

stant, does not necessarily indicate a difference of intrinsic acidity. Future measurements in solvents other than water may increase this uncertainty.

Aromatic hydrocarbon radicals, when introduced into aliphatic acids, produce no measurable change of acidity.

Either the lengthening or the branching of the hydrocarbon chain in the aliphatic acids produces a definite weakening effect. Probably both effects are real.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR  
MEDICAL RESEARCH]

## A POTENTIOMETRIC STUDY OF WURSTER'S RED AND BLUE

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In a rather large number of cases there have been found compounds intermediary, with respect to the level of oxidation, between a compound of the quinoid type and one of the hydroquinoid type. In a previous paper<sup>1</sup> it could be shown by a potentiometric method for three organic dyestuffs of the oxyphenazine series, that this intermediary compound is a molecule of the same size as either the holoquinoid form or the hydroquinoid form and differs from the hydroquinoid only by one oxidation equivalent (or hydrogen atom or electron). It must be considered as a radical-like compound with an odd number of electrons. Those three dyes offered a particularly favorable opportunity for the proof of such a statement because the intermediary compounds were very stable and permitted a thorough potentiometric study of the system, there being no drift in the potentials in time. The conclusions were based on observations of systems in a true thermodynamical equilibrium and therefore were scarcely liable to a misinterpretation.

This observation suggested the idea that other examples of half-reduced quinoid substances might be accessible to a similar potentiometric analysis. The difficulty in most of these cases is the fact that these intermediary compounds are as a rule not very stable in aqueous solution but undergo irreversible reactions and so cause a drift of the potentials. An attempt to utilize the potentiometric method for such a purpose was made by Clark, Cohen and Gibbs,<sup>2</sup> who studied the so-called meriquinones formed from aromatic diamines. They took for granted the current idea that these intermediary compounds are meriquinones according to Willstätter's<sup>3</sup>

<sup>1</sup> Michaelis, *J. Biol. Chem.*, in press, July (1931).

<sup>2</sup> W. Mansfield Clark, Barnett Cohen and H. D. Gibbs, *Public Health Repts.*, Suppl. No. 54, 1 (1926).

<sup>3</sup> Willstätter and Mayer, *Ber.*, 37, 1494 (1904); Willstätter and Pfannenstiel, *ibid.*, 37, 4605 (1905); Willstätter and Piccard, *ibid.*, 41, 1458 (1908).

definition as being molecular compounds of the holoquinoid and the hydroquinoid form.

For some years an increasing number of papers has been published advocating the formula of a free radical in such cases in which formerly double molecules were supposed to exist. In some of these cases an equilibrium between the free radical and its polymeric saturated form was assumed. This holds for instance for Gomberg's triphenylmethyl and for Wieland's biphenylnitride. In other cases the existence of the free radical without its polymerized form was assumed. This holds, for instance, for the case of the aromatic diamines, the subject also of this paper. Weitz and Fischer<sup>4</sup> showed by determination of the boiling point in solutions of such compounds that only the formula of a free radical is compatible with the data observed. A thorough compilation of the whole subject has been published by Weitz<sup>5</sup> in which many other examples are enumerated. Yet never has a potentiometric method been applied for the proof of such a contention. Such a method may not be applicable for every case, but in those cases in which it can be used this method is much superior to any other. All those assumptions with respect to incomplete dissociation which have to be considered in order to correct the boiling or freezing point data for electrolytes do not appear in the potentiometric method. This method whenever it is available may be considered as the best method for the determination of a molecular weight for an ionic compound.

The potentiometric analysis presented in this paper was suggested by, and is based on, a set of half-quantitative, preliminary observations which will first be described. These observations hold for asymmetric dimethyl-*p*-phenylenediamine and tetramethyl-*p*-phenylenediamine. There is no doubt that the method can be extended to other substances of this type but as we have to deal with very labile systems, each of these cases should be studied separately and may require long experimentation before a definite understanding is attained. Therefore this study will be restricted to the two substances mentioned.

When either of the two mentioned diamines is titrated with an oxidant such as bromine or chlorine, a deep color is developed, called Wurster's red in the case of the dimethyl compound and Wurster's blue for the tetramethyl one. When the titration is performed rather rapidly and farther extended, the color disappears again. When, after reaching the point of color discharge, the solution is allowed to stand, the color gradually turns back, though not to its maximum intensity, at a rate largely dependent on concentration and *PH*. The spectroscopic analysis shows that it is the same substance which reappears, as recognizable from the characteristic

<sup>4</sup> Weitz and Fischer. *Ber.*, 59, 432 (1926).

<sup>5</sup> Weitz, *Z. Elektrochem.*, 34, 538 (1928).

double band, which differs in Wurster's red and blue only by the spectral location of the two bands. It should not be asserted, however, that the return of the color is due only to the reappearance of Wurster's red or blue. According to the conditions other dyes may or may not be developed besides.

The interpretation of this phenomenon is this. Wurster's red or blue differs from the mother substances, the respective diamines, only by one oxidation equivalent (or hydrogen atom, or electron) as Willstätter and his co-workers<sup>3</sup> have shown long ago. The disappearance of the color in the second step of titration indicates that the dye is oxidized to a higher level which has practically no, or very little, color. One might expect this substance to be the second step of oxidation, analogous to diiminoquinone, and very likely it is. But these substances are extremely labile, as Willstätter has shown; in aqueous solution they spontaneously undergo irreversible changes and are converted into substances to which we must attribute a great inclination to still further oxidation. So these secondary substances will reduce those molecules of the diiminoquinone still present in the solution, to Wurster's red (or blue) over again. From these rough observations we may expect that the second half of the titration is characterized by a very labile system which at no point of the titration is in any chemical equilibrium within reasonable time. So we may expect that even in the best case only in the first half of the titration steady potentials might be established.

This is exactly what happens. When during the titration the potential at a blank platinum electrode is read, there are sufficiently constant and reproducible potentials in the first half of the titration. This holds at least for a certain range of *PH*. The most suitable *PH* for constant potentials proved to be 4.6 for both substances. In the second part of the titration no constant potentials can be obtained under any condition. The potentials always drift back to the negative side as though the oxidized form (the diiminoquinone) would spontaneously and irreversibly disappear in time. When the second half of the titration is performed rather hastily, the potential will stay within a small, not very well reproducible, range and the end of the titration will sometimes be indicated by a sudden though often not very big jump, which, however, drifts back at a rate depending upon the conditions, such as the time required for the whole titration, the number of steps in which the whole titration had been subdivided and the pause between the successive steps. The color vanishes simultaneously with this potential jump and, on standing, reappears, simultaneously with the back drift. If it happens that no jump of the potential appears, no complete discharge of color will be observed either.

Thus the end-point of the first step of titration can, with a fair approximation, be recognized by the fact that the potentials, which were constant

up to this point, begin to drift; and the end of the second step can be recognized, provided the titration in the second step is rapidly performed, by the point of coincidence of potential jump and transient discharge of color, if there is such a point at all. The amount of oxidant used for each of the two steps turns out to be the same, within the limits of error in such a labile system.

A theoretical analysis of the titration curve is, therefore, not difficult for the first half of the titration, but impossible at the present time for the second half. When the titration curve of the first step is analyzed, it turns out to be the curve for a regular reversible oxidation-reduction system, and the difference between the reduced and oxidized form turns out to be only one electron. It is very important to add that the mid-point potentials  $E_0$  of this step of oxidation for different experiments, at the same  $P_H$ , coincide, independently of the initial concentration of the diamine.<sup>6</sup> Hereby it is proved that Wurster's red or Wurster's blue differs from its particular diamine only by one electron, without any change in molecular size and that it is not a meriquinone according to Willstätter's definition, namely, a compound of one or several molecules of the holoquinoid form with one or several molecules of the completely reduced form. These two dyes, Wurster's red and blue, therefore are of the type of a half-reduced quinone, or semiquinone, a molecule with an odd number of electrons. We may also say that one of the two nitrogen atoms is bivalent as in Wieland's biphenylnitride. In contrast, however, to these biphenylnitrides, or to Gomberg's triphenylmethyl, the unsaturated radical-like compound does not seem to undergo to any measurable extent a polymerization to a double molecule in which the state of unsaturation is abolished. This radical-like compound in aqueous solution of a  $P_H$  around 4.6, is, though not strictly stable, yet a fairly stable substance, provided there is no excess of oxidant which can oxidize it partly to a higher level. If this is the case, the whole system becomes unstable, and the radical-like compound will partake in the chemical processes which go on with greater or less rapidity. The radicals do not combine with each other to form double molecules or with the original diamine to form quinhydrone, but they undergo condensation or other reactions with the other molecules in the solution, especially with the very unstable substances which are on the oxidation level of diiminoquinones.

In formulating radicals of the described kind one may accept a point of view proposed already by Weitz, which is best presented in this way. In the static Formula I, where R is either a methyl group or hydrogen, it is indicated that one amino group has one electron less than would correspond to an electroneutral state.

<sup>6</sup> As to significance of the independence of  $E_0$  of the initial concentration, see Ref. 1.



This static model should be replaced by a more dynamic one (Formula II). One electron has a circuit around both N atoms, or the two nitrogen atoms share one electron. This, then, is a chemical bond consisting in one shared electron, instead of the two in the ordinary chemical bond of G. N. Lewis.

### Experimental

The purest commercial grades of the hydrochlorides of dimethyl-*p*-phenylenediamine and of tetramethyl-*p*-phenylenediamine (preparations of Eastman) were recrystallized by dissolving in methyl alcohol and precipitating with benzene. A suitable amount of the crystals was dissolved in deaerated water, and a suitable portion added to 15 cc. of acetate buffer of *PH* 4.62 (solution 0.1 normal both with respect to sodium acetate and acetic acid). A freshly prepared solution of bromine was used as oxidant, in such a concentration that 1 to 2 cc. was used to the complete titration of the first step. The titration was performed in a constant temperature chamber at 30° in a stream of nitrogen purified over copper at 450°, though this precaution might not have been imperative in working on such relatively positive potential ranges as we have to deal with here. Three blank platinum electrodes were immersed in the solution. Whenever the potential was steady it was observed for all three electrodes, without there ever being a difference of more than 0.1 millivolt. As soon as the potential began to drift, in the progress of titration, the readings had to be hastened and according to the circumstances only one electrode was used for the potential readings. In the diagrams all potentials, constant over a reasonable time within one or two tenths of a millivolt, are marked with plain circles. For all potentials with a drift the direction of the drift is indicated by an arrow. The short arrows indicate a drift of some tenths of a millivolt per minute; the long arrows indicate a drift of several millivolts per minute. The drawn out curves are those calculated according to

$$E = E_0 + 0.0601 \log \frac{X}{A - X}, \text{ volts}$$

where  $E_0$  is a constant,  $X$  the amount of bromine solution in cc., and  $A$  that amount of bromine solution used up at the end of the first reversible step of the oxidation. The value of  $A$  was determined by the following three methods.

1. The first method is only roughly approximate and cannot be applied in every case; it can only be used when the second step of titration is performed within a few seconds without reading the potentials except for the very last part. This method can only be applied when the end of the second step of titration can be recognized by a transient complete discharge

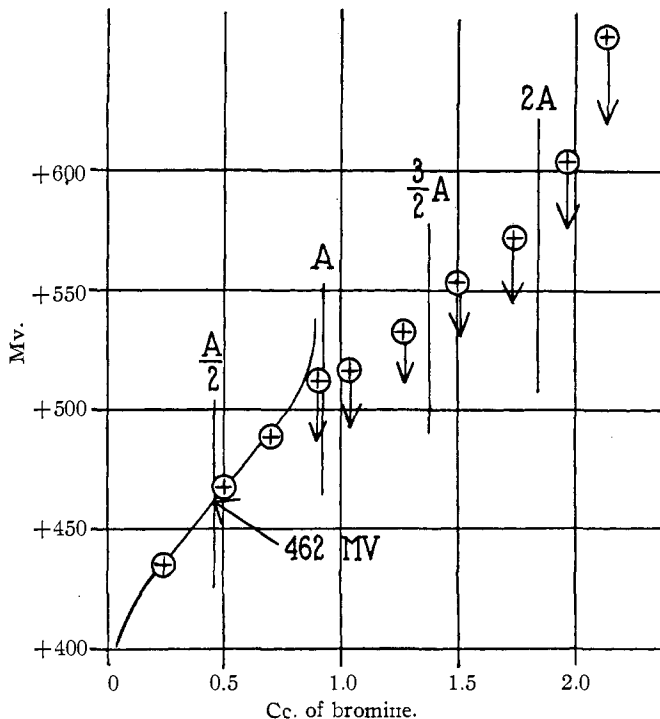


Fig. 1.— $2 \times 10^{-4}$  mole of dimethyl-*p*-phenylenediamine hydrochloride dissolved in 20 cc. of acetate buffer of  $P_H = 4.62$  (a solution 0.1 molar both for sodium acetate and for acetic acid) is titrated at  $30^\circ\text{C}$ . with an aqueous solution of bromine. Abscissa, cubic centimeters of bromine. Ordinate, potentials, in millivolts, referred to the normal hydrogen electrode. Arrows signify drift of potential. Potentials without arrow are stable.  $A$  is the total theoretical amount of bromine used for the complete oxidation to the level of the semiquinone.

of color and a transient jump of the potential. These two phenomena coincide. On account of the unavoidable secondary reactions during the second half of titration even on rapid titration, the observed end-point, if there is one at all, will always come a little later in the curve than where the theoretical end-point should lie. If such an end-point can be recognized, one may assume that the amount of oxidant at this end-point is approximately equal to, or, more precisely speaking, is somewhat greater than,  $2A$ .

2. That point of titration where the previously steady potentials become inclined to a backward drift, can in the first approximation be taken as the value of  $A$ . This method, also, is an approximative one, because a little overlapping of the two steps of titration takes place. The correction of the true value for  $A$  lies in such a direction that the first drifting potential must occur somewhat before, but never after, the theoretically required amount,  $A$ , of the oxidant has been added. The result of this method agreed with that of the first within the limits to be expected, namely, that the first method furnished always a somewhat higher value for  $A$  than the second. The true value of  $A$  may be estimated as lying between those obtained with the first and those obtained with the second method.

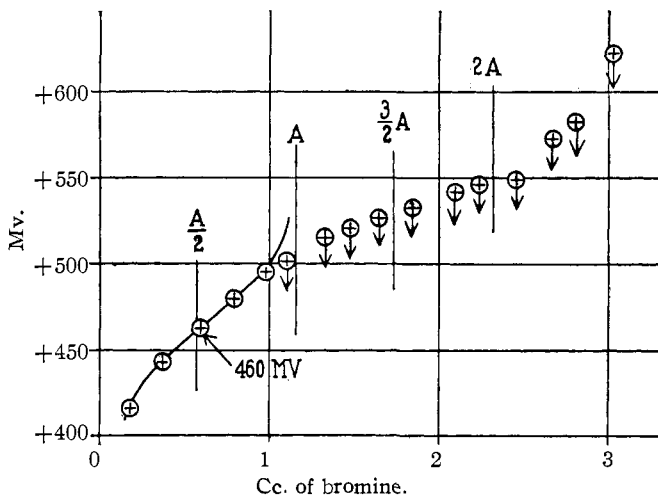


Fig. 2.— $4 \times 10^{-5}$  mole of dimethyl-*p*-phenylenediamine hydrochloride dissolved in 20 cc. of acetate buffer titrated with a bromine solution. Designations the same as in Fig. 1.

3. After the value of  $A$  had been evaluated approximately by one or both of these two methods, a correction was applied in the following way. By a graphical method of trial and error a value of  $A$  was chosen which furnished the best fitting curve for the first half of the titration where the potentials show no drift. It was postulated that there exists some value of  $A$  that will furnish an entirely fitting curve, and that this value of  $A$  should be very close to the one obtained with the two other methods, the deviation lying in the expected direction. This postulate was fulfilled in every case.

So the final and definite method is the third one, and the two others were only used to show that the value,  $A$ , obtained with this method can be shown, in suitable cases, to be compatible with those values which might have been approximately determined by the two others.

In any event, the third method furnished a theoretical curve which, except for the very end of this curve, for understandable reasons, fitted perfectly with the observations, and which furnished  $E_0$  values agreeing satisfactorily for different experiments even on varying the initial concentration in the ratio 1:10. There is, then, every justification for utilizing these curves for an interpretation based on thermodynamical considerations.

There is a slight difference between the two amines with respect to the third method. In the tetramethyl compound the overlapping of the first

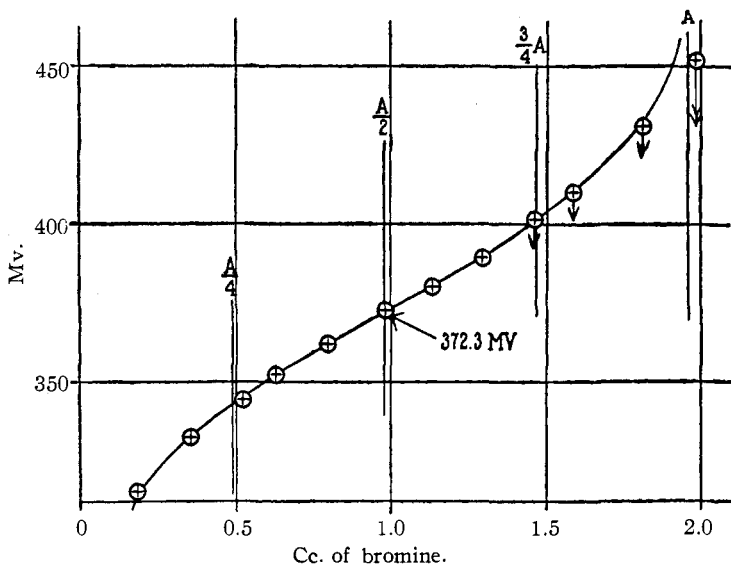


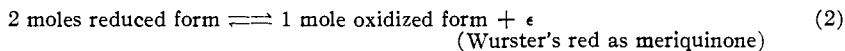
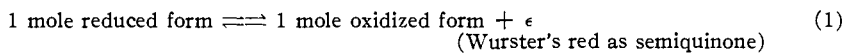
Fig. 3.— $1.0 \times 10^{-5}$  mole of tetramethyl-*p*-phenylenediamine hydrochloride dissolved in 15 cc. of acetate buffer and titrated with bromine. Designations as in Fig. 1. The short arrows signify a drift of the potential of about 0.1 millivolt per minute; the long arrow, a drift of several millivolts per minute. Potentials without arrow are perfectly stable.

and second steps of oxidation is somewhat greater than in the dimethyl compound. This is recognizable by the relatively earlier beginning of the drifting part of the curve. This disadvantage is, however, compensated by the fact that the potentials of the tetramethyl compound, before the drifting part of the curve begins, are even more stable than for the dimethyl compound. The tetramethyl compound, during the first, not drifting, part of the curve, can be titrated with the same leisure as any good reversible system; furthermore, even when the drift begins, this drift is so slow (within some tenths of a millivolt per minute) that the uncertainty of the potential value may lie only within one millivolt. Here the drift does not cause so much a time distortion of the curve, but



rather shows the beginning of an overlapping and marks that part of the curve beyond which the potentials can no longer strictly obey the simple formula calculated for a one-step oxidation without overlapping.

These  $E_0$  values must be considered as being strictly indicative of a free energy level of the system, and from the shape of the curve it can be decided with safety which one of the two reactions



( $\epsilon$  is one electron) takes place. The first of these two possibilities, then, is found to be the correct one.

Two titration experiments are shown for dimethyl-*p*-phenylenediamine graphically in Figs. 1 and 2. The initial concentrations differ in these two cases in the ratio 1:5, the greater one being 0.01 molar. Two experiments are shown for tetramethylphenylenediamine, one as a graph (Fig. 3) and another in the form of Table I. The initial concentrations in these two experiments differ in the ratio 1:7.5, the greater one being 0.003 molar.

TABLE I

$1.3 \times 10^{-6}$  MOLES OF TETRAMETHYLPHENYLENEDIAMINE HYDROCHLORIDE DISSOLVED IN 15 CC. OF ACETATE BUFFER, PH 4.62, AND TITRATED WITH BROMINE

$E$  calculated according to the formula  $E = 0.1303 + 0.0601 \log \frac{X}{1.660 - X}$  volts

$X$ (cc. of Br solution)	Percentage of oxidation, the whole first step of oxidation taken as 100%	Drift of the potential in millivolts per minute (approximately)	$E$ in volts	
			referred to the normal hydrogen electrode Observed	Calcd.
0.280	16.9	0	+0.0882	+0.0887
.465	28.0	0	.1048	.1057
.620	37.3	0	.1160	.1168
.805	48.5	0	.1285	.1287
.990	59.6	0	.1401	.1405
1.154	69.5	0	.1517	.1518
1.320	79.4	0.1	.170	.1658
1.610	98.0	5.0	.201	.1961

### Summary

It is shown by mathematical analysis of the potential curve obtained by oxidative titration with bromine that Wurster's red and Wurster's blue are not molecular compounds of one molecule of a quinoid type with another molecule of a hydroquinoid type, but true semiquinones, *i. e.*, radical-like compounds intermediary between quinone and hydroquinone and of the same molecular size as each of these two. Such a compound must possess an odd number of electrons. One may express the situation

by saying that the two nitrogen atoms of the dye are linked by a chemical bond which consists of a single electron instead of a pair.

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## THE REACTION BETWEEN OXYGEN AND ACETYLENE IN THE PRESENCE OF NITROGEN OXIDES

BY SAMUEL LENHER

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Comparatively little work has been done on the catalyzed oxidation of the simple hydrocarbons. Study of the slow combustion of acetylene<sup>1</sup> led to isolation of the intermediate compounds, glyoxal, formaldehyde, and formic acid, and indicated the probable steps in the reaction. As the influence of a homogeneous catalyst is to lower the temperature at which measurable reaction begins, and thus to increase the stability of the partially oxidized products, study of the effect of gas catalysts in oxidations promised to give further information on the course of reaction.

The present investigation was a study of the effect of nitric acid vapor and its decomposition products on the slow thermal oxidation of acetylene. The oxides of nitrogen have been used repeatedly in the partial oxidation of the hydrocarbons.<sup>2</sup> It was assumed in these papers and patents that the action of the nitrogen oxides was catalytic, that is, that the nitrogen oxides were not destroyed in the reaction. This assumption was not directly tested, although Frolich, Harrington and Waitt<sup>2f</sup> stated that in the oxidation of methane with nitrogen peroxide and oxygen the loss of nitrogen peroxide by complete decomposition to elementary nitrogen was of the order of 1% per pass, and Bibb and Lucas<sup>2g</sup> indicated in an experiment that nitric acid was consumed in the oxidation of methane. It appears now from a recent paper by Smith and Milner<sup>3</sup> that in the partial oxidation of methane in the presence of nitrogen oxides the nitrogen oxides are consumed in the reaction and that their action cannot be considered catalytic. The writer has found in an investigation of the oxidation of ethylene, which will be communicated shortly, that nitrogen oxides react chemically with ethylene at the temperature of the slow oxidation reaction and that their action is not one of catalysis.

<sup>1</sup> (a) Kistiakowsky and Lenher, *THIS JOURNAL*, **52**, 3785 (1930); (b) Spence and Kistiakowsky, *ibid.*, **52**, 4837 (1930).

<sup>2</sup> (a) Bailey, U. S. Patent 1,319,748 (1919); (b) Bibb, U. S. Patent 1,392,886 (1921), reissue 15,789 (1924); (c) Chemische Fabriken Worms A. G., British Patent 156,252 (1921); (d) Atack, British Patent 182,843 (1921); (e) Layng and Soukup, *Ind. Eng. Chem.*, **20**, 1052 (1928); (f) Frolich, Harrington and Waitt, *THIS JOURNAL*, **50**, 3216 (1928); (g) Bibb and Lucas, *Ind. Eng. Chem.*, **21**, 633 (1929); (h) Bibb, Canadian Patent 302,672 (1930).

<sup>3</sup> Smith and Milner, *Ind. Eng. Chem.*, **23**, 357 (1931).