stilbene, the melting point was not depressed, thus determining the identity of the product. The yield was 85%.

Summary

1. α- and β-*p*-Dimethylaminobenzoin have been synthesized by the Grignard method, leaving no reasonable doubt as to their structures.

2. The reduction products of these isomers have been studied and correlated with the corresponding substances produced by reducing *p*-dimethylaminobenzoin as prepared by condensing the corresponding aldehydes in the presence of potassium cyanide.

3. *p*-Dimethylaminobenzoin, as prepared by the condensation method, is shown to be the β-isomer, and not the α-derivative, as was hitherto supposed. It has the structure $p\text{-}(CH_3)_2NC_6H_4COCHOHC_6H_5$.

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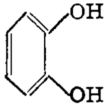
[Contribution from the Chemical Laboratory of Bryn Mawr College]

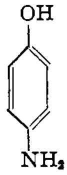
AN INDIRECT METHOD OF STUDYING THE OXIDATION-REDUCTION POTENTIALS OF UNSTABLE SYSTEMS, INCLUDING THOSE FROM THE PHENOLS AND AMINES

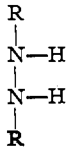
By Louis F. Fieser

Received August 2, 1930 Published December 18, 1930

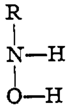
With certain unstable oxidation–reduction systems it has been found possible to measure the potentials with a reasonable degree of accuracy even though decomposition of the oxidant occurs so rapidly that the half-life period is less than one minute.[1] A limit was reached, however, in the application of the method in its present form. Such substances as amphi-naphthoquinone and *o*-quinone-di-imine decompose so very rapidly that no adequate measurements could be made. The number of such failures of the direct method, to be sure, is comparatively small. In over two hundred cases the simultaneous removal by oxidation of two hydrogen atoms from hydroxyl or amino groups which are ortho or para or adjacent to one another, or which bear some similar relationship, gives rise to a fairly stable oxidant and the system formed by the two components is electromotively active and its potential can be determined by one means or another which involves the direct observation of that potential. The following substances thus belong to what may be termed the "hydroquinone type."



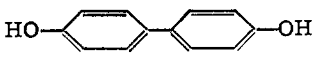




$$R\text{-}NH\text{-}NH\text{-}R$$



$$R\text{-}NH\text{-}OH$$



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[1] Fieser, This Journal, 52, 4915 (1930).

On the other hand, there is a second type of compound, to which the monatomic phenols and amines belong, the partial oxidation of which produces an oxidation–reduction system with which a high degree of instability is the rule rather than the exception, for the oxidant is a free radical. Thanks to the brilliant investigations of Wieland, of Pummerer, and of Goldschmidt, the existence of these radicals and the nature of the systems of which they are components is not a question for speculation but one of proof. Since the existence of the diphenyl nitrogen radical was established by Wieland,[2] several bivalent nitrogen radicals[3] and aroxyls[4] have been isolated. Some of these have been obtained by the direct oxidation of the corresponding amine or phenol, and it has been proved in a highly ingenious manner that the primary oxidation product of aniline is a radical containing bivalent nitrogen.[5] With few exceptions the radicals are highly unstable, but the information concerning the nature of their decompositions is very complete. The nitrogen radicals generally polymerize to hydrazines; the aroxyl radical either polymerizes to a peroxide or isomerizes to a keto-methyl radical, which may enter into various subsequent reactions. Careful studies of these reactions have led the workers in this field to conclude that the primary step in the oxidation in neutral medium of all phenols or amines consists in the removal of one hydrogen atom from oxygen or nitrogen.

With respect to the mechanism, then, there is no difference between the oxidation of the monatomic substances and that of the compound of the hydroquinone type. The oxidation products differ to the extent that those of the first class are usually much less stable than those of the second type, but the difference is hardly a significant one, for exceedingly unstable quinones have been described, as well as very stable radicals.

The property most characteristic of the quinones, the azo and similar compounds, is that they respond almost instantly to reduction at a low temperature and in dilute solution. The reverse reaction takes place with equal ease, and it may be said that the hydroquinone–quinone system is an unusually mobile one. No less mobile is the system 9-chloro-10-phenanthrol (I)–9-chloro-10-phenanthroxyl (II).[6]

Possibly because the blocking of the positions ortho and para to the oxygen atom prevents a wandering of the free valence to carbon, and because the high molecular weight retards the velocity of association, the radical,

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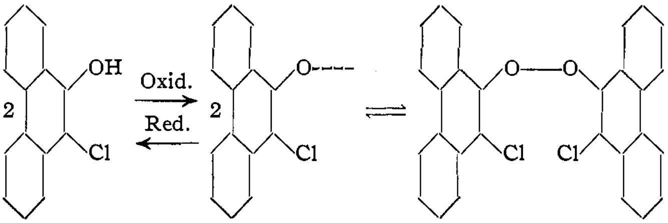
[2] Wieland, *Ann.*, **381**, 214 (1911).

[3] See particularly Goldschmidt and collaborators, *Ber.*, **53**, 44 (1920); **55**, 616, 628 (1922); *Ann.*, **437**, 194 (1924).

[4] Pummerer and collaborators, *Ber.*, **47**, 1472 (1914); **59**, 2161 (1926); Goldschmidt and collaborators, *ibid.*, **55**, 3197 (1922); *Ann.*, **438**, 202 (1924); **445**, 123 (1925); **478**, 1 (1930).

[5] Goldschmidt and Wurzschmitt, *Ber.*, **55**, 3216 (1922).

[6] Goldschmidt and Steigerwald, *Ann.*, **438**, 202 (1924).



I II III

II, is far more stable than the average and in this and other respects it is strikingly similar to the quinones. It does slowly polymerize at ordinary temperatures to the peroxide, III, but Goldschmidt was able to isolate the substance and to characterize it very completely. Outstanding among its properties is the great ease of reduction; the oxidation of I to II may be reversed quantitatively with such reagents as hydrazobenzene, hydroquinone and phenylhydrazine. So great, indeed, is the velocity of reduction of some of the bivalent nitrogen radicals that Goldschmidt and Bader were able to effect a quantitative determination of the radical by titration at −80° with hydrazobenzene solution.[7]

All of the evidence thus shows that there is no essential difference between the systems produced on partial oxidation of compounds of the hydroquinone and of the phenol type, even though the ultimate fate of the oxidant is usually different. It is reasonable to infer that, since the one is electromotively active, the other would share this property, and preliminary experiments with 9-chloro-10-phenanthroxyl have shown that this is the case.[1] It may even be possible to measure the potentials of such systems, but whether or not a few substances of special structure may be capable of study in this way, it does not seem at all likely that any direct measurements will be possible with compounds such as phenol and aniline. Consequently, we believe that it is worth while to develop an indirect method of study which is entirely general in application, if limited in accuracy.

The Theory of the Method

The general method may be called that of potentiometric indicators and it was originated by Conant.[8] It consists in measuring the potential of a solution of some stable oxidation–reduction system, usually an inorganic one, and then adding a sample of, say, a phenol. If the potential of the solution is so low that the phenol is incapable of becoming oxidized by the oxidant of the system which is being used for reference,

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[7] Goldschmidt and Bader, *Ann.*, **473**, 137 (1929).

[8] (a) Conant and Lutz, This Journal, **45**, 1047 (1923); (b) *ibid.*, **46**, 1254 (1924); (c) *ibid.*, **49**, 1083 (1927); (d) Conant and Pratt, *ibid.*, **48**, 2468 (1926); (e) *ibid.*, **48**, 3178 (1926); (f) *ibid.*, **48**, 3220 (1926); (g) Conant, Aston and Tongberg, *ibid.*, **52**, 407 (1930); (h) Conant, *Chemical Reviews*, **3**, 1 (1926).

no change in the potential of the system will occur; but if the phenol becomes oxidized, it will obviously consume some of the oxidant, and the potential will change and thus indicate that a reaction has proceeded. The experiment can, of course, be made quantitative, so that the decrease in the potential of the inorganic, or "reference system" as we shall call it, indicates the amount of phenol which is oxidized in a given period of time. Now the potential begins to fall at once, but it does not rapidly reach a constant level, as in the interaction of two stable oxidation–reduction systems, but continues to fall at a measurable rate. The reason for this is that the reaction between the two reversible systems, say, those from α-naphthol and potassium ferricyanide (1)

$$\mathrm{ROH} + \mathrm{K_3Fe(CN)_6} \rightleftharpoons \mathrm{RO}\text{——} + \mathrm{K_3HFe(CN)_6} \qquad (1)$$

$$\mathrm{RO}\text{——} \longrightarrow \text{Decomposition products} \qquad (2)$$

cannot come to a point of equilibrium because the oxidant of the organic system is unstable and changes over more or less rapidly into other substances according to (2). The destruction of the radical by (2) allows more of it to be formed by (1), and the potential, which is determined by the relative concentrations of the ferri- and ferrocyanides, continues to decrease. The rate at which the potential of the solution decreases is a measure of the rate of Reaction 2, for the first reaction is much more rapid; for practical purposes it may be regarded as instantaneous.

Now Conant has presented evidence in support of the altogether reasonable theoretical conception that the velocity of Reaction 2 is dependent upon the equilibrium constant of Reaction 1. The concentration of the radical available at any instant for Reaction 2 is determined by the extent to which Reaction 1 has proceeded to the right. In other words, the first reaction (rapid) feeds the second (slow). Since the equilibrium constant of Reaction 1 may be expressed in terms of the normal oxidation–reduction potentials and concentrations of the two interacting systems, there is obviously a relationship between the velocity of the decomposition reaction, the potential of the solution, and the normal potential of the arol–aroxyl system. It is desirable to evaluate the last-named quantity, but unfortunately there is one other unknown and undeterminable quantity: the velocity of the un-fed decomposition reaction. For each radical there must be an intrinsic rate of decomposition; the rate which can be measured by the above method is proportional both to this intrinsic rate and to the equilibrium constant of Reaction 1.

If this equilibrium constant is represented in terms of the normal potential of the ferri–ferrocyanide system, E_0(Fe), and of the unstable organic system, E_0, the situation may be summed up by means of the equation

$$(1) \quad \text{Observed velocity} = \text{Constant} \times \frac{[\mathrm{ROH}][\mathrm{K_3Fe(CN)_6}]10^{\left(\frac{E_0(\mathrm{Fe}) - E_0}{0.0591}\right)}}{[\mathrm{K_3H(CN)_6}]}.$$

This shows that the velocity of oxidation will be increased by the substitution of another reference system of normal potential greater than E_0(Fe). It is also clear that there are two unknowns, E_0 and the constant which defines the true rate of decomposition of the oxidant.

In order to gain some idea of the potential of the unstable organic system, Conant prepared a series of solutions containing various reference systems so chosen that there was a progression in the potentials of these solutions. A quantity of a given phenol was added to each solution and the potential was followed. Below a certain potential no reaction occurred, above that the potential dropped at a rate which increased as the potential of the solution was increased. By measuring the rates of the reactions and applying certain approximate equations, Conant was able to estimate the potential at which 20–30% of the phenol would be oxidized in the course of thirty minutes; this value he termed the "apparent oxidation potential." The value is dependent upon two factors: the normal oxidation–reduction potential of the phenol–phenoxyl system and the intrinsic rate of decomposition of the phenoxyl radical.

A separation of these two factors is not easily accomplished, but until this is done there can be no adequate means of estimating, even approximately, the true potentials of the unstable systems. To illustrate the point we may quote the example of two substances of the hydroquinone type which form unstable systems on partial oxidation, and for which the potentials, as well as the true velocities of decomposition of the oxidants, have been measured by direct means. The potentials of the systems from *p*-methylaminophenol and from *p*-benzylaminophenol are very nearly identical at P_H 3.5 and yet the velocity constant is about seven times as great in the second case as it is in the first.[1] If the "apparent oxidation potentials" were determined for these substances it would be found, on comparing the action of *p*-methylaminophenol and of *p*-benzylaminophenol on identical solutions of a given reference system, that the drop in potential occurred much more rapidly with the benzyl than with the methyl derivative, and a lower value for the "apparent oxidation potential" would be assigned to this than to the methyl derivative. The "apparent oxidation potentials" would thus indicate a difference between the two systems when there is no appreciable difference in the actual normal potentials.

Thus, even as a means of indicating the relative (true) potentials of a series of closely related compounds, the "apparent oxidation potential" is unreliable. It reflects not only all of the characteristics peculiar to the rate of decomposition of each oxidant, but also the very marked influences on reaction velocities of changes in temperature and environment.

If the facts were otherwise and if the velocity of the reaction were the same for all members of a given series of substances, then Conant's "apparent oxidation potentials" would give an accurate measure of the relative normal potentials of the various systems. Ordinarily, however, the velocities differ considerably. Now it will be observed that the velocity of the reaction is, in part, dependent upon the potential of the reference system and this can be adjusted to progressively lower values and the reaction can thus be made progressively slower and finally brought practically to a stop. Under these conditions the velocities of reaction for a series of compounds all approach the limiting value of zero and hence they are all very nearly the same at some point representing a small percentage of oxidation in a brief period of time. It follows from these considerations that, while the rate factor may influence greatly the "potential at which 20–30% oxidation occurs in thirty minutes," it should have a slight, possibly an inappreciable, effect on the potential at which the velocity becomes vanishingly small.

Critical Oxidation Potentials

We have thus sought to develop a method of determining the potential at which the velocity of the reaction between a given oxidizable substance and a suitable reference system reaches some limiting, small value. We believe that a means of accomplishing this end has been found and that, although the method is of a purely empirical character, it answers to certain reliable tests which may be applied. The method will be described in detail in the Experimental Part; it may be explained here briefly by quoting some experiments with α-naphthol in a neutral 37% alcoholic solution at 25°. The alcohol was included to increase the solvent power; neutral buffer salts were used in order to avoid dissociation phenomena. The potentials given all refer to the difference in potential between the oxidation–reduction electrode and a hydrogen electrode in the same solvent.

The potential of the molybdicyanide–molybdocyanide system may be varied from about 1.0 v. to 1.2 v., but at any potential in this range α-naphthol becomes oxidized with great rapidity. Using the ferri–ferrocyanide system, a rapid oxidation is observed at a potential of 0.870 v., but no reaction can be detected in a reasonable length of time at a potential of 0.770 v. After thus limiting the range to be studied more carefully, a series of solutions of ferri- and ferrocyanides is prepared in such a way that their potentials lie in this range and differ by about 5–10 mv. The total concentration of the cyanides is kept exactly the same, but the ratio of oxidant to reductant is varied. Each solution is brought to thermal and electrochemical equilibrium and the potential is carefully determined. A sample of α-naphthol is then added, the amount taken being just equivalent to the potassium ferricyanide present in each experiment, and the potential is followed for five minutes. At the potentials 0.780 v. and 0.790 v. no oxidation occurs, but at 0.800 v. and above a drop in potential is noted and this becomes progressively greater as the potentials of the solutions increase. There is thus a potential range of 0.790–0.800 v. above which oxidation occurs, below which the extent of the reaction is so limited that no reaction at all can be detected with the apparatus employed. It may be noted that the period of observation may be extended to about thirty minutes and still the reaction fails to become detectable at 0.780 v.

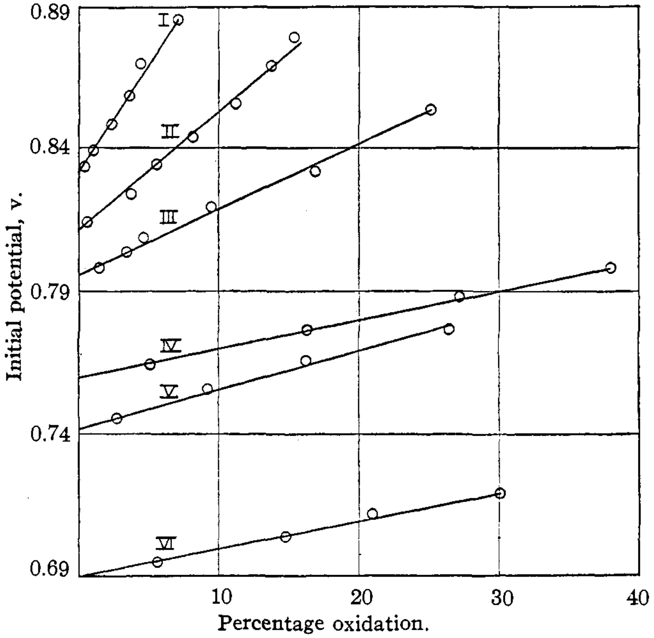

Fig. 1.—The determination of critical oxidation potentials: I, eugenol; II, 2,3-dihydroxy-naphthalene; III, α-naphthol; IV, pyrogallol dimethyl ether; V, catechol; VI, 2,6-dihydroxynaphthalene. Reference systems for I–V, ferro- and ferricyanides; for VI, *p*-hydroxydiphenylamine–N-phenylquinone-imine.

A narrowing of the potential range which thus appears to be critical may be accomplished as follows. The drop in the potential is an indication of the amount of ferricyanide which has entered into reaction and, hence, of the amount of α-naphthol which has been oxidized. One can calculate the percentage oxidation from the equation

$$\text{Percentage oxidation} = 100([\text{Oxid.}]_i - [\text{Oxid.}]_t)/[\text{Oxid.}]_t \qquad (2)$$

where $[\text{Oxid.}]_i$ is the concentration of ferricyanide at the start of the experiment and $[\text{Oxid.}]_t$ is that at time, *t*. These quantities are calculated from the normal potential of the ferri–ferrocyanide system and the potentials at the beginning and end of the experiment, by means of the usual electrode equation. Results of the following nature are obtained (Table I).

Table I

The Oxidation of α-Naphthol

Potential, E(v.)	0.7915	0.7985	0.8040	0.8087	0.8190	0.8321	0.8535
ΔE (mv)	.0	.9	2.2	3.2	7.3	18.1	38.8
Oxidation, %	.0	1.5	3.4	4.6	9.4	16.8	25.0

While the drop in potential is not directly proportional to the initial potential of the solution, the relationship between the potential and the percentage oxidation is unmistakably linear. These results are represented by Curve III, Fig. 1, and Figs. 1 and 2 give similar graphs for several other compounds. Included in the list are phenols, primary and secondary amines, and compounds of the hydroquinone type (catechol and 2,6-dihydroxy-naphthalene). Two inorganic and one organic reference systems are represented. It is clear that the relationship noted holds good in each case. In fact with over seventy compounds studied it appears to be quite generally true that when equimolecular quantities of the oxidizable substance and the oxidant of a reference system are allowed to interact over a brief period of time, the percentage oxidation is a linear function of the initial potential of the solution.

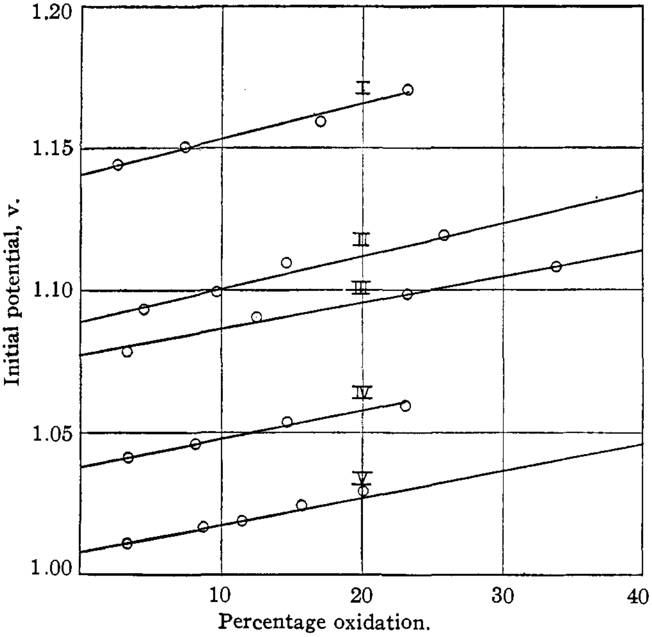

Fig. 2.—The determination of critical oxidation potentials: I, 2-nitro-1-naphthol; II, phenol; III, *p*-toluidine; IV, *p,p'*-dihydroxydiphenylmethane; V, diphenylamine. Reference system: cyanides of molybdenum.

We have not been able to solve the complicated problem of deriving this relationship from theoretical principles, but the relationship does exist and use may be made of it in the following way. On extrapolation of the percentage oxidation—potential curve, a potential is obtained which corresponds, on the curve, to the point of "zero oxidation." It really does not correspond to the point at which there is absolutely no reaction but rather to the potential at which the oxidation ceases to be detectable in a short period of time with the particular instruments employed. If these instruments were refined this "zero-oxidation" potential would be shifted to somewhat lower values. Theoretically there is no potential at which the reaction completely comes to a stop. What this extrapolation value does represent is thus the potential at which, with a particular technique and apparatus, the rate of the reaction becomes so small as to be just detectable. We shall call this the critical oxidation potential and designate it by the symbol E_c. If it is a reasonably reproducible constant with which to characterize a series of substances, it is evident that this critical oxidation potential meets precisely the requirements defined above, for it is a constant determined both by the potential-factor and the rate-factor, but for which, since the rate is made very small, the rate-factor must be exceedingly small.

The accuracy with which the critical oxidation potential can be determined may be judged from the following results. Two series of experiments with α-naphthol both gave the value 0.796 v. When the concentrations of all of the reactants were halved, the value obtained was 0.799 v. In a further series another reference system having a different normal potential was employed; with the complex cyanides of tungsten the E_c value found was 0.798 v. The percentage oxidation–potential curve in this case had a slightly different slope. It is probable that catalysts would also change the slope of the curve without changing the point of origin.

The only limitation discovered in the application of this method is that there are not enough suitable reference systems to cover the entire range of potential. The potentials of the systems which we have used are represented in Fig. 3. The most satisfactory results are obtainable when the potential desired can be secured without resorting to either very high or very low values for the ratio of oxidant to reductant. It will be seen that this can be done in the lower potential zone, for the curves for four systems overlap each other. There is a range, however, between the systems from tungsten and molybdenum which cannot be covered. The upper and lower limits of the usefulness of these systems are indicated on the graph; critical oxidation potentials falling between 0.91 v. and 1.01 v. cannot be determined until other systems of suitable potential are discovered.

The slopes of the potential–oxidation curves vary over wide limits, indicating quite different reaction velocities. This difference probably is not entirely due to the nature of the unstable substances produced on oxidation, for there is a general disposition for the curves to become steeper as the relative amount of the oxidant of the reference system is increased. Thus Curves I–V of Fig. 1 all refer to experiments in which the complex cyanides of iron were employed, and the ratio of ferri- to ferrocyanide varied from values of about 4–5 for Curve I, to 0.1–0.3 for Curve V. The slopes of the curves seem to reflect this variation.

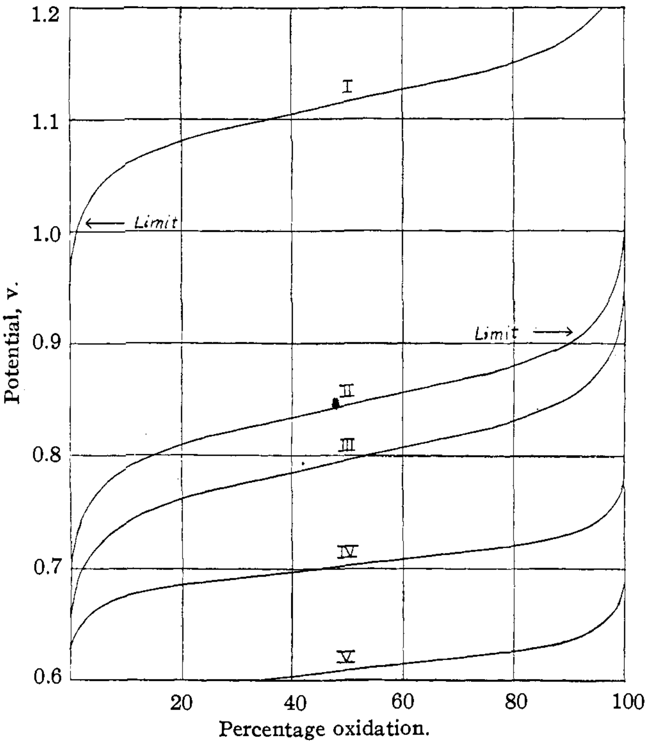

Fig. 3.—The potentials of the reference systems: systems, named as reductant, I, potassium molybdocyanide; II, potassium tungstocyanide; III, potassium ferrocyanide; IV, *p*-hydroxydiphenylamine; V, 2,4-diaminodiphenylamine.

Tests of the Reliability of the New Constant.—According to the reasoning developed above, the critical potentials which have been determined should bear some definite relationship to the normal oxidation–reduction potentials of the unstable systems to which they refer. For a group of similar substances the critical potentials would be expected to lie at some approximately constant distance below the normal potential. We have been fortunate enough to find a few systems for which both of these potentials may be determined, and the results are summarized in Table II. The determinations were all made in a neutral phosphate buffer solution containing 37% of alcohol. The potentials are those measured against a hydrogen electrode in the same solvent. The compounds listed are all of the hydrogen type (two hydrogens involved).

TABLE II

THE RELATIONSHIP BETWEEN THE NORMAL OXIDATION-REDUCTION POTENTIAL (E_0) AND THE CRITICAL OXIDATION POTENTIAL (E_c)

System, named as reductant	E_0^1, v.	E_c, v.	Difference, v.
p,p'-Dihydroxydiphenyl	0.954	0.882	0.072
p,p'-Dihydroxystilbene	.854	.786	.068
p-Phenylenediamine	.783	.710	.073
p-Aminophenol	.733	.673	.060
		Av.	.068

Although these results are not very extensive, they do indicate a constant difference between the two potentials. The variation in the difference is no greater than the uncertainty in the experimental results. The decomposition of two of the oxidants here concerned is a monomolecular reaction; with the other two it is a catalytic second-order reaction. The half-life periods vary from sixty seconds to 234 seconds.[1] When these great differences are considered, it seems quite clear that the rate-factor has been reduced to a minimum in the new term which has been called the critical oxidation potential.

Where direct determinations of normal potentials have not yet been possible it appears admissible to estimate approximate values from the critical potential values and the average difference found up to the present time for similar systems, that is, for systems of the same oxidizing equivalence. Table III gives values calculated in this manner for all of the compounds of the hydroquinone type which have been studied.[9] The normal potential for *o*-benzoquinone has been measured[10] in alcoholic hydrochloric acid solution by a method which very probably yields low results; the value found was 0.784 v.

TABLE III

NORMAL POTENTIALS (CALCD.) AT 25° IN NEUTRAL ALCOHOLIC SOLUTION

System, named as oxidant	E_0, v.
o-Benzoquinone	0.810
Amphi-naphthoquinone	.758
Nitro-*p*-benzoquinone	.765
3-Hydroxy-1,2-benzoquinone	.677
Isatin	.813
Quinone from aesculetin	.827

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[9] A more accurate estimate would be obtained by taking the mean of the critical oxidation potential of the reductant and the critical reduction potential of the oxidant if the latter quantity could be evaluated.

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

Another test of the soundness of considering the critical oxidation potential as a potential-factor from which the rate-factor has been very nearly separated is in determining the effect of temperature. One valuable feature of this test is that it may be applied to each compound individually, rather than to a series. The few measurements which we have made at 40° are not as accurate as those at 25°, but they will serve to show the order of magnitude of the effect of this variable. The results are described in the Experimental Part and summarized in Table IV. A 15° increase in the temperature has relatively little effect on the critical oxidation potential; this quantity decreases by from 3 to 21 mv. The direction of the change and its magnitude are entirely comparable with the change in the normal oxidation–reduction potentials of the quinones.[11]

TABLE IV

THE EFFECT OF TEMPERATURE

Compound	Critical oxidation potential, E_c, v. 25°	 40°	 Difference
4-Nitro-1-naphthol	...	1.123	...
2-Nitro-1-naphthol	1.141	1.120	−0.021
2,4,6-Trichlorophenol	1.103	1.097	.006
1-Naphthol-2-carboxylic acid	1.065	1.062	.003
Hydroquinone monomethyl ether	0.848	0.833	.015
2,3-Dihydroxynaphthalene	.812	.809	.003
α-Naphthol	.797	.784	.013
Phloroglucinol	.799	.791	.008
p,p'-Dihydroxystilbene	.786	.773	.017
1,3-Dihydroxynaphthalene	.754	.744	.010

The effect of a temperature change is thus that normal to true potentials. Where a rate-factor is involved as in Conant's "apparent oxidation potentials," it has been found[8f] that a 37° increase in temperature causes a decrease in the "potential" of as much as 150–400 mv.

One other standard by which the critical potential may be judged is that of the consistency of the results, and we shall now attempt to determine whether the figures obtained reveal any regularities and form a consistent pattern.

The Relationship between Critical Oxidation Potentials and Structure.—The values found for the critical oxidation potentials at 25° are recorded in Table XIII of the Experimental Part. From these figures tables have been constructed which will simplify the comparisons. The first of these, Table V, shows the effect produced on the critical potential of phenol and of α-naphthol of substituting various groups in the ortho, para or meta position to the hydroxyl group. The influence of a given group is very nearly the same for ortho or para substitution, that of a meta group is in the same direction but only 16–18% as great, and this is true whether the potential is increased or decreased.

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[11] Conant and Fieser, THIS JOURNAL, **44**, 2480 (1922).

TABLE V

A COMPARISON OF ISOMERIDES

Substituent	Substance	Effect of substituent on E_c of substance Ortho	Para	Meta
Methyl	Phenol	−0.049	−0.050	−0.009
Phenyl	Phenol	.041	.043	...
Methoxyl	Phenol	.221	.241	.037
Nitro	α-Naphthol	.336	.339	...

Table VI gives a comparison of the oxidation of the hydroxyl and the amino group when attached to an aromatic nucleus. It is seen that the amines become oxidized only at a higher potential than that required for the corresponding phenols. The difference is so nearly constant that one could make a fairly accurate estimate of the potential of an amine from a knowledge of the potential of a phenol of similar structure.

TABLE VI

A COMPARISON OF PHENOLS AND AMINES

Amines	E_c, v.	Phenols	E_c, v.	Difference
Aniline	1.135	Phenol	1.089	0.046
p-Toluidine	1.077	*p*-Cresol	1.039	.038
p-Anisidine	0.892	*p*-Methoxyphenol	0.848	.044
β-Naphthylamine	1.064	β-Naphthol	1.017	.047

In constructing Table VII, which summarizes the data on the influence of substituent groups, we have regarded ortho and para substitution to be identical, and we have considered and combined the results in the phenol and in the amine series. The figure representing the effect of the nitro group should be accepted with some reservation. A comparison of a substituted with an unsubstituted compound, in this case 2-nitro-1-naphthol with α-naphthol, is only valid when the hydroxyl group is un-ionized in each case. It is not unlikely that the nitro derivative is ionized to some extent in the buffer solution employed; hence the observed difference which we have attributed to the nitro group represents only the order of magnitude of the true effect.

TABLE VII

THE EFFECT (V.) ON THE CRITICAL OXIDATION POTENTIAL OF ORTHO OR PARA SUBSTITUENTS

Group	Effect	Group	Effect
$—NO_2$	0.344	$—CH_2CH{=}CH_2$	−0.037
—COOH	.268	$—CH_2COOH$	− .038
—CHO	.212	$—C_6H_5$	− .042
$—SO_3H$	.084	$—CH_3$	− .052
—Cl	.005	$—OC_6H_5$	− .059
$—CH_2OH$	− .037	$—OCH_3$	− .235
$—CH_2C_6H_5$	− .037	$—N(CH_3)_2$	− .371

In general, unsaturated groups increase the potential, saturated ones decrease it; the nitro group has the greatest positive effect, the modified hydroxyl and amino groups the greatest effect in the negative direction. Ortho–para directing groups usually weaken the bond holding the hydrogen atom to oxygen or nitrogen, meta directing groups have the opposite effect.

When the few results for polysubstituted substances are considered, it is found that the influence of a given group increases as the number of such groups in the molecule is increased. The effect of a meta hydroxy group may be estimated in two ways: phenol may be compared with resorcinol; α-naphthol may be compared with 1,3-dihydroxynaphthalene. The differences found in E_c are 0.046 v. and 0.043 v., respectively. A comparison of resorcinol with phloroglucinol, on the other hand, indicates that the introduction of one more meta hydroxyl group lowers the potential 0.244 v. Other substituents usually behave in the same fashion. We do not yet know how to account for this increased effect with increasing substitution, but the same thing was observed among the oxidation–reduction potentials of substituted phenanthrenequinones.[12]

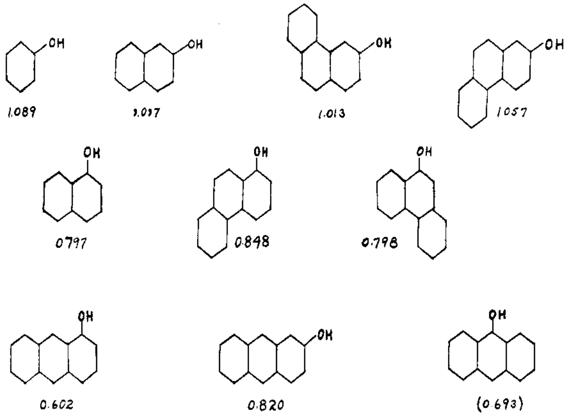


Fig. 4.—Critical oxidation potentials of phenols.

The next comparison is of the phenols derived from the various aromatic hydrocarbons, and the data are recorded in Fig. 4. According to the potentials, the substances fall into definite groups. The four phenols at the top differ relatively little in potential; they are structurally similar in that the oxidizable group is either in the unreactive β-position to a second benzene ring, or else no such ring is present. This may be called the β-naphthol type. The second group consists of α-naphthol, 1-phenanthrol and 9-phenanthrol, and their potentials are all nearly 0.2 v. lower than those of the compounds of the β-naphthol type. In each of these three substances the hydroxyl group is adjacent to a benzene ring, which

[12] Fieser, This Journal, 51, 3101 (1929).

is thus in a position to exert an activating influence. In these two series the nature of the hydrocarbon skeleton appears to be of little consequence and the dominating influence is that which may be exerted by an adjacent aromatic nucleus.

In the last line are to be found results for three anthracene derivations. On account of the uncertainty introduced by its extensive ketonization, the value for anthranol is not reliable. The figures for α- and β-anthrol clearly show that neither compound fits into the α- or β-naphthol series. It will be observed, however, that each is lower in potential than the corresponding naphthalene derivative by almost exactly the same amount, 0.195 v. for the α-derivative and 0.197 v. for β-anthrol. The difference between the α- and β-positions of anthracene is thus the normal one, but in this case the hydrocarbon structure appears to have a specific activating influence which is quite appreciable. This influence may be related to the other unique properties of anthracene.

Another interesting comparison is that given in Table VIII, which gives the potentials for a few secondary amines which result from the replacement of one of the amino hydrogen atoms of aniline by various groups. Alkyl groups cause a rather slight lowering of the potential, indicating that they tend to weaken the nitrogen–hydrogen linkage; the unsaturated phenyl group has an effect which is similar but greater, while the presence of a carbon–nitrogen double bond adjacent to the oxidizable group appears to produce a very marked change in the potential. In view of this fact, it appears odd that the azo group of diazoaminobenzene has such a moderate influence.

TABLE VIII

THE EFFECT OF N-SUBSTITUTION ON THE CRITICAL OXIDATION POTENTIAL OF ANILINE

Subst.	$C_6H_5N{=}N—$	$C_6H_5CH_2—$	$CH_3—$	$C_2H_5—$	$C_6H_5—$	$C_6H_5CH{=}N—$
Effect, v.	−0.077	−0.078	−0.082	−0.097	−0.127	−0.344

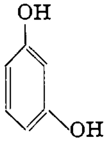
Some Theoretical Speculations

It is evident that, on the whole, the critical oxidation potentials of a large number of substances reveal many regularities and reasonable relationships; the constant responds just as well to this criterion of reliability as it does to specific experimental tests. We thus feel confident that this new constant gives a dependable, if approximate, indication of the relative normal potentials of the compounds concerned and that it may be taken as a true measure of the tendency of a given substance to become oxidized. Because of this demonstrated reliability, we shall now venture to present a few deductions of a somewhat speculative nature.

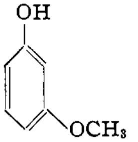
1. **The Possibility of Quinone Formation.**—The property of forming a quinone on oxidation is not shared by all dihydroxyl derivatives of the aromatic hydrocarbons, and it is important to determine the requirements

for this type of reaction and the limitations. Whether or not 2,3-dihydroxynaphthalene possesses this property is a question which has received considerable attention and one to which some of the present results may be applied, for the ability of a substance to yield a quinone, azo compound or similar oxidant, rather than a univalent radical, appears to be reflected in the potential.

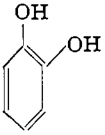
With resorcinol (IV) the formation of a quinone is impossible and the relation of the potential to that of phenol gives a measure of the effect of one meta hydroxyl group. The potential of the monomethyl ether,



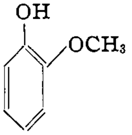
E_c = 1.043 v.
IV



E_c = 1.052 v.
V



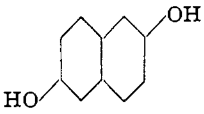
E_c = 0.742 v.
VI



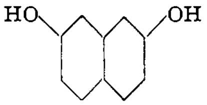
E_c = 0.868 v.
VII

V, gives a measure of the influence of a meta methoxyl, and it will be observed that the effect is practically the same for these two groups. Turning to the ortho derivatives, catechol (VI) would be expected to have a potential very close to that of guaiacol (VII) if the oxidation involved a single hydrogen atom and the formation of a univalent radical. The observed potential, however, is very much below that of guaiacol, and the obvious reason for this is that the oxidation of catechol is different and results in the formation of a quinone. Even the transitory existence of the most unstable of quinones should affect the potential in this way.

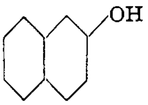
A further example of the manner of applying this criterion of quinone formation is the case of the oxidation of 2,6-dihydroxynaphthalene (VIII). If this substance is to be imagined as a β-naphthol derivative which will become oxidized at a single hydroxyl group, we need a means of predicting the effect on this oxidation of the hydroxyl in the second nucleus. A comparison of 2,7-dihydroxynaphthalene (IX) with β-naphthol (X) indicates that this effect ordinarily is practically negligible. The potential of VIII, however, is not at all close to that of β-naphthol, but far below it. This may be interpreted as the result of the formation on oxidation of the highly unstable *amphi*-naphthoquinone.



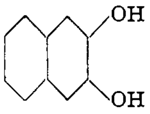
E_c = 0.690 v.
VIII



E_c = 1.007 v.
IX



E_c = 1.017 v.
X

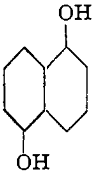


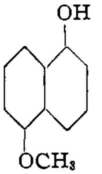
E_c = 0.812 v.
XI

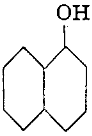
The possible existence of "2,3-naphthoquinone" may now be considered. The oxidation potential of 2,3-dihydroxynaphthalene (XI) is only 0.205 v.

below that of β-naphthol (X). It has been shown that the effect of a hydroxyl group is about the same as that of a methoxyl, where the oxidation is of the univalent type, and it is known that the effect on the potential of phenol of an ortho-methoxyl group is 0.221 v. The value is so close to the difference between X and XI that a completely adequate conception of the potential of XI is given by the assumption that the oxidation is of the univalent type, that it is simply an ortho substituted naphthol which cannot form a quinone.

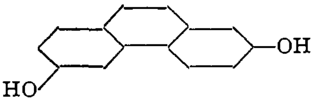
The opposite decision is reached in the case of 1,5-dihydroxy-naphthalene (XII). A comparison of the ether, XIII, with α-naphthol (XIV) indicates that a methoxyl in the 5-position, and hence by inference a hydroxyl in that position, has little effect upon the potential for the oxidation at the single hydroxyl group in the 1-position. Since the potential of 1,5-dihydroxynaphthalene is 0.124 v. below that of α-naphthol, it must be concluded that the oxidation is not similar to that of α-naphthol and that a quinone is formed, however brief its existence.

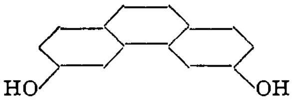

$E_c = 0.673$ v.
XII

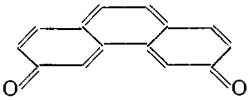

$E_c = 0.792$ v.
XIII


$E_c = 0.797$ v.
XIV

In the phenanthrene series it is found that an hydroxyl group in one terminal ring has little influence on the potential of oxidation at an hydroxyl in the other terminal nucleus. The 2,6-dihydroxy derivative (XV) is to be regarded as a substituted 3-phenanthrol, and its potential is practically identical with that of this compound. On the other hand, the potential of the 3,6-derivative (XVI) is well below that for its isomer and this suggests that the quinone, XVII, is the primary oxidation product. Preliminary qualitative tests with 3,6-dihydroxyphenanthrene have failed to reveal any indication of the formation of a quinone,[13] but this problem will now bear closer study.


$E_c = 1.010$ v.
XV


$E_c = 0.832$
XVI


XVII

2. The Nature of the Compounds of the Hydroquinone Type.—Some comparison of the systems involving one and those involving two hydrogens in the oxidation process has been made above in a qualitative way,

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[13] Fieser, This Journal, 51, 2480 (1929).

but when a closer relationship between the two types is desired, the critical oxidation potentials do not furnish an adequate basis for comparison. This can only be obtained through a knowledge of the normal potentials and the free energies of the oxidation.

It has been shown that for a few substances of the hydroquinone type it is possible to relate the critical potential (E_c) to the normal potential (E_0) experimentally. On the average, the former is 0.068 v. below the latter. From the electrode equation, which must apply to E_c as well as to any potential of the system, one may write

$$E_c - E_0 = -0.068 = 0.02957 \log [\text{Oxid.}]/[\text{Red.}] \qquad (3)$$

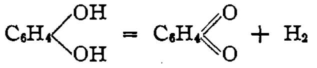
A calculation from this equation shows that the potential represented by E_c corresponds to a point at which 0.5 part of the oxidant is in equilibrium with 99.5 parts of the reductant; in other words, we have determined in E_c the potential at which 0.5% of the reductant becomes oxidized in five minutes. Though the amount is quite small, it appears that this represents quite closely the extent of the reaction in each case.

The difference, $E_c - E_0$, was determined for systems with which two hydrogens are removed on oxidation, hence the difference would not be the same where a monatomic phenol or amine is concerned. In the latter case the equation becomes

$$E_c - E_0 = 0.05915 \log [\text{Oxid.}]/[\text{Red.}] \qquad (4)$$

The experiments, however, establish that the reaction proceeds to the extent of 0.5% in five minutes. We have shown that the variation in the rate of the reaction is insignificant when the rate is so very small and we are thus justified in assuming that the extent of oxidation would be very nearly the same for all similar systems. Since there is an abundance of evidence to show that the hydroquinone–quinone and arol–aroxyl systems are entirely similar, we may assume 0.5% reaction for the latter system and thus calculate from Equation 4 that the difference between E_c and E_0 is 0.136 v. We regard this value, which gives a means of estimating the normal potentials for the systems containing radicals, as uncertain only to the extent that it is an approximation which may be subject to some revision as more data accumulate.

Having a method of estimating approximate values for the normal potentials, the free energy changes in the oxidations can be calculated. Thus for phenol the critical potential is 1.089 v., hence the normal potential for the phenol–phenoxyl system is 1.089 + 0.136 = 1.225 v. The normal potential for the quinone–hydroquinone system is 0.715 v. The free energy changes are as follows

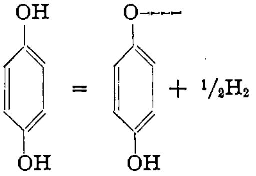


$$C_6H_4\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} = C_6H_4\begin{matrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{matrix} + H_2 \qquad \Delta F = 33.0 \text{ Cal.}$$

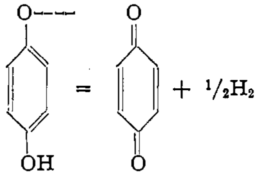
$$C_6H_5OH = C_6H_5O\text{---} + {}^1/_2H_2 \qquad \Delta F = 28.3 \text{ Cal.}$$

Not much more energy is required for the removal of two hydrogens from hydroquinone than for the oxidation of the single hydrogen of phenol.

One interesting application of these calculated free energy changes is to the question of the possibility of carrying out the step-wise oxidation of hydroquinone. Estimates of the free energy changes for the removal of each hydrogen atom may be made in the following way. Considering the first step in the reaction, hydroquinone may be regarded as a substituted phenol which is converted into a univalent radical. The hypothetical critical potential for this oxidation would be close to that of its monomethyl ether (E_c = 0.848 v.), and one can estimate from the known relationship between hydroxy and methoxy compounds (resorcinol and its ether) that the value would be 0.839 v. The normal potential would be 0.136 v. greater, or 0.975 v., and the increase in free energy 22.5 Cal. For the complete oxidation of hydroquinone to quinone the energy change is 33.0 Cal. The difference between these quantities gives the free energy change in the second step of the process. We may thus write



ΔF = 22.5 Cal.



ΔF = 10.5 Cal.

This shows that considerably less energy is required for the removal of the second hydrogen atom than for the first. If the energy level in a given oxidation experiment is great enough to produce the radical, it will be more than sufficient to complete the oxidation. The free radical is thermodynamically unstable except when it is present at very low concentrations. If it were possible to prepare it by some other method, it would disproportionate to give quinone and hydroquinone. The situation may be expressed in terms of the equilibrium constants of the two reactions (3×10^{-17} and 2×10^{-8}), and it may be shown that the concentration of the radical in a solution containing 0.1 M each of quinone and hydroquinone is 4×10^{-6}.

By following similar processes of reasoning we have estimated the corresponding free energy changes for other substances which yield quinones, and the figures are given in Table IX.

TABLE IX

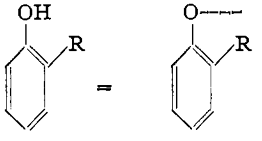
CALCULATED FREE ENERGY CHANGES IN THE OXIDATION OF HYDROQUINONES

Reductant	ΔF, Cal. First hydrogen	ΔF, Cal. Second hydrogen
Hydroquinone	22.5	10.5
Catechol	23.0	14.4
2,6-Dihydroxynaphthalene	26.4	8.6
p,p'-Dihydroxydiphenyl	27.0	17.0

Invariably the energy required to complete the oxidation of the radical is very much less than that required to produce it. This not only serves to explain why radicals or their reaction products (other than quinones) have never been observed in the oxidation of this type of compound, but it also gives a new insight into the nature of these substances. When one hydrogen atom has been separated from the hydroxylic oxygen atom, the free valence on this oxygen transmits to an ortho or para hydroxyl or amine group a reactivity, a mobility, which it did not before possess.

3. **The Effect of Substituents on the Normal Potentials of the Quinones.**—Throughout the entire investigation of the subject named it has been a perplexing problem to decide whether the observed shifting in the normal potential of an oxidation–reduction system as the result of the introduction of a substituent group, or of other structural change, is to be regarded as connected with the structural change in the oxidant or in the reductant. Thus the normal potential of the quinone–hydroquinone system is lowered 0.121 v. by the introduction of a methoxyl group;[14] but there has been no way of telling whether this pronounced change results from the fact that the methoxyl group weakens the oxygen–hydrogen bond of the hydroxyl groups of hydroquinone, or if it is because of an effect of this group on the unsaturated system of quinone, causing the molecule to have a diminished tendency to add hydrogen in the 1,6-positions. Possibly both factors are of importance. On account of the great contrast in the structure of the oxidant and reductant, oxidation cannot be visualized as the exact reverse of reduction. This is, however, true of the oxidation of a phenol to a free radical, for each substance retains the truly aromatic structure and it is immaterial whether one considers the activation of the functional hydrogen atom of the reductant or the affinity of the univalent oxygen atom of the oxidant for hydrogen.

One may compare guaiacol with phenol and thus obtain a difference in the free energy changes which represents the effect of the methoxyl group



$+ \, {}^1/_2H_2$

$-\Delta F$ (Cal.) $\left\{ \begin{array}{ll} R = H: & 28.3 \\ R = OCH_3: & 23.2 \end{array} \right.$
Difference = 5.1

The effect of the methoxyl group in guaiacol, which is thus determined, must be very nearly the same as the effect of that group on the hydroxyl group ortho to it in methoxyhydroquinone. The influence of the substituent on the second hydroxyl group cannot be very great, because this group is in the meta position and groups which are meta to each other have very little effect on one another. A comparison of the hydroquinone system with the methoxy-substituted system gives the following results

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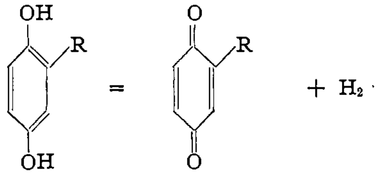
[14] The value for the normal potential of methoxyquinone (0.594 v.) was kindly supplied by Dr. J. B. Conant.



$-\Delta F$ (Cal.) $R = H$: 33.0
$R = OCH_3$: 27.4
Difference = 5.6

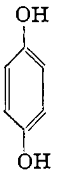
The effect of substitution is hardly any greater than that found above for guaiacol, and this means that almost the entire change brought about by introducing this group is to be attributed to the influence of that group on the character of the hydroquinone, and that the change produced in the quinone molecule is relatively insignificant.

The inference which the present results suggest, namely, that the normal potential of a quinone–hydroquinone system is influenced much more by the change produced in the reductant as the result of substitution than by the corresponding change in the oxidant, is an important one and one which will be investigated further.

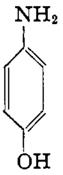
While the effect of simple substitution now appears traceable largely to the character of the hydroquinone in question, there can be no doubt that the influence of some structural changes must be attributed to the nature of the quinone in question. Thus, for example, the pronounced difference in the normal potentials of the quinone–hydroquinone and the *o*-benzoquinone–catechol systems results from a difference inherent in the two quinones and not in their reduction products, for there is good evidence that ortho and para substitution produce the same effect on the oxidation potential of a phenol.

4. **The Relationship between Various Oxidizable Substances.**—With the information supplied by the present study of phenols and amines, we are in a position to understand somewhat better the relationship between the various types of compounds which yield more or less stable oxidation products by the loss of two hydrogen atoms.

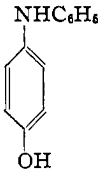
Since a given primary amine is oxidized only at a potential higher than that required for the oxidation of the corresponding phenol, we may conclude that the hydrogen is the more firmly bound in the primary amino group. This gives a rational explanation of the fact that the normal potential of the hydroquinone–quinone system is progressively increased by the substitution of amino and imino groups for the hydroxyl and ke-



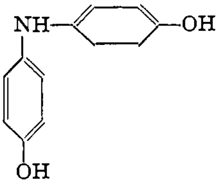
E_0 = 0.715 v.
XVIII



E_0 = 0.733 v.
XIX



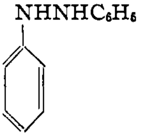
E_0 = 0.703 v.
XX



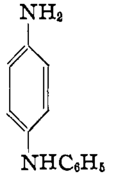
E_0 = 0.656 v.
XXI

tone groups, respectively (Compare XVIII and XIX).[1] That diphenylamine is lower in potential than aniline accounts for the relationship between XIX and XX. The structural difference between XX and XXI is that the latter substance has one additional para hydroxyl group. Since such a group has been found to impart a considerable mobility to a hydroxylic or amino hydrogen, the shifting of the potential of the system of which XXI is the reductant to a lower level is easily understood. Thus the systems from the quinones, the quinone-imines and di-imines, the quinone-anils, the indophenols and indamines are all closely related to one another and in a qualitative way their relative potentials are now understood.

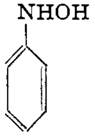
On considering the structures of hydrazobenzene and phenylhydroxylamine, which form systems with azobenzene and nitrosobenzene, respectively, one is impressed by the relationship of these substances to *p*-aminodiphenylamine and to *p*-aminophenol. The first two compounds are amines in which there is, adjacent to the amino group, a group which appears to impart a considerable reactivity to the amino hydrogen. Once this hydrogen has been removed by oxidation, the resulting free valence in turn aids in the immediate oxidation of the group which caused the activation. The other two substances, XXIII and XXV, are exactly similar except that their activating group which eventually becomes oxidized is across the benzene ring from the first group, rather than adjacent to it. One may roughly estimate how the activating effect of a group would compare when it is in these two situations by considering the critical potentials of aniline (1.135 v.), N-methylaniline (1.053 v.) and *p*-toluidine (1.077 v.). Attaching the methyl group to nitrogen, and substituting it in the para position, both cause a lowering in the potential but the effect of N-substitution is the greater of the two. Consequently it is understandable that the potentials for hydrazobenzene and phenyl hydroxylamine are lower than those for their isomers.



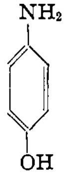
E_0 = 0.420 v.[15]
XXII



E_0 = 0.751 v.
XXIII



E_0 = 0.562 v.
XXIV



E_0 = 0.727 v.
XXV

5. A Possible Reason for Certain Molecular Rearrangements.—The comparisons which have just been made suggest an interesting relationship in the field of the molecular rearrangements. This can be made

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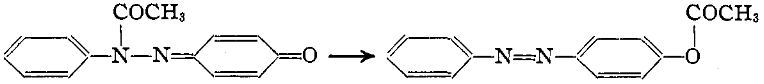
[15] This value is estimated from the potentials for 3,3′-diaminoazobenzene (0.4095 v.) and azobenzene-4,4′-disulfonate (0.424 v.). Compare: Biilmann and Blom, *J. Chem. Soc.*, **125**, 1719 (1924); Conant and Pratt, Ref. 8d.

clear by the following statements. Under certain conditions N-methylaniline (E_c = 1.053 v.) can be caused to rearrange into *p*-toluidine (E_c = 1.077 v.); phenylhydroxylamine (E_0 = 0.562 v.) yields *p*-aminophenol (E_0 = 0.733 v.); the hydrazobenzenes (hydrazobenzene, E_0 = 0.420 v.) rearrange either to benzidines (benzidine, E_0 = 0.921 v.[16]), or semidines (*p*-aminodiphenylamine, E_0 = 0.751 v.). In each case the rearrangement involves the formation of a less oxidizable isomer, a substance of higher potential. The converse of this proposition appears equally true as, for example, in the case of the rearrangement of acetylquinonephenylhydrazone, XXVI, into acetoxy-azobenzene, XXVII. From the known potentials for quinone-imines and for azo compounds it is quite safe to assume that the azo compound has the lower reduction potential, so that the change represented here is from one reducible substance to an isomer which is less reducible. This reaction constitutes one of the few exceptions to Latimer's theory of molecular rearrangements,[17] and yet it falls into line with the other reactions noted. It has been shown that a given reducible substance tends to tautomerize, if this is possible, into a less reducible form, a form of lower reduction potential.[18] There is a suggestion in the present observations that a given reducible (or oxidizable) substance possesses a tendency to rearrange, where possible, into an isomeric form which is less reducible (or oxidizable).


XXVI XXVII

Experimental Part

Buffer Solution.—The solvent employed in all of the experiments was 0.038 *M* in potassium dihydrogen phosphate and 0.067 *M* in disodium hydrogen phosphate, and contained approximately 37% of alcohol. It was prepared by diluting 534 cc. of a solution 0.07 *M* in potassium dihydrogen phosphate and 0.105 *M* in disodium hydrogen phosphate to a volume of 1 liter with 95% alcohol. When diluted with water instead of alcohol, the solution had a PH value of 7.04. The alcoholic solution contains about the maximum quantity of salts, and crystallization is likely to occur if it is allowed to stand for any length of time at a temperature below 25°.

Potassium Molybdocyanide, $K_4Mo(CN)_8 \cdot 2H_2O$.—After carrying out several preparations of this material according to the method outlined by Rosenheim,[19] the following procedure was adopted as being rapid and reliable.

One hundred grams of molybdic acid (85% MoO_3) and 210 cc. of concentrated hydrochloric acid were added to a solution of 210 g. of sodium thiocyanate in 1.2 liters of water and the mixture was boiled under the reflux condenser for three hours. The deep red solution of the basic molybdenum-IV-thiocyanate was filtered by suction and

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[16] Clark, Cohen and Gibbs, Supplement No. 54 to *Pub. Health Repts.* (1926).

[17] Latimer, This Journal, **51**, 3185 (1929).

[18] Fieser, *ibid.*, **50**, 439 (1928).

[19] Rosenheim, *Z. anorg. Chem.*, **54**, 97 (1907); see also, *ibid.*, **49**, 149 (1906).

60 cc. of pyridine was added slowly to the well-stirred solution. A dark red oil was thus precipitated, and toward the end of the addition a light yellow solid began to separate. On thorough cooling in an ice-bath the red oil solidified (dry weight, 148 g.). Without drying the product or breaking up the lumps the pyridine compound was stirred into a solution of 300 g. of potassium cyanide in 500 cc. of water. Noxious gases were evolved and the material rapidly dissolved to give a solution which was first green and then yellow-brown. The mixture was heated on the steam-bath and stirred for one-half hour, filtered from a certain amount of black material, and evaporated on the water-bath until a large crop of amber-colored crystals had separated. After cooling, the material was collected and washed with a small amount of potassium chloride solution. The crystals collected in this way were usually contaminated with a considerable amount of black material, but the latter is not soluble in water and is easily removed. The crude product was dissolved in warm water, the solution was treated with animal charcoal, filtered, and to it there was added one to two volumes of alcohol. The potassium molybdocyanide soon separated in the form of golden-yellow crystals of great purity; yield, 100 g. Further evaporations of the cyanide mother liquor yielded, after two or three recrystallizations, 9 g. more of the pure product.

Potassium Molybdicyanide Solution, $K_3Mo(CN)_8$.—Oxidation to the pentavalent cyanide was carried out according to Olsson.[20] A solution of 4.4 g. of potassium molybdocyanide in 20 cc. of water and 10 cc. of 6 *N* sulfuric acid was titrated with a 10% solution of potassium permanganate until a pink color indicated complete oxidation. Fifty cc. of 10% silver nitrate solution was then added to precipitate the molybdicyanide in the form of the fine, brown-red silver salt. This was collected on a Büchner funnel washed with water, suspended in 50–100 cc. of water, and treated with 50 cc. of 10% potassium chloride solution. By shaking the mixture vigorously in a stoppered flask the silver salt was soon decomposed. The solution was filtered by suction from the silver chloride, clarified with animal charcoal and diluted to a volume of 250 cc. As the pentavalent molybdenum compounds are sensitive to light, the above operations were carried out in the dark-room.

The strength of the molybdicyanide solution was determined by electrometric titration with potassium ferrocyanide, and it was found to vary from 0.032 to 0.034 *M*. The solution was diluted to 0.030 *M* and stored in the dark. The fresh solution always contained a small amount of molybdocyanide, as revealed by the titration curve, and when exposed to the light of the laboratory the concentration of molybdicyanide decreased at the rate of about 0.2% per hour.

Potassium Ferricyanide and Ferrocyanide Solution.—These solutions were prepared by dissolving 0.03 mole of the salt in 200 cc. of water and diluting to 1 liter with the alcoholic buffer solution. The solutions decompose slowly and should be rejected after the second day.

Procedure for the Determination of Critical Oxidation Potentials.—The five reversible oxidation–reduction systems which were employed as reference systems are listed in Table X. Since the potentials of the complex cyanides vary considerably with dilution, it was essential to determine the normal potential under conditions comparable with those of the oxidation tests. For this purpose 20 cc. of the 0.03 *M* potassium ferrocyanide solution was added to 200 cc. of the buffer solution and titrated electrometrically with 0.03 *M* molybdicyanide solution, giving a curve from which the normal potential could be calculated. The potential of

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[20] Olsson, *Ber.*, **47**, 917 (1914).

Table X

Normal Potentials of the Reference Systems

0.0016 *N* solution of oxidant and reductant in neutral alcoholic phosphate solution

System, named as reductant	Abbreviation	E_0 25°	E_0 40°
Potassium molybdocyanide	Mo	1.1160	1.111
Potassium tungstocyanide	W	0.8450	0.833
Potassium ferrocyanide	Fe	.7965	.786
p-Hydroxydiphenylamine	A	.7030	..
2,4-Diaminodiphenylamine	B	.6090	..

the oxidation–reduction half-cell was measured against a hydrogen electrode immersed in some of the same solvent, and the value found when [Oxid.] = [Red.] is that reported as the normal potential. In the case of potassium tungstocyanide, a solution of 0.0006 *M* of the salt in 20 cc. of water was added to 200 cc. of the buffer solution and titrated with potassium molybdicyanide, while 0.0003 *M* of each of the organic compounds was dissolved in 220 cc. of the solution and titrated with the same reagent. The potential of the molybdicyanide–molybdocyanide solution was determined by titration of the oxidant with ferrocyanide solution and correcting the titration curve for a small amount of the reductant which was invariably present.

The molybdenum system reaches a constant potential with great rapidity while such constancy is reached relatively slowly in the case of *p*-hydroxydiphenylamine and, when the proportion of the reductant is small, with the complex cyanides of iron. Solutions of 2,4-diaminodiphenylamine should be protected from the air, for the rate of oxidation is sufficient to cause trouble.

The potentials recorded in the table are all subject to a slight inaccuracy owing to the fact that it was necessary to prepare the 0.03 *M* complex cyanide solutions either with water (Mo, W) or with a mixture of water and buffer solution (Fe), rather than with the latter solution alone.

In performing the oxidation tests the solutions were prepared in exactly the same manner, and with the same amounts and concentrations, as in these determinations of the normal potentials, but the titration was discontinued when the desired potential had been reached. The relationship between the potential of the system and the ratio of oxidant to reductant is conveniently expressed in the form of a large graph showing the potential plotted against Equivalents of oxidant $\times 10^5$. When completely oxidized, each solution contains 6×10^{-4} equivalent of the oxidant, and the curves may be constructed from the normal potentials given and the theoretical equations. Having titrated a solution to the potential desired, the number of equivalents of oxidant present was found by reference to the chart and the equivalent amount of the substance to be studied was dissolved in 30 cc. of the buffer solution. While releasing the stop watch, this solution was poured through a funnel into the oxidation–reduction vessel (three seconds required for the addition) and the potential was recorded after one minute and after five minutes. When a progressive drop in potential occurred, the extent of the reaction after five minutes was determined from the potential at that time and the chart.

It was usually necessary to apply a correction to the potentials actually noted after adding the sample under investigation. In most cases it was observed that at potentials well below that at which oxidation quite evidently occurred, the potential dropped almost immediately about 1 mv. and then remained constant indefinitely. Such a drop in potential can hardly be indicative of an oxidation, for such a reaction is not instantaneous and proceeds at a regular rate. As will be shown later, the potential is decreased to a certain extent as the result of diluting the solution of the reference system by the addition of the sample, but this does not account for the entire effect. It is probable that a further factor is the change in the activities of the oxidant and reductant produced by the organic material added. A correction for the effect was applied in the following manner. With each substance studied experiments were carried out at such a potential that this small change in potential during the first minute to a constant value could be observed, that is, at a potential 5–10 mv. below that fixed for E_c. This change in potential was then subtracted from the initial potential of the solution in each of the other experiments with the compound in question, for the same drop, which is not due to oxidation, must occur in each case. In calculating the percentage oxidation these corrected potentials were employed. The correction was greatest with the molybdenum system, amounting usually to about 2 mv., and it was scarcely perceptible with the organic systems.

The Use of Various Reference Systems and the Effect of Changing the Concentrations.—The procedure may be illustrated by quoting in full the measurements with α-naphthol at 25°. In Series I, Table XI, the first two experiments show that the potential of the ferri–ferrocyanide system falls 1 mv. on adding one equivalent of α-naphthol and then remains constant. In the next experiment the potential might be expected to fall 1 mv. whether or not a reaction occurs; the corrected initial potential is thus 0.7985 v. But the potential falls progressively, hence a reaction occurs at this potential level. From the corrected initial potential and the potential at the five-minute interval it was calculated that 1.5% of α-naphthol was oxidized during this period of time. On plotting the corrected initial potentials against the percentage oxidation for the entire series, a value of 0.796 v. was found for the critical oxidation potential. It should be noted that the second and third experiments fix this value as between 0.7930 v. and 0.7990 v. and that the remaining experiments serve merely to give a means of interpolating accurately be-

Table XI

Determination of the Critical Oxidation Potential of α-Naphthol (25°)

	Potential of reference system, v.				
	Initial	Initial (corr.)	1 Min.	5 Min.	% oxidation
	0.7864	0.7854	0.7854	0.7854	0.0
	.7940	.7930	.7930	.7930	.0
Series I	.8000	.7990	.7990	.7980	1.6
System: Fe	.8113	.8103	.8100	.8070	4.7
	.8210	.8200	.8185	.8120	9.9
	.8321	.8311	.8260	.8150	15.0
	E_c = 0.796 v.				
Series II. Duplicate of I.	E_c = 0.796 v				
	0.7915	0.7905	0.7905	0.7905	0.0
	.8052	.8042	.8041	.8037	2.8
Series III	.8132	.8122	.8115	.8105	5.2
System: W	.8214	.8204	.8198	.8167	10.8
	.8273	.8263	.8236	.8200	16.8
	.8306	.8296	.8283	.8222	18.2
	E_c = 0.798 v.				
Series IV	0.7913	0.7913	0.7913	0.7913	0.0
System: Fe	.8057	.8057	.8053	.8040	2.3
	.8156	.8156	.8147	.8113	5.8
Using one-half the usual quantities of oxidant and of α-naphthol	.8192	.8192	.8178	.8116	9.4
	.8233	.8233	.8218	.8143	10.2
	.8328	.8328	.8295	.8174	13.2
	.8515	.8515	.8330	.8160	23.3
	E_c = 0.799 v.				

tween these figures. The second series of experiments is that referred to in the first part of this paper. In connection with Series III it may be pointed out that the normal potential of the tungsten system differs considerably from that of iron, which means that the amount of oxidant present at a given potential was less than half that used in Series I. In spite of this difference, the percentage oxidation at a given potential was only slightly greater and very nearly the same result was obtained for E_c. Series IV shows that halving the concentrations of both the oxidant and the α-naphthol does not materially alter the value for E_c or the percentage oxidation at a given potential.

In deciding upon a time interval at which to compose the extent of oxidation at different potentials it was felt that, aside from the theoretical considerations which have been mentioned earlier, this interval should be fairly short in order to avoid secondary oxidations and in order that the potential of the reference system should not fall so far as to diminish greatly the initial driving force of the reaction. Comparison of the results for the one-minute and the five-minute intervals showed that the latter were much more consistent and regular, and this period of time was thus adopted for all of the experiments at 25°.

The Effect of Varying the Ratio of Oxidant to Substance Oxidized.—In each of the experiments just described the amount of α-naphthol taken was that equivalent to the oxidant of the reference system. Since there is no theoretical reason for preferring this particular ratio, experiments were undertaken to determine the effect of varying the ratio indicated. Table XII summarizes the critical oxidation potentials found for six compounds under different conditions of concentration. Each figure represents the results of extrapolating a curve constructed from the results of five or six experiments similar to those described above. The total amount of the reference system was kept the same (0.0006 mole), and the amount of the sample was varied in each series in the proportions shown in the Table. Though the results are not recorded in detail, it may be said that it was invariably found that as the proportion of the sample to the oxidant was increased, the percentage oxidation at a given potential above the critical potential became progressively less. That is, a greater percentage of the sample was oxidized in five minutes when the total amount of substance was small than when a large excess was present.

TABLE XII

CRITICAL OXIDATION POTENTIALS (25°)

Compound	Reference system	E_c (v.) when equiv. ratio of oxidant to sample was 1:05	1:1	1:2	1:3	1:4
Aniline	Mo	1.137	1.135	1.121	1.116	...
p-Toluidine	Mo	1.080	1.077	1.063	1.059	...
p-Cresol	Mo	...	1.038	1.023	...	1.021
β-Naphthol	Mo	...	1.016	1.006	...	...
Aesculetin	Fe	...	0.766	0.759	...	...
Catechol	Fe	...	.754	.742	0.739	...

The results show that E_c decreases as the relative amount of phenol or amine is increased. This is in accord with the prediction from the electrode potential equation. The greatest difference seems to occur between the results for the 1:1 and the 1:2 ratios, though the difference appears to be fairly constant (av., 12 mv.) for all six compounds and to be independent of the nature or the potential of the reference system. The results in themselves furnish no basis for preferring any particular set of conditions for carrying out a large number of determinations, and considerations of a practical nature governed the choice. Several of the compounds which it seemed desirable to study are so sparingly soluble in the buffer solution employed that it would not be possible to adopt the concentrations called for by the higher ratios. Thus in all subsequent evaluations of critical potentials the 1:1 ratio was adopted.

General Application of the Method.—On the basis of the orienting experiments which have been described, the following general procedure was adopted as being that most suitable for a wide survey of oxidizable substances. A solution of 0.0006 equivalent of the completely oxidized or reduced form of the reference system in 220 cc. of the alcoholic buffer solution (or in a mixture of 200 cc. of this solution and 20 cc. of water) was titrated to the potential desired with a suitable reagent. The substance to be studied in amount equivalent to the oxidant present, and dissolved in 30 cc. of buffer solution, was added, the percentage oxidation at five minutes was determined and the critical potential found in the usual way.

In studying ortho or para dihydroxy or diamino compounds, and substances of similar structure, it was assumed that the primary oxidation is of the 2-hydrogen type. Thus for each mole of a complex metal cyanide one-half mole was taken of catechol, pyrogallol, *p*-phenylenediamine, 1,5- and 2,6-dihydroxynaphthalene, *p*,*p'*-dihydroxystilbene, *p*-hydroxyphenylglycine and similar substances. The percentage oxidation in these cases was calculated on the basis of the assumption made.

A complete record of the experiments will not be given, but rather a summary of the significant results. In Table XIII, under the symbol E, there is given for each compound the initial potentials of the reference system, corrected for the drop observed when no progressive reaction occurred, and the corresponding percentages of oxidation observed in five minutes ("% Oxid."). The correction applied ("Corr.") and the critical oxidation potential, E_c, follow these figures. In the one or two cases in which it was not possible to determine the magnitude of the correction term, this was estimated from the behavior of similar compounds under similar conditions.

Though experiments quoted above indicate that about the same amount of α-naphthol is oxidized at a given potential by either potassium ferricyanide or potassium tungsticyanide, there is little assurance that this would be true in every case, and thus it was considered advisable to use a single reference system in determining the potential for each substance studied. The nature of the reference system employed is indicated in the heading of each small table, using the abbreviations listed in Table X.

The majority of the compounds studied are simple substances which are easily obtainable in a state of purity. Many of them, purchased from the firms of Kahlbaum, Schuchardt and Eastman, required no further purification. A few of the compounds have been described in recent publications of the author, others were supplied by the E. I. du Pont de Nemours & Company, while some were prepared according to known methods. In each case the sample was purified until it corresponded to the literature description of the pure material, and it does not appear necessary to record the physical constants. While the present method of determining oxidation potentials makes some use of the velocity of oxidation, it is very improbable that catalysts would appreciably influence the results. It is conceivable that one sample of a phenol might contain a catalyst which would accelerate the oxidation and that the slope of the percentage oxidation–potential curve would be different from that obtained with the pure compound, but the extrapolations to the point of zero oxidation should give very nearly the same results in each case.

TABLE XIII

CRITICAL OXIDATION POTENTIALS AT 25°

I. PHENOLS

Phenol

E, Mo, v.	% oxid.
1.0875	0.0
1.0935	4.5
1.0995	9.7
1.1098	14.6
1.1192	25.8
1.1375	42.0

Corr. = 1.5
E_c = 1.089 v.

o-Cresol

E, Mo, v.	% oxid.
1.0313	0.0
1.0420	2.7
1.0469	9.4
1.0541	14.5
1.0586	23.3

Corr. = 1.4
E_c = 1.040 v.

p-Cresol

E, Mo, v.	% oxid.
1.0293	0.0
1.0400	3.8
1.0465	11.3
1.0531	24.2
1.0593	38.6

Corr. = 2.0
E_c = 1.038

m-Cresol

E, Mo, v.	% oxid.
1.0765	0.0
1.0867	7.3
1.0927	13.5
1.0985	19.8
1.1083	32.8

Corr. = 1.5 mv.
E_c = 1.080 v.

2,4-Dimethylphenol

E, W, v.	% oxid.
0.8877	0.0
.9023	0.8
.9135	1.9
.9255	3.2

Corr. = 2.5 mv.
E_c = 0.895 v.

p-Hydroxyphenylacetic acid

E, Mo, v.	% oxid.
1.0467	0.0
1.0452	3.9
1.0570	7.2
1.0667	12.5
1.0707	20.6
1.0770	29.5

Corr. = 1.3 mv.
E_c = 1.051 v.

p-Hydroxydiphenylmethane

E, Mo, v.	% oxid.
1.0466	0.0
1.0537	2.4
1.0572	3.4
1.0620	11.2
1.0734	19.8

Corr. = 1.8 mv.
E_c = 1.052 v.

p,p'-Dihydroxydiphenylmethane

E, Mo, v.	% oxid.
1.0278	0.0
1.0414	3.3
1.0460	8.1
1.0534	14.6
1.0593	23.0
1.0673	47.5

Corr. = 2.2 mv.
E_c = 1.038 v.

Saligenin

E, Mo, v.	% oxid.
1.0512	0.0
1.0582	3.2
1.0660	5.0
1.0720	9.2
1.0812	10.8

Corr. = 1.5 mv.
E_c = 1.052 v.

o-Hydroxydiphenyl

E, Mo, v.	% oxid.
1.0256	0.0
1.0378	1.7
1.0426	3.8
1.0478	4.9

p-Hydroxydiphenyl

E, Mo, v.	% oxid.
1.0214	0.0
1.0368	4.0
1.0415	6.1
1.0470	12.5

Guaiacol

E, Fe, v.	% oxid.
0.8588	0.0
.8684	.1
.8748	.2
.8780	.5

TABLE XIII (*Continued*)

E, Mo, v.	% oxid.
1.0556	15.2
1.0660	34.0

Corr. = 1.9 mv.
E_c = 1.038 v.

E, Mo, v.	% oxid.
1.0520	23.5
1.0570	37.9

Corr. = 2.0 mv.
E_c = 1.036 v.

E, Fe, v.	% oxid.
.8848	.9

Corr. = 1.2 mv.
E_c = 0.868 v.

Hydroquinone monomethyl ether

E, Fe, v.	% oxid.
0.8400	0.0
.8507	.4
.8561	.7
.8630	1.5
.8738	2.6

Corr. = 1.7 mv.
E_c = 0.848 v.

Resorcinolmonomethyl ether

E, Mo, v.	% oxid.
1.0380	0.0
1.0555	1.5
1.0593	4.8
1.0622	6.6
1.0695	9.5
1.0787	11.8

Corr. = 2.0 mv.
E_c = 1.052 v.

Pyrogallol dimethyl ether

E, Fe, v.	% oxid.
0.7510	0.0
.7643	5.1
.7765	16.2
.7883	27.1
.7780	38.0

Corr. = 1.2 mv.
E_c = 0.760 v.

p-Hydroxydiphenyl ether

E, Mo, v.	% oxid.
1.0040	2.0
1.0108	10.0
1.0143	11.1
1.0185	23.6
1.0258	29.4
1.0363	46.4

Corr. = 1.7 v.
E_c = 1.030 v.

Cresol

E, Fe, v.	% oxid.
0.8198	0.0
.8311	.9
.8398	2.2
.8501	3.7
.8598	5.1

Corr. = 1.2 mv.
E_c = 0.825 v.

Eugenol

E, Fe, v.	% oxid.
0.7905	0.0
.8343	.4
.8398	1.0
.8485	2.3(5)
.8585	3.6
.8698	5.3
.8863	7.0

Corr. = 0.7 mv.
E_c = .831 v.

Isoeugenol

E, Fe, v.	% oxid.
0.7535	0.0
.7600	5.7
.7700	13.8
.7790	25.1
.7900	34.6

Corr. = 0.5 mv.
E_c = .757 v.

m-Aminophenol

E, W, v.	% oxid.
0.8917	0.0
.9037	.5
.9142	.8
.9245	1.1

Corr. = 2.3 mv.
E_c = 0.894 v.

p-Dimethylaminophenol

E, A, v.	% oxid.
0.7123	0.0
.7230	1.7
.7273	6.0
.7310	7.1
.7400	8.9

Corr. = 3.5 mv.
E_c = 0.718 v.

2,4,6-Trichlorophenol

E, Mo, v.	% oxid.
1.1000	0.0
1.1103	6.9
1.1191	9.5
1.1293	20.9
1.1390	30.2

Corr. = 1.7 mv.
E_c = 1.103 v.

Vanillin

E, Mo, v.	% oxid.
1.0778	0.0
1.0878	12.7
1.0985	32.7
1.1071	48.8
1.1247	65.5

Corr. = 2.2 mv.
E_c = 1.080 v.

Catechol

E, Fe, v.	% oxid.
0.7277	0.0
.7454	2.7
.7554	9.2
.7654	16.2
.7754	24.6

Corr. = 0.6 mv.
E_c = .742 v.

TABLE XIII (*Continued*)

Resorcinol

E, Mo, v.	% oxid.
1.0160	0.0
1.0460	2.8
1.0471	4.0
1.0515	8.8
1.0565	12.9
1.0659	28.8
1.0790	46.6

Corr. = 2.0 mv.
E_c = 1.043 v.

Nitro-hydroquinone

E, A, v.	% oxid.
0.6935	0.0
.7020	5.2
.7110	10.1
.7222	12.4
.7297	19.7
.7380	22.0

Corr. = 0.0
E_c = .697 v.

Aesculetin

E, Fe, v.	% oxid.
0.7554	0.0
.7622	3.2
.7698	6.1
.7797	12.6
.7940	26.7

Corr. = 0.3 mv.
E_c = .759 v.

Phloroglucinol

E, Fe, v.	% oxid.
0.7980	0.0
.8207	2.5
.8330	3.5
.8520	4.6
.8624	5.5
.8745	7.0

Corr. = 1.0 mv.
E_c = 0.799 v.

Pyrogallol

E, B, v.	% oxid.
0.6052	0.0
.6132	3.1
.6188	6.8
.6235	12.9
.6313	16.6

Corr. = 0.0 mv.
E_c = .609 v.

II. NAPHTHOLS

β-Naphthol

E, Mo, v.	% oxid.
0.9935	0.0
1.0167	1.4
1.0208	3.5
1.0240	5.4
1.0275	11.4
1.0370	18.5

Corr. = 1.5 mv.
E_c = 1.017 v.

2-Nitro-1-naphthol

E, Mo, v.	% oxid.
1.1285	0.0
1.1442	2.6
1.1505	7.4
1.1597	17.0
1.1708	23.2

Corr. = 1.8 mv.
E_c = 1.141 v.

1-Naphthol-2-carboxylic acid

E, Mo, v.	% oxid.
1.0570	0.0
1.0692	5.5
1.0728	8.0
1.0820	19.6
1.0917	27.0

Corr. = 2.0 mv.
E_c = 1.065 v.

Sodium 1-naphthol-2-sulfonate

E, W, v.	% oxid.
0.8765	0.0
.8875	0.7
.8933	1.3
.9017	2.2
.9113	3.4

Corr. = 2.5 mv.
E_c = 0.881 v.

5-Methoxy-1-naphthol

E, Fe, v.	% oxid.
0.7800	0.0
.7960	1.5
.7990	2.9
.8070	6.7
.8118	9.1
.8142	11.0

Corr. = 1.0 mv.
E_c = 0.792 v.

1,3-Dihydroxynaphthalene

E, Fe, v.	% oxid.
0.7480	0.0
.7592	5.4
.7692	12.7
.7790	23.3
.7980	38.4

Corr. = 1.0 mv.
E_c = 0.754 v.

1,5-Dihydroxynaphthalene

E, A, v.	% oxid.
0.6650	0.0
.6763	4.5
.6835	14.1
.6876	22.6
.6955	34.4
.7030	46.3

Corr. 0.0
E_c = 0.673 v.

2,3-Dihydroxynaphthalene

E, Fe, v.	% oxid.
0.7965	0.0
.8140	.7

2,6-Dihydroxynaphthalene

E, A, v.	% oxid.
0.6860	0.0
.6950	5.7

2,7-Dihydroxynaphthalene

E, Mo, v.	% oxid.
1.0065	6.1
1.0145	7.0

TABLE XIII (*Continued*)

E, Fe, v.	% oxid.	*E*, A, v.	% oxid.	*E*, Mo, v.	% oxid.
.8240	3.7	.7040	14.8	1.0202	13.4
.8343	5.5	.7120	21.0	1.0249	23.9
.8438	8.1	.719	30.0	1.0302	30.7
.8558	11.2				
.8690	13.7				
.8787	15.3				
Corr. = 0.9 mv.		Corr. = 0.0		Corr. = 1.5 mv.	
E_c = .812 v.		E_c = .690 v.		E_c = 1.007 v.	

III. ANTHROLS

Anthranol (anthrone)		α-Anthrol		β-Anthrol	
E, A, v.	% oxid.	*E*, B, v.	% oxid.	*E*, Fe, v.	% oxid.
0.6878	0.0	0.6036	2.5	0.8143	0.0
.6982	10.5	.6098	9.1	.8240	3.2
.7058	26.8	.6145	15.2	.8316	4.8
.7085	41.0	.6220	18.8	.8365	7.2
		.6255	22.4	.8472	14.4
Corr. = 0.0		Corr. = 0.0		Corr. = 1.0 mv.	
E_c = .693 v.		E_c = .602 v.		E_c = 0.820 v.	

IV. PHENANTHROLS

1-Phenanthrol		2-Phenanthrol		3-Phenanthrol	
E, Fe, v.	% oxid.	*E*, Mo, v.	% oxid.	*E*, Mo, v.	% oxid.
0.8438	0.0	1.0494	0.0	1.0145	3.6
.8563	.9	1.0584	1.7	1.0195	8.0
.8675	1.8	1.0659	8.6	1.0250	21.2
.8896	4.1	1.0612	10.2	1.0310	23.4
		1.0707	10.5		
		1.0769	29.6		
Corr. = 0.9 mv.		Corr. = 2.3 mv.		Corr. = 2.0 mv.	
E_c = .848 v.		E_c = 1.057 v.		E_c = 1.013 v.	

9-Phenanthrol		2,6-Dihydroxyphenanthrene		3,6-Dihydroxyphenanthrene	
E, Fe, v.	% oxid.	*E*, Mo, v.	% oxid.	*E*, Fe, v.	% oxid.
0.7945	0.0	1.0000	0.0	0.8224	0.0
.8026	2.0	1.0123	6.3	.8321	.4
.8101	2.6	1.0178	9.7	.8412	2.7
.8196	6.3	1.0247	22.4	.8521	5.0
.8265	7.4	1.0315	34.7	.8654	8.1
.8331	10.9				
Corr. = 0.7 mv.		Corr. = 2.0 mv.		Corr. = 1.3 mv.	
E_c = .798 v.		E_c = 1.010 v.		E_c = 0.832 v.	

V. OTHER HYDROXY COMPOUNDS

p,p'-Dihydroxydiphenyl		*p,p'*-Dihydroxystilbene		Dioxindole	
E, W, v.	% oxid.	*E*, Fe, v.	% oxid.	*E*, Fe, v.	% oxid.
0.8778	0.0	0.7712	0.0	0.7330	0.0
.8921	1.6	.7940	5.4	.7465	.6
.9069	2.7	.7987	6.0	.7566	2.7

TABLE XIII (*Continued*)

E, W, v.	% oxid.
.9221	3.7

Corr. = 2.4 mv.
E_c = 0.882 v.

E, Fe, v.	% oxid.
.8103	13.9
.8223	21.2
.8355	25.4

Corr. = 1.0 mv.
E_c = 0.786 v.

E, Fe, v.	% oxid.
.7695	6.5
.7773	8.0

Corr. = 2.0 mv.
E_c = 0.745 v.

VI. AMINES

Aniline

E, Mo, v.	% oxid.
1.1282	0.0
1.1387	2.3
1.1472	3.6
1.1525	5.3
1.1650	11.5

Corr. = 1.8 mv.
E_c = 1.135 v.

N-Methylaniline

E, Mo, v.	% oxid.
1.0430	0.0
1.0578	3.0
1.0627	7.0
1.0680	11.4
1.0778	25.0

Corr. = 2.0 mv.
E_c = 1.053 v.

N-Ethylaniline

E, Mo, v.	% oxid.
1.0366	0.0
1.0431	2.3
1.0484	4.0
1.0576	5.6
1.0678	7.2
1.0784	16.5

Corr. = 1.6 mv.
E_c = 1.038 v.

N-Benzylaniline

E, Mo, v.	% oxid.
1.0520	0.0
1.0556	1.4
1.0646	4.3
1.0708	5.4
1.0759	6.3
1.0831	8.4
1.0886	15.2

Corr. = 1.4 mv.
E_c = 1.057 v.

Diphenylamine

E, Mo, v.	% oxid.
1.0042	0.0
1.0116	3.3
1.0170	8.7
1.0189	11.3
1.0246	15.7
1.0294	20.0
1.0492	45.2

Corr. = 1.8 mv.
E_c = 1.008 v.

p,p'-Diethoxydiphenylamine

E, Fe, v.	% oxid.
0.8284	0.0
.8396	.5
.8533	3.7
.8645	5.7
.8770	8.0
.8906	10.6

Corr. = 0.9 mv.
E_c = .836 v.

p-Toluidine

E, Mo, v.	% oxid.
1.0636	0.0
1.0785	3.3
1.0903	12.5
1.0986	23.1
1.1083	33.8
1.1148	41.3

Corr. = 1.7 mv.
E_c = 1.077 v.

p-Anisidine

E, W, v.	% oxid.
0.8898	0.0
.9001	.5
.9098	.8
.9308	1.5

Corr. = 2.4 mv.
E_c = 0.892 v.

m-Toluylenediamine

E, Fe, v.	% oxid.
0.8580	0.0
.8685	.3
.8772	.6
.8872	1.5

Corr. = 2.0 mv.
E_c = 0.864 v.

Benzalphenylhydrazine

E, Fe, v.	% oxid.
0.7883	0.0
.7938	1.4
.7981	5.6
.8083	9.6
.8211	13.0

Corr. = 1.7 mv.
E_c = 0.791 v.

Diazoaminobenzene

E, Mo, v.	% oxid.
1.0562	0.0
1.0642	8.1
1.0682	12.0
1.0772	21.6
1.0924	43.2

Corr. = 1.3 mv.
E_c = 1.058 v.

Phenylglycine

E, Fe, v.	% oxid.
0.7976	0.0
.8350	.7
.8452	2.1
.8557	3.3
.8645	3.9
.8867	5.5

Corr. = 0.0
E_c = .833 v.

β-Naphthylamine

E, Mo, v.	% oxid.
1.0552	0.0
1.0696	8.7
1.0794	17.2
1.0889	31.6
1.0962	45.0

Corr. = 1.8 mv.
E_c = 1.064 v.

TABLE XIII (*Concluded*)

VII. AMINOPHENOLS AND PHENYLENEDIAMINES (ORTHO AND PARA)

p-Aminophenol		*p*-Phenylenediamine		*p*-Amino-diphenylamine		*p*-Hydr phenylg
E, A, v.	% oxid.	*E*, A, v.	% oxid.	*E*, A, v.	% oxid.	*E*, B, v.
0.6687	0.0	0.7093	0.0	0.6950	0.0	0.6000
.6765	4.5	.7113	3.8	.7010	1.8	.6060
.6818	5.3	.7150	5.0	.7075	3.2	.6107
.6920	11.7	.7220	8.3	.7115	8.7	.6155
.7070	14.6	.7308	12.2	.7205	9.8	.6255
.7395	28.8	.7428	13.2	.7330	11.3	
Corr. = 0.0		Corr. = 0.7 mv.		Corr. = 0.0		Corr. = 1.
E_c = .673 v.		E_c = .710		E_c = .696 v.		E_c = 0.

VIII. THIOPHENOLS AND MERCAPTANS

n-Propyl mercaptan		Isopropyl mercaptan		Mercapto-benzothiazo	
E, Fe, v.	% oxid.	*E*, Fe, v.	% oxid.	*E*, Fe, v.	% oxid
0.8125	0.0	0.8197	0.0	0.7839	0.0
.8190	.9	.8299	1.2	.7928	3.2
.8250	1.9	.8431	1.5	.8105	5.0
.8335	2.0	.8528	1.6	.8200	5.7
.8430	3.7	.8672	1.9	.8335	5.3
.8525				.8487	6.0
1.0900 (Mo)	49.0				
Corr. = 1.0 mv.		Corr. = 0.6 mv.		Corr. = 0.5 mv.	
E_c = 0.812 v.		E_c = .819 v.		E_c = .785 v.	

While no special effort was made to exclude all traces of catalyt active impurities, it was absolutely essential to free the sample of easily oxidizable substances. Thus preliminary experiments with mercial samples of the monomethyl ethers of the dihydroxyben gave irregular results which were very probably due to the presence small amount of unmethylated material. When this was removed extracting the ethereal solution of the substance with water, and distilling and crystallizing the product, no irregularity was noted.

Measurements at 40°.—At the beginning of this research we hope provide for the study of even very sparingly soluble substances, and this end in view the early procedure called for a relatively small vo (100 cc.) of buffer solution as solvent for the reference system (in 20 while the sample was dissolved in 130 cc. of the buffer.

A temperature of 40° was chosen in order to further increase the am of material which could be accommodated. It was observed, how that the potential of the molybdenum system often dropped as muc 15 mv. even when no progressive reaction occurred, and blank determ tions soon showed that the drop in potential is largely the result of tion. The potential of the molybdenum system was found to be less positive by about 12 mv. when the volume was increased from cc. to 250 cc., and the change was independent of the ratio of oxidant to reductant. Since the ratio of the concentrations of the two components of the system is not influenced by dilution, the observed change in potential must be the result of a change in the ratio of their activities, and the direction of the effect is such as to indicate that the activity coefficient of the reductant increases more rapidly with dilution than that of the oxidant. The same was true of the ferri–ferrocyanide system, though the effect was less pronounced. The decrease in potential on dilution ranged from 1.5 mv. to 7.5 mv. as the ratio of oxidant to reductant varied from $^1/_9$ to 9.

When determinations of critical oxidation potentials were carried out it was found that the rapid decrease in potential to a constant value, which was observed at a region well below that at which a progressive reaction occurred, was always somewhat greater than that attributable solely to dilution. The components of the system thus appear to be affected by the oxidizable substance even when no oxidation occurs. While no means of eliminating this effect was found, the effect of dilution was reduced to a minimum in the determinations which have been described above. The original procedure was thus soon abandoned, for the large correction term which had to be applied to the initial potentials rendered the results subject to an unnecessary source of error. The few determinations which had been made before the method was modified have been summarized in Table IV of the Theoretical Part.

It should be stated that when working at 40° the velocity of oxidation is much greater than at the lower temperature. Consequently the time interval over which the fall in potential of the reference system was observed was made shorter, namely one minute instead of five minutes. The reference systems used were those of iron, molybdenum and tungsten, and their potentials at 40° are recorded in Table X.

Normal Oxidation–Reduction Potentials of Stable Systems.—In the course of this survey of oxidizable substances a constant watch was kept for electromotively active oxidation–reduction systems of sufficient stability to permit direct potentiometric study. Such a system may reveal itself in the determination of the critical oxidation potential by causing a very rapid drop in potential to a constant value. A few such cases were discovered, and it was found that the reductant could be titrated in the ordinary way with molybdicyanide. Sharp, reproducible potentials were established in the mixtures of the oxidant and reductant and there was no drift in potential which would indicate a destruction of the oxidant. A summary of the results for this group of substances is given in Table XIV, and two more compounds of this type have been listed in Table X. The figures represent the averages of several closely agreeing determinations. The solutions of the amines (0.0003 mole in 220 cc.)

TABLE XIV

NORMAL POTENTIALS (25°) IN NEUTRAL ALCOHOLIC SOLUTION

System, named as reductant	E_0, v.
p-Aminodiphenylamine	0.751
Hydroquinone	.715
p-Hydroxyphenyl-β-naphthylamine	.701
p-Methyl-*p*′-hydroxydiphenylamine	.684
p,*p*′-Dihydroxy-diphenylamine	.656
2,4-Diamino-4′-hydroxydiphenylamine	.568
β-Phenylhydroxylamine	.562

were prepared from freshly crystallized or distilled material and kept in an atmosphere of nitrogen. In the case of *p*-methyl-*p*′-hydroxydiphenylamine it was necessary to reduce catalytically a small amount of the oxidant which was found to be present.

The potential of the quinone–hydroquinone system was determined by the use of quinhydrone. The potential of such a solution is initially 5–10 mv. above the normal potential. Within one to two minutes it falls to a point where it remains constant for about six minutes, and then it falls off at the rate of about seven mv. per hour. The reading during the period of constancy is reproducible on various electrodes and with different preparations, and this point was taken as the normal potential. On titration of hydroquinone with potassium molybdicyanide, the electrode equilibrium is established slowly and the results are not satisfactory.

β-Phenylhydroxylamine behaved in a very curious manner. The potential of a fresh solution was about 20 mv. higher than the normal potential of the nitrosobenzene-β-phenylhydroxylamine system, whereas one would expect the solution containing none of the oxidant to have a potential considerably below the point of half-oxidation. The initial potential was not constant, but fell off fairly rapidly as the solution was stirred and treated with a steady stream of nitrogen, and in about an hour a fairly constant level had been reached which was 47 mv. below the normal potential. A titration commenced after this or a longer period of time gave perfectly normal results, though electrode equilibrium was somewhat slow. After each addition of molybdicyanide the potential reached a constant value (from below) only after about three minutes. On the other hand, when the titration was commenced ten minutes after preparing the solution, that is, before the low, constant level had been reached; the same amount of oxidizing agent was consumed, but the curve was flat, as though some oxidant were present at the outset, and the value found for E_0 was about 10 mv. too high.

Summary

The unstable systems formed by phenols or amines and the free radicals formed as their immediate oxidation products have been characterized

by a new term called the critical oxidation potential. This is the potential of some oxidizing solution which will cause a certain small amount of the amine or phenol to become oxidized in five minutes when equivalent amounts of the sample and of the oxidizing agent are employed. This value, which may be determined with reasonable accuracy, represents the potential at which the velocity of oxidation becomes vanishingly small, and hence the result is influenced by the reaction rate to an extent which is insignificant. This has been demonstrated experimentally, for the critical oxidation potential bears a definite relationship to the normal potential, and it is influenced no more by temperature changes than is the latter quantity.

The critical oxidation potentials of over seventy compounds have been determined and many relationships, conclusions and deductions have been pointed out in discussing the results.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

SOME ERRORS IN ANALYTICAL BROMINATION. THERMAL CLEAVAGE OF HYDROGEN BROMIDE FROM BROMINATED SUBSTANCES. A NEW PROCEDURE FOR DETERMINATION OF ORGANIC UNSATURATION[1]

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RECEIVED AUGUST 20, 1930 PUBLISHED DECEMBER 18, 1930

I. Introduction

Halogenation methods for the determination of organic unsaturation are in general referable to three types, based upon the nature of the agent and the medium: (1) iodine–halide methods, such as those of Hübl, Wijs and Hanus, conducted in non-aqueous solvents;[2] (2) bromination in non-aqueous solvent, especially carbon tetrachloride, the best-known method being that of Schweitzer–Lungwitz–McIlhiney;[3] (3) the bromide–bromate method, conducted in the presence of water, and due to Koppeschaar.[4]

[1] Thesis presented by Howard M. Buckwalter to the Graduate School of the University of Pennsylvania in partial satisfaction of the requirements for the degree of Doctor of Philosophy.

[2] Hübl, *Dingler's Polytech. J.*, **253**, 281 (1884); *J. Soc. Chem. Ind.*, **3**, 641 (1884); Ingle, *ibid.*, **21**, 587 (1902); **23**, 422 (1904); Wijs, *Ber.*, **31**, 750 (1898); Marshall, *J. Soc. Chem. Ind.*, **19**, 213 (1900); Kemp, *Ind. Eng. Chem.*, **19**, 531 (1927); Hanus, *Z. Nahr. Genussm.*, **4**, 913 (1901).

[3] Schweitzer and Lungwitz, *J. Soc. Chem. Ind.*, **14**, 130 (1895); McIlhiney, THIS JOURNAL, **16**, 275 (1894); **21**, 1084 (1899); **24**, 1103 (1902).

[4] Koppeschaar, *Z. anal. Chem.*, **15**, 233 (1876).