medium. This material is probably what is loosely termed β-titanic acid. An X-ray diffraction examination would probably classify this material, although such an examination was not made. The effect which produced the precipitate is apparently not syneresis, since the volume of the granular precipitate is only a small fraction of the volume of the liquid.

A peculiar effect was discovered when a gel which had set at a higher temperature was suddenly cooled. The material liquefied. If this was again raised to the higher temperature, it was found to regel. This cycle was repeated five times for one mixture which set at 80°. This phenomenon is being reinvestigated.

In spite of the peculiarities in the setting of these hydrogels of titania, we believe that the values of the energy of activation, using three different methods of mixing, are approximately correct. These hydrogels set more rapidly as the temperature is raised. A value of the energy of activation of 22,000 calories appears reasonable.

In these acidic mixtures, the gels set more rapidly, as the pH increases, for a given concentration of titania. They also set more rapidly, with a given pH, as the titania concentration increases. The behavior here resembles that of silicic acid gels.

The formation of β-titanic acid appears to prevent the formation of the gel; in fact, when the gels broke down, apparently the β-titanic acid was formed. The β-acid is thus, apparently, a form with lower energy content than either the gelatinous α-acid or the form present in the gel. There are not sufficient data here to contribute much information to clarify relations between the α- and β-acids and the gel.

If a monotitanic acid is first formed when the alkali carbonate reacts with the acid titanate solution, as was suggested by Brintzinger,[7] the condensation process must be rapid. It should be noted here that considerably more evidence is at hand to show the amphoteric character of titanium hydroxide than is available to show the amphoteric character of silicon hydroxide.[8] This amphoteric nature of the hydroxide affords an easy way of explaining the condensation mechanism.

Summary

A study of some properties of the hydrogel of titania has been made.

These gels are softer than silicic acid gels of equivalent concentration. They also break down on standing to give a granular precipitate.

An approximate value of 22,000 calories for the energy of activation was obtained. This is higher than the value of 17,000 calories for silicic acid gels.

Acidic mixtures set more rapidly with increases in the pH, the titania content or the temperature.

Gels set at a higher temperature were liquefied by rapid cooling.

SCHENECTADY, N. Y. RECEIVED NOVEMBER 18, 1940

[A CONTRIBUTION FROM THE PHYSICAL CHEMISTRY RESEARCH LABORATORY OF NORTHWESTERN UNIVERSITY]

The Theory of the Glass Electrode. V. The Influence of Negative Ions

BY MALCOLM DOLE, RICHARD M. ROBERTS AND CHARLES E. HOLLEY, JR.

Introduction

It has long been believed that the type or relative concentration of negative ions is without influence on the behavior of the glass electrode either in acid or alkaline solutions.[1] However, we have been informed by an industrial research chemist that the use of the glass electrode in solutions containing borate or fluoride ions encounters difficulties, in the latter case in solutions too alkaline for hydrogen fluoride attack on glass (according to this chemist). Furthermore, no careful investigation has been carried out on the effect of the smallest negative ions such as the hydroxyl, fluoride or chloride ions which might be expected to be the negative ions most likely to interfere with the hydrogen electrode function of glass electrodes. Finally, a certain discrepancy between some of the data of Dole and of Dole and Wiener[2] was thought possibly to be due to a difference in the type of negative ions in their buffer solutions, as the other experimental condi-

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[1] A complete discussion of the theory of the glass electrode with references is to be found in the monograph by Dole, "The Glass Electrode," to be published by John Wiley and Sons, Inc.

[2] (a) M. Dole, THIS JOURNAL, **53**, 4260 (1931); (b) M. Dole and B. Z. Wiener, *Trans. Electrochem. Soc.*, **72**, 107 (1937).

tions of the two investigations were presumably identical. For all these reasons we decided to study the influence, if any, of negative ions on the glass electrode e. m. f., particularly in alkaline solution.[3]

Thanks to the courtesy of Dr. Arnold Beckman, we are also able to report in this paper on the behavior of his new type of sodium-error free (nearly free) glass electrode.

Experimental

Salts and Solutions.—All salts were purified by recrystallization except tetraethylammonium bromide and the water content determined where necessary. The bases used were not repurified; the 10% solution of tetraethylammonium hydroxide was brownish in color due to the attack of the base on the brown glass bottle in which it was shipped.

Concentrations in this paper are expressed in terms of equivalents per liter of solution at 25°.

Electrodes.—The hydrogen and silver chloride electrodes were made as in previous investigations of this series. A buffer solution approximately 0.1 *N* each in acetic acid, sodium acetate and sodium chloride served as the reference solution inside the glass electrodes which were of the MacInnes and Dole type. A separate measurement was made of the e. m. f. of the cell

$$\mathrm{H_2} \mid 0.1\ N\ \mathrm{HAc, NaAc, NaCl} \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad \text{(A)}$$

so that, apart from the asymmetry potentials and alkaline errors, the e. m. f. of the glass electrode cell

$$\mathrm{H_2} \mid \text{test solution} \mid \text{glass} \mid 0.1\ N\ \mathrm{HAc, NaAc, NaCl} \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad \text{(B)}$$

would be known.

The Beckman 4990-E glass electrode of the sodium error free type had a resistance of 550 megohms at 25°; the resistances of the Corning 015 glass electrodes varied between 25 and 75 megohms depending on the thickness of the membrane.

Electrometer.—The e. m. f. of the glass electrode cells was measured with a Rubicon potentiometer to 0.1 mv. with the aid of a Cherry electrometer[4] employing the inverted triode Westinghouse RH-507 tube. Numerous difficulties were encountered in the use of the electrometer, particularly during the hot humid summer months when accurate e. m. f. readings could be obtained only after an additional gauze bag filled with dehydrite had been placed in the vacuum tube well, after a rubber gasket had helped to make the cap to the tube well more nearly air-tight[5] and after the air about the quartz insulation had been maintained in a desiccated condition by means of a special drying tube fastened to the quartz insulator (the surface resistance of quartz falls from 10^{14} ohms/sq. cm. at 40% relative humidity to 10^9 ohms/sq. cm. at 75% relative humidity). It was found that irregular fluctuations in the galvanometer deflections might occur if the tension on the screw heads on the top panel of the electrometer was altered, possibly because of changes in contact resistances or changes in the resistance settings by the changing tension. The electrometer and particularly the input circuit proved to be extremely sensitive to external electrostatic and electromagnetic fields; even bringing the hand within a foot of the unshielded input circuit would swing the galvanometer light image off the scale, or starting an electric motor with sparking commutator brushes even in another room 50 feet away would produce the most erratic behavior. For these reasons all electric motors and transformers near the instrument were disconnected while making the e. m. f. readings, and the entire input circuit including the glass electrode cell was carefully shielded, the copper shields being connected to the shield binding post on the electrometer panel and grounded.

Other experimental conditions were the same as described in previous papers of this series.

Fluoride and Chloride Ions.—The method of investigating the influence of negative ions consisted in the measurement of the error (ΔE) of the glass electrode over a *p*H range in alkaline solutions containing different types of negative ions. Any deviation of the constant value of cell (B) from its value in acid solutions, E^0_B, where the glass electrode is supposed to function without error is the error of the electrode, or

$$E_\mathrm{B} - E^0_\mathrm{B} = \Delta E \qquad (1)$$

The value of E^0_B should be equal to the e. m. f., E_A, of cell (A) 0.5632 v., except for any asymmetry potential of the glass electrode (in the case of the experiments involving the sodium salt solutions a different reference liquid inside the glass electrode was used, giving E_A, 0.3680 v.). Alkali having the same positive ion concentration as the buffer solution in the cell was used to increase the *p*H, thereby maintaining the positive ion concentration constant.

Figures 1 and 2 illustrate values of E_B obtained in the case of 0.5 *N* sodium fluoride and acetate and 1.0 *N* sodium fluoride and acetate, respectively. No significant difference exists in the data for the two types of negative ions, but the errors produced by the sodium ions are so large that the effect of changing the type of negative ion might be masked. For this reason it was decided to investigate solutions containing potassium as the positive ion, because potassium-errors of the glass electrode are small.

Values obtained for E_B for 1 *N* potassium solutions are shown in Fig. 3 while the corresponding ΔE values are plotted in Fig. 4. It is immediately apparent that the errors of the glass electrode in alkaline solutions are the same whether the

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[3] No influence of negative ions in acid solutions had been demonstrated previously by M. Dole, THIS JOURNAL, **54**, 3095 (1932).

[4] R. H. Cherry, *Trans. Electrochem. Soc.*, **72**, 173 (1937).

[5] We are indebted to Professor Malcolm Haring for this suggestion.

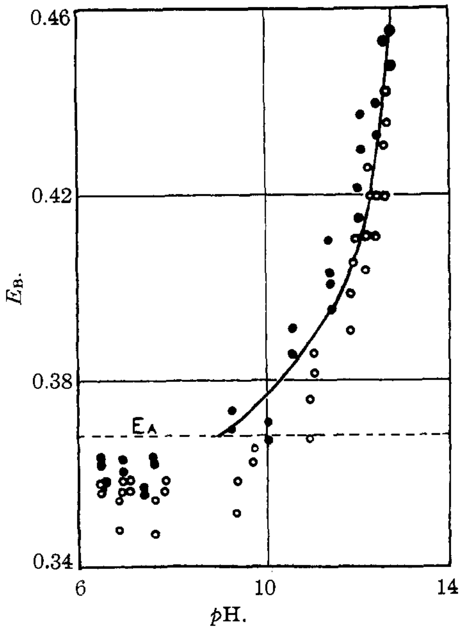

Fig. 1.—○, 0.48 N NaF, 0.01 M NaH_2PO_4 + 0.5 N NaOH; ●, 0.48 N NaAc, 0.01 M NaH_2PO_4 + 0.5 N NaOH.

negative ion of the solute is the fluoride, chloride or acetate ion. It is interesting to observe that the E_B values more nearly coincide at the high *p*H values than do the ΔE data, which indicates that the asymmetry potentials possibly change with rising *p*H to become more nearly similar for different electrodes.

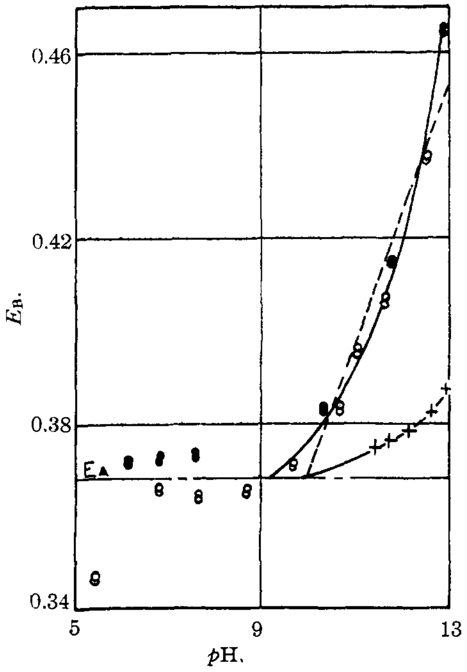

Fig. 2.—○, 0.9 N NaF, 0.1 M NaH_2PO_4 + 1 N NaOH; ●, 0.9 N NaAc + 1 N NaOH; +, Beckman electrode 4990-E in 1 N NaAc +1 N NaOH.

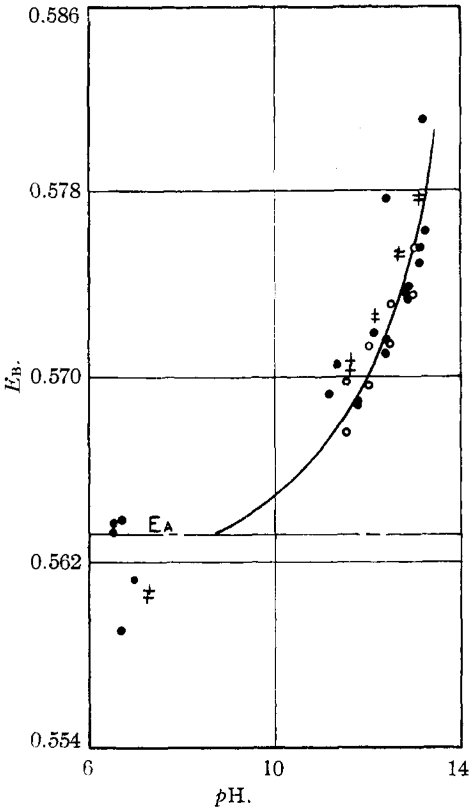

Fig. 3.—All solutions 1 N in K^+; ○, chloride + 1 N KOH; ●, acetate + 1 N KOH; +, fluoride + 1 N KOH.

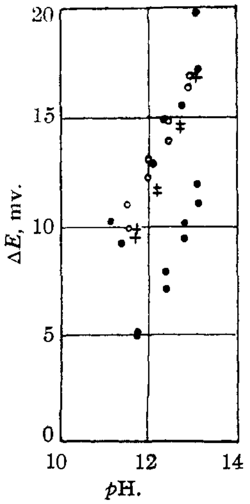

Fig. 4.—All solutions 1 N in K^+: ○, chloride + 1 N KOH; ●, acetate + 1 N KOH; +, fluoride + 1 N KOH.

An astonishing observation was made when a glass electrode which had been in the fluoride solution at a *p*H of 6.34 (curve 3, Fig. 5) was compared over the high *p*H range with a glass electrode which had never been in a fluoride solution more acid than *p*H 6.85 (curve 1, Fig. 5). Curve 2 illustrates similar data starting at *p*H 7.29. In the previous fluoride studies acid solutions were avoided, because of the well-known destructive action of hydrogen fluoride on glass. By referring to Fig. 5 it can be seen that the *alkaline* errors were greatly increased by virtue of the contact of the glass membrane with a

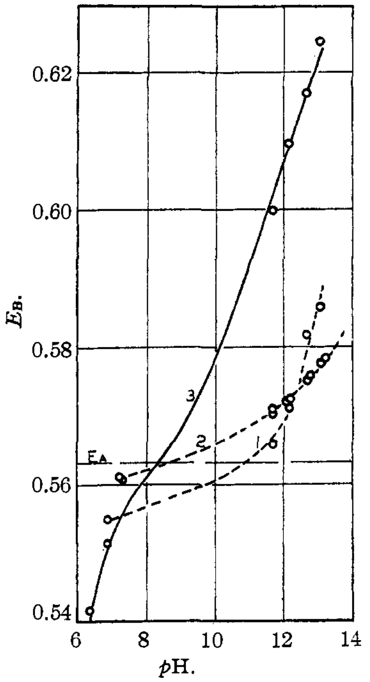

Fig. 5.—Curve 1, 0.985 N KF, 0.015 N KAc + 1 N KOH starting at pH 6.85; curve 2, the same, starting at pH 7.29; curve 3, the same, starting at pH 6.34.

0.9846 N potassium fluoride solution (also 0.0154 N in potassium acetate). This effect was investigated further by placing a glass electrode momentarily in a fluoride solution having a pH of 4.14. E_B for this electrode at first rose toward its theoretical value of 0.5632 v., but quickly reversed its trend, falling rapidly to a value of 0.4402 v. At this point 1 N potassium hydroxide was added to bring the pH to 12.25 where E_B became 0.6324 v., giving an error of 69 mv. as compared to the value of 49 mv. exhibited by the glass electrode which originally had been in contact with a potassium fluoride solution of pH 6.34 (curve 3, Fig. 5). Thus, it is clear that exposure of the glass electrode to solutions containing hydrogen fluoride impairs the hydrogen electrode function of the glass not only in acidic solutions but also when used subsequently in basic solutions. From Figs. 4 and 5 it can be seen that if the glass electrode is not exposed to fluoride solutions below a pH of 7, the glass is not damaged detectably. At a pH of 6 the molecular hydrogen fluoride concentration is approximately 0.0013 molar in our potassium fluoride solution as can be calculated from the equilibrium equation[6] at 25°

$$[H^+][F^-]/[HF] = 7.4 \times 10^{-4}$$

We conclude that while the smallest negative ions are without influence on the potentials of the glass electrode, solutions containing molecular hydrogen fluoride above a concentration of 0.0001 molar should be avoided.

When the sodium acetate and fluoride solutions were investigated, no such effect was observed, see Figs. 1 and 2 (relatively thick Haber-type glass electrodes were employed for these experiments—which explains why the glass electrodes were not destroyed by the action of the fluoride solutions). In this case the rate of attack of the glass surface by the basic sodium solutions is probably rapid enough[7] to dissolve off the surface corroded by the hydrogen fluoride, or perhaps the error of the glass electrode is already so large because of the sodium ions that the impairment of the surface by the hydrogen fluoride cannot be detected by the method adopted here. However, the behavior of the glass electrode in sodium fluoride solutions below a pH of six can be seen from Fig. 2 to be definitely affected by the hydrogen fluoride, so that our admonition to avoid hydrogen fluoride is applicable also to solutions containing sodium ions and presumably to all acid fluoride solutions.

Borate Ions.—A solution 0.05 molar in $Na_2B_4O_7 \cdot 10H_2O$[8] having a pH of 9.18 is recommended as a standard buffer solution for glass electrode calibrations.

As this pH is at the borderline of the pH range where glass electrodes begin to exhibit sodium errors, some experiments were first carried out to ascertain the accuracy with which the pH of this solution can be measured with Corning 015 glass electrodes. Three glass electrodes and two hydrogen electrodes were placed in an acetate buffer of pH 4.58 and their e. m. f.'s measured. On replacing the acetate buffer with 0.05 M $Na_2B_4O_7$, the change in e. m. f., δE, for the five electrodes was found to be the same for all except glass electrode number 26; see Table I. We can conclude, therefore, that the borax buffer is suit-

TABLE I

Electrode	δE
Hydrogen 1	0.2710
Hydrogen 2	.2710
Glass electrode 26	.2675
Glass electrode 29	.2710
Glass electrode 30	.2710

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[6] J. H. Simons, *Chem. Rev.*, **8**, 232 (1931).

[7] For the rate of attack of Corning 015 glass see Hubbard, Hamilton and Finn, *J. Research Natl. Bur. Standards*, **22**, 339 (1939).

[8] This decahydrate may be brought to constant weight by exposure in a desiccator to the aqueous vapor of a saturated solution of potassium bromide. Kolthoff, THIS JOURNAL, **48**, 1447 (1926).

able for glass electrode standardizations, with an uncertainty of possibly 1 mv.

Membrane type glass electrodes were next studied in 1 *N* $K_2B_4O_7$ solutions using a technique similar to that described in the acetate, chloride and fluoride studies. No difference between the behavior of the glass electrode in the borate and acetate buffers could be detected, at least over the *p*H range 9.50 to 12.85, see Fig. 6. Incidentally the good agreement obtained for these separate studies indicates that the previous conclusion of one of us concerning the irreproducibility of the glass electrode in solutions containing the potassium ion is invalid for Corning 015 glass electrodes.[2a] However, on adding concentrated hydrochloric acid to the 1 *N* $K_2B_4O_7$ solution at *p*H 9.57 large errors of the glass electrode were observed, the values of E_B being 0.5711 and 0.5615; 0.5575 and 0.5570; 0.5544 and 0.5472 for two different electrodes at *p*H's 9.57, 9.00 and 8.32, respectively. At still lower *p*H values the hydrogen electrode e. m. f. became erratic; on removing the platinum electrodes from the solution at *p*H 5.4, they, as well as the glass electrodes, were found to be thickly coated with solid boric acid. Yet, the boric acid or the borate ions did not impair the hydrogen electrode function of the glass electrodes for on placing the glass membranes in a 1 *N* potassium ion solution at *p*H 13.02 after they had stood for ten minutes or even one hour in the boric acid solution of *p*H 5.4, E_B was found to be reproduced within 1 mv. of its original value. The correct value for cell E_B (within limits of asymmetry potential error, 2–3 mv.) was found when glass electrodes were studied in a saturated boric acid solution at *p*H 4.57, in a 1 *N* $K_2B_4O_7$ solution saturated with boric acid at *p*H 9.15, and in a 0.1 *N* hydrochloric acid solution saturated with boric acid at *p*H 1.14. Thus it appears that neither acid nor alkaline borate or boric acid solutions appear to impair the hydrogen electrode function of the glass electrode.

Hydroxyl Ions.—It is almost impossible to answer the question concerning the extent to which hydroxyl ions enter into the electrochemical reactions at the glass–aqueous solution interface inasmuch as the transfer of an equivalent of hydroxyl ions on the passage of one faraday of electricity in one direction can be shown to be thermodynamically equivalent to the transfer of one equivalent of hydrogen ions in the opposite direction except for one factor, the free energy of transfer of water. Unfortunately the value of ΔE calculated on the basis of a decrease in the activity of the water and resulting from the assumed migration of hydroxyl ions has the same sign as the positive ion error in alkaline solutions and cannot be separately distinguished from the latter.

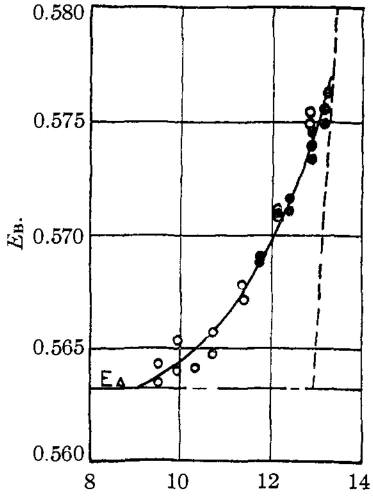

Fig. 6.—All solutions 1 *N* in K^+ ion: ○, borate buffer + 1 *N* KOH; ●, acetate buffer + 1 *N* KOH.

Another approach to the hydroxyl ion problem consists in studying the influence of hydroxyl ion migration on the positive ion error; it can be shown mathematically that in solutions of high *p*H the slope of the ΔE-*p*H curve should approach 29.5 mv. per *p*H unit instead of the maximum value of 59 mv. per *p*H unit if the hydroxyl ion participates significantly in the electrochemical reaction at the glass electrode surface. The dotted lines of Figs. 2 and 6 have been drawn with a slope of 29.5 mv. per *p*H unit and it can be seen that in the first case the experimental slope is much greater, nearly 59 mv. per *p*H unit, and in the second case much less than the calculated 29.5 mv. per *p*H unit. We conclude that there is no evidence of hydroxyl ion migration across the aqueous glass solution interface.

Alkaline Errors of the Beckman 4990-E Glass Electrodes.—The crosses of Fig. 2 illustrate the sodium errors of the new Beckman No. 4990-E glass electrode.[9] The data of Table II also prove that this new type of glass is superior to Corning 015 glass in the alkaline range. This striking

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[9] Supplied by the National Technical Laboratories, Pasadena, Calif.

difference would probably not be observed in lithium salt solutions.

Table II

Solution	pH		ΔE in mv. Beckman electrode	Corning electrode
0.7 N $(C_2H_5)_4NOH$	13.78		0.8	38.0
			2.7	35.3
		Av.	1.7	36.7
0.7 N $(C_2H_5)_4NOH$			3.3	68.1
+1.7 N $(C_2H_5)_4NBr$	14.23		7.6	65.4
		Av.	5.4	66.7

Acknowledgments.—The authors gratefully acknowledge grants from the National Society of Sigma Xi for the purchase of the Cherry electrometer, from the Penrose Fund of the American Philosophical Society for the support of one of us (R. M. R.) during a six-month period and from the Abbott Research Fund of Northwestern University which supplied a fellowship held for one month only by C. E. H., Jr.

Summary

1. The influence of fluoride, chloride, borate and hydroxide ions on the glass electrode has been studied.

2. No negative ion as such appears to affect the alkaline errors of the glass electrode, but in certain cases these errors in solutions of high pH are greatly increased if the glass surface is exposed to one normal fluoride solutions having pH values lower than 7.0.

3. A new Beckman sodium-error free glass electrode has been investigated in one normal sodium solutions. In agreement with unpublished data of Dr. Beckman and his co-workers we find the sodium errors to be materially reduced by this new kind of glass.

Evanston, Illinois Received November 25, 1940

[Contribution from the Chemical Laboratories of the University of New Hampshire and Trinity College (Conn.)]

The Preparation of Symmetrical Biaryls by the Action of Reducing Agents on Diazotized Amines. Reducing Agents

By Edward R. Atkinson, H. J. Lawler, J. C. Heath, E. H. Kimball and E. R. Read

In beginning our detailed study of the reaction outlined in an earlier paper,[1] we have selected as a standard diazotized amine that derived from anthranilic acid and have examined its conversion to diphenic acid by the action of a number of reducing agents. This paper reports our results using those containing cuprous copper. For each we have determined the necessary mole ratios and concentrations. Where reducing agents had been used in this reaction by previous workers, their stated procedures were in general followed at first, but desirable modifications were made in all cases and the procedures given in the experimental part of this paper represent those which we have found to be the optimum.

Experimental Part

General Experimental Procedure.—With the exception of the work using solutions of cuprous chloride in hydrochloric acid, the reactions were carried out by suspending or dissolving the reducing agent in the appropriate solvent (dilute ammonium hydroxide in most cases) and then adding the diazonium solution to the well-stirred reducing solution by means of the addition tube already described.[1] If desirable, the reaction mixture was cooled by immersion in an ice-bath. At the conclusion of the reaction the solution was acidified with concentrated hydrochloric acid at a temperature specified for the individual case.

Hydrated Cuprous Oxide in Dilute Ammonium Hydroxide.—A mixture of hydrated cuprous and ferric oxides, prepared by the action of ferrous sulfate on ammoniacal solutions of cupric sulfate as described by Vorländer and Meyer,[2] was used in three experiments; the procedure and quantities of materials were as specified by these workers. Impure diphenic acid, m. p. 215–225°, was obtained in 57% yields.

When cuprous chloride was converted to the hydrated oxide by the action of aqueous sodium hydroxide as described by Huntress[3a] and the oxide so prepared used as described below, the results were essentially the same as those obtained by Huntress; a tarry by-product was often present and in one experiment we isolated *o*-chlorobenzoic acid from the lower melting by-products. Since acetic acid had been used in diazotization, the reducing agent was analyzed for chloride and was found to contain 80–90% unconverted chloride. This was the case even when freshly precipitated cuprous chloride had been used. By

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[1] Atkinson and Lawler, This Journal, **62**, 1704 (1940).

[2] Vorländer and Meyer, *Ann.*, **320**, 122–144 (1902).

[3] (a) Huntress, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1932, Coll. Vol. I, page 216; (b) This Journal, **55**, 2561 (1933); (c) **55**, 4268 and 4270 (1933).