

εϊδική ταχύτης αντίδρασεως αυξάνεται σημαντικώς μετά της ελαττώσεως της διηλεκτρικής σταθεράς του διαλύτου, και ελαττούται μετά της αύξησεως της ιοντικής ισχύος, κατά τρόπον ύποδηλούντα ότι η ρυθμίζουσα την ταχύτητα αντίδρασης λαμβάνει χώραν μεταξύ μονοσθενών ιόντων αντιθέτου φορτίου.

Είς μηχανισμός αντίδρασεως εν συναρτήσει μετά των ως άνω πειραματικών δεδομένων θεωρείται ως πιθανός. Ο μηχανισμός ούτος οδηγεί εις την έπιτυχή πρόβλεψιν ότι ύδατικά διαλύματα του διφαινυλο-ύδροξυβορανίου δύνανται να σταθεροποιηθούν διά της προσθήκης ισχυρού όξέος.

Προσδιωρίσθησαν αι σταθεραι της πρωτολυτικής διαστάσεως του διφαινυλοβορικού όξέος, δίδουσαι την μετά της θερμοκρασίας μεταβαλλομένην συνάρτησιν: $pK_a = 1.85 + \frac{1293}{T}$, εκ της οποίας ελήφθησαν αι θερμοδυναμικαι συναρτήσεις της πρωτολύσεως. Η μεταβολή της έντροπίας κατά την πρωτόλυσιν δεικνύει ότι ισχυρά επίδρασις των μορίων του ύδατος άσκειται επί του όξέος πρό της πρωτολύσεως.

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The precision of the quantitative determination of hyponitrous acid by the precipitation method.

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The concentration of $H_2N_2O_2$ is determined by precipitation with $AgNO_3$ in a 100ml volumetric flask in weakly acid solution, and back titration of Ag^+ in the half of the filtrate. The mean, standard, and 90% - chance deviations of the method are found to be 2.15, 2.80, and 4.5×10^{-4} mole/l respectively.

Three methods are available for the quantitative determination of hyponitrites in aqueous solution: precipitation as $Ag_2N_2O_2$ (1), oxidation by $KMnO_4$ (2) and the spectrophotometric method (3). They have been used for determination of $N_2O_2^{2-}$ in alkaline solution.

Hyponitrous acid itself, in acid solution, has recently been the subject of a systematic kinetic investigation (4) by the authors. During this work the precipitation method was standardized as follows:

A sample (20-25ml) of the solution of $H_2N_2O_2$ is transferred to a 100 ml volumetric flask. Then an excess of a standard solution of $AgNO_3$ (20-25 ml, 0.1 N) is added and the mixture is, without undue delay, neutralized with 0.1 N NaOH up to the appearance of a brown precipitate (Ag_2O). The latter is redissolved with a few mls of 0.1 N CH_3COOH , and, finally, 5-10 ml of an acetate buffer solution (0.1 M CH_3COOH

and 0.1 M CH_3COONa) are added and the volume is brought to 100 ml. Thus a pH of about 4.5-5 is established, at which silver hyponitrite is practically insoluble (5) whereas silver oxide and carbonate are soluble.

The solution is next filtered through a dry hard filter paper into a dry conical flask. The first 1/3 - 1/4 of the filtrate is discarded. In 50 ml of the rest of the filtrate the excess of Ag^+ is titrated with 0.1N KSCN, after the addition of 10 ml 6N HNO_3 , and 2 ml of a saturated solution of ferri-ammonium sulfate.

The results are not influenced by the order of mixing the solutions of $H_2N_2O_2$ and $AgNO_3$. The same results are also found if the solution of $H_2N_2O_2$ is first added dropwise to an excess of NaOH, and precipitation follows. But slow neutralization of $H_2N_2O_2$ up to pink phenolphthaleine prior to the addition of $AgNO_3$, as frequently recommended by early investigators

(6), should be avoided, because hyponitrites, as it has recently been shown (4,7), are much more unstable in neutral than in acid solution.

The precision of the method, as estimated below, is based on 37 sets of measurements each of which consisted of about 9 determinations. The concentration of $H_2N_2O_2$ varied in the range 0.005-0.060 mole/l.

Within each set of measurements the probable value of the concentration of $H_2N_2O_2$ was estimated by a least square method (8a), and the difference from the actually determined value was computed. The absolute value of this difference is referred to as Δ .

The mean value of Δ was 2.15×10^{-4} mole/l and the largest 9.8×10^{-4} mole/l. The standard deviation ($s = [\sum \Delta^2/n]^{1/2}$) is $s = 2.80 \times 10^{-4}$ mole/l.

The number of analyses whose Δ fell within a certain range is shown in Table I. The distri-

Table I.— Distribution of the deviations

$a < \Delta \times 10^4 < b$		n	$a < \Delta \times 10^4 < b$		n
a	b		a	b	
0.00	— 0.50	47	5.00	— 5.50	3
0.50	— 1.00	56	5.50	— 6.00	3
1.00	— 1.50	56	6.00	— 6.50	4
1.50	— 2.00	25	6.50	— 7.00	2
2.00	— 2.50	31	7.00	— 7.50	4
2.50	— 3.00	31	7.50	— 8.00	0
3.00	— 3.50	25	8.00	— 8.50	2
3.50	— 4.00	21	8.50	— 9.00	0
4.00	— 4.50	17	9.00	— 9.50	1
4.50	— 5.00	9	9.50	— 10.00	2
Total $n = 339$					

Δ in mole/l, n = number of determinations

bution of Δ is very nearly as expected theoretically (8b). This is better shown in Fig. 1, in which the curve is theoretical (for the present value of s) and the points express the results of Table I summed up successively and divided by 3.39.

The percent number of determinations whose Δ is less than $1s$, $2s$, and $3s$ is 68.7, 94.7, and 98.5% respectively, as compared to the theoretically expected (8b) values 68.27, 95.45, and 99.73%.

There is a 90% chance for the error to be less than 4.5×10^{-4} , i.e., about 1% for moderately concentrated solutions of $H_2N_2O_2$.

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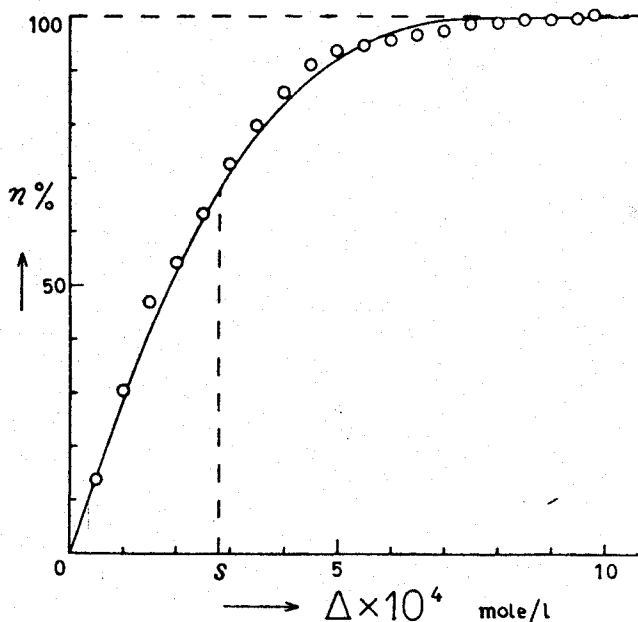


Fig. 1. Percent number of determinations having Δ less than the value shown on the abscissa.

Π Ε Ρ Ι Λ Η Ψ Ι Σ

Ἡ ἀκρίβεια τοῦ ποσοτικοῦ προσδιορισμοῦ τοῦ ὑπονιτρώδους ὀξέος διὰ τῆς μεθόδου τῆς κατακρημνίσεως.

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Τὸ ὑπονιτρώδες ὀξύ εἰς ἀσθενῶς ὀξινὸν διάλυμα προσδιορίζεται διὰ κατακρημνίσεως διὰ 0.1N $AgNO_3$ ἐντὸς ὀγκομετρικῆς φιάλης τῶν 100 ml, προσθήκης ὀξικοῦ ρυθμιστικοῦ καί, μετὰ διήθησιν, ὀπισθογκομετρήσεως τῆς περισσεύσεως τῶν Ag^+ εἰς τὸ ἥμισυ τοῦ διηθήματος. Ἡ ἀκρίβεια τῆς μεθόδου ὑπολογίζεται ἐκ τῶν ἀποτελεσμάτων 339 προσδιορισμῶν. Ἡ μεγίστη σημειωθεῖσα ἀπόκλισις ἦτο 9.8×10^{-4} mole/l καί, ἀντιστοίχως, ἡ μέση 2.15 καὶ ἡ πρότυπος (standard deviation) 2.80. Τὸ σφάλμα ἔχει πιθανότητα 90% νὰ μὴ ὑπερβαῖν τὴν τιμὴν 4.5×10^{-4} mole/l, ἦτοι, διὰ μετρίως ἀραιὰ διαλύματα $H_2N_2O_2$, τὸ σφάλμα τῆς μεθόδου δὲν ὑπερβαίνει τὸ 1%.

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