[Contribution from the Department of Chemistry of the Oregon State Agricultural College]

THE ELECTROMETRIC TITRATION OF HYDRAZINE AND ITS SALTS

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Introduction

Hydrazine is a base which forms two distinct and stable series of salts, in one of which it functions as a mono-acid base and in the other as a di-acid base. The dissociation constant for the ionization of the first hydroxyl group is given as 3×10^{-6} which shows it to be slightly weaker than ammonium hydroxide.[1] The constant for the ionization of the second hydroxyl group has apparently not been determined with any great degree of exactitude.[2] *Bredig*[3] and *Bach*[4] conclude that the second base is so weak that the corresponding salts are almost completely hydrolyzed. It is a question, therefore, whether to consider hydrazine as a mono- or di-acid base. Landolt-Börnstein interpret it on the basis of the former. Curtius and Schulz,[5] however, state that cryoscopic measurements made by them indicate the presence of the dihydrate in a water solution of the hydrazine, since they obtain a molecular weight of 68. However, this does not seem very conclusive since cryoscopic data can be interpreted either on the basis of the monohydrate or the dihydrate.[6] Indeed, the cryoscopic method is of as little value here as it is in the case of ammonia and ammonium hydroxide in water solution. In dilute solution the ratio of hydrazine to total water is too small and in concentrated solution the data cannot be interpreted.

On the other hand, the so-called electrometric titration using a hydrogen electrode would yield evidence of the hydroxyl groups of a poly-acid base (or hydrogen for acid) provided the base is not too weak and furthermore the method can be used to give an approximation of the ionization constant. It was therefore thought that the electrometric titration of hydrazine with acids might throw light on both these points; first, the conditions of formation and existence of hydrazine dihydrate and the salts corresponding

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[1] Landolt-Börnstein "Tabellen," Julius Springer, Berlin, 5th ed., **1923**, p. 1122.

[2] Kolthoff [This Journal, **46**, 2009 (1924)] in an article which appeared after this paper was written states that he calculates $K_2 = 2.8 \times 10^{-13}$ but gives no figures.

[3] Bredig, *Z. physik. Chem.*, **13**, 191, 314 (1894).

[4] Bach, *ibid.*, **9**, 241 (1892).

[5] Curtius and Schulz, *J. prakt. Chem.*, [2] **42**, 521 (1890).

[6] A solution containing 0.156 g. of hydrazine (N_2H_4) in 33.35 g. of water gave in this Laboratory depressions of the freezing point of 0.295°, 0.287° and 0.290°. Calculating on the basis of $N_2H_4.H_2O$ this gives an observed mol. wt. of approximately 47 (actual = 50), and on the basis of $N_2H_4.2H_2O$, the observed mol. wt. of 64 (actual = 68), neither agreeing with that calculated on account of ionization and traces of impurity.

to it; and second, an approximation of the second ionization constant. The work described in this paper was begun on that basis and then extended to examine briefly the electrometric titration of hydrazine with oxidizing agents.

Theoretical

Electrometric titration (using the hydrogen electrode) of a di-acid base should lead to a completed voltage-volume curve having two inflections provided the base is not too weak. If the base is so weak that sufficient hydrolysis takes place the expected inflection will not be found. In order to determine the limiting value for the ionization constant which would give a noticeable inflection in a titration curve, arbitrary values were set for the second ionization constant K_2 of hydrazine dihydrate and the corresponding (H^+) calculated upon the addition of 1%, 3% and 10% of acid or base to solutions of hydrazine hydrochloride (0.1 and 1.0 *M* concentration), neglecting dilution due to added reagent. The corresponding logarithms of (H^+) were plotted against the percentage of base or acid added, with the result shown in Fig. 1. It is evident that for 0.1 *M* con-

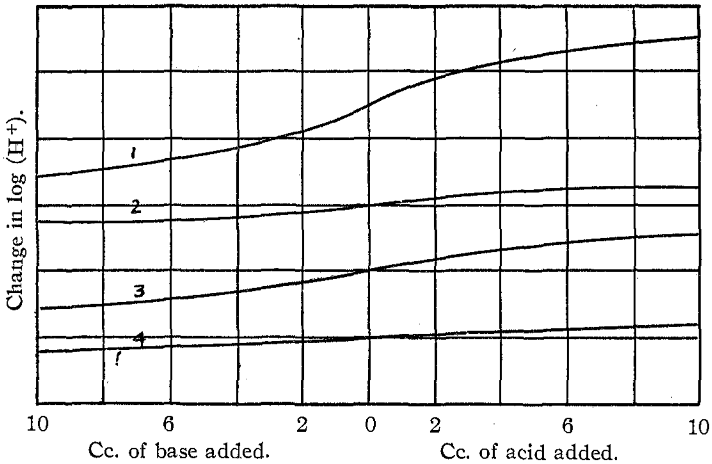

Fig. 1.—The inflection theoretically to be obtained in titrating bases or acids of small ionization constants. (1) Concn. = 1 *M*; $K_2 = 1 \times 10^{-10}$. (2) Concn. = 1 *M*; $K_2 = 1 \times 10^{-12}$. (3) Concn. = 0.1 *M*; $K_2 = 1 \times 10^{-10}$. (4) Concn. = 0.1 *M*; $K_2 = 1 \times 10^{-11}$. One vertical division signifies a change in log (H^+) of one unit. The location of the individual curves in respect to one another on the plot is without significance.

It is evident that these do not represent the actual voltage-volume curves obtained in practise since log (H^+) or rather log $\frac{1}{(H^+)}$ is only one of several factors entering into the equation for the e.m.f. It is, however, the factor which determines the inflection or its absence and was therefore used in these curves, for the sake of simplicity.

centration, K_2 must be of the order of 10^{-10} or possibly 10^{-11}, else the hydrolysis will be sufficient to prevent a noticeable inflection in the curve. For a concentration of 1 *M*, however, an inflection may be obtained when K_2 is of the order of 10^{-11} or perhaps even 10^{-12}. The degree of hydrolysis necessary to eliminate the inflection is apparently only about 10% at this concentration. Absence of the second inflection in the titration curve of hydrazine might be interpreted in two ways, that is, either as presumptive evidence that the dihydrate is largely dissociated into the monohydrate and water at ordinary concentrations or, more probably, that it is too weak a base to fall within the range of applicability of the method.

Titration of Hydrazine with Acids

Experimental.—A solution of hydrazine hydrate (approximately 0.08 *M* in N_2H_4) was made up from a 40% solution of the hydrate and recently boiled distilled water.

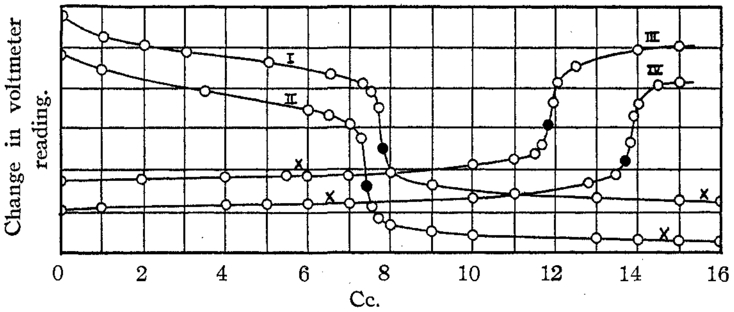

Fig. 2.—Curves for the electrometric titration of hydrazine hydrate against acids: (1) H_2SO_4 added to the hydrazine; (2) HCl added to the hydrazine; (3) hydrazine added to H_2SO_4; (4) hydrazine added to HCl.

Ordinates represent change in voltmeter reading, (1 division = 100 mv.); abscissas represent cc. of one reagent added to 10 cc. of the other. The methyl orange end-point is shown by the black dot.

The hydrazine solutions are not all of the same normality and the acids are not of equal concentration.

X shows the points at which a second inflection in the curve would occur.

The base was quite unstable and the titer changed from day to day on account of oxidation. Solutions of the base were titrated against standard hydrochloric and sulfuric acids, first by adding the base to the acid and second by adding acid to base.[7] Finally, a solution of the hydrate approximately 2 *M* in N_2H_4 was made up and titrated against 3 *M* hydrochloric acid. A hydrogen electrode of the Hildebrand-Wendt type was used.[8] For the more concentrated solution a potentiometer accurate to 0.5 mv. was used, instead of a voltmeter. The solution was protected from the atmosphere during the titra-

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[7] Hydrochloric acid was standardized gravimetrically as silver chloride and the sulfuric acid gravimetrically as ammonium sulfate. All measuring apparatus was calibrated although the purpose of the investigation was to determine the shape of the curves rather than the exact analytical data.

[8] Hildebrand, THIS JOURNAL, **35**, 847 (1913). Central Scientific Co., *Bulletin* **86**, (1920).

tion and methyl orange was added to check the colorimetric with the electrometric end-point.

Typical curves for the titrations of the more dilute solutions are shown in Fig. 2. The curves for the more concentrated solution though not shown are entirely similar, particularly in the fact that no indication is given of any second inflection.

Discussion.—The point on each curve in Fig. 2 corresponding to the ratio 2:1 of acid to hydrazine is marked by (X). It was hoped that at least in the concentrated solution an inflection would be obtained, but all the curves are entirely flat at this point. This indicates that the second ionization constant K_2 of the base must be smaller than 1×10^{-12} (see Fig. 1).[9]

Titration of Hydrazine Salts with a Base

Stollé recommends hydrazine sulfate as a standard in alkalimetry giving a sharp end-point with one equivalent of base when methyl orange is used as indicator.[10]

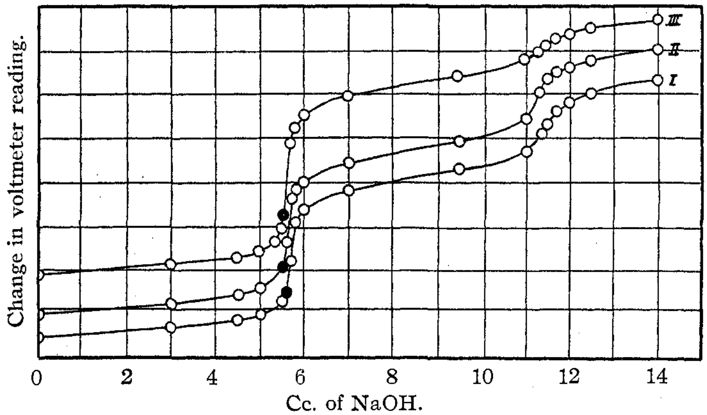

Fig. 3.—Curves for the titration of hydrazine salts and acid ammonium sulfate with sodium hydroxide: (1) hydrazine sulfate; (2) hydrazine dihydrochloride; (3) acid ammonium sulfate. Twenty-five cc. of a 0.025 *M* solution of the salt was used in each case. The normality of NaOH was 0.1112. The methyl orange end-point is indicated by the black dot.

Each vertical division represents a change of 100 millivolts in voltmeter reading.

Experimental.—Solutions of the sulfate and dihychloride were made up (0.025 *M*) and titrated with carbonate-free sodium hydroxide, using the same apparatus as described above. These solutions were found to be quite stable and kept well. Typical curves are shown in Fig. 3. The behavior of these salts was so like that of the acid salts of the monovalent bases that a solution of an acid sulfate quite analogous to hy-

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[9] This, however, gives qualitative agreement with the calculation of Kolthoff (Ref. 2) which appeared after this work had been completed.

[10] Stollé, *J. prakt. Chem.*, [2] **66**, 332 (1902).

drazine sulfate, namely, ammonium acid sulfate, was made up in the same concentration and titrated with sodium hydroxide. The curve for this titration is also included in Fig. 3.

Discussion.—In these titrations we find two inflections in the curve, one corresponding to the addition of the first equivalent of base and the other to the second equivalent. This confirms the conclusions of the earlier investigators,[3,4] that the hydrazine salts containing two equivalents of acid are largely hydrolyzed in dilute solution, or dissociated into the mono-salt and free acid. The first inflection corresponds to the neutralization of the hydrogen ion thus produced and the second to the formation of the un-ionized base, N_2H_5OH or $N_2H_6(OH)_2$. The first inflection is sufficiently sharp to indicate that the use of hydrazine in alkalimetry as recommended by Stollé is practicable.

It is interesting to note that in all the titrations the methyl orange end-point comes slightly before the electrometric end-point and is theoretically, at least, not so accurate. Perhaps the personal equation may enter in choosing end-point color, though most of the end-points recorded in this paper occurred at P_H 4 to 5.

Titration of Hydrazine with Oxidizing Agents

Hydrazine is customarily determined by oxidimetric titration, and to complete the investigation a number of these were studied by the electrometric method. A very careful study of the various other methods has been made by several investigators, the most recent being that of Bray and Cuy[11] which appeared just as this paper was being written and to avoid needless repetition the reader is referred to their paper for the summary of previous work. As they state in their discussion nearly all of the methods heretofore available have been tedious and none too accurate. The methods proposed by Bray and Cuy represent a great improvement both as to rapidity and accuracy but were not available when this work was done.

A large number of oxidizing agents were tried by us which are known to react with hydrazine but the only ones that proved satisfactory on the basis of rapidity of action and stability were iodine in neutral solution and potassium bromate in the presence of strong hydrochloric acid. Iodine in alkaline solution reacted more rapidly but no break occurred in the curve at the end-point. This agrees with the work of Bray and Cuy.

The Iodine Hydrazine Titration

Of all the previous methods for the determination of hydrazine this seemed to be the most susceptible to "speeding up." It was studied by Stollé[10] and Rupp[12] and is believed to give fairly accurate results if fifteen

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[11] Bray and Cuy, This Journal, **46**, 858 (1924). Kolthoff, Ref. 2, has also just published a similar paper.

[12] Rupp, *J. prakt. Chem.*, [2] **67**, 140 (1903).

minutes is allowed for the reaction to become complete, although Bray and Cuy are inclined to modify it, in order to cut down this time. It was thought by us that the slower addition of iodine in the electrometric method might serve this same purpose and this indeed seems to be the case. In our work very concordant results were obtained particularly when disodium phosphate was used as a buffer instead of sodium bicarbonate or sodium potassium tartrate as recommended by the earlier investigators.

Experimental.—The typical electrometric apparatus for such work was used, the electrodes being a small platinum wire and a 0.10 *N* calomel half-cell. The solutions were protected from the air during the titration by an atmosphere of carbon dioxide. The phosphate buffer solution was made up as 100 g. of the crystalline disodium phosphate per liter and neutralized to phenolphthalein with phosphoric acid. A volume of it equal to the volume of the hydrazine solution was used in each titration.

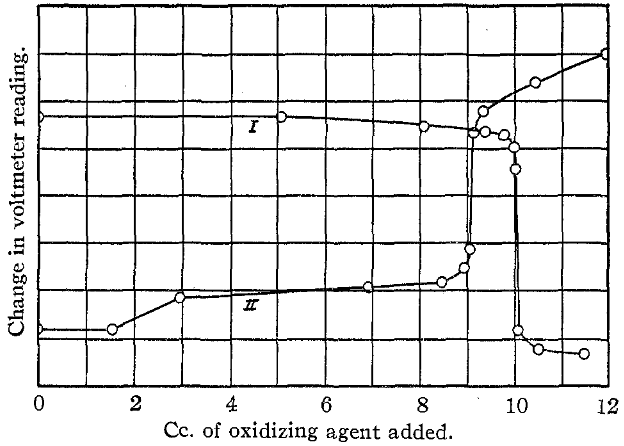

Fig. 4.—Curve I represents the addition of I_2 to hydrazine or its salts; Curve II, the addition of $KBrO_3$. Each vertical division represents a change of 100 millivolts in the reading of the voltmeter. (The iodine and bromate are not of the same concentration.)

A very sharp break was obtained in the curve at the end-point and in general the method seemed to be satisfactory, obviating as it did the 15-to-

TABLE I

COMPARISON OF ELECTROMETRIC AND COLORIMETRIC END-POINTS AND EFFECT OF DILUTION ON THE HYDRAZINE-IODINE TITRATION

H_2O added to 10 cc. of $N_2H_4.H_2SO_4$ and of 10 cc. buffer Cc.	I_2 required for— (a) Elect. end-point Cc.	(b) Color. end-point Cc.	Diff.
0	11.06	11.07	+0.01
25	11.05	11.06	+0.01
50	11.07	11.06	−0.01
50	11.05	...	....
100	11.07	11.06	−0.01

30-minute wait required by other methods. A representative curve is shown in Fig. 4. The accuracy of the method as compared with the colorimetric method (using starch indicator) was determined and the effect of dilution was also studied. Some of these results are shown in Table I. The colorimetric end-point was determined by titrating back in each case with standard thiosulfate solution, after the addition of a little acid.

The Bromate Hydrazine Titration

Kurtenacker and Wagner[13] found that an excess of potassium bromate in the presence of 6 *N* hydrochloric acid quantitatively oxidizes hydrazine to nitrogen and hydroxylamine to nitrate. In their procedure the hydroxylamine solution was treated in a stoppered flask with an excess of potassium bromate solution (0.1 *N*) and then acidified with 40 cc. of 1:1 hydrochloric acid. After 15 minutes, potassium iodide solution was added and the liberated iodine titrated with thiosulfate solution. The bromate excess was about 10–30 cc. of 0.1 *N* solution. With hydrazine the liberated nitrogen was measured.

This method was modified to meet the requirements of electrometric titration. The standard potassium bromate was run into the hydrazine salt in the presence of a large excess of 6 *N* hydrochloric acid, in an atmosphere of carbon dioxide. Chlorine was probably the real oxidizing agent here. A good curve was obtained, as shown in Fig. 4, the end-point agreeing with that obtained by the iodine method, but the titration was slow and tedious and therefore not desirable for practical use. For this reason experimental data are omitted.

An attempt was also made to adapt this method to the use made nitrometrically by Kurtenacker and Wagner, that is, to the determination of hydrazine and hydroxylamine in a mixture of the two. A curve was obtained showing two breaks, one corresponding to the completed oxidation of each of the two compounds, but whereas they obtained a quantitative oxidation of hydroxylamine to *nitrate*, the electrometric titration (adding the bromate slowly to a mixture of hydroxylamine and hydrochloric acid) used an amount of bromate corresponding almost quantitatively to the amount required to oxidize hydroxylamine to *nitrous oxide*. This was true whether a mixture of hydrazine and hydroxylamine, or hydroxylamine alone, was titrated. As noted above, Kurtenacker and Wagner added the 6 *N* acid to the mixture of hydroxylamine and excess of bromate, whereas our method called for the addition of the bromate slowly to the mixture of hydroxylamine and acid, the two procedures with the same reagents and same concentrations yielding different end-products. In one titration 10 cc. of hydroxylamine solution containing 0.0806 g. of the hydrochloride required 23.20 cc. of 0.100 *N* potassium bromate solution.

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[13] Kurtenacker and Wagner, *Z. anorg. allgem. Chem.*, **120**, 261 (1922).

The calculated amount needed for oxidation to nitrate would be 69.62 cc. and for oxidation to nitrous oxide would be 23.21. This apparently accurate result was due probably to a combination of errors as the presence of small but variable quantities of nitrite could always be detected. The reaction proved to be very sensitive to dilution and acid concentration so that it was given up. Other oxidizing agents failed to do as well as the bromate. For the determination of hydroxylamine alone the volumetric methods of Bray, Simpson and McKenzie leave nothing to be desired in the way of accuracy but they are not very adaptable to electrometric treatment.[14]

The foregoing attempts to titrate hydroxylamine are mentioned to call attention to the apparent difference in the product of the reaction of bromate and hydroxylamine, depending only on the way and order in which the reagents are brought together.[15]

Summary

1. Representative curves are given for the titration of hydrazine hydrate in various concentrations with acids, which show but one inflection.
2. Calculations are made and a graph has been drawn which show that this being the case, the second ionization constant K_2 of hydrazine hydrate should be less than 1×10^{-12}; Kolthoff calculates it to be 2.8×10^{-13}.
3. Curves are given for the titration of hydrazine salts with bases and similarity to the acid salts of ammonia is pointed out.
4. Curves are given for the titration of hydrazine with oxidizing agents such as iodine and potassium bromate. Mention is made of a variation in the reaction of *hydroxylamine* and potassium bromate in acid solution, depending on the order in which they are brought together.

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[14] Bray, Simpson and McKenzie, THIS JOURNAL, **41,** 1368 (1919).

[15] The writer wishes to express his indebtedness to Professor Bray for many valuable suggestions in the preparation of this paper.