

The Journal of the American Chemical Society

VOL. 52

NOVEMBER, 1930

No. 11

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

PROPERTIES OF DIPHENYLAMINE AND DIPHENYLBENZIDINE AS OXIDATION-REDUCTION INDICATORS

BY I. M. KOLTHOFF AND L. A. SARVER

RECEIVED MARCH 4, 1930

PUBLISHED NOVEMBER 5, 1930

Introduction

Knop¹ was the first to propose the use of diphenylamine as an indicator in the titration of ferrous iron by potassium dichromate, whereas Cone and Cady² recommended either diphenylamine or diphenylbenzidine as internal indicators in the titration of zinc by ferrocyanide. Several workers³ have since shown that these indicators are reliable and useful in oxidation-reduction titrations, but Sarver⁴ pointed out that end-points are often passed without any color formation, whereupon the addition of a trace of ferrous iron will then produce it instantly. Moreover, Watson⁵ has recently shown that mercuric chloride has a powerful inhibiting effect on the color production.

Since diphenylamine and diphenylbenzidine now belong among the common analytical laboratory indicators it appeared desirable to make an extensive study of their properties in order to know in what cases they can be applied, under what conditions they give reliable results, and what corrections must be made under different circumstances. The physico-chemical part of this investigation will be presented here, while the analytical significance of the work will be reserved for a future paper.

I. Speed of Color Development.—Pure products of diphenylamine (m. p. 52–53°, uncorr.) and diphenylbenzidine (m. p. 242–243°, uncorr.) have been used throughout this work, stock solutions being prepared by dissolving 0.1 g. of the substance in 100 cc. of concentrated sulfuric acid.

¹ J. Knop, *THIS JOURNAL*, **46**, 263 (1924).

² W. H. Cone and L. C. Cady, *ibid.*, **49**, 356 (1927).

³ W. W. Scott, *ibid.*, **46**, 1396 (1924); N. H. Furman, *Ind. Eng. Chem.*, **17**, 314 (1925); J. P. Mehlig, *J. Chem. Ed.*, **3**, 824 (1926); I. M. Kolthoff, *Rec. trav. chim.*, **45**, 745 (1926); *Chem. Weekblad*, **24**, 203 (1927); H. H. Willard and P. Young, *Ind. Eng. Chem.*, **20**, 764 (1928).

⁴ L. A. Sarver, *THIS JOURNAL*, **49**, 1472 (1927).

⁵ F. J. Watson, *Chem. Eng. Min. Review*, **20**, 355, 396 (1928).

The oxidation was first studied qualitatively, various amounts of acid, indicator and dichromate being mixed at different temperatures, and the time noted at which the color first became perceptible. The results were not very exact since it was hard to perceive the first tinge of violet, due to a green which often accompanied it. The hue is somewhat dependent upon the acidity, being violet at low hydrogen-ion concentrations, and more blue in acid concentrations higher than 4 *N*.

The speed of oxidation is approximately proportional to the amount of dichromate added for a given amount of indicator, and to the amount of indicator used for a given amount of dichromate. Furthermore, the reaction velocity increases rapidly with the temperature, being about four times as great at 55 as at 25°.

Acids increase the speed of reaction very markedly, and the color develops much more quickly in hydrochloric than in sulfuric acid of the same normality, on account of the greater activity of the hydrogen ions in the former. This increased speed of oxidation in larger hydrogen-ion concentrations is explained by the fact that the oxidation potential of the dichromate increases rapidly with the acidity, whereas as we shall see later the potential of the system diphenylbenzidine and its violet oxidation product is practically independent of the concentration of the hydrogen ions. This explanation is supported by the behavior of diphenylamine and diphenylbenzidine with stronger oxidizing agents; *e. g.*, with potassium permanganate the violet appears instantly at all acidities.

Mercuric chloride has a pronounced inhibiting effect, whereas traces of ferrous iron show an enormous accelerating effect; when both are present at the same time the iron only partially neutralizes the adverse action of the mercuric chloride. It may be mentioned that ferric iron is without any effect. Hence the oxidation is induced by the reaction between ferrous iron and potassium dichromate, which is in harmony with the primary oxide theory of Manchot. First, the ferrous ion is oxidized to an intermediate unstable higher oxidation state than ferric iron, which in turn reacts rapidly with diphenylbenzidine.

Finally it should be mentioned that in all cases where a large excess of oxidant was added, the violet color was quickly destroyed, becoming first red, then yellow, with dark flocks precipitating out after standing for some time, leaving a colorless solution in which it was impossible to get the violet again. The diphenylbenzidine violet is therefore decomposed in an irreversible way by excess oxidant.

II. Light Absorption by Diphenylbenzidine Violet.—The light absorption of the violet oxidation product of diphenylamine and diphenylbenzidine (which will be called diphenylbenzidine violet and abbreviated D.B.V.) in hydrochloric and sulfuric acids of various concentrations was determined by means of a Keuffel and Esser spectrophotometer and, in

agreement with the experiments of Thiel,⁶ the curves were found to be nearly flat between 5400 and 5700 Å., the absorptions differing by less than 1% over this range. The intensities of the colors increased more or less slowly with the time, according to the concentration of the acid, and later decreased, so that it was difficult to obtain comparable readings for the whole absorption curve at one time: at one stage they were practically constant for a few minutes, however, and by working rapidly fairly comparable values were obtained; but it was not possible to derive transmission coefficients under these conditions. A definite shift of the absorption maximum toward the longer wave lengths was observed in the stronger acid solutions, from 5600 Å. for the colored oxidation product from either indicator in 0.5 *N* hydrochloric or sulfuric acid to 5850 Å. for 6 *N* acid solutions. This agrees well with Thiel's value of 5870 Å. for diphenylamine in 50% sulfuric acid, considering that he worked at a still higher acidity. The fact that the colored oxidation products of both diphenylamine and diphenylbenzidine have identical absorption spectra is one proof that the two bases give identical compounds (see discussion, Section V).

III. Solubility of Diphenylbenzidine and the Order of its Ionization Constant.—The solubilities of diphenylbenzidine in water, in various concentrations of hydrochloric acid, sulfuric acid and sodium chloride, and in saturated mercuric chloride have been determined by a nephelometric method. A freshly prepared solution containing 0.04 mg. of diphenylbenzidine per cc. in a mixture of concentrated sulfuric and glacial acetic acids (10 and 90% by volume, respectively) was dispensed from a microburet, 0.01 cc. at a time, into 50 cc. of water or solution contained in a small beaker.⁷ After each addition the solution was stirred, poured carefully (to avoid formation of air bubbles) into Nessler tubes, and compared with other tubes containing only the solvent, in a dark room in a simple nephelometer constructed from a photographic dark-room lamp. Solubilities were estimated from the minimum volume of standard solution required to give the faintest perceptible permanent cloud, and could be reproduced with an accuracy of about 10%, which is quite satisfactory for such extremely small values; the concentrations were so low that the solutions did not show any perceptible color with oxidizing agents. Solubilities estimated in this way for water both at room temperature and at 50° were 0.06 mg. per liter, while those for 0.5 *N* and *N* sodium chloride, and saturated mercuric chloride were 0.05 mg. per liter. Solubilities of diphenylbenzidine in various concentrations of hydrochloric acid and the corresponding hydrolysis constants of the base are given in Table I.

Although diphenylbenzidine is a diacid base, its first ionization constant

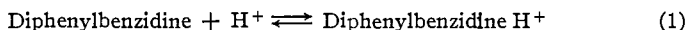
⁶ A. Thiel, *Z. Elektrochem.*, **35**, 274 (1929).

⁷ Soon after the preparation of diphenylbenzidine standard solutions, a green compound separated out; hence it was necessary to use fresh solutions.

TABLE I
SOLUBILITIES IN HYDROCHLORIC ACID AND HYDROLYSIS CONSTANT OF DIPHENYL-
BENZIDINE AT 25°

Normality of HCl	Mg. D.B. per liter	Mg. D.B.H ⁺ per liter	$K_{\text{Hydrolysis}}$	$K_{\text{Hydrolysis}}$ (corr. for salting out)
0.1	0.07
.25	.09	0.03	0.50	0.50
.5	.12	.06	.50	.45
1.0	.17	.11	.55	.50
2.0	.28	.22	.55	.51

is so small that the solubility in acids will be mainly determined by the magnitude of this constant, according to the equations:



and

$$\frac{[a\text{D.B.}][a\text{H}^+]}{[a\text{D.B.H}^+]} = \frac{[a\text{D.B.}][\text{H}^+]f\text{H}^+}{[\text{D.B.H}^+]f\text{D.B.H}^+} = K_{\text{Hydrolysis}} \quad (2)$$

where $[a\text{D.B.}]$ is the activity of diphenylbenzidine and equals the solubility in water, $[a\text{H}^+]$ is the activity of the hydrogen ion and $[a\text{D.B.H}^+]$ that of the diphenylbenzidine cation. Since $f\text{H}^+$ and $f\text{D.B.H}^+$ represent the activity coefficients of univalent ions at the same ionic strength, their magnitude will be of the same order, and the ratio of activities can be assumed to be equal to the ratio of ionic concentrations; this may introduce an uncertainty of 5–10% at higher acidities, but it is not serious when the approximate nature of the solubility determinations is considered. The concentration $[\text{D.B.H}^+]$ is equal to the difference between the solubilities of diphenylbenzidine in acid and in water, but should be corrected for the salting out effect of the electrolyte. In order to approximate the magnitude of this correction, the solubility of diphenylbenzidine was determined in N and $0.5 N$ sodium chloride solution, and the salting out effect was assumed to be the same in hydrochloric acid of corresponding concentrations. The activity of the diphenylbenzidine is not changed by the salting out, although the actual concentration may be reduced; hence it may be assumed to be equal to the solubility in water. So it follows that

$$\frac{[S_w] \cdot [\text{H}^+]}{[S_A - S_w]} = K_{\text{Hydrolysis}} \text{ (uncorrected)} \quad (3)$$

and

$$\frac{[S_w] \cdot [\text{H}^+]}{[S_A - S_s]} = K_{\text{Hydrolysis}} \text{ (corrected)} \quad (4)$$

where S_w represents the solubility of diphenylbenzidine in water, S_A the solubility in acid and S_s that in salt solution, while the hydrogen-ion concentration is assumed to be equal to the normality of the acid.

In this way the hydrolysis constant (corrected for salting out effect) has been determined and found to be remarkably constant in acid concentrations between 0.1 and 2.0 N , with an average magnitude of 0.50 at 25°.

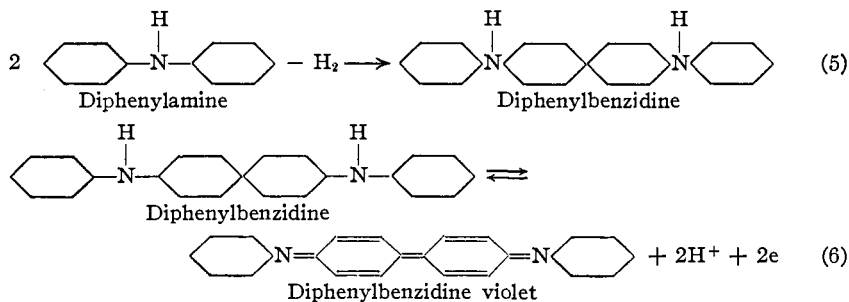
Hence the constant of the first ionization of diphenylbenzidine is 2×10^{-14} at 25° , whereas Thiel⁶ found a value of 7.6×10^{-14} for diphenylamine at 15° .

The solubility of diphenylbenzidine in sulfuric acid is much smaller than in hydrochloric acid of corresponding normality, on account of the lower activity of the hydrogen ions in the former acid. In 4 *N* hydrochloric acid and 6 *N* sulfuric acid the solubility of diphenylbenzidine is much greater than could be expected from its behavior as a monoacid base; the activity of the hydrogen ions in these strongly acid solutions is much larger than the corresponding concentrations, and also the second basic group may play an important part in strong acid medium.

Finally, it is of interest to point out that since the solubility of diphenylbenzidine in saturated mercuric chloride is approximately the same as in water, we cannot explain the great inhibiting effect of this salt on the color development by the formation of a complex between it and diphenylbenzidine; so it seems more reasonable to suppose that it reacts in some way with the colored compound or intermediate products.

IV. Potentiometric Titrations.—Freshly prepared solutions of diphenylamine and diphenylbenzidine in various concentrations of sulfuric acid were titrated potentiometrically with 0.01 *N* potassium dichromate solutions containing the same concentrations of sulfuric acid as the titration mixtures, both at room temperature ($24-30^\circ$) and at 50° . The bright platinum gauze electrode was ignited before each titration, and used in conjunction with a saturated calomel electrode with salt bridge of agar and saturated potassium chloride.

The experiments were not very satisfactory from the stoichiometric point of view, because of the slowness with which equilibrium is established and the occurrence of side reactions. However, it was found that the main reactions could be represented thus



The oxidation of diphenylamine to diphenylbenzidine is irreversible, and it even seems doubtful whether the reversible system, diphenylbenzidine \rightleftharpoons diphenylbenzidine violet, ever reaches a constant potential. In the first place they react with each other to form an extremely slightly

soluble green meriquinoid (a molecular compound of diphenylbenzidine and diphenylbenzidine violet). Moreover, the diphenylbenzidine violet itself easily undergoes further oxidation by an irreversible reaction. Therefore the potentials observed in direct titrations depend upon the time which has elapsed since the addition of the oxidant, the temperature, the acidity and the amount of excess oxidant. Yet it is possible to obtain reproducible results when the titrations are made under similar conditions. When the dichromate is added rapidly the violet appears before complete oxidation of diphenylamine to diphenylbenzidine, but the color fades on standing and the potential drops. After the quantitative formation of the diphenylbenzidine, a continued addition of dichromate oxidizes it to diphenylbenzidine violet, but part of this reacts with unchanged diphenylbenzidine to form the green meriquinoid. This meriquinoid formation is less at higher temperatures than at room temperature.

The potentials observed during the oxidation of diphenylamine to diphenylbenzidine have no exact significance, because the reaction is irreversible and the electrode behaves more or less like an oxygen electrode, with the values decreasing on long standing. At the beginning of the oxidation of diphenylbenzidine to diphenylbenzidine violet the potentials are reproducible, although the meriquinoid formation and the decomposition of the violet are responsible for the fact that the potentials are never constant for an indefinite time.

In Table II a summary is given of the results found in a few examples taken from a large number of direct titrations of 1.69 mg. of diphenylamine with 0.01 *N* potassium dichromate at different acidities and temperatures. The table is self-explanatory with the exception of the last two columns; of these, the former gives the number of equivalents of oxidant added before a violet color was perceptible in the solution (which point could be only approximated, since the green greatly obscured the violet), and the latter column indicates the potential (against saturated calomel electrode) at which the violet was first visible in the solution. Probably there was already some violet in the solution before it could be perceived, on account of being masked by the green; this could be inferred from the results of the back titrations, as will be shown later. The violet was generally first observed at potentials of 0.510–0.525 v. (against saturated calomel electrode) when the titrations were made in the presence of ferrous iron.

These results show that in the direct titration of diphenylamine two jumps in potential are observed under the proper conditions, the first corresponding to the complete oxidation of diphenylamine to diphenylbenzidine, the second to the complete oxidation of the latter to diphenylbenzidine violet. The last does not correspond exactly to the stoichiometric value on account of the fact that the green insoluble meriquinoid formed during the titration is attacked very slowly (tending to cause low

TABLE II

DIRECT TITRATIONS OF DIPHENYLAMINE WITH POTASSIUM DICHROMATE
50-cc. portions of acid of the designated normality containing 1.69 mg. of diphenylamine
used for each titration

H_2SO_4 , N	Temp., °C.	First jump (D.A. \rightarrow D.B.)		Second jump (D.B. \rightarrow D.B.V.)		Violet first perceptible	
		Equiv. of oxidant required (calcd. 1.0)	Approx. e. m. f. (against satd. C.E.), v.	Equiv. of oxidant required (calcd. 2.0)	Approx. e. m. f. (against satd. C.E.), v.	Equiv. of oxidant required (calcd. 1.0)	Approx. e. m. f. (against satd. C.E.), v.
0.1	27	1.0	0.550	2.0	0.580	1.1	0.555
.1	25	0.95	.530	2.2	.580	1.2	.560
.1	50	.9	.525	1.9	.570	0.9	.590
.1	50	.9	.535	1.9	.580	.95	.530
.25	25	1.0	.545	2.2	.590	1.1	.558
.25	50	1.0	.550	2.2	.600	1.1	.550
.25	50	1.0	.550	2.2	.600	1.1	.555
.5	25	1.1	.535	2.2	.600	1.0	.530
.5	25	1.1	.540	2.3	.605	1.1	.538
.5	50	0.95	.530	2.1	.600	0.6	.510
.5	50	1.0	.530	2.1	.605	.4	.505
.5	50	1.0	.525	2.1	.605	.8	.518
1.0	28	1.0	.530	2.0	.600	.9	.524
1.0	50	1.1	.520	2.0	.590	.7	.530
1.0	50	1.1	.530	2.0	.595	.8	.520
1.0	50	1.1	.530	2.2	.600	.9	.530

results), and because part of the diphenylbenzidine violet is oxidized irreversibly to other products (tending to cause high results).

Similar titrations have been made with diphenylbenzidine under the same conditions of time and acidity, which confirm the results obtained with diphenylamine; but, owing to the slight solubility of the former, still more difficulties were encountered. Of course, only one jump in potential occurs in this titration, after the complete oxidation to diphenylbenzidine violet.

On account of the fact that equilibrium is established fairly slowly in direct titrations, with much opportunity for side reactions, it was thought desirable to add the diphenylamine or diphenylbenzidine to a small excess of dichromate and then back-titrate as quickly as possible. It is inevitable that some of the diphenylbenzidine violet will be further oxidized by the excess dichromate when working in this way; but by making the excess small and working rapidly it has been possible to obtain reproducible results which confirm the proposed theory of the reaction mechanism. The oxidized solutions were kept at room temperature until the excess dichromate had been reduced with ferrous iron, in order to minimize further oxidation of the diphenylbenzidine violet; they were then warmed to 50° for the rest of the titration, to hasten the establishment of equilibrium. Two jumps in potential were observed, the first corresponding to the complete reduction of the excess dichromate, and the second to the completion

of the reduction of the diphenylbenzidine violet to the meriquinoid, diphenylbenzidine green. Averaging the results of a large number of titrations of diphenylamine at different acidities, it was estimated that after the removal of excess dichromate, 2.01 equivalents of the oxidant had been consumed by the diphenylamine (calcd., 2.0), and that the potential at the equivalence point was 0.575 v. (against saturated calomel electrode); likewise, the second jump, corresponding to the complete reduction of the

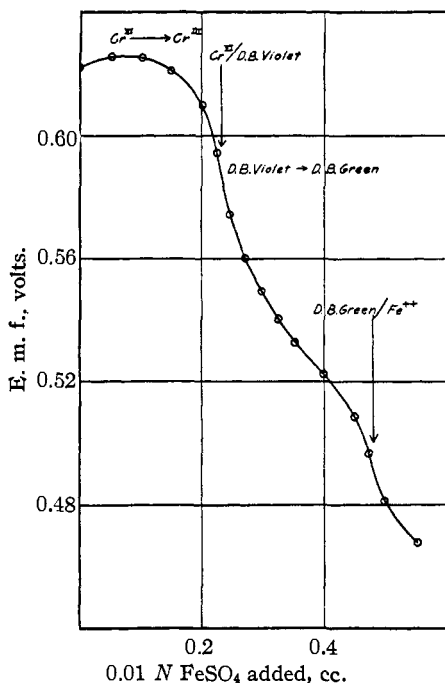


Fig. 1.—Back titration of diphenylbenzidine violet and excess potassium dichromate in 0.6 *N* sulfuric acid.

to green took place at the same potential as with diphenylamine, 0.51 ± 0.01 v. (against saturated calomel electrode), or 0.76 ± 0.01 v. (against normal hydrogen electrode). It is striking that the potential at which this color change takes place is very constant, and quite independent of the acidity. Hence, it may be concluded that diphenylamine and diphenylbenzidine give their violet oxidation product in solutions having higher oxidation-reduction potentials than those mentioned above, at all reasonable acid concentrations. In general, the curves representing the potentials during the reduction of diphenylbenzidine violet to diphenylbenzidine green have the same shape, and corresponding points have the same potentials at all acidities between 0.1 and 1.0 *N*.

diphenylbenzidine violet to diphenylbenzidine green, indicated that 1.62 equivalents of oxidant were required to oxidize the original diphenylamine to diphenylbenzidine green (calcd., 1.5), and the potential at this equivalence point was 0.510 v. (against saturated calomel electrode). Such a back-titration is shown graphically in Fig. 1, where the first part of the curve represents the reduction of the excess dichromate by ferrous sulfate, and the portion following the first break shows the reduction of diphenylbenzidine violet to the meriquinoid, diphenylbenzidine green, the second break indicating this equivalence point.

Similar experiments were made with diphenylbenzidine, but were less satisfactory from the stoichiometric point of view, for the reasons previously given; in all cases, however, the color change from violet

Further, although the results have no exact quantitative significance, they confirm the reaction mechanism represented by Equations 5 and 6.

V. Discussion.—1. The potentiometric experiments show that upon slow addition of a strong oxidizing agent to a solution of diphenylamine in an acid medium, one equivalent of oxidant is consumed before the violet is formed. Moreover, before the solution becomes colored, a milky cloudiness is observed, probably from diphenylbenzidine, which is very slightly soluble. That diphenylbenzidine is indeed the first oxidation product obtained from diphenylamine was proved by the following experiment. To a liter of a solution of 100 mg. of diphenylamine in 0.1 *N* sulfuric acid, 90% of the theoretical amount of dichromate necessary for the oxidation to diphenylbenzidine was added slowly at 50°. The solution soon became opalescent, with a tinge of green from the chromic salt formed. The white insoluble substance coagulated immediately upon boiling, and was filtered off and washed first with water and then alcohol. The residue was recrystallized from boiling toluene and dried at 105°. The melting point of this product was 244–245° (uncorr.), and the same value (within 2°) was found for a mixture of this with pure diphenylbenzidine.⁸

This experiment partly confirms the important work of Kehrmann and Micewicz,⁹ who were the first to clear up the reaction mechanism in the oxidation of diphenylamine. Although the colored oxidation products of diphenylamine had been known and studied for a long time, the interpretations of the reaction given by various writers¹⁰ were quite contradictory. Kehrmann and Micewicz obtained tetraphenylhydrazine, then diphenylbenzidine, then a green oxidation product of diphenylbenzidine which they called a half-quinoid salt, or quinhydrone, and, finally, the blue holoquinoid salt. Further strong oxidation gave a yellow solution, and then, by molecular rearrangement, a red solution. Dilute acid solutions of all these quickly became colorless, with precipitation of greenish-black flocks. These results were confirmed in the main by a number of writers, especially Marqueyrol and Muraour,¹¹ except that the latter obtained only traces of

⁸ It should be mentioned that there is some confusion in the literature as to the correct melting point of diphenylbenzidine. R. Gnehm and H. Werdenburg [*Z. angew. Chem.*, **43**, 1027, 1051, 1128 (1899)] gave it as 246–248°; V. Kadiera [*Ber.*, **38**, 3575 (1905)] reported it as 242°, corrected; and M. Marqueyrol and H. Muraour [*Bull. soc. chim.*, **15**, 186 (1914)] found 250.5–251.5°.

⁹ F. Kehrmann and St. Micewicz, *Ber.*, **45**, 2641 (1912).

¹⁰ A. W. Hoffmann, *Ann.*, **132**, 160 (1864); V. Merz and W. Weith, *Ber.*, **5**, 283 (1872), communicated by O. Meister; R. Gnehm and H. Werdenburg, *Z. angew. Chem.*, **43**, 1027, 1051, 1128 (1899); A. Baeyer, *Ber.*, **38**, 583 (1905); V. Kadiera, *ibid.*, **38**, 3575 (1905); F. D. Chattaway and H. Ingle, *J. Chem. Soc.*, **67**, 1090 (1895); H. Wieland and S. Gambarjan, *Ber.*, **39**, 1499 (1906).

¹¹ M. Marqueyrol and H. Muraour, *Bull. soc. chim.*, **15**, 186 (1914); *Ann. chim. anal. appl.*, **19**, 174 (1914); H. Wieland, *Ber.*, **46**, 3296 (1914); *ibid.*, **52**, 886 (1919); H. Wieland and C. Müller, *ibid.*, **46**, 3304 (1914).

diphenylbenzidine when tetraphenylhydrazine was taken as the starting substance. At first Wieland believed that each molecule of diphenylamine splits off one molecule of hydrogen (as H_2O) upon oxidation, to give the bivalent radical $[Ph-N=C_6H_4]_2$, which then polymerizes to the blue product $Ph-N=C_6H_4=C_6H_4=N-Ph$; but Marquoyrol and Muraour showed by quantitative experiments that diphenylbenzidine is indeed the main product, and Wieland later concurred in their conclusions.

An interpretation similar to the original one of Wieland has recently been offered by Thiel,⁶ but he assumes that not the free amines, but the corresponding cations, enter into reaction. Although it is quite possible that the formation of the bivalent cation depends upon working conditions (acidity, temperature, solvent, etc.), the present paper shows definitely that at fairly low acidities (0.1–2.0 *N*) with slow addition of the oxidizing agent, diphenylbenzidine is the first product which can be isolated.

Hence, it is felt that the first stage in the oxidation of diphenylamine is correctly represented by Equation 5 (Section IV), since the formation of diphenylbenzidine in nearly stoichiometric amounts has been proved, while no evidence of the formation of intermediate compounds has been found.

2. Diphenylbenzidine may be further oxidized to the violet or blue holoquinoid salt, diphenylbenzidine violet, by a reversible reaction Equation 6, (Section IV). This diphenylbenzidine violet is a very unstable compound, and is easily oxidized further to yellow or red compounds whose composition is as yet unknown; or it may react with unchanged diphenylbenzidine to form the greenish-black meriquinoid, diphenylbenzidine green. In fact, it is possible to titrate the color out of an oxidized diphenylbenzidine solution by adding a solution of pure diphenylbenzidine. While it is impossible to state with certainty, it is believed that diphenylbenzidine green is an equimolecular compound of oxidized and unoxidized diphenylbenzidine.

3. This meriquinoid, diphenylbenzidine green, which was first mentioned by Kehrmann and Micewicz,⁹ is an extremely slightly soluble green substance, and obscures the perception of the violet in the solution. A saturated solution of it in water or acid is colorless, and contains so little diphenylbenzidine that it is not colored by an oxidizing agent. A suspension of the green product is, however, changed to violet by dichromate or any strong oxidizing agent, which shows the presence of diphenylbenzidine in the compound. On account of its extremely slight solubility, it is hard to reduce it with ferrous sulfate, but stronger reducing agents like stannous chloride discharge the color rapidly, and a milky white opalescence from the diphenylbenzidine remains. If diphenylbenzidine violet is titrated potentiometrically with ferrous sulfate, a jump in potential occurs at the point where all the violet has been reduced to the green meriquinoid; if, however, the ferrous sulfate is added very rapidly, the formation of the

green product is prevented, and the reduction goes as far as diphenylbenzidine. The stability of a suspension of the merquinoid decreases with the temperature; at 50° it shows a weak violet color, which indicates that the dissociation of the molecular compound is greater at 50° than at room temperature.

4. If a small excess of potassium dichromate is added either to diphenylamine or diphenylbenzidine, both indicators behave identically upon back-titration with ferrous sulfate, which shows that the oxidation product is the same in both cases; this conclusion is also confirmed by the similarity of the absorption spectra (Section II).

5. It seems very remarkable that the potential at which the violet changes to green is independent of the acidity, at about 0.51 ± 0.01 v. against saturated calomel electrode, or at about 0.76 ± 0.01 v. against the normal hydrogen electrode, even the temperature having a negligible effect on this value. It was shown by special experiments that even at P_H values of 3 to 4, the change from violet to green takes place at approximately the same potential, although the diphenylbenzidine violet itself is extremely unstable at these low acidities.

According to Equation 6 (Section IV) the oxidation-reduction potential should be

$$E = E_0 + \frac{0.060}{2} \log \frac{[aD.B.V.]^2 [aH^+]^2}{[aD.B.]}, \text{ at } 30^\circ \quad (7)$$

where a designates the activity of the specified substance or ion. Therefore one would expect that E would increase 60 millivolts for each decrease of 1 in the P_H .

Now if we consider the system diphenylbenzidine violet \rightleftharpoons diphenylbenzidine green, especially at the moment when the violet changes to green, we can safely assume that $[aD.B.]$ is a constant, because diphenylbenzidine is very slightly soluble and its activity in a saturated solution will be a constant (*cf.* Section III). The diphenylbenzidine violet, on the other hand, had a variable concentration; further, part of it is present as cation (also violet or blue), and part as the free base, the latter determining the potential, according to the equations



$$[aD.B.V.] = \frac{[aD.B.V.H_2^{++}]}{[aH^+]^2} \cdot K \quad (9)$$

Now, if diphenylbenzidine violet is a relatively strong base, as compared with diphenylbenzidine itself (which seems probable), practically all the dyestuff will be present as cation in the fairly strong acid solution. Therefore, if we consider the $[D.B.V.]$ at different P_H values, but at the same total concentration of dyestuff (free base + ions), then we may assume that $[D.B.V.H_2^{++}]$ is practically the same in all the solutions, while the concentrations of the free base are quite different.

Assuming $[aD.B.]$ a constant, we have from Equation 7

$$E = E'_0 + \frac{0.060}{2} \log [aD.B.V.][aH^+]^2 \quad (10)$$

or, since

$$[D.B.V.] = \frac{[\text{Total dyestuff}]}{[aH^+]^2} K \text{ approximately} \quad (11)$$

we derive by substitution

$$E = E'_0 + \frac{0.060}{2} \log \frac{[\text{Total dyestuff}][aH^+]^2}{[aH^+]^2} = E'_0 + 0.03 \log [\text{Total dyestuff}] \text{ approximately} \quad (12)$$

It thus becomes comprehensible why the oxidation-reduction potential is independent of the acidity, although it must be emphasized that the above relations hold only approximately.

6. It has already been mentioned that diphenylbenzidine violet can be oxidized to other products; at low acidities, especially, it is very unstable. In solutions with a P_H of 7 to 2, potassium dichromate is not able to oxidize diphenylamine or diphenylbenzidine to the violet; but potassium permanganate, on the other hand, oxidizes both indicators easily at these acidities, due to its higher oxidation-reduction potential. The violet is the more easily destroyed, the lower the P_H and the higher the oxidation-reduction potential; in acetic acid medium, the violet produced by oxidizing diphenylamine with permanganate disappears almost instantly.

7. Potentiometric titrations have been made in the presence of mercuric chloride in order to see whether this substance has a specific effect upon oxidation-reduction potentials, but it was not possible to make satisfactory measurements. Even the ferrous iron-dichromate titration was impossible; the electrode was slow, and no jump in potential occurred at the equivalence point. It seems that the electrode takes up some mercury by polarization, and does not respond quickly to excess of oxidant. This may be of significance in the use of a bimetallic electrode system.

Summary

1. At acidities between 0.1 and 2.0 N , diphenylamine is oxidized quantitatively to diphenylbenzidine by potassium dichromate if the oxidant is added slowly to the former solution. Further addition of dichromate oxidizes the diphenylbenzidine to a violet quinoid salt, which quickly combines with unchanged diphenylbenzidine to form an extremely slightly soluble green meriquinoid salt.

2. In titrating diphenylbenzidine violet with ferrous sulfate the color change, violet to green, takes place at a potential of about 0.51 v., against saturated calomel electrode; or at 0.76 v., against the normal hydrogen electrode, regardless of the hydrogen-ion concentration of the solution. An explanation has been offered to account for this.

3. The results of the analytical study are not very satisfactory from the stoichiometric point of view, because side reactions may occur, diphenylbenzidine and diphenylbenzidine green are very slightly soluble, and diphenylbenzidine violet decomposes rapidly, especially at low acidities.

4. The absorption spectra of oxidized diphenylamine and diphenylbenzidine solutions have been determined and found to be identical; the maxima of the curves are very flat, and shift toward the longer wave lengths in stronger acid solutions.

5. The solubility of diphenylbenzidine in water is 0.06 ± 0.005 mg. per liter at $25\text{--}50^\circ$; and its ionization constant at 25° is of the order of 2×10^{-14} .

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

STUDIES IN INTENSIVE DRYING¹

BY E. JUANITA GREER²

RECEIVED JUNE 16, 1930

PUBLISHED NOVEMBER 5, 1930

The following is an account of an experimental study of the intensive drying, and therewith "the catalytic" effect of small traces of water, mainly in liquid benzene, which leads to an explanation of the phenomenon observed. Since Baker's work was published in 1922 there has been a constant stream of theoretical explanations of intensive drying, as well as a large number of experimental studies dealing with this strange phenomenon.

It is unnecessary in this paper to give even a synopsis of either the theoretical or the experimental aspects of this problem, inasmuch as quite recently this whole subject has been carefully and most adequately reviewed in book form under the title of "The Effects of Moisture on Chemical and Physical Changes," by J. W. Smith.³

Suffice it to say that since Baker's⁴ paper data have accumulated which tend to support, and lately some as justly to contest, the view that when the last traces of water are removed from certain liquids, there occur physical changes in the latter that are consistent with the assumption of an association of the molecules in the liquid. The properties investigated have been such as the boiling point, freezing point, density, vapor density, surface tension, latent heat of vaporization and vapor pressure. However,

¹ Based on a dissertation submitted June, 1929, to the Board of University Studies of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Holder of the Boston Alumnae Fellowship of the American Association of University Women for 1929-1930, when this work was completed.

³ Longmans, Green and Co., 1929.

⁴ Baker, *J. Chem. Soc.*, 121, 568 (1922).