

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

**DIPHENYLAMINE SULFONIC ACID AS A NEW
OXIDATION-REDUCTION INDICATOR**

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

RECEIVED MAY 12, 1931

PUBLISHED AUGUST 5, 1931

Introduction

It was shown in a recent paper¹ that the first product of the oxidation of diphenylamine is the very insoluble white diphenylbenzidine, and that all but a trace of the indicator precipitates out with the completion of this stage of the reaction. The precipitate remains suspended in a finely divided condition, however, and is oxidized somewhat slowly by excess oxidant to the highly colored holoquinoid compound, diphenylbenzidine violet; but when the attempt is made to start with a solution of diphenylbenzidine, instead of producing it by the oxidation of diphenylamine, practically all of the indicator precipitates and settles out in large flocks. This suspension yields the violet color only after contact with a considerable excess of oxidant for several minutes. Therefore, while diphenylbenzidine is very satisfactory for reverse titrations, it does not work so well in direct titrations.

Furthermore, diphenylbenzidine violet reacts quickly with any unchanged diphenylbenzidine to form the very insoluble greenish-black meriquinoid compound, diphenylbenzidine green, which under certain circumstances imparts a muddy appearance to the solution, due to a mixture of considerable white and greenish-black precipitate with the violet solution. In addition, neither diphenylamine nor diphenylbenzidine give their color changes in the presence of even traces of tungstate,² a property which greatly limits their usefulness in the analysis of alloy steels. The present authors have ascertained that tungstate forms blue insoluble compounds with the colored oxidation products of diphenylamine, thus removing them from the solution. Hence, it was thought that some of the objectionable features might be corrected by introducing a strongly polar group like $-\text{SO}_3\text{H}$ into the molecule, thereby increasing its solubility and that of its oxidation products.

I. Preparation of Barium Diphenylamine Sulfonate.—Equimolecular quantities of diphenylamine and acetic anhydride were treated with a few cubic centimeters of concentrated sulfuric acid and refluxed for one hour, after which the excess acetic acid was removed by washing with cold water and the acetyldiphenylamine recrystallized from ether and dried at 100° .³ Then 200 g. of 20% fuming sulfuric acid was cooled to 5° , and

¹ I. M. Kolthoff and L. A. Sarver, *THIS JOURNAL*, **52**, 4179 (1930).

² H. H. Willard and Philena Young, *Ind. Eng. Chem.*, **20**, 764 (1928).

³ A. Claus, *Ber.*, **14**, 2365 (1881).

100 g. of the pulverized acetyldiphenylamine added in small portions, with constant stirring. The mixture was warmed to 45° on a water-bath for two hours, with continued stirring, then poured into 250 cc. of water and boiled for three hours to hydrolyze the acetyl compound, after which it was poured into a large volume of water and the unchanged diphenylamine filtered off. The filtrate was neutralized with barium carbonate, the barium sulfate filtered off⁴ and the white barium diphenylamine sulfonate removed from barium acetate by fractional crystallization. The barium salt of diphenylamine sulfonic acid is sufficiently soluble for the preparation of indicator solutions, and has been used for subsequent work.

An analysis of the salt showed 21.88% barium, whereas the theoretical value for the anhydrous salt of the monosulfonic acid is 21.64%. Being primarily interested in the purity of the product, no attempt was made to secure a quantitative yield, though it may be mentioned that Gnehm and Werdenburg⁴ obtained 80% of the theoretical amount of the monosulfonic acid, with 17% of the diphenylamine recovered unchanged.

II. Indicator Properties.—All the experimental evidence confirms the assumption that the mechanism of the oxidation of diphenylamine sulfonic acid is similar to that of diphenylamine; that it is first oxidized to diphenylbenzidine sulfonic acid, and then to diphenylbenzidine sulfonic acid violet, which forms a meriquinoid compound, diphenylbenzidine sulfonic acid green, with unoxidized diphenylbenzidine sulfonic acid.

Potentiometric titrations of diphenylamine sulfonic acid with potassium dichromate (similar to those of diphenylamine and diphenylbenzidine described in a previous paper¹) were not very satisfactory from the stoichiometric point of view; nevertheless, it has been possible to determine the potential at which the color change takes place. Since the oxidation by dichromate is very slow in the absence of ferrous iron, it was more advantageous to add an excess of the dichromate to the acidified solution of diphenylamine sulfonic acid, and then titrate back with ferrous solution. For the details of the performance of these experiments the reader is referred to the previous paper. Further addition of ferrous solution after the reduction of the reddish-violet to diphenylbenzidine sulfonic acid green changes the color to a pale yellow, whereas diphenylbenzidine green was not affected by an excess of ferrous ions. The color change green to reddish-violet, and the reverse, takes place at a potential of about 0.59–0.60 v. (against the saturated calomel electrode, or 0.83–0.84 v., against the normal hydrogen electrode) in sulfuric acid solutions between 0.5 and 2.0 normal, whereas the color change for diphenylbenzidine occurs at about 0.51 v. (against the saturated calomel electrode, or 0.76 v., against the normal hydrogen electrode) under the same conditions. This difference of

⁴ R. Gnehm and H. Werdenburg, *Z. angew. Chem.*, **43**, 1027 (1899); V. Merz and W. Weith, *Ber.*, **5**, 283 (1872), communicated by O. Meister.

oxidation potential was confirmed by the following experiment. A portion of a ferrous solution in normal sulfuric acid, but without any phosphoric acid, was titrated potentiometrically in one case, 20.23 cc. of 0.1 *N* dichromate being required; a similar sample showed a faint trace of color with 20.20 cc., and a good color with 20.25 cc., when diphenylamine sulfonic acid was used as indicator; but when diphenylamine was used as indicator in another similar sample, a muddy green precipitate appeared when about 19.00 cc. had been added, with more and more violet from 19.50 cc. on.

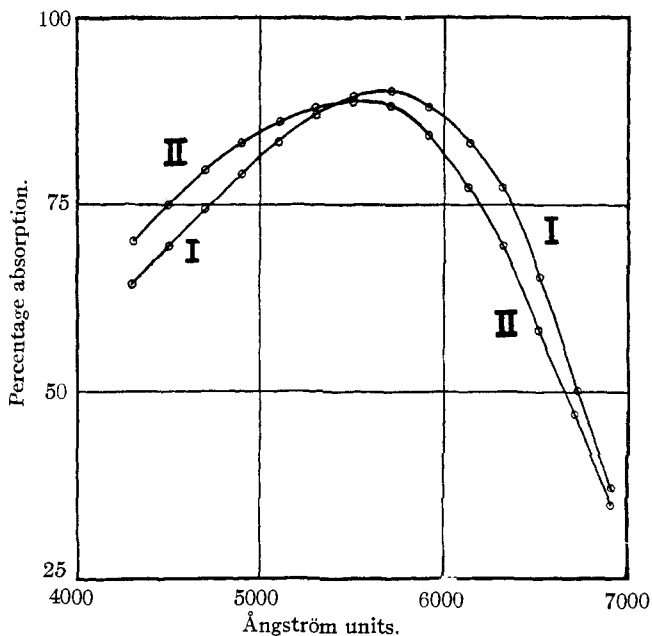


Fig. 1.—Absorption spectra of diphenylbenzidine violet and diphenylbenzidine sulfonic acid violet. I, diphenylbenzidine violet; II, diphenylbenzidine sulfonic acid violet.

The diphenylbenzidine sulfonic acid violet has a reddish-violet color resembling that of a dilute permanganate solution, and its absorption spectrum in the visible region resembles that of diphenylbenzidine violet (*cf.* Fig. 1), except that the former absorbs more in the red.

The speed of formation of the diphenylbenzidine sulfonic acid violet depends upon the oxidation potential of the solution, as is the case with diphenylamine and diphenylbenzidine. With permanganate or vanadate an acidified solution of the diphenylamine sulfonic acid is colored almost instantly; but with dichromate the coloration is very slow, even at high hydrogen-ion concentrations and with a relatively large excess of oxidant;

with this reagent the speed of oxidation is much less than in the case of diphenylamine or diphenylbenzidine. The presence of ferrous iron (see also the previous paper¹) accelerates the oxidation of diphenylamine sulfonic acid tremendously; for example, with 0.1 cc. of 0.005 *M* indicator and 0.2 cc. of 0.01 *N* dichromate in 50 cc. of 2 *N* hydrochloric acid the violet color appeared within fifteen to twenty seconds in the case of diphenylamine, and after two to three minutes in the case of diphenylamine sulfonic acid; but if 0.2 cc. of 0.01 *N* ferrous solution are first added to the acid solution of the latter indicator, and then 0.4 cc. of 0.01 *N* dichromate, the color appears after about one second with diphenylamine, and instantly with diphenylamine sulfonic acid.

The color change in the titration of ferrous iron by dichromate is very brilliant and sharply reversible; indeed, the coloring power of the substance is so great that titrations may be made in highly colored solutions where diphenylamine and diphenylbenzidine are not satisfactory. The presence of mercuric chloride has no influence upon the speed of formation of the reddish-violet oxidation product, whereas it retards the oxidation of diphenylamine and diphenylbenzidine very markedly. Finally—and this is the main advantage of the new indicator—its indicator properties are not affected by the presence of tungstate, whereas diphenylamine and diphenylbenzidine are useless in the presence of even traces of this substance.

The indicator corrections for diphenylamine, diphenylbenzidine and diphenylamine sulfonic acid in dilute solutions will be considered in a future paper.

Summary

Diphenylamine sulfonic acid has indicator properties similar to those of diphenylamine, but its color change is more sharp and brilliant. It can be used in the presence of tungstate, whereas diphenylamine and diphenylbenzidine cannot. Ferrous iron has an enormous accelerating effect upon the speed of its oxidation, while mercuric chloride has no harmful effect. The absorption spectrum has been determined, and the electrochemical properties investigated.

MINNEAPOLIS, MINNESOTA