

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE IRREVERSIBLE OXIDATION OF ORGANIC COMPOUNDS II. THE APPARENT OXIDATION POTENTIAL OF CERTAIN PHENOLS AND ENOLS

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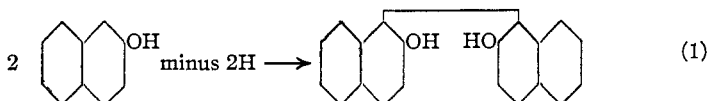
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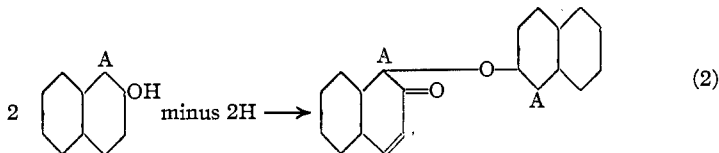
The methods outlined in the first paper of this series¹ are applicable to the study of the rate of oxidation of any substance which is attacked by a reversible reagent that rapidly gives a definite potential to an inert electrode. Many phenols and enols are readily oxidized by reagents which are suitable for use in our quantitative method. We have studied, therefore, the rate of oxidation of certain of these hydroxy compounds in buffer solutions of known acidity. Only oxidizing agents of definite potential were employed. The results indicate that the rate of reduction of these reagents by phenols and enols depends on the oxidation-reduction potential of the reagent if the temperature and hydrogen-ion concentration are constant. Therefore, the electrochemical formulation of these particular oxidations is feasible and we have estimated the apparent oxidation potential of a number of phenols and enols.

The Oxidation of Phenols and Naphthols

It is well known that the chief product of the oxidation of phenols and naphthols in acid or neutral solution by ferric chloride is a dinuclear compound as illustrated by the following reaction of β -naphthol. Other



products may also be formed particularly by alkaline oxidation with ferricyanide as shown by Pummerer. In the case of alkyl and halogenated phenols and naphthols the final products indicate that one of the intermediate products may be an ether which can undergo further rearrangements and reactions. The reader is referred to the work of Pum-



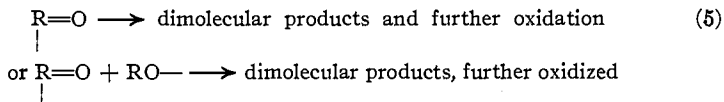
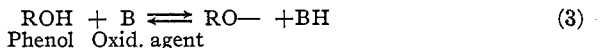
merer and Hunter² for a detailed consideration of the products formed on oxidizing naphthol derivatives and halogenated phenols.³ It is extremely

¹ Conant and Pratt, *THIS JOURNAL*, **48**, 3178 (1926).

² Pummerer and Hunter, *Ber.*, **47**, 1472, 2957 (1914); **52**, 1392, 1403, 1414, 1416 (1919); **55**, 3116 (1922); **58**, 1808 (1925).

³ *THIS JOURNAL*, **48**, 1608, 1615 (1926).

probable in view of Goldschmidt's⁴ and Pummerer's work, that the initial step in all these cases is the formation of a free radical containing univalent oxygen which may then enter into a variety of reactions. If the interaction of the hydroxy compound and the oxidizing agent were rapid and reversible, the rate of the entire process might be controlled by the amount of free radical formed by the reversible reaction (Equation 3). In this case the speed of the entire irreversible process (or processes) would depend on the potential of the reagent employed. This we have found to be essentially the case. We have further found that the rate of the irreversible process is nearly independent of the *total* concentration of the reactants. This fact points to some rate-controlling monomolecular reaction which may be the rearrangement of the free radical. Thus, without attempting to state the nature of the products formed under a variety of conditions, we may postulate the following general mechanism in which Reaction 3 is rapid and reversible, Reaction 4 *relatively* slow, and Reaction 5 fast and irreversible. As we have no information at present in regard to the products formed with each of our reagents, it is not worth while to consider the



various ways in which Reaction 5 may proceed. In this paper we shall content ourselves with investigating the connection between the rate of the oxidation and the potential of the reagent employed.

The most readily oxidized phenolic substance we have examined is α -naphthol. We have studied its behavior in considerable detail. The results obtained with an acid solution at 60° (0.2 *N* hydrochloric acid, $P_{\text{H}} = 0.76$) are given in Table I which illustrates our method and the calculation of the results. In Table II are shown the results of varying the total concentration. It will be noted that with all the substances except resorcinol the rate is only slightly affected by a change of 10-fold in the total concentration if the relative concentrations of substance and reagent are constant.

In all these experiments and in those to be reported later in this paper, the material under investigation was added to an equimolecular mixture of the oxidizing agent and its reduced form (for example, ferric chloride + ferrous chloride) dissolved in a solution of definite acidity contained in the usual electrochemical cell. The potential of two platinum electrodes immersed in the cell was measured against a saturated calomel electrode

⁴ Goldschmidt, *Ann.*, **438**, 202 (1924); see also *Ber.*, **55**, 3216 (1922).

at definite intervals of time after the substance was added. The change in potential corresponded to a reduction of the oxidizing agent (an oxidation of the organic substance). In these experiments one mole of substance per oxidizing equivalent of oxidized form of reagent was used so that even if only one hydrogen atom were involved in the change, the reaction would involve the eventual complete reduction of the oxidizing agent. The extent of the reaction at a given time can be calculated by means of Equation 6, from the observed change of potential, since at the start, an equimolecular mixture of oxidizing agent and reduced form was present in the cell. In this equation n is the number of equivalents involved in

$$\Delta E = \frac{0.000198 T}{n} \log \frac{1+S}{1-S} \quad (6)$$

the reduction of the oxidizing agent and S the fraction of reagent that has reacted. Assuming the course of the reaction to be approximately expressed by the usual monomolecular formula (Equation 7, time in minutes), the constant of the reaction may be calculated. Such constants calcu-

$$k = (2.30/t) \log 1/(1 - S) \quad (7)$$

lated for 5-, 15- and 30-minute periods express the general order of magnitude of the reaction rate. The probable error of this type of work is large

TABLE I

THE OXIDATION OF α -NAPHTHOL BY REAGENTS OF DEFINITE POTENTIAL. TEMP., 60;
 $P_H = 0.76$ (0.2 N HCl)

Reagent (contained equi- molar amount of reduced form)	E_0' ($P_H = 0.76$ $t^{\circ} = 60$)	Change of potential in min.			Fraction (S) of reagent reduced			$k \times 10^2$ calcd. from S at			Av.
		5 min.	15 min.	30 min.	5 min.	15 min.	30 min.	5 min.	15 min.	30 min.	
Pot. molybdicyanide	0.692	27	73	125	0.42	0.84	> 0.95	11	12	11
2,6-Dichloroquinone	.639	20	48	79	.60	.92	> .95	19	17	18
Quinone	.612	20	50	65	.60	.94	.98	19	19	19
Pot. ferricyanide	.598	6	8	9	.08	.12	.14	1.7	0.9	0.04	1.0
Xyloquinone	.510	0	0	0							
Pot. tungsticyanide	.451	0	0	0							
1,4-Naphthoquinone	.388	0	0	0							
Indigo-tetrasulfonate	.287	0	0	0							

In each experiment with reagents of one oxidizing equivalent, 0.0002 mole of solid compound was dropped into 0.0002 mole of oxidized and 0.0002 mole of reduced reagent dissolved in 100 cc. of 0.2 N HCl. With reagents of two oxidizing equivalents (for example, quinone) 0.0001 mole of reagent and 0.0001 of reduced reagent were taken.

The standard of reference for the potential measurements at 60° was the quinhydrone electrode. The temperature coefficient as determined in this Laboratory for the range 25–40° [THIS JOURNAL, 44, 2484 (1922)] was used in extrapolating to 60°; the value for the normal potential in normal hydrogen-ion concentration at 60° was thus calculated to be 0.662 at 60° (compared with 0.699 at 25°). It was arbitrarily assumed that the activity coefficient of the hydrogen ion in 0.2 N hydrochloric acid at 60° was the same as at 25°. On this basis the quinhydrone electrode in 0.2 N HCl was assigned a value of +0.612 on the hydrogen electrode scale at 60°. The saturated calomel electrode we employed at 60° had a value of +0.217 on the basis of the above assumptions as compared with +0.253 at 25°. The errors involved in the above assumptions are probably not great.

TABLE II

EFFECT OF DILUTION ON THE RATE OF OXIDATION OF CERTAIN PHENOLS AND ENOLS
AT $23^{\circ} \pm 2^{\circ}$

F = potassium ferricyanide; M = potassium molybdicyanide

P_H of solution	Reagent (containing equimol. amt. of reduced form)	Concn., moles per liter $\times 10^3$	Substances oxidized	Concn., moles per liter $\times 10^3$	Fraction oxidized in		
					5 min.	15 min.	30 min.
6.9	F	20	α -Naphthol	20	0.24	0.52	0.70
6.9	F	2	α -Naphthol	2	.18	.46	.64
8.5	F	2	Hydroquinone monomethyl ether	2	.61	.92	.97
8.5	F	0.2	Hydroquinone monomethyl ether	0.2	.65	.80	.90
8.5	F	20	Resorcinol	20	.36	.52	.58
8.5	F	2	Resorcinol	2	.10	.19	.26
6.9	M	2	Ethyl acetoacetate	2	.78	.86	.98
6.9	M	0.2	Ethyl acetoacetate	0.2	.38	.66	.82
4.0	M	2	β -Naphthol	280
4.0	M	0.2	β -Naphthol	0.2	.1065

The solutions of fixed hydrogen-ion concentration used throughout this work were all 0.1 to 0.05 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. 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 concentration 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.

and there is no reason to believe that the reactions involved are strictly monomolecular; therefore no significance is attached to variations of k of 25 to 50%, and no attempt has been made to calculate k for values of S larger than 0.9.

It is evident from Table I that in a general way one can classify the reaction of the reagents with α -naphthol on the basis of their potential; this is true in spite of the fact that some of the reagents are quinones, others complex salts. When one pushes the inquiry further and examines the different observed rates with the first four reagents, there are certain inconsistencies. The dichloroquinone and quinone act essentially alike although differing by 22 millivolts in potential, and potassium molybdicyanide is less effective than dichloroquinone although above it on the potential scale. This latter inconsistency is apparent and not real since we

are comparing two reagents with one of which $n = 1$, with the other $n = 2$. The equations which are developed below on the basis of our postulated mechanism would lead one to predict that a reagent with which $n = 1$ would be less effective than one of the same potential where $n = 2$. The difficulty in regard to the action of the two quinones must be left for the present unexplained. Such slight irregularities probably reflect secondary disturbing influences of a catalytic nature.

The development of the approximate equations for calculating the relative rates with two reagents follows the general scheme outlined in the previous paper. It assumes the mechanism we have given above.

The equilibrium of the first step (Equation 3) can be formulated electrochemically by Equation 7a.

$$(E_0')_B - (E_0')_{ROH} = \frac{0.000198 T}{m} \log \frac{[RO-]^m [BH_m]}{[ROH]^m [B]} \quad (7a)$$

In this equation m is the number of moles of substance reacting with one of reagent. With the inorganic reagents $m = 1$; the reduced form of the reagent in this case is an ion and not BH_m , but this does not alter the equation as constant hydrogen-ion concentration is assumed. Initially $[BH_m] = [B] = [ROH]$; therefore, if we let S be the fraction of B which has reacted at a given time we have the resulting relative concentrations: $[BH_m] = (1 + S)$; $[B] = (1 - S)$; $ROH = 1 - S$ (provided no further oxidation of the products occurs). If we let X be the fraction of oxidizing agent reduced by virtue of the rapid equilibrium which is adjusted after the fraction S of material has reacted we may write Equation 8 by substitution

$$(E_0')_B - (E_0')_{ROH} = 0.0002 T \log \frac{[X(1 - S)] [1 + S + X - XS]}{[1 - S - X + XS] [1 - S - X + XS]} \quad (8)$$

in Equation 7a. For small values of X we may write Equation 8a which is approximately valid for the $n = 1$ reagents we have employed. Similarly

$$(E_0')_B - (E_0')_{ROH} = 0.0002 T \log X + 0.0002 T \log (1 + S)/(1 - S) \quad (8a)$$

we may derive Equation 9 which is approximately valid when quinones are employed (if the ratio of material to oxidizing *equivalent* of reagent is the same as with the inorganic reagents and $2X$ is the fraction of reagent reversibly reduced).

$$(E_0')_B - (E_0')_{ROH} = 0.0002 T \log X + 0.0002 \log \frac{(1 - S)}{(2 - S)} + 0.0001 T \log \frac{1 + S}{1 - S} \quad (9)$$

If the irreversible slow step of the reaction is monomolecular and if we assume X to be constant, we may write

$$k = k'X = 2.3/i \log 1/(1 - S) \quad (9a)$$

It is evident that X really varies with S , and Equation 9a and the subsequent equations developed from it are approximations representing an average rate. The results indicate that in many cases k decreases as S increases, as would be predicted.

For two different reagents of potentials $(E_0')_B^1$ and $(E_0')_B^2$ we can write

the following equations for the relative speeds (values of k) measured over the same range of S values. Equation 10 applies where the two reagents are of the same type; Equation 11 where one is of the quinone type, the other of the ferricyanide type, $(E_0')_B^1$ being the potential of the reagent where $n = 2$. The value of the last two terms of Equation 11 which we may call Z is as follows:

at 23° $S = 0.3$, $Z = -30$ mv.; $S = 0.5$, $Z = -45$ mv.; $S = 0.8$, $Z = -75$ mv.
 at 60° $S = 0.3$, $Z = -34$ mv.; $S = 0.5$, $Z = -48$ mv.; $S = 0.8$, $Z = -84$ mv.

$$(E_0')_B^1 - (E_0')_B^2 = 0.0002 T \log k_1/k_2 \quad (10)$$

$$(E_0')_B^1 - (E_0')_B^2 = 0.0002 T \log \frac{k_1}{k_2} + 0.0002 T \log \frac{1-S}{2-S} - 0.0001 T \log \frac{1+S}{1-S} \quad (11)$$

Applying these equations to the oxidation of α -naphthol at 60° one is led to the following predictions in regard to the approximate value of the ratio k_1/k_2 : dichloroquinone *versus* molybdicyanide, calcd. 3, found 1.6; dichloroquinone *versus* quinone, calcd. 2.6, found 1; quinone *versus* ferricyanide, calcd. 10, found 19. Considering the experimental difficulties and the approximations involved in deriving and applying Equations 10 and 11, the agreement is satisfactory.

In particular it should be noted that the apparent discrepancy between molybdicyanide and quinone is accounted for by the correction involved in the last two terms of Equation 11.

It is convenient to express such results as those given in Table I in terms of an apparent oxidation potential (A. O. P.). This may be defined as the potential of the hypothetical reagent (of the ferricyanide type) which will just cause 20–30% oxidation in 30 minutes. This rate corresponds to a value of $k \times 10^2$ of 1. It happens that in 0.2 N hydrochloric acid at 60° with α -naphthol such a critical reagent is potassium ferricyanide. We may therefore place the A. O. P. as +0.600 for α -naphthol under these conditions. Since the rate is nearly independent of the dilution, this value is essentially independent of the total concentration. It does depend on the temperature, the acidity, the ratio of material to oxidizing agent (one mole to one equivalent), and *on the use of an oxidizing reagent which is an equimolar mixture of the oxidized and reduced forms of the reagent*. Changes in the ratio of material to reagent affect only slightly the rate (and therefore the A. O. P.) so that for practical purposes the numbers representing the A. O. P. of a series of compounds are of value in characterizing their behavior.⁵

The Effect of Varying the Acidity

Up to this point in the discussion we have assumed constant hydrogen-ion concentration and considered only the results obtained at one definite Sørensen (P_H) value. The next point of interest is the effect of varying the

⁵ For a discussion of the use of "pure" reagents as commonly employed in the laboratory, see *Chem. Reviews*, 3, 1 (1926).

hydrogen-ion concentration. By employing a series of solutions of definite Sørensen value it is possible to study the effect of the variation of acidity on the oxidation. The potential of the hypothetical reversible step of our mechanism should vary with the hydrogen-ion concentration according to Equation 12. K_1 is the acid dissociation constant of the phenolic group.

$$E = E_0 - 0.0002 T \log \frac{[\text{Phenol}]}{[\text{Free Radical}]} + 0.0002 T \log (K_1 + [\text{H}^+]) \quad (12)$$

For Sørensen values where $[\text{H}^+] > K_1$ the last term is $0.0002 T \log [\text{H}^+]$ and the $E_0' : PH$ curve parallels that of the hydrogen electrode. When $[\text{H}^+] = K_1$ there will be an inflexion and for more alkaline solutions the potential will be independent of the hydrogen-ion concentration. It will be recalled that $E = E_0'$ when $[\text{phenol}] = [\text{free radical}]$ and that in terms of our hypothesis the A. O. P. depends on the value of E_0' for the reversible step. Therefore it would be expected that the change of A. O. P. with change in hydrogen-ion concentration would parallel the hydrogen electrode for some distance and then be independent of the Sørensen value of the solution.

In Fig. 1 we have plotted the $E_0' : PH$ curves for a number of the reversible systems we have used as reagents. These curves are based on our own data at 25° and apply to dilute solutions (about $0.001 M$); they are essentially the same as the results already recorded in the literature. The slope of the quinone lines is the same as that of the hydrogen electrode. The action of quinones as oxidizing agents on phenols should therefore be independent of the hydrogen-ion concentration until either the quinone line or that of the hypothetical reversible system bends. Since the potential of the complex cyanides is nearly independent of the hydrogen-ion concentration (ferricyanide between $PH = 1$ and 4 is an exception) the action of these reagents on phenolic substance should be greatly influenced by change in acidity. This is, indeed, the case, and it has enabled us to locate the A. O. P. line with considerable assurance in many instances.

In Table III are given the results of our experiments on the oxidation of α -naphthol at 60° in different buffer solutions. The values of E_0' for the reagents at this temperature are somewhat different from those at 25° plotted in Fig. 1, but the general relationship of the inorganic and organic reagents is the same. As will be shown below, at 25° the A. O. P. of α -naphthol is a little too high to enable us to employ as many reagents as at 60° . The experiments summarized in Table III are therefore the most drastic test we could devise of the consistency of our formulation.

In the last column are given the values of the A. O. P. of α -naphthol at 60° in each buffer calculated by Equation 10 or 11 from that datum recorded on the same line. The value of S in Equation 11 was taken as that recorded under the 15-minute heading. The apparent inconsistencies between the action of quinone and the complex cyanides (for example,

TABLE III

THE OXIDATION OF α -NAPHTHOL AT 60° IN DIFFERENT BUFFER SOLUTIONS

Oxid. agent (containing equimol. amount of reduced form)	E_0'	Fraction reacted (S) at			$k \times 10^2$ calcd. at				A. O. P.
		5 min.	15 min.	30 min.	5 min.	15 min.	30 min.	Av.	
A. $P_H = 2.6$									
Dichloroquinone	+0.507	0.20	0.88	>0.95	5	14	...	10	+0.475
Quinone	+ .490	.32	.62	.81	8	7	6	7	+ .470
Pot. ferricyanide	+ .350	0	0	0					<.05
Pot. tungsticyanide	+ .441	0	0	0					<.05
									Av. = +0.472
B. $P_H = 3.6$									
Pot. tungsticyanide	+ .425	.01	.04	.04	0.2	0.2	.15	.2	+ .471
Quinone	+ .422	.60	.60	.74	(20)	6	5	6	+ .420
									Av. = + .445
C. $P_H = 5.2$									
Pot. tungsticyanide	+ .420	.32	.60	.80	8	6	5	6	+ .369
Quinone	+ .320	.32	.72	.90	8	8	7	8	+ .344
Pot. ferricyanide	+ .320	0	0	0					
									Av. = + 0.356
D. $P_H = 5.8$									
Pot. tungsticyanide	+ .425	> .95							>60
Quinone	+ .277	.46	.90	> .95	12	15		13	+ .290
Pot. ferricyanide	+ .325	.06	.21	.38	1.3	1.6	1.5	1.4	+ .315
									Av. = + .305
E. $P_H = 6.9$									
Pot. tungsticyanide	+ .435	.90	> .98	> .98	50	50	
Pot. ferricyanide	+ .320	.68	.90	> .95	24	16		16	+ .240
Quinone	+ .205	.74	.90	.96	26	16	10	16	+ .215
									Av. = + .232

In addition to the above results the following facts were established: potassium molybdicyanide and dichloroquinone rapidly oxidized α -naphthol in all buffers and xyloquinone was without action. The Sørensen value of the buffer solutions at 60° was calculated from the quinhydrone potential assuming the value in 0.2 *N* HCl at 60° to represent P_H 0.76 (See Table I, note).

quinone *versus* tungsticyanide at $P_H = 3.6$ and quinone *versus* ferricyanide at $P_H = 5.2$ and 5.8) are explained to a large degree by the terms in Equation 11. A consideration of this equation shows that when $S = 0.8$ (80% reaction) a quinone ($n = 2$) should act like a complex cyanide ($n = 1$) of about 85 mv. higher potential. Actually, the difference is somewhat greater even than this. Thus at $P_H = 5.2$, quinone and tungsticyanide are essentially alike in their action, though the quinone has a potential 0.100 mv. lower than the inorganic reagent. This is typical of the discrepancy between the facts and our calculations concerning the action of reagents of different type. Considering the approximations involved in deriving the equations, we do not regard the discrepancy as serious;

it may well be due to some secondary influence that we have not taken into account in the development of our simple theory. The failure of Equation 11 to correct adequately for the difference in type of quinone and a complex cyanide causes the A. O. P. calculated from two different reagents to differ by 20 to 60 mv. We shall use an average value in the discussion that follows.

The fact that in all the solutions used, quinone oxidizes α -naphthol and xyloquinone does not, shows that the A. O. P.: P_H curve parallels the quinone line. According to our theory, the change of A. O. P. should be 66 mv. per P_H unit. Taking the value at 0.76 as +0.600 (Table I) this would give the following values in the different solutions which are to be compared with the average values in Table II: $P_H = 2.6$, calcd. +0.475, found +0.472; $P_H = 3.6$, calcd. +0.410, found +0.445; $P_H = 5.2$, calcd. +0.310, found +0.356; $P_H = 5.8$, calcd. +0.270, found +0.305; $P_H = 6.9$, calcd. +0.200, found +0.232. It should be pointed out that because of the peculiar shape of the E_0' : P_H curve for ferricyanide, it is crossed twice by the A. O. P. curve of α -naphthol at 60°. Thus at $P_H = 0.76$, ferricyanide oxidizes α -naphthol, at $P_H = 3.0$ and $P_H = 5.0$ it is without action, but in solutions more alkaline than $P_H = 5.7$ it reacts and with increasing rapidity as the acidity is decreased. Since E_0' : P_H curve of tungsticyanide is parallel to the P_H axis, the A. O. P. line crosses it only at one point, namely at about $P_H = 4.0$. These and similar relationships which follow from the data in Table III afford a very satisfactory confirmation of the essential correctness of our electrochemical formulation of the oxidation of α -naphthol.

The Oxidation of Certain Phenols and Enols at 23° and 60°

We have been interested in determining the apparent oxidation potential of a number of different types of hydroxy compounds, as a first step in our general inquiry concerning the relative "ease of oxidation" of organic compounds. The only suitable reagents which were sufficiently powerful oxidizing agents to be useful at 25° were potassium molybdicyanide, potassium tungsticyanide and potassium ferricyanide. Potassium permanganate and dichromate do not give sufficiently reproducible potentials to be employed in our work; the relation of their behavior to those of the other reagents will be discussed in another paper.

By using a series of buffer solutions it was possible to decide at what acidity the substance in question was first attacked at an appreciable rate by each of our three reagents. In Table IV, we have recorded only those experiments, the results of which were of service in estimating the A. O. P. Many more experiments were performed under different conditions in which there was either very rapid oxidation or no oxidation. All these unrecorded results were in entire accord with those given in Table IV and our electrochemical formulation. The bands shown in Fig. 1 represent

the A. O. P.: P_H curve plotted from the data in Table IV. With the exception of resorcinol, they approximately parallel the quinone line as would be expected on the basis of the theory outlined in the first part of this paper.

TABLE IV

DETERMINATION OF A. O. P. OF CERTAIN PHENOLS, NAPHTHOLS AND ENOLS AT $23^\circ \pm 2^\circ$
IN DIFFERENT BUFFER SOLUTIONS

F = potassium ferricyanide; M = potassium molybdicyanide; T = potassium tungsticyanide

Substance	Reagent	P_H of soln.	E_s' of reagent	Fraction reacted (S) in		Reaction constant $k \times 10^2$		A. O. P.
				5 min.	30 min.	5 min.	30 min.	
α -Naphthol	M	0.76	+0.775	0.36	>0.95	9	...	+0.708
	T	5.7	+ .510	0.35	.84	9	6	+ .455
	F	6.9	+ .42565	...	3.5	+ .393
	F	7.8	+ .422	.46	>.95	14	...	+ .354
Hydroquinone monomethyl ether	M	0.76	+ .775	.90	>.95	(50)	...	
	T	5.7	+ .510	.18	.60	4	3	+ .480
	F	7.8	+ .422	.28	.62	6	3	+ .380
β -Naphthol	M	4.0	+ .77580	...	32	+ .685
	T	8.9	+ .500	.26	.70	6	4	+ .460
	F	9.7	+ .425	.05	.30	1.0	1.2	+ .425
	F	11.3	+ .425	.72	>.95	26	...	+ .330
Ethyl malonate	M	7.8	+ .71026	...	1.0	+ .710
	T	13.0	+ .500	<.01	<.01			
Resorcinol	M	5.0	+ .77524	...	0.9	+ .775
	T	7.8	+ .510	.36	.70	9	4	+ .460
	F	8.5	+ .425	.10	.33	2.0	1.4	+ .415
Phenol	M	5.0	+ .77520	...	0.8	+ .780
	F	13.0	+ .425	<.01	<.01			
Ethyl acetoacetate	M	5.0	+ .77510	...	2	+ .755
	M	6.9	+ .775	...	>.95			
	T	9.7	+ .500	.02	.05	.3	.2	+ .540
	F	13.0	+ .425	.01	.10	.2	.3	+ .455
Dibenzoylmethane	M	9.7	+ .775	>.95				
	F	13.0	+ .425	<.01	<.01			

The oxidation of the enolic substances deserves a few words of comment. The product of the oxidation of dibenzoylmethane we have shown to be tetrabenzoylthane,⁶ by isolation of the product obtained by oxidizing 1 g. in alkaline solution with 10 g. of potassium molybdicyanide (somewhat more than the calculated amount). Preliminary experiments indicate that ethyl benzoylacetate is similarly oxidized and yields ethyl dibenzoyl-fumarate. The first product of the oxidation of ethyl benzoylacetate is undoubtedly ethyl dibenzoylsuccinate which we have found to

⁶ Andres, *Thesis*, Strassburg, 1911.

be readily oxidized to the unsaturated ester by molybdicyanide in alkaline solutions. In the case of tetrabenzoylthane this further oxidation does not take place as this compound does not form a sodium derivative⁶ (strangely enough). We are continuing a study of the oxidation of enolic

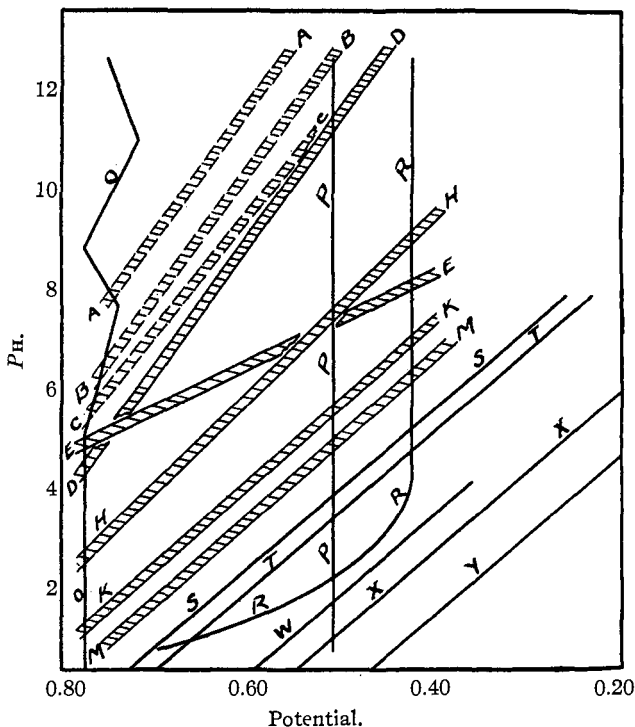


Fig. 1.—The A. O. P. of certain enolic and phenolic substances at various Sørensen values. The cross-hatched bands show the approximate position of the A. O. P. at different Sørensen values as follows: A = dibenzoylmethane; B = malonic ester; C = phenol (all shown as broken bands to indicate some uncertainty at P_H 10–11); D = ethyl aceto-acetate; E = resorcinol; H = β -naphthol; K = hydroquinone monomethyl ether; M = α -naphthol. The normal potentials of the reagents employed are shown by the following lines: O = potassium molybdicyanide; P = potassium tungsticyanide; R = potassium ferricyanide; S = 2,6-dichloroquinone; T = quinone; W = xyloquinone; X = 1,2-naphthoquinone; Y = 1,4-naphthoquinone.

substances by means of the complex cyanides and hope to report in another paper concerning the preparative aspects of the work. The mechanism of the reaction we believe to be the same as that postulated for the phenols and naphthols since the rate is nearly independent of the dilution (Table II).

The influence of change of temperature on the A. O. P. is of interest since we often carry out oxidations in the laboratory at temperatures considerably above 25°. The results already reported for α -naphthol at 60° (Table III) and 23° (Table IV) show that the actual numerical value of the A. O. P. is considerably lowered by an increase in temperature of 35°. Similar results were obtained with other phenols and enols and are briefly summarized in Table V. It must be remembered that this change of A. O. P. is somewhat illusory since the normal potentials of the reagents are also lowered by an increase in temperature. Unfortunately, the potentials of the different reagents do not have a uniform temperature coefficient (though all the quinones seem to be alike) and there is no satisfactory way of referring all the potentials to a standard temperature. Thus, while the A. O. P. of α -naphthol at $P_H = 6.9$ is only +0.232 at 60°, compared with +0.393 at 23°, at both temperatures potassium ferricyanide oxidizes the compound at an appreciable rate. The rate is somewhat faster at 60° than at 23° ($k \times 10^2$ of 16 instead of 3.5) and this corresponds to a real shift in the A. O. P. band as compared to the ferricyanide $E_0':P_H$ line. Similarly the numerical values for the A. O. P. of β -naphthol, phenol and ethyl aceto-acetate are very different in Table IV from the corresponding values in Table III, yet the action of the various reagents is not very different at the two temperatures. To be sure, phenol and ethyl aceto-acetate are very slowly oxidized by ferricyanide in the extremely alkaline solutions at 60°, while at 23° there is no evidence of a reaction. However, it is evident from Fig. 1 that this does not correspond to very much of a shift of the A. O. P. bands of phenol and ethyl aceto-acetate relative to the ferricyanide line.

In terms of our theory, a change in temperature varies three factors, (1) the E_0' value of the reversible step, (2) the E_0' value of the reagent, and (3) the rate of the irreversible step (k' Equation 9a). The speed of the reaction would be expected to increase with temperature, the potential of the reversible step would probably be lower and the potential of most reversible reagents is certainly decreased by rise in temperature. The summation of these three effects in the case of phenolic and enolic substances lowers the A. O. P. bands a little with respect to the potentials of the complex cyanides and somewhat more with respect to the quinones.

Preliminary Experiments with Other Hydroxy Compounds

Finally, we should report our attempts to include in our study the oxidation of alcohols, hydroxy acids, aldehydes, and certain unsaturated compounds. Even in strongly alkaline solution ($P_H = 13$) the following substances were not appreciably attacked by molybdicyanide at 25°: isopropyl alcohol, glycine, lactic acid, mandelic acid, fumaric acid, cinnamic acid, acrylic acid.

Formaldehyde and acetaldehyde are slowly attacked in a solution of *PH* 13 at 25°. At 60°, acetaldehyde is rapidly oxidized in strongly alkaline solution, and slowly in a solution of *PH* 8.5. This shift in the position of the A. O. P. with respect to the potentials of the complex cyanides is greater than what we have observed with the phenols and aceto-acetic ester (Table V). We are continuing a study of the oxidation of aldehydes by reagents of known potential and in another paper we shall discuss the effect of catalysis on such reactions and the use of Fehling's solution and ammoniacal silver nitrate as reagents.

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TABLE V
DETERMINATION OF A. O. P. OF CERTAIN PHENOLS AND ENOLS AT 60°

Substance	Reagent	<i>PH</i> of soln.	<i>E</i> ' of reagent	Fraction reacted		Reaction constant $k \times 10^3$		A. O. P.
				5 min.	(S) in 30 min.	5 min.	30 min.	
α -Naphthol	M	2.0	+0.694	0.05	0.26	1	2	+0.690
	F	2.6	+ .694	.35	.80	9	5	+ .640
β -Naphthol	F	8.3	+ .322	.01	.01			
	F	9.5	+ .331	.30	.70	8	4	+ .275
Phenol	M	4.0	+ .694	.01	.01			
	M	5.2	+ .690	.38	.70	11	4	+ .635
	F	12.0	+ .340	.01	.08	...	0.25	+ .380
Ethyl aceto-acetate	M	4.0	+ .694	.01	.052	
	M	5.2	+ .690	.05	.38	1	1.5	+ .690
	F	12.0	+ .340	.04	.18	0.9	0.8	+ .350

Summary

1. The rate of irreversible oxidation of α -naphthol in acid solution at 60° has been determined, using a number of reversible reagents of known potential. The results show that the speed of oxidation is related to the potential of the reagent employed.

2. The rate of oxidation of a number of phenolic substances and aceto-acetic ester varies only slightly on ten-fold dilution. It is suggested that a reversible formation of a free radical is followed by a monomolecular irreversible isomerization of the free radical followed by polymerization.

3. The relative rates of oxidation of α -naphthol at 60° with reagents of different potential are of the same order of magnitude as those calculated from the electrochemical equations based on the suggested mechanism.

4. The apparent oxidation potential of a number of phenolic and enolic substances has been determined in buffer solutions of varying acidity at 25° and at 60°.