίσεως του ύγρου ήλεκτρολύσεως. Πρός τόν σκοπόν τούτον προετάθη υπό του Michel τó πρώτον, ή έμβάπτισις του όλου ήλεκτροφορητικού συστήματος έντός τολουολίου άποφενυγομένης ούτω της έξατίσεως και θερμάνσεως του διηθητικού χάρτου.

Η χρησιμοποίησις όμως τολουολίου, ιδίως κατά τας ήλεκτροφορήσεις πρωτεϊνών και πεπτιδών καθ' ός λαμβάνεται ως ρυθμιστικόν διάλυμα ήλεκτροφορήσεως μίγμα πυριδίνης ύδατος και όξεικού όξέος, έχει δύο μειονεκτήματα, πρώτον ότι μετά πέντε ή έξ ήλεκτροφορήσεις τó τολουόλιον πρέπει να έκπλυθή έκ της εις αυτό διαλυθείσης πυριδίνης και όξεικού όξέος και είτα άποσταχθή, και δεύτερον ότι ή τιμή αύτου είναι λίαν ύψηλή, ούτως ώστε ένεκα των άπωλειών κατά την πλύσιν και την άπόσταξιν ή χρησιμοποίησις αύτου δέν είναι σύμφορος.

ελεύθερον προσμίξων. Διαλύματα Al, Cr (III), Fe (III), Sn (II) και Sn (IV) κατακρήμνίζονται ως ύδροξειδια, άνεξαρτήτως της παρουσίας ή μη υπονιτρώδους όξέος (Σχ. 4). Πιθανός σχηματισμός FeN₂O, φαίνεται έκ της καμπύλης όγκομετρήσεως. Τό καστανόχρουν όμως τούτο ίζημα διασπάται ταχέως υπό έκλυσιν άερίων, μη έπιτρέπον άναλυτικήν έπαλήθευσιν της συστάσεως αύτου.

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Διά τόν λόγον αύτον προσπαθήσαμεν να εύρωμεν έν μέσον άδρανές ήλεκτροφορήσεως δεικνύον μικράν άγωγιμότητα και δυσδιάλυτον εις ύδατικά διαλύματα πυριδίνης. Κατόπιν σχετικών άναζητήσεων προεκρίναμεν τó πινένιον ως έκπληροϋν άπολύτως τούς διά την ήλεκτροφόρησιν άπαραιτήτους όρους.

Τό τρισεποταχθέν πινένιον τó όποϊον έχρησιμοποίησαμεν προέρχεται έκ του τερεβινθελαιου της περιοχής Κασάνδρας της Χαλκιδικής και δεικνύει τας έξης φυσικας σταθεράς: Σταθερός βαθμ. ζέσ. 154°—155°, ειδ. βάρ. 0.837gr./cm³, δείκτην διαθλ. 1.459 και ειδ. άγωγιμότητα εις 22° $\lambda < 1,5110^{\circ}$. Είναι όπτικώς άδρανές και ως έκ τούτου τó χρησιμοποιηθέν πινένιον είναι ρακεμικόν άποτελούμενον από ίσα μέρη δεξιοστρόφου και άριστεροστρόφου πινενίου.

Διά της χρησιμοποίησεως του πινενίου έπετύχαμεν τόν έξαιρετον διαχωρισμόν πρωτεϊνών και πεπτιδών, της θερμοκρασίας κατά την ήλεκτροφόρησιν παραμενύσης μεταξύ 20° και 22°.

Τό προτέρημα της διά πινενίου ήλεκτροφορήσεως έγκειται άφ' ενός μεν εις τó ότι τούτο διαλύει πολύ όλιγώτερον την πυριδίνην και τó άραιτόν όξεικόν όξύ παρ' όσον τó τολουόλιον και ως έκ τούτου δέν άπαιτείται ή έκπλυσις και άπόσταξις αύτου μετά πέντε ήλεκτροφορήσεις, άφ' έτέρου δέ εις τó εύωνον αύτου (4