[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE IRREVERSIBLE OXIDATION OF ORGANIC COMPOUNDS

I. THE OXIDATION OF AMINOPHENOLS BY REAGENTS OF DEFINITE POTENTIAL

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RECEIVED SEPTEMBER 23, 1926 PUBLISHED DECEMBER 16, 1926

This is the first of a series of papers dealing with the oxidation of organic compounds in solution by means of soluble oxidizing agents. The object of this study is to discover to what extent such oxidations may be formulated in electrochemical terms. In the last few years a number of investigations have shown that certain types of organic oxidations are strictly reversible and definite oxidation-reduction potentials may be measured.[1] In such cases both the oxidation and reduction reactions are very rapid in solution and therefore an equilibrium is soon established when the reduced form (for example, hydroquinol) is treated with a reversible oxidizing agent or the oxidized form is treated with a reversible reducing agent. The analytical composition of such an equilibrium is readily calculated from the normal potentials of the organic system (for example, quinone + hydroquinol) and that of the oxidizing or reducing agent. The potentials of the organic systems may be measured electrochemically or calculated from the equilibria which result when the components are treated with reagents of known potential.

This precise and convenient treatment of oxidations can be employed *only* if the system is strictly reversible under the experimental conditions Unfortunately, many of the oxidation reactions of organic chemistry are not strictly reversible—no equilibrium is established when the reduced form is treated with reversible oxidizing agents. Can such reactions be studied profitably from the electrochemical standpoint? We are in these instances concerned with rates but if the rate bears some regular relation to the potential of the oxidizing agent an approximate but convenient electrochemical formulation becomes possible. One can determine what reagent will oxidize the compound at a definite rate under certain conditions and if the electrochemical point of view is applicable, all reagents of higher potential should oxidize the compound more rapidly and those of lower potential less rapidly or not at all. A similar method of formulating cases of irreversible reduction has been used with some success in connection with a number of reduction reactions in organic chemistry.[2]

The aminonaphthols (1,2 and 1,4) are rapidly and almost quantitatively oxidized in aqueous acidic solutions to the corresponding quinones by such reagents as ferric chloride. The process is irreversible. We have studied the rate of these oxidations with eleven different reversible oxidizing agents

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[1] For a recent review of such work, see Clark, *Chem. Reviews*, **2**, 127 (1925).

[2] (a) THIS JOURNAL, **48**, 2468 (1926); (b) *Chem. Reviews*, **3**, 1 (1926).

by an electrochemical device which amounts to measuring the rate of reduction of the reagent by the organic compound. We have also included the 1,2- and 1,4-aminophenols in our study although the product in the case of the first compound is probably not the quinone but some more complicated compound of uncertain composition. The results are given in Tables I–IV.

The experimental method consisted of dropping a weighed sample of the hydrochloride of the aminonaphthol or aminophenol into an electrochemical cell containing a rapidly stirred mixture of equimolar amounts of the oxidizing agent and its reduced form in dilute solution of known acidity (in most cases 0.2 N hydrochloric acid). This mixture of oxidizing agent and its reduced form was prepared either by weighing the requisite amounts of the two forms or by titrating the oxidized form with half the amount of titanous chloride required for reduction. The electrochemical cells were identical with those previously used in our studies on irreversible reduction and need not be again described. Two platinum electrodes (one bright and one platinized or gold-plated) dipped into the cell, and their potentials against a saturated calomel electrode were determined at definite intervals of time after the solid compound had been introduced. In the case of those reagents which were sensitive to oxygen, the cells were kept filled with nitrogen.

If the compound under investigation is oxidized during the experiment, the composition of the reversible system in the cell is changed by reason of the reduction of the oxidizing agent and the potential falls. The rate of fall of potential under such conditions is a function of the rate of the reduction of the oxidizing agent and thus a measure of the speed of the oxidations. The potential of the cell at 23° varies with the relative proportion of oxidized and reduced forms of the oxidizing agent according to Equation 1.

$$E\ (\text{obs. pot.}) = E_0' - \frac{0.06}{n} \log \frac{[\text{red. form of reagent}]}{[\text{oxidizing reagent}]} \qquad (1)$$

At the start of the oxidation the two forms are present in equimolar amounts and therefore Equation 2 relates the change of potential ΔE and the fraction (S) of reagent which has reacted. With quinones and other organic oxidizing systems $n = 2$; with most inorganic oxidizers $n = 1$.

$$\Delta E = \frac{0.06}{n} \log \frac{1 + S}{1 - S} \qquad (2)$$

The rate of the oxidation of the aminonaphthols and aminophenols appears to be essentially independent of the dilution, as shown by the results given in Table III. In these experiments and in all the others recorded in this paper (unless otherwise specified) the material to be oxidized was taken in such an amount that in each experiment there was one mole of it per oxidizing equivalent of the oxidized form of the reagent.

This large excess of the substance undergoing oxidation insured complete reduction of those oxidizing agents which acted rapidly. Since the speed of the reaction (the fraction oxidized in a given time) appears to be independent of the dilution, the usual constant for a monomolecular reaction may be calculated according to Equation 3 (t being the time in minutes).[3]

$$k = \frac{2.30}{t} \log \frac{1}{1 - S} \tag{3}$$

To illustrate our general method the actual change in potential with time is given in Table I for a series of reagents and the two aminonaphthols. Table II illustrates the calculation of S and of k. In the other tables in this paper and following papers we shall save space by giving only values of S, or in some cases only of k calculated from the potential change 5,

TABLE I

OXIDATION OF AMINONAPHTHOLS IN 0.2 N HCl AT 23° ± 2°

Oxidizing agent containing equimolar amount of reduced form	Pot. in 0.2 N HCl $(E_0')_B$	Change in potential (millivolts) on adding hydrochloride of aminonaphthol: 1,4-Aminonaphthol, 5 min.	15 min.	30 min.	1,2-Aminonaphthol, 5 min.	15 min.	30 min.
$K_3Mo(CN)_8$	+0.776	325	330	332	270	276	280
Ferric chloride	+ .726	250	270	280	220	225	228
1,4-Benzoquinone	+ .656	185	198	...	136	139	...
Pot. ferricyanide	+ .631	170	180	185	126	130	132
Toluquinone	+ .587	135	...	147	...	...	...
p-Xyloquinone	+ .549	70	88	95	38	41	43
1,2-Naphthoquinone	+ .506	17	36	50	7	11	14
2,6-Dimethoxyquinone	+ .471	3	7	12	0	0	0
1,4-Naphthoquinone	+ .426	0	0	0	0	0	0

The solutions were 0.002 molar in oxidized reagent and 0.002 molar in the reduced form of the reagent, when reagents of the ferricyanide type were employed. With quinones half this concentration was used. In each case 1 mole of substance was added per oxidizing equivalent present.

TABLE II

ILLUSTRATING THE METHOD OF CALCULATING THE RATE OF OXIDATION FROM THE OBSERVED CHANGE IN POTENTIAL

(Oxidation of 1,4-Aminonaphthol in 0.2 N HCl; see Table I)

A REAGENT = 2,6-DIMETHOXYQUINONE

$(E_0')_B = +0.471$

Time, min.	Change in potential, mv.	Fraction oxid. (Eq. 2)	$k \times 10^2$ (Eq. 3)
5	3	0.07	1.5
15	7	.26	1.7
30	12	.45	1.8

B REAGENT = 1,2-NAPHTHOQUINONE

$(E_0')_B = +0.506$

5	17	.55	17
15	36	.88	15
30	50	.96	18

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[3] The calculations can be rapidly performed if curves of Equation 2 (m = 1 and n = 2) are at hand and a nomogram of Equation 3 is constructed.

TABLE III

EFFECT OF DILUTION OF THE RATE OF OXIDATION OF 1,2-AMINONAPHTHOL AND 1,4-AMINOPHENOL

Reagent	Concn., moles per liter × 10^3	Substance	Concn., moles per liter × 10^3	Fraction oxidized in 5 min.	15 min.	30 min.
Ferric chloride	2	1,4-Aminophenol	2	0.36	0.46	0.54
Ferric chloride	20	1,4-Aminophenol	20	.56	.72	.78
1,2-Naphthoquinone	1	1,2-Aminonaphthol	2	.26	...	.50
1,2-Naphthoquinone	0.1	1,2-Aminonaphthol	0.2	.38	...	.62

In each experiment the reagent consisted of an equimolar mixture of the oxidized and reduced form (for example, ferric chloride and ferrous chloride).

TABLE IV

THE RATE OF OXIDATION OF AMINONAPHTHOLS AND AMINOPHENOLS IN 0.2 *N* HCl AT 23° ± 2°

Substance	Reagent (containing equimolar amounts of reduced form)	$(E_0')_B$ (P_H = 0.76)	$k \times 10^2$ (Eq. 3) calcd. from obs. change in potential at 5 min.	15 min.	30 min.	Av.
1,4-Aminonaphthol	2,6-Dimethoxyquinone	+0.471	1.5	1.7	1.8	1.7
	1,2-Naphthoquinone	+ .506	17	15	18	17
	p-Xyloquinone	+ .549	100	....	....	....
1,2-Aminonaphthol	1,2-Naphthoquinone	+ .506	5.5	3.3	2.2	3.7
	p-Xyloquinone	+ .549	50	17	9	25
1,4-Aminophenol	Pot. ferricyanide	+ .631	0.1	0.08	0.08	0.08
	1,4-Benzoquinone	+ .656	.5	.25	.25	.33
	2,6-Dichloroquinone	+ .681	2.0	1.8	1.6	1.8
	Ferric chloride	+ .726	10	4.1	2.7	6
1,2-Aminophenol	Pot. ferricyanide	+ .631	....	0.08	0.18	0.13
	1,4-Benzoquinone	+ .656	0.6	.8	1.0	.8
	2,6-Dichloroquinone	+ .681	4.2	3.9	3.0	3.7
	Ferric chloride	+ .726	2.0	1.3	2.0	1.7

In each experiment in which a quinone was the reagent 0.0002 mole of the solid hydrochloride of the aminophenol or aminonaphthol was dropped into 100 cc. of 0.2 *N* hydrochloric acid containing 0.0001 mole of the quinone and 0.0001 mole of the hydroquinone. In the experiments with ferricyanide and ferric chloride, 0.0002 mole of solid hydrochloride was used and the solution contained 0.0002 mole of ferric compound and 0.0002 mole of ferrous compound in 100 cc.

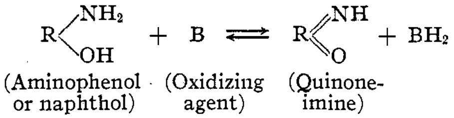
15 or 30 minutes after the reaction started. Many duplicate experiments convinced us that the results were reproducible within about 1 or 2 mv. for slight changes and within 3 or 4 mv. for larger changes. In terms of the fraction oxidized in a given time our results are probably significant within 20% over the range $S = 0.2$ to 0.95. No attempt was made to evaluate k for values of S larger than 0.95, and for very small values of S the results may be 50 or 100% in error since a 2 mv. change corresponds to about 7% oxidation with a quinone. The probable significance of the values for k can be judged from Table IV; in some instances the three values are in good agreement but in others the variations are so large that the average value must be regarded as only indicating the order of magnitude of the speed of the reaction.

The normal potential of the reagent (that is, the potential of an equimolar mixture of the oxidized and reduced forms) in the buffer solution and at the dilution employed will be designated as E_0' throughout this paper. These values were determined in this Laboratory and were in agreement with the values already published for these systems. All potentials are referred to the normal hydrogen electrode and the European convention in regard to sign has been employed (the chlorine electrode is regarded as positive).

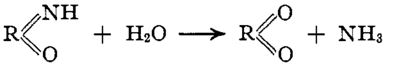
Our electrochemical method of following the course of the reaction assumes that there is no appreciable lag in the establishment of electrode equilibrium. From our experience with the electrochemical behavior of a variety of systems, we believe that this assumption is justified in the case of the reagents we have chosen. We have avoided the use of those reversible systems which only slowly establish definite potentials. This is an important point which must always be borne in mind in future extensions of our methods.

Tables I and IV show that on the whole the rate of oxidation of the aminonaphthols and aminophenols is a regular function of the potential of the oxidizing agent which is employed. It is evident that a great variety of organic and inorganic oxidizing agents show a surprising regularity in these reactions. Therefore, one can conclude that in these cases of irreversible oxidation the potential of the oxidizing agent is the predominant factor in determining the rate.

It has been pointed out in previous papers[2] that there is no reason to suppose that in general the rate of an irreversible process will be a function of the potential of the reagent. Indeed, we shall present instances in later papers of oxidation reactions in which specific properties of the reagent are more important than their potentials. However, in cases like those at hand, where the behavior of a reagent can be predicted from its potential, it seems probable that some reversible step controls the rate of the entire process,[4] and this reversible step is the same with all reagents. The following mechanism for the oxidation of aminophenols and naphthols provides such a reversible step.



$$\mathrm{R}{<}^{\mathrm{NH_2}}_{\mathrm{OH}} + \mathrm{B} \rightleftharpoons \mathrm{R}{\ll}^{\mathrm{NH}}_{\mathrm{O}} + \mathrm{BH_2} \qquad (4a)$$



$$\mathrm{R}{\ll}^{\mathrm{NH}}_{\mathrm{O}} + \mathrm{H_2O} \longrightarrow \mathrm{R}{\ll}^{\mathrm{O}}_{\mathrm{O}} + \mathrm{NH_3} \qquad (4b)$$

This hypothesis assumes that Reaction 4a is rapid and reversible and Reaction 4b is *relatively slow* and irreversible. It is also probable that other more complex products are formed, particularly with the aminophenols,

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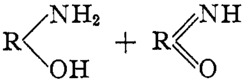
[4] Compare Ref. 2 b.

by the interaction of the quinone-imine and the amino compound. We cannot claim that with each reagent we are measuring the rate of formation of quinone but rather the rate of oxidation of the amino compound by the reagent. The amount of quinone-imine formed in Reaction 4a would control the rate of the entire irreversible change (4b) which would be a monomolecular reaction and independent of the dilution. The extent of Reaction 4a would be determined by the unknown potential of the reversible system  $R{<}^{NH_2}_{OH} + R{\ll}^{NH}_{O}$ and that of the oxidizing agent ($B + BH_2$). With a series of reagents B_1, B_2, etc., of increasing potential increasing amounts of quinone-imine would be formed and thus the rate of Reaction 4b would be increased. Wieland[5] has suggested that quinone-imine is an intermediate in the oxidation of aminophenol. We shall now present further evidence which seems to us to be very convincing at least insofar as the oxidation of 1,4-aminophenol is concerned.

The Reversible Oxidation of 1,4-Aminophenol to Quinone-imine

In solutions more alkaline than about *P*H 7, 1,4-benzoquinone-imine is sufficiently stable to enable one to obtain evidence as to the reversibility of the aminophenol—quinone-imine system. Even in these neutral and alkaline solutions, however, decomposition is so rapid that special precautions must be taken and the value of the oxidation-reduction potential cannot be determined accurately.

We have studied the system both by the titration method and by the method of mixtures. In solutions of *P*H 7.8–11.3 one can obtain a fairly satisfactory titration curve by adding increments of a powerful oxidizing agent rapidly to a dilute solution (0.002 *M*) of 1,4-aminophenol. The oxidizing agents we employed were potassium ferricyanide and potassium molybdicyanide. Such a titration curve at *P*H 9.7 is shown by the dotted line in Fig. 1; the end-point corresponded within 10% with the amount of oxidizing agent equivalent to the removal of two hydrogen atoms. We also prepared an ethereal solution of quinone-imine by Willstätter's procedure[6] (he was never able to obtain pure *solid* material) and added definite amounts of it and 1,4-aminophenol to the buffer solutions. The results of these experiments by the "method of mixtures" are shown by crosses in Fig. 1. It is evident that they fall on the curve within the limits of the experimental errors incident to the handling of such sensitive material. In Fig. 2 are shown the results of our attempts to evaluate E_0' at different Sörensen values (*P*H) both by the method of mixtures and in the alkaline range by a rapid titration (complete in a few minutes).

[5] Wieland, *Ber.*, **43,** 718 (1910).

[6] Willstätter, *Ber.*, **42,** 2166 (1909).

TABLE V

ILLUSTRATING THE DRIFT OF THE POTENTIALS OBSERVED WITH QUINONE-IMINE IN VARIOUS BUFFER SOLUTIONS AT 25°

Quinone-imine added (2 cc. of 0.002 *M* ether soln. per 100 cc. of buffer)

*P*H of soln.	Recorded potentials at (volts, hydrogen electrode = 0)				Extrapolated potential, zero time
	10 sec.	20 sec.	40 sec.	60 sec.	
0.76	+0.717	+0.707	+0.697	+0.689	+0.731
2.0	+ .643	+ .623	+ .598	+ .584	+ .667
5.7	+ .371	+ .366	+ .353	+ .338	+ .377
7.8	+ .289	+ .279	+ .268	+ .263	+ .307
9.7	+ .205	+ .193	+ .183	+ .175	+ .225

Quinone-imine and aminophenol
2 cc. of an ether soln. added to 100 cc. of buffer; ether soln. 0.0004 *M* in regard to quinone-imine and about 0.001 *M* in aminophenol (satd. solution)

*P*H of soln.	Recorded potentials at (volts, hydrogen electrode = 0)				Extrapolated potential, zero time
	10 sec.	20 sec.	40 sec.	60 sec.	
0.76	+0.707	+0.697	+0.685	+0.677	+0.717
2.0	+ .639	+ .621	+ .601	+ .589	+ .663
5.7	+ .353	+ .321	+ .289	+ .273	+ .403
7.8	+ .257	+ .251	+ .245	+ .243	+ .261
9.7	+ .147	+ .145	+ .145	+ .145	+ .149

The drift in potential was so rapid in the experiments with the quinone-imine that a special procedure had to be employed. A definite amount of the ethereal solution of the quinone-imine and a weighed quantity of the

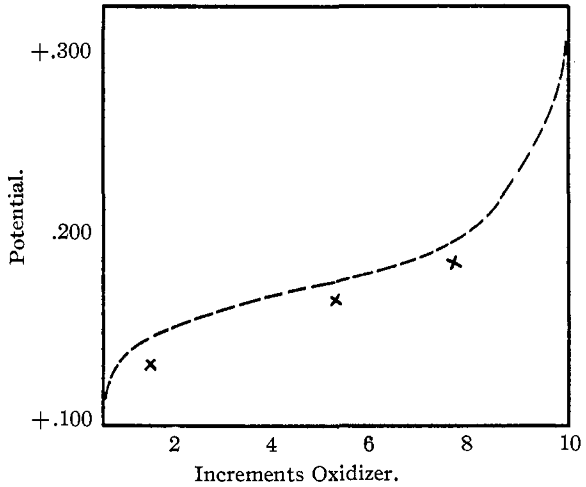
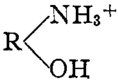


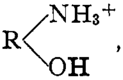
Fig. 1.—Potential of benzoquinone-imine + aminophenol at *P*H 9.7. The dotted curve was drawn through the ten points obtained in the rapid titration of aminophenol with molybdicyanide. The crosses represent potentials by the method of mixtures extrapolated to zero time.

aminophenol were placed in a thin-walled bulb of about 2 cc. capacity. This bulb was fitted to the end of a glass rod by means of a rubber stopper and was placed in the usual electrochemical cell. By pushing down the rod the bulb could be forced against the stirrer and thus broken. The time was recorded by a stop watch and the potential noted 9, 15, 30 and 60 seconds after the bulb was broken. Some typical results are given in Table V which indicate the rapid drift of potential which usually occurred. The values plotted in Figs. 1 and 2 were obtained by extrapolation to the moment of breaking the bulb.

The potentials changed so rapidly in solutions more acid than *P*H 6.9 that the extrapolated values are mere approximations and are almost certainly too low. This is particularly the case with the almost pure imine with which the drop occurred chiefly in the first ten seconds. This rapid decomposition accounts for the fact that we could obtain no titration curves in such solutions. Willstätter has shown that quinone-imine rapidly hydrolyzes to quinone in acid solution, and probably this is the main decomposition reaction in the acid solution as postulated by our mechanism for the irreversible oxidation. The relatively great stability of practically pure quinone-imine in *P*H 5.7 as compared with the rapid decomposition of mixtures of quinone-imine and aminophenol in the same solutions (Table V) suggests that in this buffer an interaction of these two substances is the chief reaction; the highly colored solutions that result indicate that complex products are formed.

Not much significance can be attached to the results plotted in Fig. 2 in the range *P*H 0.76 to 7.8, but it is interesting to compare them with what would be expected for the reversible system. The potential of this system would be expected to vary with acidity in much the same way as many other reversible systems which have been studied.[7] If we consider in this discussion the aminophenol ion,  $R<^{NH_3^+}_{OH}$, rather than the free aminophenol, we arrive at Equation 5 for the variation with the acidity of the potential of this system.

$$E_h = E_0 - 0.03 \log \frac{[\text{am.phenol}]}{[\text{quin.-imine}]} + 0.03 \log \left(1 + \frac{K_2}{H^+} + \frac{[H^+]}{K_1}\right) + 0.06 \log [H^+] \quad (5)$$

In this equation the quinone-imine has been treated as a neutral substance and the aminophenol ion,  $R<^{NH_3^+}_{OH}$, as a dibasic acid with the constants

$$K_1 = \frac{[H^+]\,[RNH_2OH]}{[RNH_3OH^+]};\quad K_2 = \frac{[H^+]\,[RNH_2O]}{[RNH_2OH]}.$$

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[7] Conant, Kahn, Fieser and Kurtz, THIS JOURNAL, **44**, 1382 (1922). Clark, *U. S. Public Health Repts.*, **38**, 666 (1923).

The first dissociation constant represents the formation of the free base and has a value[8] of about 10^{-5}. This would lead to a shift in the E_0' P_H curve near P_H 5; before this point the slope of the curve would be steeper than that of the hydrogen electrode (90 mv. per Sörensen unit). After this inflexion the curve would be expected to parallel that of the hydrogen electrode until the Sörensen value approximately equal to —log K_2 was reached when another inflexion (in the opposite direction) would be expected. The first inflexion seems to be indicated by the data given in Fig. 1; the second is missing, which may mean that aminophenol is so weak an acid that $K_2 < 10^{-11}$.

The oxidations of 1,4-aminonaphthol and 1,2-aminonaphthol appear to be reversible in P_H 8.7 since satisfactory titration curves were obtained using ferricyanide and working rapidly. The amount of oxidizing agent required, however, was only about 60% of that calculated for two equivalents. This may be due to the rapid removal of both the quinone-imine and the aminonaphthol by their interaction. The values for E_0' are as follows: 1,4-aminonaphthol, $P_H = 7.8$, $E_0' = +0.085$; $P_H = 9.7$, $E_0' = +0.015$; 1,2-aminonaphthol, $P_H = 9.7$, $E_0' = +0.073$; $P_H = 7.8$, $E_0' = +0.150$.

The Quantitative Formulation of the Rates of the Irreversible Oxidations

The mechanism of the irreversible oxidation of aminophenols and naphthols given in the first part of the paper can be made the basis of certain quantitative predictions. It can be shown that the composition of the equilibrium in Equation 4a is related to the normal potential of the aminophenol—quinone-imine system $(E_0')_A$ and that of the oxidizing agent $(E_0')_B$ according to Equation 6 (at constant Sörensen value),

$$(E_0')_B - (E_0')_A = \frac{0.06}{nm} \log \frac{[RNHO]\,[BH_{nm}]^m}{[RNH_2OH]\,[B]^m} \qquad (6)$$

where n is the number of equivalents involved in the reduction of the oxidizer and m is the number of moles of oxidizing agent entering into the reaction. Where the oxidizing agent is a quinone $n = 2$ and $m = 1$. Where the reagent is an inorganic ion usually $n = 1$ and $m = 2$ and Equation 6 then takes the form 6a.

$$(E_0')_B - (E_0')_A = \frac{0.06}{2} \log \frac{[RNHO]\,[B^-]^2}{[RNH_2OH]\,[B]^2} \qquad (6a)$$

If we start with the concentrations $[B] = [BH_2] = C$ and $RNH_2OH = 2C$, and let S be the fraction of oxidizing agent which has been reduced, we have the following resulting concentrations: $[B] = C(1-S)$; $[BH_2] = C(1+S)$; $[RNH_2OH] = C(2-S)$. For the equilibrium which instantaneously adjusts at time t, we can substitute these concentrations in Equation 6 ($n = 2$) and let X be the fraction of oxidizing agent reduced by this instantaneous

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[8] Scudder, "The Conductivity Ionization Constants of Organic Compounds," D. Van Nostrand Co., New York, **1914.**

equilibrium; then $XC(1-S)$ will be the concentration of quinone-imine and Equation 7 results.

$$(E_0')_B - (E_0')_A = 0.03 \log \frac{[XC(1-S)]\,[C(1+S)+XC(1-S)]}{[C(2-S)-XC(1-S)]\,[C(1-S)-XC(1-S)]} \qquad (7)$$

This on simplification gives Equation 7a and if X is less than 0.1 we may

$$(E_0')_B - (E_0')_A = 0.03 \log \frac{X(1-S)\,(1+S+X-XS)}{(2-S-X+XS)\,(1-S-X+XS)} \qquad (7a)$$

without much error write, Equation 7b as an approximation. *This equation holds for reagents of the quinone type.*

$$(E_0')_B - (E_0')_A = 0.03 \log X + 0.03 \log \frac{1+S}{2-S} \qquad (7b)$$

Similarly from Equation 6a we may derive Equation 8 and the approximate Equation 8a which are valid for reagents like ferricyanide (in this instance we employed one mole of oxidizing agent per mole of substance, and let $2X(1-S)$ be the fraction of reagent reduced by the instantaneous equilibrium).

$$(E_0')_B - (E_0')_A = 0.03 \log \frac{X(1-S)\,(1+S+2X-2XS)^2}{(1-0.5S-X+XS)\,(1-S-2X+2XS)^2} \qquad (8)$$

$$(E_0')_B - (E_0')_A = 0.03 \log X + 0.06 \log (1+S) - 0.03 \log (1-S)\,(1-0.5S) \qquad (8a)$$

The concentration of the quinone-imine undergoing the *relatively* slow monomolecular change is $XC(1-S)$; therefore, we may write Equation 9, and, assuming X to be constant, the integrated form Equation 10.

$$\mathrm{d}c/\mathrm{d}t = k'XC(1-S) \qquad (9)$$

$$k'X = 2.3/t \log 1/(1-S) \qquad (10)$$

The $k'X$ in Equation 10 is the constant of the entire irreversible process and by combining Equations 10 and 3 we may write

$$k = k'X = 2.3/t \log 1/(1-S)$$

It is evident from the above equations that it is only an approximation to consider X constant as S varies. A rigorous development would lead to the conclusion that X and therefore k will decrease as the reaction proceeds. Such a decrease we meet with experimentally (Table IV); our simplified treatment considers the average values.

By combining Equation 10 with 7b or 8a it should be possible to predict the relative rates of reaction with two reagents of potentials $(E_0')_B{}^1$ and $(E_0')_B{}^2$, respectively. If both reagents are of the same type (n and m the same), Equation 11 results; if of different types, Equation 12, where $(E_0')_B{}^1$ corresponds to a quinone and $(E_0')_B{}^2$ to an inorganic ion where $n = 1, m = 2$. Both equations are only approximations and are rigorously valid only if the value of S is about the same in both cases, that is, if the

$$(E_0')_B{}^1 - (E_0')_B{}^2 = 0.03 \log k_1/k_2 \qquad (11)$$

$$(E_0')_B{}^1 - (E_0')_B{}^2 = 0.03 \log k_1/k_2 + 0.03 \log \frac{(1+S)\,(1-S)\,(1-0.5S)}{(2-S)} - 0.06 \log (1+S) \qquad (12)$$

rates are compared over the same range of oxidation (for example, 0–50%). The values of the combined last two terms of Equation 12, which we may call Z, for different values of S are: $S = 0$, $Z = -0.009$; $S = 0.3$, $Z = -0.020$; $S = 0.5$, $Z = -0.024$; $S = 0.7$, $Z = -0.041$.

According to Equation 11, the rate of oxidation should increase about 10 fold if a given reagent is replaced by one of 30 mv. higher potential, while the increase would be 30 fold for 45 mv. and 100 fold for 60 mv. Reference to Table IV shows that the actual experimental results are of the same order of magnitude as those predicted by our hypothesis and the equations. Thus in the two experiments with 1,4-aminophenol $(E_0')_B{}^1 - (E_0')_B{}^2 = 0.035$ and the rate with the more powerful oxidizing agent is ten times greater than that with the reagent of lower potential. This excellent agreement must be regarded as partly fortuitous in view of the results with other compounds. The relative rates with two reagents as actually measured (the ratio of $k \times 10^2$ in Table IV) and calculated from Equations 11 and 12 are given below.

Substance	k_1/k_2, found	k_1/k_2, calcd.
1,4-Aminonaphthol (rates with 2 quinones)	10	10
1,2-Aminonaphthol (rates with 2 quinones)	8	30
1,4-Aminophenol (rates with 2 quinones)	6	6
1,4-Aminophenol (ferricyanide *versus* quinone)	4	12
1,4-Aminophenol (ferric chloride *versus* dichloroquinone)	3.3	2
1,2-Aminophenol (two quinones)	9	6
1,2-Aminophenol (ferricyanide *versus* quinone)	6	12
1,2-Aminophenol (ferric chloride *versus* dichloroquinone)	0.45	2

On the whole the agreement is all that could be expected considering the accuracy of the method and the approximations involved in the derivation and use of Equations 11 and 12. Furthermore, the oxidation of 1,2-aminonaphthol with 1,2-naphthoquinone and 1,4-aminophenol with benzoquinone probably really require special formulations as the product of oxidation may be in these cases identical with the oxidizing agent. In only one case (the oxidation of 1,2-aminophenol with ferric chloride and dichloroquinone) is the order of the reagents different from that predicted on the basis of the theory. It seems safe to consider that the validity of the electrochemical formulation of aminophenols and naphthols has been established. Unless some mechanism such as we have suggested is involved in this reaction, it seems hardly possible that such regularities would result with a variety of oxidizing agents.

The Apparent Oxidation Potential

For practical purposes it is convenient to summarize results such as those given above by determining the "apparent oxidation potential" of each compound. This may be defined as the normal potential of the hypothetical oxidizing system of the ferricyanide type ($n = 1$) which will cause 20–30% oxidation in 30 minutes; with such a reagent $k \times 10^2$ is about 1. Assuming Equations 11 and 12 to hold, apparent oxidation potentials (A. O. P.) at 23° in 0.2 N HCl can be calculated by interpolation from the data in Table IV: 1,4-aminonaphthol = +0.480; 1,2-aminonaphthol = +0.510; 1,4-aminophenol = +0.680; 1,2-aminophenol = +0.670. Reagents of the ferricyanide type higher than the A. O. P. will cause rapid oxidation; those of lower potential very slow oxidation. Since the rate is nearly independent of the total concentration, the values of the A. O. P. are approximately also independent of the dilution at constant temperature and hydrogen-ion concentration. They are not significant to more than 10 mv. Because of the "Z terms" in Equation 11, a quinone with a potential about 15 mv. lower than the A .O. P. would be expected to cause oxidation at such a rate that $k \times 10^2 = 1$. Thus if the A. O. P. were defined in terms of reagents with which $n = 2$, the values would be about 15 mv. lower.

If different proportions of oxidizing agent and substances are used, the value of the A. O. P. will change somewhat. Thus, Equation 13 can be derived from Equation 6 for a case where one equivalent of oxidizing mixture is employed and the initial concentrations are: $[B] = [BH_2] = [RNH_2OH] = C$. The difference in the last terms, in this Equation 13 and in Equation 7b only amounts to 9 mv. at the start of the reaction and 15 mv. when $S = 0.5$. Therefore, as a convenient approximate description of the phenomena, the concept of apparent oxidation potential has general validity; it can be used in predicting qualitatively the action of reagents on a compound without regard to the relative proportions of the reagent and substance. It is only necessary to bear in mind that the A. O. P. varies with temperature, acidity, and probably large changes in total salt concentrations, and that an exact definition of it presupposes an oxidizing agent containing an equal amount of the reduced form.[9]

$$(E_0')_B - (E_0')_A = 0.03 \log X + 0.03 \log \frac{(1+S)}{(1-S)} \qquad (13)$$

It is interesting to compare the apparent oxidation potentials with the values of E_0' for the reversible quinone-imine system extrapolated from $P_H = 7.8$ to 0.2 N hydrochloric acid by means of Equation 5 (taking K_1 as 10^{-5}). This comparison is made in Table VI. The A. O. P. in each

Table VI

Comparison of A. O. P. and Estimated Potential of Reversible Step

Compound	A. O. P. $P_H = 0.76$	Estimated E_0' at $P_H = 0.76$ of reversible step
1,4-Aminophenol	+0.680	+0.746
1,2-Aminonaphthol	+ .510	+ .636
1,4-Aminonaphthol	+ .480	+ .571

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[9] For a discussion of the difference between such reagents and the "pure" reagents commonly used in the laboratory see Ref. **2** b.

case is 70 to 120 mv. below the estimated normal potential of the hypothetical step. These are reasonable values as they correspond to a very small amount of quinone-imine which would be formed by the critical oxidizing agents and which would then undergo the irreversible hydrolysis to the quinone. If the relationships shown in Table VI are correct, the value of X in Equation 8a would be 10^{-3} to 10^{-4}. In other words, 0.1 to 0.01% of the aminophenol is initially oxidized to the quinone-imine by virtue of the reversible step when the reagent is the critical reagent whose potential is the A. O. P. of the compound. Substituting this value into the expression $k = k'X$ and taking k as 1×10^{-2}, we find that k' is about 10. This corresponds to a half life of about four seconds, a value for the speed of hydrolysis of the quinone-imine which does not seem improbable in view of our experiments with the benzoquinone-imine in acid solution.

The A. O. P. of 1,4-Aminophenol in Buffer Solutions

In Table VII are recorded the results of some experiments on the oxidation of 1,4-aminophenol in buffer solutions of various acidities in which the oxidation is irreversible. It will be noted that since the ferricyanide E_0':P_H line is practically straight in solutions more alkaline than P_H

TABLE VII

THE OXIDATION OF 1,4-AMINOPHENOL IN BUFFER SOLUTIONS AT 23°

Reagent	P_H, soln.	E_0'	Fraction oxidized (S) in 5 min.	15 min.	30 min.	Reaction constant $k \times 10^2$ calcd. at 5 min.	15 min.	30 min.	A. O. P.
Pot. ferricyanide	3.9	+0.425	0.01	0.03	0.10	0.2	0.2	0.3	+0.445
2,6-Dichloroquinone	3.9	+ .516	.10	....	.78	2.0	....	5	
Xyloquinone	3.9	+ .381	< .01	< .01	< .01				
Pot. ferricyanide	4.7	+ .425	.61	.80	.90	18	10	7	+ .390
2,6-Dichloroquinone	5.7	+ .368	> .95	> .95	> .95				
Xyloquinone	5.7	+ .248	< .01	< .01	< .01				Estimated at about .300

The solutions of fixed hydrogen-ion concentration used throughout this work were all 0.1 to 0.2 M with respect to the buffering ion. The hydrogen-ion concentration of each solution was determined by means of the hydrogen electrode. The following materials were used in preparing the various solutions: P_H 0.76, hydrochloric acid; P_H 2.0 and 3.0, glycine, sodium chloride, hydrochloric acid; P_H 4.0 and 5.0, potassium acid phthalate and sodium hydroxide; P_H 5.7, citric acid, potassium hydrogen phosphate; P_H 6.9, potassium dihydrogen phosphate, sodium monohydrogen phosphate; P_H 7.8 and 8.5, borax, boric acid, sodium chloride; P_H 9.0 and 9.8, boric acid, sodium hydroxide, potassium chloride; P_H 11.3, 0.2 M ammonium hydroxide and potassium chloride; P_H 13.0, 0.2 M sodium hydroxide solution. The proportions taken were in general those recommended by Clark ("The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore); the total concentrations, however, were much greater since we desired to insure a constancy of hydrogen-ion concentrations during the course of a chemical reaction. As our buffering ion was nearly a thousand times more concentrated than the reacting substances, we felt confident of a nearly constant acidity.

3.9, the A. O. P. curve of 1,4-aminophenol crosses this line at about *P*H 4. The results shown in Table VII together with the A. O. P. at *P*H 0.76 are plotted in Fig. 2. The slope of the curve between *P*H 0.76 and 4.7 is 72 mv. per Sörensen unit. The curve of E_0' for the hypothetical quinone-imine system in this range should have a slope of 90 mv. per Sörensen unit. If our interpretation is correct, the difference is to be attributed to the less rapid hydrolysis of the quinone-imine in the less acid solutions.

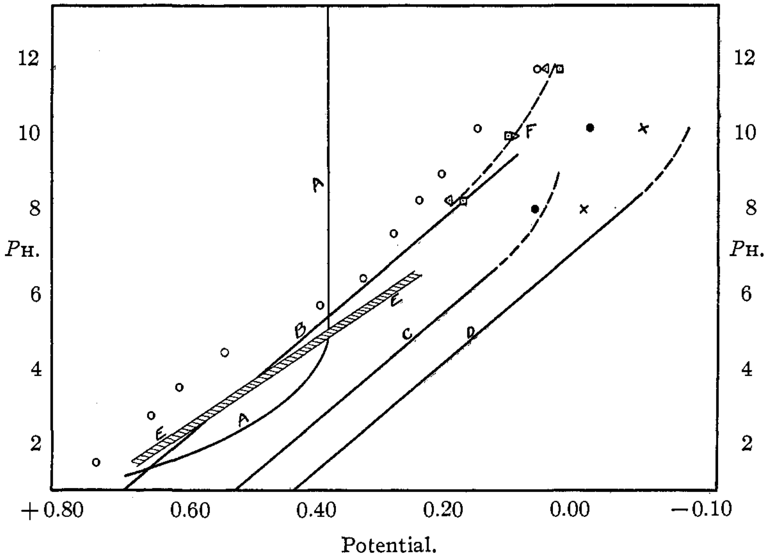

Fig. 2.—Showing the A. O. P. of aminophenol (crosshatched band E) in acidic solutions and the quinone-imine reversible potential in alkaline solutions (dotted line F). The circles represent the estimated quinone-imine potential with nearly pure material. The squares and triangles represent the normal potential of the reversible quinone-imine system by the method of titration and mixtures (respectively). The titration results with 1,2-aminonaphthol are shown by black circles, with 1,4-aminonaphthol by crosses. The normal potentials of the reversible systems used as reagents are: A = $K_3Fe(CN)_6$; B = quinone; C = 1,2-naphthoquinone; D = 1,4-naphthoquinone.

Such a slowing down of the irreversible step would have the effect of raising the A. O. P. Where the rate of irreversible step is affected by change in acidity it is obviously impossible to predict from the electrochemical equations the slope of the A. O. P.: *P*H curve with reference to the E_0': *P*H curve of the reversible system. The general trend of the curve, in this instance, is in accord with our interpretation.

We are indebted to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for a generous grant which has aided this work.

Summary

1. The rates of the irreversible oxidation of 1,2- and 1,4-aminophenol and 1,2- and 1,4-aminonaphthol have been studied using reversible reagents of definite potential. The rate is independent of the dilution and is related to the oxidation-reduction potential of the reagent employed.

2. We have suggested that the irreversible oxidation of aminophenols or aminonaphthols proceeds through the reversible formation of the quinone-imine which then irreversibly hydrolyzes. This mechanism is made probable by the evidence which we have obtained of the reversibility of the aminophenol—quinone-imine system in alkaline solutions. The oxidation-reduction potential of this unstable system may be estimated in certain buffer solutions both by the method of mixtures and by titration.

3. The relative rates of oxidation of each amino compound with several reagents of different potentials have been measured and found to be of the order of magnitude predicted from the electrochemical equations which we have developed.

4. It appears that these examples of irreversible oxidation may be formulated in electrochemical terms. This we have done by determining the rates of oxidation of each compound by each member of a graded series of reagents and estimating the potential of the oxidizing agent which should just cause "appreciable oxidation." The potential of this hypothetical reagent (with an oxidizing power of one equivalent) we have defined as the apparent oxidation potential of the substance under investigation.

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THE REACTIVITIES OF SOME TERTIARY BROMIDES

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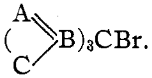
RECEIVED SEPTEMBER 25, 1926 PUBLISHED DECEMBER 16, 1926

The work here reported was undertaken with the idea of comparing the reactivities of the halogen atoms in the compounds $(C_6H_5)_3CBr$ (I), $(C_6H_5)_2CBr(CO_2CH_3)$ (II), $(C_6H_5)CBr(CO_2CH_3)_2$ (III) and $CBr(CO_2CH_3)_3$ (IV). These compounds have a certain structural similarity: they may all be represented by the formula  $(\overset{A}{\underset{C}{>}}B)_3CBr$. The phenyl and carbalkoxy groups are both negative, and both are activating groups in the sense that they increase the reactivity of methyl halide when they replace one of its hydrogen atoms. From the data presented in recent papers by Conant and his students[1] it appears that the activating influence of the

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[1] Conant and Kirner, THIS JOURNAL, **46,** 232 (1924). Conant and Hussey, *ibid.*, **47,** 476 (1925). Conant, Kirner and Hussey, *ibid.*, **47,** 488, 587 (1925).