ing 3.00 and 4.90% of organic carbon, a muck containing 30% and a peat containing 53% organic carbon. These soils varied in reaction from P_H 4.7 to 8.3.

The uronic acid carbon dioxide varied from 0.07 to 1.80% of the soil, and this, when calculated to the equivalent uronic acid, varied from 0.308 to 7.94% of the soil.

The uronic acid carbon calculated from these figures varied from 0.113 to 2.86% of the soil and this uronic acid carbon varied from 5.15 to 28.4% of the total organic carbon.

The presence of uronic acids or complex substances containing them (polyuronides) was confirmed by the separation from two of the soils of colloidal material having all the properties of such uronic acid complexes.

This separation was made both by hot water extraction and extraction with dilute sodium hydroxide.

The bearing of the presence of uronic acids in soils on certain analytical operations has been pointed out. These are the determination of carbonates in soils, and methods proposed for the proximate analysis of the organic matter of soils.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

THE POTENTIALS OF SOME UNSTABLE OXIDATION–REDUCTION SYSTEMS

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Although a considerable amount of data concerning the oxidation–reduction potentials of well-defined organic systems has accumulated during the past ten years, relatively few efforts have been made to study by direct potentiometric measurement those systems which are alterable and with which the potential of a solution is subject to a definite drift with time as the result of some reaction which consumes either the oxidant or the reductant, or both. Such systems, to be sure, have been studied by colorimetric and electrometric indicator methods, but these are to be classed as indirect methods inasmuch as they involve the observation of the effect of the unstable system upon the color or the potential of an oxidation–reduction system of unalterable components, and it is the potential of the latter, rather than that of the former, which actually is measured.

The potential of the alterable system has been the basis of observation in only a few investigations. Biilmann and Blom[1] have recorded the equilibrium potentials, together with the velocity constants, for the disappearance of the reductant, for two azo–hydrazo systems. They followed the

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[1] Biilmann and Blom, *J. Chem. Soc.*, **125**, 1719 (1924).

fairly slow drift in the potentials of solutions prepared from equimolecular amounts of the oxidant and reductant and extrapolated the values to zero time. Relying not upon extrapolation but upon initial potentials obtained as soon as potentiometric balance could be reached, Clark, Cohen and Gibbs[2] obtained data for the systems from benzidine, *o*-tolidine and *p*-aminodimethylaniline, but their "attempts to measure the system of which *p*-phenylenediamine is the reductant were frustrated by the extreme instability of the system." In addition to these studies, Conant and Fieser[3] have reported approximate results obtained by rapid titration for the *o*-benzoquinone–catechol system, while Conant and Pratt[4] give some record of their attempts to measure the potential of the system formed by *p*-aminophenol and its highly alterable oxidation product, quinone-imine, and state that even under the most favorable conditions "the value of the oxidation–reduction potential cannot be determined accurately."

It is an unfortunate circumstance that the instability of the simple quinone-imines, quinonedi-imines and certain of the quinones has imposed such limitations upon the investigator as to prevent the accurate evaluation of the free energy of reduction of these substances, for some of the most interesting compounds fall into this group. On the more practical side, it will be recalled that the substances in question, in the form of their reduction products, have been used extensively as oxidation–reduction indicators and as photographic developers. Their suitability for these purposes is determined largely by the potentials of the systems.[5]

There is thus abundant reason for attempting to extend to some extent the limits in the field of the direct measurement of the oxidation–reduction potentials of unstable systems. We have examined several such systems with which, while the reductant is perfectly stable, the oxidant undergoes decomposition with greater or less rapidity when it is prepared in aqueous solution or in a mixture of water and alcohol. It did not appear expedient to prepare the oxidant in non-aqueous medium even where this is known to be possible, for a certain unnecessary period of time would be required for the dissolution of the material in the electrolytic solvent. It seemed much more rational to start with a solution of the reductant and to produce the oxidant in the solution at the time desired by the addition of an oxidizing agent. Ordinary electrometric titration of the reductant, however, is out of the question when a highly alterable oxidant is concerned. The decrease in potential between successive increments of the oxidizing agent is often so rapid that the results are meaningless.

The method which we have adopted as being the most satisfactory of any

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[2] Clark, Cohen and Gibbs, *Pub. Health Repts.*, Supplement No. 54, **1926**.

[3] Conant and Fieser, THIS JOURNAL, **46**, 1858 (1924).

[4] Conant and Pratt, *ibid.*, **48**, 3179 (1926).

[5] Compare Frary and Nietz, *ibid.*, **37**, 2246 (1915).

yet developed may be called that of discontinuous titration. To a solution of the reductant there is added an amount of oxidizing agent estimated to produce a certain amount of the oxidant and thus to fix, at least momentarily, the ratio of oxidant to reductant. The potential of the solution is observed and followed with time. In further experiments the same quantity of reductant is treated with varying amounts of oxidizing agent so that, when all of the experiments are grouped together, a composite titration curve may be constructed and from it the normal oxidation–reduction potential and other constants may be calculated. This general scheme was employed to a certain extent by Clark, Cohen and Gibbs in the work cited, and its advantages over the continuous titration method are apparent. The most important point of difference in the present work lies in the manner of interpreting the potential readings. The choice lay between extrapolating the time–potential curve, after the manner of Biilmann, or in taking the first measurable potential, according to Clark, but the experiments themselves soon furnished reasons for giving preference to the former method. This will be shown directly, in connection with a description of some of the results obtained.

The Method of Procedure

In performing each experiment a solution of 0.0003 mole of the reductant was employed. In the case of the amines it was found convenient to prepare a 0.015 *M* solution of the amine hydrochloride and to add 20 cc. of this to 190 cc. of the buffer solution. Well-poised buffer solutions having a high concentration of salts (usually 0.2 *M*) were chosen in order to prevent any but very slight changes in hydrogen-ion concentration as a result of the dilution or the presence of the sample. When 0.1 *M* hydrochloric acid was the solvent, the P_H employed was that found for the diluted solution. As the electrode vessel a tall 400-cc. beaker was employed, and the solution of the reductant was agitated vigorously in the thermostat with an efficient mechanical stirrer. The oxidizing agent used was a 0.03 *M* aqueous solution of potassium molybdicyanide, $K_3Mo(CN)_8$.[6] Since an unnecessary amount of time is consumed in running in the reagent from a buret, the addition was made in the following way. The reagent was carefully measured into a small dropping funnel having a wide-bore stopcock, and the stem of the funnel was inserted through the stopper of the electrode vessel. A rapid-delivering Mohr buret containing buffer solution was clamped just above the dropping funnel so that the latter could be rinsed out quickly into the vessel. When all was in readiness the stopcock was turned and the stop watch was released just as the stream of the oxidizing solution entered the stirred solution. With this arrangement it was possible to introduce 3–20 cc. of molybdicyanide solution in not more than three seconds, with about one second more for the rinsing. The potential readings were made on a student's type potentiometer and with an enclosed glass and scale galvanometer. By placing the stop watch in line of vision with the galvanometer scale and having this directly behind the potentiometer dial, the unassisted observer had little difficulty in following a very rapidly changing potential. Readings were made at intervals of fifteen seconds.

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[6] Some observations concerning the preparation and stability of this reagent will be published in another paper.

The average volume of the solution at the time of the measurement was 220 cc. and the total concentration of the organic system 0.0014 *M*. When it was desirable to keep the volume the same in all experiments the amount of buffer solution used for washing out the funnel was so adjusted as to make the final volume just 230 cc.; total concentration, 0.0013 *M*. The temperature was 25° in all of the experiments.

***p*-Benzylaminophenol[7]-N-Benzyl-quinone-imine.**—The potential of a solution of these components in every case decreased rapidly with time, but the rate of change usually varied with the nature of the solvent and with the ratio of oxidant to reductant. The simplest behavior noted is illustrated by Curve II of Fig. 1. It will be observed that for one and one-fourth minutes the relationship between the decrease in potential and the time is linear.

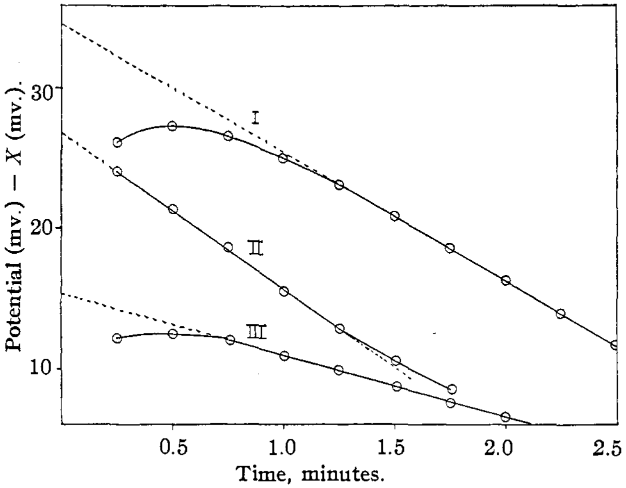

Fig. 1.—The system: *p*-benzylaminophenol–N-benzyl-quinone-imine. Curve I. P_H 7.57. [Oxid]/[Red] = 6.25: Curve II. P_H 1.10, [Oxid]/[Red] = 0.387; Curve III, P_H 7.57. [Oxid]/[Red] = 0.403.

The fact that the potential decreases indicates that it is the oxidant which is being destroyed, and the nature of the relationship points to a first order reaction, for both the monomolecular velocity constant and the potential of the solution are logarithmic functions of the concentration of the oxidant. The velocity constant may be defined by the following equations

$$k' = \frac{2.3026}{t} \log \frac{[\text{Oxid}]_i}{[\text{Oxid}]_i - x} \tag{1}$$

$$E_i - E_t = \frac{RT}{nF} \log \frac{[\text{Oxid}]_i}{[\text{Oxid}]_i - x} \tag{2}$$

$$\text{Let } k = k'RT/2.3026\, nF$$

$$k = (E_i - E_t)/t \tag{3}$$

The initial concentration of the oxidant is denoted by $[\text{Oxid}]_i$, x is the amount which has disappeared in t minutes, E_t is the potential at that time

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[7] The material was crystallized as the hydrochloride.

and E_i is the initial potential of the solution. If the initial potential is taken as that found on extrapolating Curve II to zero time, the following values are obtained for the velocity constant, k (Table I). Up to one and one-fourth minutes the constancy is very good; the velocity then progressively decreases. Though the period over which the monomolecular reaction rate holds good is very brief, it may be estimated from other data on hand that the potential is a linear function of the time up to the point where 52% of the oxidant originally present has disappeared. The constancy is thus maintained for a considerable part of the life of the oxidant. It is clear that the reaction is monomolecular in the early stages, and one is consequently justified in making the extrapolation indicated by the dotted line. The only uncertainty is concerned with the timing of the experiment, but every effort was made to reduce this uncertainty to a minimum. The possible error in fixing the zero time is about two seconds, which in the case at hand would amount to an error of 0.0005 v. in the value for the initial potential.

TABLE I

VELOCITY CONSTANTS FOR REACTION PLOTTED IN CURVE II. FIG. 1

Minutes	Potential	k	Minutes	Potential	k
0	0.6880 (Extrap.)	....	1.50	0.6717	(0.0108)
0.25	.6852	0.0112	1.75	.6697	(.0104)
.50	.6825	.0110	2.00	.6677	(.0101)
.75	.6798	.0109	2.25	.6654	(.0100)
1.00	.6767	.0113	2.50	.6637	(.0097)
1.25	.6740	.0112	2.75	.6624	(.0093)

One significant conclusion to be drawn from the results just quoted is that in fifteen seconds the mixing is complete, the reaction between the reductant and the molybdicyanide has gone to completion, and electrode equilibrium has been attained. The potential at this point could hardly show the concordance with the succeeding potentials if it were otherwise. While the same observations apply equally well to many other experiments, there were other cases in which the first potential readings (15 sec.) did not fall into line with the rest in this manner, and examples of this type of behavior are given in Curves I and III of Fig. 1. Like Curve II, these results refer to the system from *p*-benzylaminophenol, but in neutral rather than acid solution. Instead of falling off at once, the potential shows a slight increase after fifteen seconds and only begins to drop in direct proportion to the time after one and one-fourth minutes for Curve I, and forty-five seconds for Curve III. In view of the conclusions drawn from the form of Curve II, this lag can hardly be due to incomplete mixing and it probably is not occasioned by a tardy establishment of electrode equilibrium. We are thus led to believe that the reaction between the reductant and the molybdicyanide is complete only after the time intervals noted. After the period of lag the reaction follows the monomolecular course for seven minutes, and we have extrapolated the straight portions of the curve (dotted lines) in order to obtain the initial potentials.

The initial potential obtained in this way is subject to some error if our interpretation of the lag is correct, for the amount of oxidant initially available for the decomposition reaction is not quite as great as that which the extrapolation curve implies. It seems unlikely that the phenomenon is the result of a slow attainment of potential balance, but if this is actually the case no error would be involved other than that occasioned by the extent of the extrapolation necessary. While we see no way of either obviating or evaluating this possible source of error, there is reason to believe that the error is very slight. Curves I and III both refer to the discontinuous titration of *p*-benzylaminophenol at *P*H 7.57 and the experiments differ only in that the value of the ratio [Oxid]/[Red] was 6.25 and 0.403, respectively. Now there is much more lag, and more error if any, in the first case than in the second and yet the calculations from both experiments indicate very nearly the same value for the normal oxidation–reduction potential of the system. The case at hand, moreover, was selected for illustration because it is an extreme one; many other experiments might be cited in which a lag in the time–potential curve occurred only when the concentration of the oxidant was relatively high, and in these instances there was no detectable difference in the results for the experiments which showed this lag. There is thus justification for regarding extrapolations of the type illustrated in Curves I and III as at least close approximations.

The method which we have adopted for fixing the initial potential of the solution thus consists in extrapolating the first observed straight portion of the time–potential curve to zero time. A comparison may now be made with the procedure of Clark, Cohen and Gibbs, who took for this value the reading obtained as soon as potentiometric balance could be reached. In their experiments this required about twenty seconds; in our work the first reading was made at exactly fifteen seconds, and we are reasonably sure that a true balance had been attained. According to the interpretation which we have made of Curve II, during the time required for the attainment of electrode equilibrium and for the mechanics of measurement a considerable amount of oxidant has disappeared and the potential has fallen an appreciable extent. In other words, the error of taking the first measurable potential as the initial potential here amounts to 2.8 mv. In the case of the experiment of Curve I the error would be more serious. If one were relying entirely upon the first "significant potential" one very probably would conclude that electrode equilibrium had been reached at thirty seconds and that the potential found here was the true potential. According to the results of extrapolation the error would amount to 7.3 mv. While we thus feel that the method of Clark, Cohen and Gibbs should not be used in the study of the systems with which we are here concerned, we do not wish to imply a criticism of their own work. Each system has its own peculiarities and may require a special method of study.

Having described our method of fixing the initial potential, E_i, we shall present in Table II a summary of a typical "discontinuous titration." The potentials given are single electrode potentials at 25° referred to the hydrogen electrode potential at P_H 0.

TABLE II

SYSTEM: *p*-BENZYLAMINOPHENOL–N-BENZYL-QUINONE-IMINE

P_H 7.57. End-point = 17.4 cc. molybdicyanide solution

Molybdicyanide soln., cc.	Initial potential, E_i, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	$0.02957 \times \log R$, v.	C	E_n, v.	k
3.0	0.2227	0.208	−0.0201	1.35	0.2506	0.0043
5.0	.2338	.403	− .0117	1.37	.2501	.0047
7.0	.2427	.673	− .0051	1.37	.2498	.0057
9.0	.2514	1.07	.0009	. .	.2502	.0066
11.0	.2595	1.72	.0070	1.38	.2498	.0072
13.0	.2695	2.95	.0139	1.42	.2502	.0082
15.0	.2831	6.25	.0235	1.42	.2504	.0092
				Av. 1.39	Av. 0.2501	

The end-point of the titration was determined in the usual way except, of course, that a number of separate experiments were required, in each of which a different amount of oxidizing agent was added to the solution of the reductant. This method was found preferable to the use of standardized solutions of the molybdicyanide and of the reductant on account of some uncertainties in these standardizations. It is not difficult to ascertain the end-point with a reasonable degree of accuracy, even with these unstable systems, and often one is aided by a distinct color change.

The initial potentials obtained by extrapolation are given in the second column of the table and they are represented graphically in Fig. 2. The full line drawn through the potentials forms a smooth curve which has the logarithmic form of the usual titration curve but not the slope. For a reductant which loses two hydrogen atoms on oxidation, the slope of the curve is normally represented by the equation

$$E = E_n + 0.02957 \log \frac{[\text{Oxid}]}{[\text{Red}]} \qquad (4)$$

in which E_n is the potential when [Oxid] = [Red] in a given solution. This equation is pictured in the figure by the dotted line. The present results may be represented by the modified Equation, 5, by the introduction of an empirical constant, C, to correct for the divergent slope

$$E = E_n + C \times 0.0295 \log [\text{Oxid}]/[\text{Red}] \qquad (5)$$

At the point of half-oxidation the two equations become identical, and the potential corresponding to this point provisionally may be taken as the value for E_n. Using this value one may now calculate from Equation 5 the value of the constant, C, as has been done in the fifth column of the table. In the fourth experiment the ratio [Oxid]/[Red] is so close to unity that a calculation of C is not admissible. The constancy is sufficiently good to show that the equation accurately expresses the results.

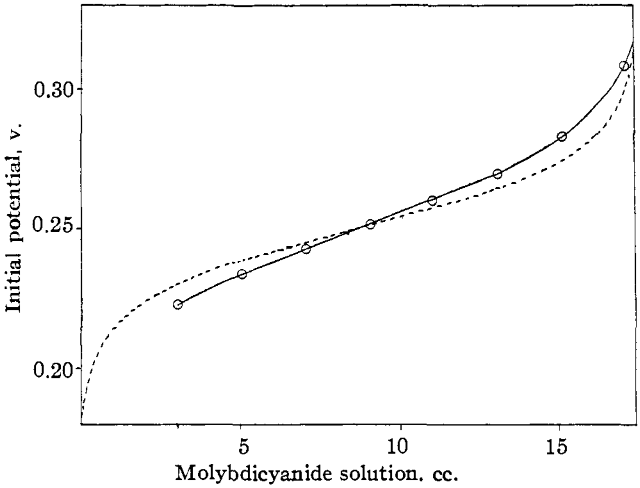

Fig. 2.—Titration curve of *p*-benzylaminophenol at *P*H 7.57.

An explanation of the abnormal slope is not far to seek. Several investigators have noted the influence on the potential of the quinone–hydroquinone system of the association between the components to form quinhydrone, and Clark, Cohen and Gibbs have found that such association is particularly marked among the systems of the *p*-phenylenediamine series, to which the system under study is closely related. Conant and collaborators[8] ascribed abnormal slopes of the titration curves of certain anthraquinones to quinhydrone formation. It is probable that quinhydrones or meriquinones are formed in the present case, and with most of the other substances reported on below. If the meriquinone, M, contains equal molecules of oxidant and reductant, Equation 4 must be modified as in 6

$$E = E_n + 0.02957 \log \frac{[\mathrm{Oxid}]_\mathrm{T} - [\mathrm{M}]}{[\mathrm{Oxid}]_\mathrm{T} - [\mathrm{M}]} \qquad (6)$$

The terms $[\mathrm{Oxid}]_\mathrm{T}$ and $[\mathrm{Red}]_\mathrm{T}$ refer to the total amounts of the components. It is evident that the removal of equivalent amounts of oxidant and reductant from the oxidation–reduction equilibrium would shift the potential to values progressively higher than the normal as the excess of oxidant over reductant increases, and to lower values as this ratio is reversed.

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[8] Conant, Kahn, Fieser and Kurtz, This Journal, **44**, 1382 (1922).

The magnitude of the effect in the present instance may be estimated by relating Equations 5 and 6, and for this purpose we shall make use of an expression similar to that developed by Conant.[8,9] If the oxidant is present in excess of the reductant, and if X is the degree of association of the complex, M, then $[\mathrm{M}] = X[\mathrm{Red}]_{\mathrm{T}}$. Expressing the concentrations of oxidant and reductant in terms of the ratio, R, of the former to the latter, the following expression is obtained.

$$E = E_{\mathrm{n}} + 0.02957 \log \frac{R - X}{1 - X} \tag{7}$$

When it is the reductant which is in excess, the equation is

$$E = E_{\mathrm{n}} + 0.02957 \log \frac{R - RX}{1 - RX} \tag{8}$$

To obtain the degree of association, X, Equation 7 may be combined with the empirical Equation 5, whence

$$C \log R = \log \frac{R - X}{1 - X} \tag{9}$$

Using the average value found for the constant, C, one finds the value of 0.36 for X when $R = 2$; 0.52 when $R = 5$. This indicates that the meriquinone formation takes place to a considerable extent.

Some caution should be exercised in respect to conclusions deduced in this way concerning meriquinone formation, for the subject is full of complications, as Clark, Cohen and Gibbs have pointed out. We have presented a possible interpretation of the peculiar titration curves, but in reporting our results we prefer to disregard the theoretical aspects of the question and to make use of the empirical Equation 5. A provisional value for E_{n}, the potential at half-oxidation, was obtained by interpolating the titration curve, and from it an average value for the constant, C, was calculated. We may now reverse the process, that is, use the average value found for C and calculate E_{n} from the results of each experiment. This has been done in the sixth column of Table II. The agreement between the individual values is very good, considering the rapid decomposition of the oxidant, the abnormal slope of the titration curve, and the lag in the time–potential curve (Curves III and I of Fig. 1 refer to the second and the last experiments of Table II).

Values for the velocity constant of the decomposition reaction are given in the last column. Since, by definition, $k = (E_{\mathrm{i}} - E_{\mathrm{t}})/t$, the values for k represent the drop in potential per minute. In each case the rate remained constant for from six to seven minutes and the values reported represent the averages during the period of constancy. It will be observed that the velocity increases very considerably as the concentration of the oxidant is increased, though the changes are not parallel. A five-fold

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[9] Conant's equation, p. 1391, holds when the reductant is in excess but not for the converse case.

increase in the concentration of the oxidant doubles the velocity constant. It is thus difficult to classify the order of the reaction as a whole, though in each individual experiment it appears to be strictly monomolecular in the early stages.

The oxidation of *p*-benzylaminophenol was not followed in the alkaline range, but a fairly complete study was made in acid and neutral solutions. A condensed summary of the results is given in Table III. The individual experiments at each *P*H are not recorded, but an indication of the agreement of the six or seven determinations of each value for E_n is given by appending the average error. Single electrode potentials on the hydrogen scale at 25° are given. Except in the first case, the solutions all contained a total of 0.2 *M* per liter of buffer salts. Some indication of the velocity constants observed is given by including in the last two columns the approximate constants for two values of the ratio [Oxid]/[Red], *R*. Experiments were not usually performed at just the ratios indicated, but the constants were obtained by interpolation.

TABLE III

VARIATION OF THE POTENTIAL OF THE SYSTEM *p*-BENZYLAMINOPHENOL–N-BENZYLQUINONE-IMINE WITH HYDROGEN-ION CONCENTRATION

*P*H[10]	Hydrogen electrode potential, E_n, v.	Constant, *C*, of Eq. 5	Potential when [Oxid] = [Red], E_n, v.	Av. error, mv.	Calcd. E_n, v.	Diff. E_n (Found − calcd.), mv.	Velocity constant, *k* when [Oxid]/[Red] =	
							0.3	3.3
1.10	−0.0648	0.82	0.6992	0.4	0.6991	0.1	0.011	0.010
1.56	.0925	.84	.6715	.4	.6708	.7	.011	.012
2.05	.1214	1.14	.6391	.4	.6407	−1.6	.011	.012
2.69	.1589	1.00	.5976	.2	.5957	1.9	.011	.016
3.22	.1903	1.24	.5609	.3	.5578	3.1	.014	.024
3.53	.2086	1.18	.5346	.3	.5332	1.4	.012	.021
3.88	.2296	1.19	.5048	.6	.5036	1.2	.008	.013
4.32	.2558	1.23	.4651	.7	.4665	−1.4	.003	.006
4.91	.2903	1.09	.4163	.3	.4195	−3.2	.002	.003
5.58	.3301	1.32	.3707	.9	.3718	−1.1	.002	.003
6.96	.4114	1.29	.2878	1.1	.2872	0.6	.007	.011
7.57	.4475	1.39	.2501	0.2	.2509	− .8	.005	.008

$E_0 = 0.6984$ $K_0 = 9.00 \times 10^{-12}$ $K_r = 1.48 \times 10^{-9}$

The first two series of experiments summarized in the table require a more detailed description. At *P*H 7 the potential of the molybdicyanide–molybdocyanide system is over 0.4 v. higher than that of the organic system, hence the reaction between potassium molybdicyanide and *p*-benzylaminophenol proceeds practically to completion at all concentrations of the reactants and a sharp inflection at the end-point of a titration is ob-

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[10] The buffer solutions were of the following compositions: *P*H 1.10, HCl; *P*H 1.56–2.05, glycine, HCl. KCl; *P*H 2.69, citric acid, NaOH, NaCl; *P*H 3.22–3.88. KH-Phthalate, HCl; *P*H 4.32–4.91, sodium acetate, acetic acid. NaCl; *P*H 5.58. citric acid. NaOH, NaCl; *P*H 6.96–7.57. Na_2HPO_4, KH_2PO_4.

tained. But the potential of the organic system, in reference to a hydrogen electrode at the same P_H, increases somewhat with increasing acidity while that of the inorganic system suffers an enormous decrease, with the result that at P_H 1.10 the potentials of the two systems overlap and the reaction between the reductant and the oxidizing agent comes to a stop when an appreciable quantity of the molybdicyanide is still unconsumed. This does not necessitate giving up this oxidizing agent, but it does require that a correction be applied for the unreacted reagent.

The fraction, m, of the potassium molybdicyanide which has failed to react may be found from the potential of the solution and Equation 10

$$E = E\,(\mathrm{Mo}) + 0.05915 \log m/(1 - m) \tag{10}$$

where E (Mo) is the potential of a half-oxidized molybdicyanide solution at P_H 1.10 on the hydrogen scale and E is the initial potential of the mixture of organic and inorganic materials, on the same scale. A rough determination of E (Mo) suffices for the purpose at hand and the value used was 0.771 v., determined by titration with potassium ferrocyanide. If the end-point in the titration of *p*-benzylaminophenol, preferably as determined in another series of experiments at a higher P_H, be represented by P and if C cubic centimeters of molybdicyanide solution is employed in a given experiment, the correct ratio of oxidant to reductant (R) is given by Equation 11

$$R = \frac{C\,(1 - m)}{P - C\,(1 - m)} \tag{11}$$

Table IV gives the details of the results and calculations at P_H 1.10. The titration curve is not as steep as one would anticipate and there is a downward trend in the values for E_n obtained by applying the usual equation (next to last column). This cannot be caused by association between the oxidant and reductant for the trend is in the wrong direction. Indeed we have failed to discover the cause for this, but we have corrected for it by means of the empirical Equation 5, and there is reason to accept the values thus obtained for E_n (last column), for the average is identical with the mid-point potential of the titration curve.

TABLE IV

TITRATION OF *p*-BENZYLAMINOPHENOL AT P_H 1.10

End-point (P) = 17.2 cc.

Molybdicyanide soln. added, cc.	Initial potential, E_i, v.	Fraction of Mo soln. unreacted, m	$\frac{[\mathrm{Oxid}]}{[\mathrm{Red}]} = R$	Constant, C, of Eq. 5	Potential when [Oxid] = [Red], E_n (uncorr.), v.	Potential when [Oxid] = [Red], E_n (corr.), v.
5.0	0.6881	0.038	0.387	0.90	0.7002	0.6991
7.0	.6949	.049	.630	.74	.7008	.6997
9.0	.6994	.057	.977	..	.6997	.6997
11.0	.7037	.067	1.49	.88	.6986	.6995
13.0	.7081	.078	2.30	.83	.6974	.6993
15.0	.7121	.091	3.77	.77	.6951	.6982

In the experiments at *P*H 1.56 there was some overlapping in the potentials of the organic and inorganic systems, except for very low values of *R*, and the correction was applied in the same way, using 0.782 v. as the value for *E* (Mo).

No general conclusions can be drawn regarding the velocity of decomposition of the oxidant, as inspection of the values for *k* in Table III will show. There is no definite trend with changing acidity; the rate is sometimes constant over a considerable range of concentration of the oxidant, but it often increases decidedly as the amount of the quinone-imine increases.

Some statement should be made regarding the color of the solutions at the conclusion of the experiments. From *P*H 1.10 to 3.53 the solutions were yellow; at *P*H 3.88 a faint purple developed, and at *P*H 4.91 and beyond a red precipitate resulted from the oxidations. In the case of the highly colored solutions or suspensions a striking and significant effect was noted. As the end-point of the titration was approached the solution became pale purple, and when this point had been reached or passed the solution was pure yellow in color. The more intense color is thus caused either by an association or an interaction of the quinone-imine or its decomposition products with the reductant.

We shall now turn to the interesting problem of determining whether the potentials of this system have been characterized accurately enough to reveal the dissociation constants of the oxidant and reductant. In Fig. 3 the potentials of half-oxidation of Table III are plotted against the *P*H of the buffer solutions. It will be observed that the points fall on a smooth curve which has certain distinct characteristics. Starting in the neutral range, there is a straight portion which is parallel to the curve for the hydrogen electrode potential and thus has the slope 0.05915 log $[H^+]$. This "0.06 slope" is characteristic, though not uniquely so, of a system in which an oxidant or reductant is either un-ionized or completely ionized, and in the present case it is altogether reasonable to assume that they are un-ionized. Close to *P*H 5 there is an upward inflection and the curve then approaches an "0.09 slope." This indicates that a dissociation of some basic group begins to occur at about this acidity. That the potential becomes higher than when the components of the system are un-ionized means that it is the reductant which dissociates, for the removal of some of the undissociated reductant from the oxidation–reduction equilibrium by ionization would increase the ratio

$$[\text{Undissociated Oxidant}]/[\text{Undissociated Reductant}]$$

and hence shift the potential to higher levels. The dissociation of the reductant is complete when the "0.09 slope" is reached, but a second inflection in the opposite direction is noted at *P*H 2.85 and the curve then swings back to a new "0.06 slope." This obviously indicates a basic ionization of the oxidant, which eventually compensates for the dissociation of the reductant and brings the curve once more parallel to that for the hydrogen electrode.

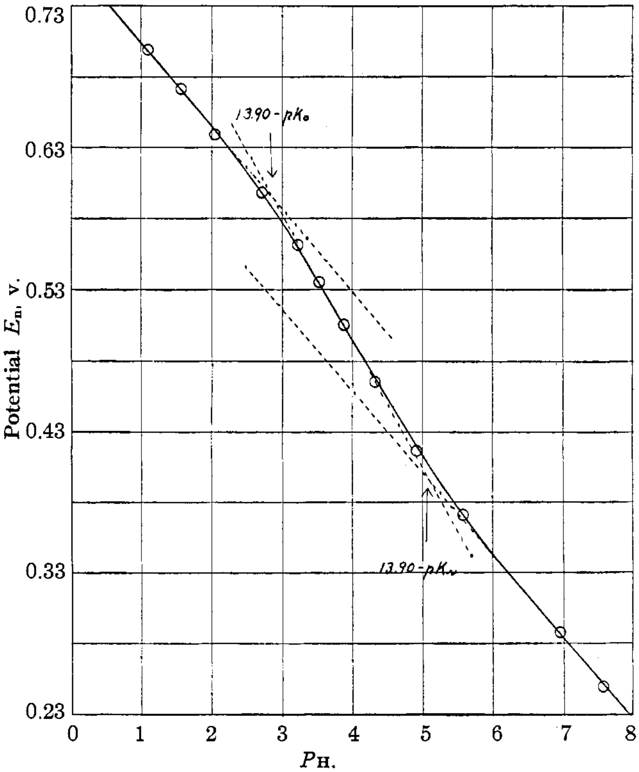

Fig. 3.—Relationship between Pн and the potential of half-oxidation of *p*-benzylaminophenol. (The line is theoretical. the points experimental.)

Since the study of the system has not been pursued into the alkaline range, we may omit all consideration of the acidic ionization of the reductant in developing an equation to cover the present observations. For the limited Pн region investigated the equation for a system in which the oxidant and the reductant have the basic dissociation constants, K_o and K_r is as follows

$$E_n = E_0 + E_h + 0.02957 \log \frac{K_w + K_r\,[H^+]}{K_w + K_o\,[H^+]} \qquad (12)$$

The term E_n is the potential when [Oxid] = [Red], E_0 is the normal oxidation-reduction potential for the undissociated components of the system, E_h is the hydrogen electrode potential, K_w is the ionization constant of water, for which we have used the value 1.26×10^{-14} and K_o and K_r are defined as follows

$$K_o = K_w \left[C_6H_4 \begin{matrix} \diagup O \\ \diagdown \overset{+}{N}HR \end{matrix} \right] \Big/ \left[C_6H_4 \begin{matrix} \diagup O \\ \diagdown NR \end{matrix} \right] [H^+] \qquad (13)$$

$$K_r = K_w \left[C_6H_4 \begin{matrix} \diagup OH \\ \diagdown \overset{+}{N}H_2R \end{matrix} \right] \Big/ \left[C_6H_4 \begin{matrix} \diagup OH \\ \diagdown NHR \end{matrix} \right] [H^+] \qquad (14)$$

With the aid of this equation we have constructed a "best curve" to fit the experimental results, and the constants which we have thus found for the system are given at the bottom of Table III. In the sixth column of this table are to be found values for E_n for each P_H as calculated from Equation 12 and the constants, and a comparison between the values found and those calculated is given in the following column. For further comparison the theoretical equation has been plotted in Fig. 3, and it will be seen that the experimental values (points) lie close to the curve. Comment on these results will be reserved until other systems have been defined.

In addition to the measurements in aqueous solution, some knowledge of the nature of the system in an alcohol–water mixture was desirable. The solvent chosen contained primary and secondary phosphates in such a ratio as to give a solution of P_H 7.03 in water, and we considered that very little ionization of either the oxidant or reductant would occur in the neutral solution and hence that the potential difference between the oxidation–reduction electrode at half-oxidation and the hydrogen electrode in the same solvent would give an adequate measure of the "normal" oxidation–reduction potential. The cell employed was that just indicated, and we shall term the e. m. f. of this cell the normal potential E_0 for the alcoholic solution. The results of a "discontinuous titration" are given in Table V. Comparison with the results in aqueous solution shows that the normal potential is very nearly the same (compare 0.6984), but that the velocity of the disappearance of the oxidant is noticeably less in the alcoholic buffer than in the neutral aqueous solutions.

TABLE V

POTENTIALS OF THE SYSTEM *p*-BENZYLAMINOPHENOL–N-BENZYL-QUINONE-IMINE

Solvent: 37% alcohol. 0.038 *M* in KH_2PO_4. 0.067 *M* in Na_2HPO_4

Initial potential, E_1, v.	$\frac{[Oxid]}{[Red]}$	Const., C, of Eq. 5	Normal potential, E_0, v.	Velocity constant, k
0.6803	0.214	1.00	0.7029	0.0027
.6897	.417	1.11	.7026	.0026
.6970	.700	1.11	.7023	.0022
.7040	1.12	..	.7023	.0024
.7113	1.83	1.19	.7024	.0021
.7205	3.25	1.22	.7031	.0020
.7330	7.50	1.20	.7033	.0020
		Av. 1.14	Av. 0.7027	Av. 0.0023

***p*-Methylaminophenol–N-Methyl-quinone-imine.**—The material used was a good, colorless commercial grade of the sulfate ("Photol"), crystallized six times from water. Brown samples of the material which are offered under the name "Metol" appeared to contain a catalytically active impurity which is not easily removed. The catalyst does not affect the potentials to any noticeable extent, but it greatly accelerates the rate of decomposition of the oxidant. Three crystallizations yielded a colorless product which showed a reaction rate which was less than that for the crude material but still almost twice as great as for the purest samples which we studied.

The results for this system are summarized in Tables VI and VII. They require little comment, for the behavior was quite similar to that already

TABLE VI

VARIATION OF THE POTENTIAL OF THE SYSTEM *p*-METHYLAMINOPHENOL-N-METHYL-QUINONE-IMINE WITH HYDROGEN-ION CONCENTRATION

PH[11]	Hydrogen elect. potential, E_h. v.	Constant, C, of Eq. 5	Potential when [Oxid] = [Red], E_n. v.	Av. error, mv.	Calcd., E_n, v.	Diff. E_n (Found—calcd.), mv.	Velocity constant, k, when [Oxid]/[Red] = 0.3	3.3
1.10	−0.0648	1.00	0.6813	0.3	0.6820	−0.7	0.0017	0.0020
1.47	.0868	1.00	.6601	.3	.6600	.1	.0018	.0020
2.69	.1589	1.00	.5880	.3	.5879	.1	.0024	.0030
3.56	.2108	1.23	.5361	.3	.5312	4.9	.0020	.0030
3.88	.2296	1.25	.5144	.7	.5087	5.7	.0016	.0026
4.32	.2558	1.16	.4749	.8	.4758	−0.9	.0006	.0008
4.91	.2903	1.11	.4236	.3	.4267	−3.1	.0004	.0005
5.56	.3290	1.27	.3736	.1	.3733	0.3	.0005	.0005
5.88	.3481	1.27	.3498	.5	.3487	1.2	.0011	.0010
6.07	.3589	1.11	.3350	.3	.3354	−0.4	.0010	.0007
6.25	.3694	1.11	.3212	.3	.3230	−1.8	.0004	.0008
6.58	.3891	1.16	.2994	.5	.3010	−1.6	.0014	.0010
6.96	.4114	1.10	.2763	.3	.2773	−1.0	.0014	.0011
7.57	.4475	1.23	.2405	1.0	.2405	0.0	.0013	.0011

$E_0 = 0.6877$ $K_0 = 1.0 \times 10^{-10}$ $K_r = 1.0 \times 10^{-8}$

TABLE VII

THE SYSTEM *p*-METHYLAMINOPHENOL-N-METHYL-QUINONE-IMINE, IN NEUTRAL ALCOHOLIC SOLUTION

Initial potential, E_i. v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Const., C, of Eq. 5	Normal potential, E_0, v.	Velocity constant, k
0.6685	0.187	1.14	0.6935	0.0003
.6777	.357	1.16	.6931	.0003
.6848	.383	1.19	.6929	.0002
.6916	.900	..	.6931	.0002
.6980	1.37	1.22	.6932	.0002
.7046	2.16	1.10	.6923	.0002
.7134	3.75	1.21	.6936	.0002
.7254	8.50	1.18	.6933	.0002
		Av. 1.17	Av. 0.6931	

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[11] The buffer solutions were similar to those described in Table III.

described. In the first two series of experiments of Table VI it was necessary to correct for incomplete interaction between the molybdicyanide and the reductant in the manner explained above. It is perhaps significant that the values for the constant, *C*, indicate that the slight association between oxidant and reductant noted in the neutral solutions vanishes in the more strongly acid region. No precipitate was formed as the result of the oxidations; the color produced varied from yellow at *P*H 1.10–3.56 to a purple-red at higher *P*H values.

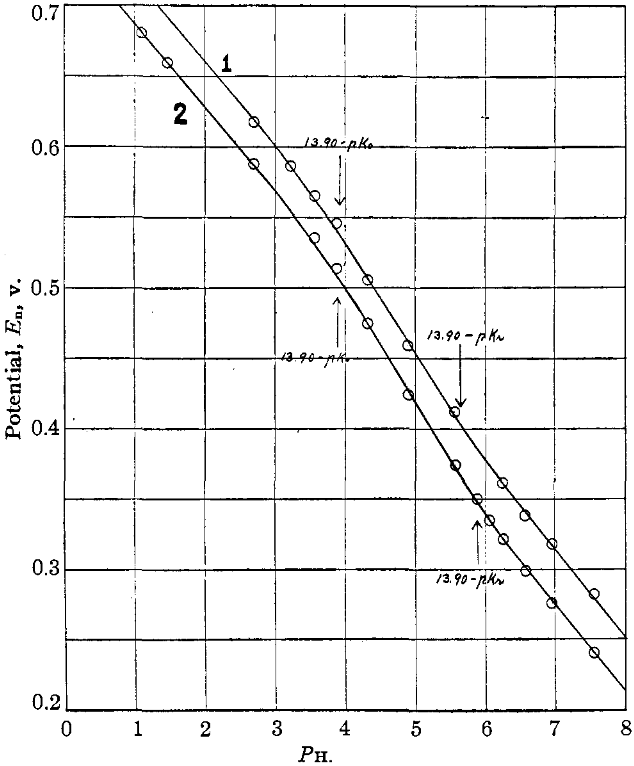

Fig. 4.—Relationship between *P*H and the potential of half-oxidation. 1,*p*-aminophenol; 2.methyl-*p*-aminophenol.

In spite of the low rate of decomposition of solutions containing N-methyl-quinone-imine, and the greater accuracy which this fact implies, the potentials found do not fit the "best curve" quite as well as in the above instance, as the calculations in the table and the graph of the theoretical equation given in Fig. 4 will show. In constructing this curve consideration was given to the fact that the two "0.06 slopes" are quite sharply defined, and the burden of the error was thus thrown onto the potentials in the intermediate regions.

p-Aminophenol–Quinone-imine.—A good grade of p-aminophenol was distilled at atmospheric pressure in an atmosphere of nitrogen and crystallized from alcohol. Tables VIII and IX summarize the results.

The exceedingly rapid decomposition of this system is evident from the velocity constants of Table VIII, which represent the drop in potential per minute. A preliminary study in a few buffers in the P_H range 2–8 at first led us to believe that satisfactory results could only be obtained by the present method in neutral solution. At P_H 7.57 the rate of change in the potential is no greater than for the system from p-benzylaminophenol, and the reaction follows the monomolecular course for about three minutes, thus permitting twelve readings for the extrapolation to each initial potential. At P_H 6.96 the reaction velocity has more than doubled, but there is still a considerable straight portion of the time–potential curve, and there is little difficulty in obtaining reproducible results. In some of the more acid buffers, however, the situation becomes critical. With the potential changing more than one millivolt per second, one can still make fairly accurate settings of the potentiometer but one is seriously hampered by the fact that the time–potential curve drawn through the first few fifteen-second readings often contains no initial straight portion, the velocity decreasing progressively with time. Some of the curves resembled those calculated for a bimolecular reaction, but the reaction does not appear to be of the second order, for the velocity was not altered by a wide change in concentration.

TABLE VIII

VARIATION OF THE POTENTIAL OF THE SYSTEM p-AMINOPHENOL–QUINONE-IMINE WITH HYDROGEN-ION CONCENTRATION

P_H	Hydrogen elect. potential, E_h, v.	Constant, C, of Eq. 5	Potential when [Oxid] = [Red], E_n, v.	Av. error, mv.	Calcd., E_n, v.	Diff., E_n (Found − calcd.), mv.	Velocity constant, k, when [Oxid]/[Red] = 0.3	3.3
2.69	0.1589	1.24	0.6180	0.8	0.6220	−4.0	0.080	0.103
3.22	.1903	1.26	.5870	.7	.5865	0.5	.082	.090
3.56	.2108	1.26	.5662	.8	.5637	2.5	.072	.080
3.88	.2296	1.21	.5437	1.2	.5414	2.3	.074	.063
4.32	.2558	1.15	.5059	0.8	.5078	−1.9	.046	.030
4.91	.2903	1.13	.4585	.7	.4604	−1.9	.060	.025
5.56	.3290	1.03	.4118	.8	.4089	2.9	...	.032
6.25	.3694	1.47	.3615	.5	.3614	0.1	.080	.041
6.58	.3891	1.24	.3382	.7	.3408	−2.6	.047	.032
6.96	.4114	1.10	.3176	.3	.3172	0.4	.023	.017
7.57	.4475	1.09	.2820	.4	.2807	1.3	.008	.007

$E_0 = 0.7280$ $K_0 = 1.05 \times 10^{-10}$ $K_r = 5.62 \times 10^{-9}$

We did note one encouraging feature of this system, namely, that there is very seldom any lag in the adjustment of the potential at the start of an experiment. This, together with the fact that the reaction appears by one rational criterion to be monomolecular, led us to a fresh attack of the problem. We suspected that the reason for the rapid decrease in the velocity so often noted is simply that a large proportion of the original quinone-imine has been destroyed by the time the first two or three readings can be made and, consequently, that more reliable results would be obtained with a high rather than a low value for the ratio [Oxid]/[Red]. One is usually faced with a greater lag in the potential under these conditions, but the present system is particularly favorable in this one respect. Our new experiments, in which particular weight was given to the experiments where the oxidant was in excess of the reductant, supported this view of the reaction. It was often observed that with a high value of R four or five of the first fifteen-second readings fell on a straight line and thus permitted an accurate extrapolation, while when R was given a low value the velocity was less at forty-five seconds than at thirty seconds. There is no way of telling whether the velocity also decreases during the first thirty seconds, but, as an experiment, we made extrapolations from the first two readings and found the results to be in agreement with the other, surer ones. The results of this type of extrapolation, however dubious in principle, usually have been included in the averages as furnishing some slight support for the none too certain characterization of the system.

Though when viewed individually some of the experiments appear questionable, it is not only true that fairly good agreement is found in the values for the potential at half-oxidation from a given series of experiments, but it will also be apparent that the complete set of results, viewed as a whole, forms a remarkably consistent picture. This can best be seen by examining Fig. 4, Curve I. There can be little question about the essential accuracy of the figure for E_n at P_H 7.57, and the value at P_H 6.96 is nearly as certain. In the next two buffers the potentials measured were shifting with extreme rapidity and the extrapolation curves were short, but the four E_n values found form a good, straight-line curve with the characteristic "0.06 slope." In fact the whole of the E_n–P_H curve conforms closely to the type which has been noted for related compounds. The occurrence of the two "0.06 slopes" connected by the "0.09 slope" could hardly be fortuitous, and we thus feel that there is justification for regarding the constants found for this highly unstable system as fairly close approximations (see Table VIII).[12] Entirely independent support of this conclusion is furnished by the comparison of Veley's value for the basic dissociation constant of *p*-aminophenol[13] with the value here deduced. By a colori-

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[12] Equation 12 was used in making the calculations in the table. It should be noted that Conant and Pratt[4] made use of an equation for the system under discussion which can now be declared incorrect. for it takes no account of the basic dissociation of the oxidant. Our own equation is limited, for by definition it does not hold for solutions of such a P_H that acidic ionization of the reductant takes place.

[13] Veley, *J. Chem. Soc.*, **93**, 2122 (1908).

metric method, Veley obtained 6.6×10^{-9} at 15°; the value here reported is 5.6×10^{-9} at 25°.

From Table IX it will be seen that the decomposition of quinone-imine in alcoholic solution is very much slower than in water, and that the rate of the reaction remains very nearly constant over a wide change of concentration. At the end of the experiments in the alcoholic buffer the solution was orange up to the end-point, then yellow. In aqueous solution the color varied from a very pale purple at *P*H 2.69 to red at *P*H 4.91, while from *P*H 5.56 to 7.57 a brown precipitate was formed until up to the point where the end of the titration had been reached.

Table IX

The System *p*-Aminophenol–Quinone-imine in Neutral Alcoholic Solution

Initial potential, E_i, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Constant, *C*, of Eq. 5	Normal potential, E_0, v.	Velocity constant, *k*
0.7089	0.190	1.12	0.7331	0.0027
.7172	.362	1.19	.7320	.0024
.7250	.593	1.15	.7326	.0023
.7381	1.51	1.02	.7321	.0022
.7443	2.24	1.13	.7326	.0021
.7535	3.95	1.18	.7334	.0020
.7663	9.44	1.17	.7335	.0020
		Av. 1.14	Av. 0.7329	Av. 0.0022

***p*-Phenylenediamine–Quinonedi-imine.**—In aqueous solution this system was less stable than that just described. We had no success with measurements attempted in solutions less acid than *P*H 5, and no *P*H region was discovered in which altogether reliable results could be obtained. There is thus little means of determining the accuracy of the few determinations which we were able to make. In view of the use of this system as an oxidation–reduction indicator, these results are reported in Table X; they probably give at least a rough idea of the true potential in the range indicated. There is a suggestion in the results that the E_n–*P*H curve has the "0.06 slope," for the sum ($E_n - E_h$) approximates a constant quantity;

Table X

Variation of the Potential of the System *p*-Phenylenediamine–Quinonedi-imine with Hydrogen-ion Concentration

*P*H	Hydrogen elect. potential, E_h, v.	Potential when [Oxid] = [Red], E_n, v.	Constant, *C*, of Eq. 5	$E_n - E_h$, v.	Velocity constant, *k* when [Oxid]/[Red] = 0.3	3.3
2.69	0.1589	0.6422	1.00	0.8011	0.084	0.104
3.56	.2108	.5859	1.68	.7967	.059	.086
3.88	.2296	.5665	1.74	.7961	.060	.060
4.32	.2558	.5491	2.04	.8049	.046	.058
4.91	.2903	.5147	2.08	.8050	.074	.090

but we do not feel justified in undertaking a theoretical analysis on the basis of such scanty information.

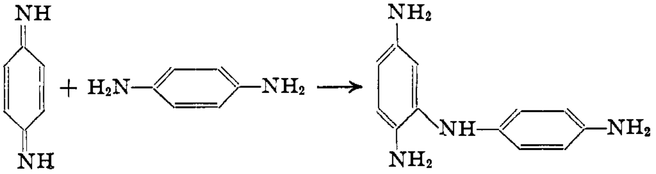
The behavior of the system in alcoholic solution was entirely different, and we are treading on much safer ground in considering the results listed in Table XI. The decomposition was not over-rapid and the time–potential curve was accurately linear up to from one and one-quarter to one and one-half minutes. The normal potential obtained is thus regarded as wholly reliable. The most interesting feature of the results is that the velocity of the destruction of the quinonedi-imine increases steadily as the concentration of the reactant decreases. The drop in potential varies from 25.5 mv. to 6.5 mv. per minute (next to last column) and the direction of the change is particularly striking. It must mean that the reductant enters into the reaction whose rate is measured and that it is the concentration of this component of the system which causes the observed effect. But experimentation showed that the concentration of the reductant is not altered as a result of the decomposition reaction. This was ascertained by performing what amounts to a titration of the reductant remaining after the decomposition reaction had run its course.

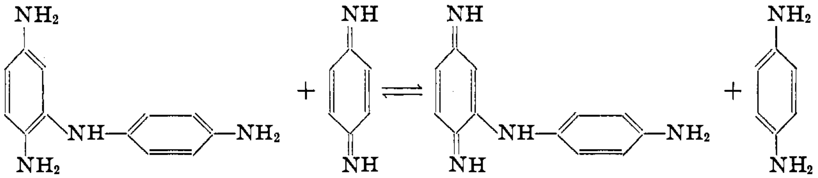
TABLE XI

THE SYSTEM *p*-PHENYLENEDIAMINE–QUINONEDI-IMINE IN NEUTRAL ALCOHOLIC SOLUTION

Initial potential, E_i, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Constant, C, of Eq. 5	Normal potential, E_0, v.	$\frac{E_i - E_t}{t}$	Velocity constant, $k' \times 10^{-3}$
0.7586	0.197	1.15	0.7836	0.0255	1.9
.7681	.379	1.16	.7830	.0232	1.9
.7751	.625	1.25	.7823	.0201	2.0
.7820	.978	..	.7824	.0170	2.0
.7900	1.53	1.34	.7834	.0150	2.3
.7968	2.50	1.20	.7826	.0109	2.3
.8061	4.68	1.23	.7823	.0065	2.2
		Av. 1.20	Av. 0.7828		Av. 2.1

Among the various types of reactions by which quinonedi-imine conceivably might be destroyed, there is one which perfectly answers the requirements which the experiments seem to imply, namely, an interaction between the oxidant and the reductant without causing a change in the concentration of the latter. That reaction is the 1,4-addition of the reductant to the oxidant, as follows





From the general knowledge of substituted and unsubstituted quinones, one can say that the equilibrium point of the second reaction would be such as to favor the products almost exclusively, so that the net result of the initial addition reaction, which would be the slower of the two, would be the destruction of two molecules of quinonedi-imine and the maintenance of the reductant at its original concentration. The reaction may, and probably does, go farther, with the ultimate conversion of three molecules of quinonedi-imine into one molecule of a dianilino-quinonedi-imine, but this would not alter the nature of the reaction.

If this mechanism is correct the reaction is of the second order and the reductant functions as a catalyst. The velocity constant may be represented thus

$$k' = \frac{2.3026}{t\,[\text{Red}]_c} \log \frac{[\text{Oxid}]_i}{[\text{Oxid}]_i - x} \tag{16}$$

where $[\text{Oxid}]_i$ is the initial concentration of the quinonedi-imine and where the subscript c indicates a concentration which may be varied from one experiment to another, but which remains unaltered as a result of the reaction. The potential at any time, E_t, may be expressed as follows

$$E_t = E_i - 0.02957 \log \frac{[\text{Oxid}]_i}{[\text{Oxid}]_i - x} \tag{17}$$

Combining Equations 16 and 17 it is seen that

$$k' = 77.87\,(E_i - E_t)/t[\text{Red}]_c \tag{18}$$

This equation calls for a linear time–potential curve for each ratio of oxidant to reductant, but a decreasing velocity with an increase in that ratio. From this equation (and the value 0.0013 M for the total concentration of the organic system in all of the experiments) values for the bimolecular reaction constant have been calculated and they are included in Table XI (last column). The concordance in the values is sufficient to show that the reaction is of the type defined.

Methyl *p*-Phenylenediamine–N-Methyl-quinonedi-imine.—The substitution of a methyl group for one of the amino hydrogen atoms of *p*-phenylenediamine produces little change in the character of the oxidation–reduction system. Measurements in aqueous solution were not very satisfactory and will not be reported. In the alcoholic buffer the decomposition reaction again appeared to be bimolecular, with the reductant functioning as a catalyst, and Equation 18 was thus used in calculating the velocity constants given in Table XII.

Table XII

The System Methyl *p*-Phenylenediamine–N-Methylquinonedi-imine in Neutral Alcoholic Solution

Initial potential, E_i, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Const., C, of Eq. 5	Normal potential, E_0, v.	$\frac{E_i - E_t}{t}$	Velocity constant, $k' \times 10^3$
0.7230	0.195	1.34	0.7506	0.0213	1.5
.7347	.373	1.34	.7508	.0220	1.9
.7430	.613	1.28	.7513	.0200	1.9
.7502	.957	..	.7512	.0170	2.0
.7572	1.49	1.20	.7505	.0138	2.1
.7661	2.41	1.30	.7508	.0114	2.3
.7759	4.41	1.36	.7508	.0094	3.0
		Av. 1.32	Av. 0.7509		Av. 2.1

***p,p'*-Dihydroxystilbene–Stilbenequinone.**—Owing to the lack of sufficient solubility, this system could not be studied in aqueous solution, but good results were obtained in the alcoholic buffer. The time–potential curve was linear up to about three minutes, but there usually was a lag of from one-half to one minute. The velocity of decomposition again increases with increasing concentrations of the reductant (Table XIII) and the constancy of the velocity constant calculated for the catalytic second order reaction is as good as could be expected.

Table XIII

The System *p,p'*-Dihydroxystilbene–Stilbenequinone in Neutral Alcoholic Solution

Initial potential, E_i, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Const., C, of Eq. 5	Normal potential, E_0, v.	$\frac{E_i - E_t}{t}$	Velocity constant, $k' \times 10^3$
0.8205	0.158	1.37	0.8554	0.0140	0.097
.8310	.294	1.42	.8542	.0124	.096
.8384	.467	1.53	.8528	.0108	.095
.8470	.692	1.36	.8540	.0096	.097
.8535	1.00	..	.8535	.0073	.088
.8611	1.44	1.63	.8541	.0059	.087
.8690	2.14	1.51	.8546	.0045	.085
.8774	6.33	1.53	.8542	.0019	.084
.908	10.0	..	...	.0015	.099
		Av. 1.48	Av. 0.8541		Av. 0.092

According to the interpretation given above of the nature of this type of reaction, this indicates that stilbenequinone forms an addition product with its reduction product, a behavior which appears to be common enough with the quinonedi-imines, but which is unique in the quinone series. It was noted that a bright yellow substance precipitated from the partially oxidized solutions, but failed to form when the reductant was no longer present. It seems probable that this is the quinone formed on oxidation of the primary addition product. The marked additive power of stilbenequinone has been noted by Zincke and Münch,[14] but little is known about the products formed.

***p,p'*-Dihydroxydiphenyl–Diphenoquinone.**—The potentials observed for this system exhibited the linear relationship up to about three minutes, and there was usually a delay of one-half minute before the regular descent started. The rate of the reaction showed no variation with a change in the concentrations of oxidant and reductant. A brown substance precipitated from the partially oxidized solutions but not when oxidation was complete. This suggests that the reductant is in some way involved in the decomposition reaction, but the exact nature of the reaction is not clear.

TABLE XIV

THE SYSTEM *p,p'*-DIHYDROXYDIPHENYL–DIPHENOQUINONE IN NEUTRAL ALCOHOLIC SOLUTION

Initial potential, E_i. v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Const., *C*, of Eq. 5	Normal potential, E_0. v.	Velocity constant, *k*
0.9325	0.197	1.04	0.9550	0.0059
.9410	.379	1.06	.9544	.0066
.9480	.625	1.05	.9544	.0061
.9538	.978	..	.9541	.0060
.9605	1.53	1.14	.9546	.0050
.9670	2.50	1.08	.9543	.0050
.9780	4.68	1.20	(.9566)	.0048
		Av. 1.08	Av. 0.9544	Av. 0.0056

Other Systems.—Oxidation experiments in the neutral alcoholic buffer solution with the following compounds were unsuccessful; the solutions were so unstable that the potentials could not be determined accurately by the present method: *o*-aminophenol, *o*-phenylenediamine, catechol, nitrohydroquinone, 2,6-dihydroxynaphthalene.

One of the purposes of this investigation was to acquire information and experience of various unstable systems which might be useful in a study of the oxidation–reduction systems which are formed when monatomic phenols and amines are oxidized. One or two such systems appear to possess a stability well above the average, and it was hoped that some such system might be discovered which would prove accessible to direct potential measurement. We have made a preliminary study by the method here described of 9-chloro-10-phenanthrol and the radical produced when it is oxidized,[15] and we have found that the system is electromotively active and that it behaves in much the same way as those which have been described above. The potentials, however, appear to be subject to a peculiar fluctuation from one experiment to another, and only a thorough investigation can determine if it is possible to characterize such systems by direct methods.

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[14] Zincke and Münch, *Ann.*, **335**, 157 (1904).

[15] Goldschmidt and Steigerwald. *ibid.*, **438**, 202 (1924).

Comparison of Results

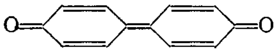
Table XV lists the rounded average values found for the normal potentials of the systems studied. This term is defined as the potential difference between a dilute solution of equimolecular quantities of the oxidant and the reductant when neither is ionized, and a hydrogen electrode in the same solvent.

TABLE XV

ROUNDED AVERAGE VALUES

System named as reductant	Normal potential, E_0 Alcohol, v.	Normal potential, E_0 Water, v.	Half-life (neutral solution) Alcohol, min.	Half-life (neutral solution) Water, min.
p-Methylaminophenol	0.693	0.688	35.6	7.4
p-Benzylaminophenol	.703	.698	3.9	1.4
p-Aminophenol	.733	.728	3.9	1.1
p,p'-Dihydroxydiphenyl	.954	..	1.6	...
p,p'-Dihydroxystilbene	.854	..	1.1	...
p-Phenylenediamine	.783	(.801)	0.5	0.1
N-Methyl-*p*-phenylenediamine	.751	..	.5	...

The potential of diphenoquinone (I) and its reduction product is the highest yet recorded for an organic system. Stilbenequinone (II), though



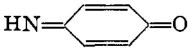
I

II

it has a more extended conjugated system of linkages, falls well below this compound in potential, though it is about equal to the polyhalogenated *o*-benzoquinones and 0.15 v. above *p*-benzoquinone on the potential scale.

Comparison of the various quinone-imines and di-imines (in alcoholic solution) with quinone shows that the substitution of the imino group for the ketonic oxygen atom progressively increases the affinity of the quinonoid substance for hydrogen

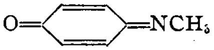
$E_0 = 0.715$ v.



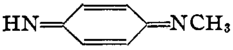
$E_0 = 0.733$ v.

$E_0 = 0.783$ v.

The N-methyl derivatives of quinone-imine and quinonedi-imine are lower in potential than the parent substances by about the same amount



$E_0 = 0.693$ v.



$E_0 = 0.751$ v.

A benzyl group has much the same effect as methyl.

A further interesting comparison is of the basic dissociation constants determined for three of the systems, and these are listed in Table XVI, along with the *pK*-values ($pK = -\log K$). We have also included in the table the data of Clark, Cohen and Gibbs for the first dissociation constants at 30° which they report for systems studied by them.

TABLE XVI

FIRST BASIC DISSOCIATION CONSTANTS

	Reductant		Oxidant	
System, named as reductant	K_r	pK_r	K_0	pK_0
p-Aminophenol	5.6×10^{-9}	8.2	1.0×10^{-10}	10.0
p-Methylaminophenol	1.0×10^{-8}	8.0	1.0×10^{-10}	10.0
p-Benzylaminophenol	1.5×10^{-9}	8.8	9.0×10^{-12}	11.1
p-Aminodimethylaniline[2]	3.9×10^{-8}	7.4	5.0×10^{-7}	6.3
o-Tolidine[2]	6.2×10^{-10}	9.2	2.7×10^{-8}	7.6

According to the present results the ionization constants for *p*-aminophenol and quinone-imine are not appreciably affected by the substitution of methyl for hydrogen, but they are both decreased by the substitution of a benzyl group. The difference between pK_0 and pK_r is fairly constant, from 1.3 to 2.2 units, and it is always in the same direction. The quinone-imine in each case has a smaller dissociation constant than its reduction product. It appears odd that in the case of the di-imines it is the oxidant which is the more highly ionized. This causes an interesting difference in the form of the E_n–P_H curves, a difference at once apparent on comparing Clark's curves with those given here.

In Table XV the systems have been listed in the order of decreasing stability. As an arbitrary basis of comparison in aqueous solution, we have taken the rates of decomposition at P_H 7.57. The half-life periods given are fairly accurate for the alcoholic solutions; for water they represent approximations. The most striking feature about these results is that the systems are all far more stable in a neutral phosphate solution when this contains 37% of alcohol than when it contains no other solvent but water. We see no way of accounting for this, but the practical implications are obvious. If a given system proves too unstable for potentiometric study in aqueous solution it is likely that the conditions will be improved on operating in a partially non-aqueous solvent. Not only is the stability greater, but it has been observed throughout this work that the velocity constants found in the various experiments of a series show much the better agreement in the case of the alcoholic solutions.

There appears to be little correlation between the velocity of decomposition and the acidity of the solution; the only marked effect noted is that quinone-imine is decidedly more stable at P_H 7–8 than in more acidic solutions. It is evident that the rate of the reaction often varies considerably according to the nature of the solution and the relative concentrations of oxidant and reductant, and that there is often a great difference in the behavior of closely related compounds.

We can say little regarding the nature of the reactions by which the oxidants suffer decomposition other than that with two quinonedi-imines and one quinone of unusual structure the reaction very probably is one of addition of the reductant to the oxidant. In the other cases there are so many possibilities that velocity measurements alone are of little assistance in establishing the complete mechanisms. It is not improbable that each of the following reactions contributes in some instances to the instability of the systems: self-condensation and self-oxidation of the oxidant, the addition of the elements of water, reaction with the reductant.

Summary

By means of a "discontinuous titration" method it has been possible to determine the oxidation–reduction potentials of systems which are so unstable that the half-life period for the decomposition of the oxidant is of the order of one-tenth to one-half minute. With the systems formed by *p*-aminophenol and two of its N-alkyl derivatives the variation of the potential with the hydrogen-ion concentration has been studied in the *P*H range 1–8, and the basic dissociation constants have been determined from the results. Seven systems have been studied and the more important constants found are summarized in Tables XV and XVI.

Bryn Mawr, Pennsylvania

[Contribution from the Chemical Laboratories of the University of North Carolina]

PRELIMINARY STUDY ON THE ANTIRACHITIC PROPERTIES OF SHRIMP OIL

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Shrimp oil is the ether-soluble oil obtained when the waste of the shrimp industry is extracted. It has been obtained by the authors[3] in their study on the utilization of shrimp waste. A later chemical study of this oil showed the presence of 19% of cholesterol, the presence of which led to the study of the oil for its antirachitic properties.

This investigation consisted in the feeding study of the oil on white rats, which had become rachitic by special feeding. Standard cod liver oil and shrimp oil were fed at the same time to get a relation of the antirachitic properties of the oil. After three generations of breeding, the selected young rats were fed on Sherman's growth diet B consisting of 66.7 g. of whole wheat, 33.3 g. of whole milk and 1.3 g. of sodium chloride, until they were twenty-eight days old. Part of the series was continued on this diet to serve as normal controls, another part was fed Steenbock's diet 2965[4] for the production of rickets. When they had developed the rickets,

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[3] F. C. Vilbrandt and R. F. Abernethy, "Utilization of Shrimp Waste," Fisheries Document 1078 (1930).

[4] H. Steenbock and A. Black, *J. Biol. Chem.*, **64**, 263 (1924).