[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

# Kinetics of the Iodination of Phenol

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The kinetics of the iodination of phenol were studied in an attempt to distinguish between the undissociated phenol and the phenoxide ion as the reacting species. The rate constants calculated for the iodination of the phenoxide ion are much greater than those for the iodination of aniline, and the activation energy is smaller. This is in accord with predictions made by the electronic theory of substitution, and supports the assumption that the phenoxide ion is involved rather than phenol. The term $(HOX)(H^+)$ appears in aqueous iodination, bromination and chlorination, and the similarity between the three reactions is emphasized.

Painter and Soper[1] have shown that the kinetics of the iodination of phenol are compatible with a reaction of either undissociated phenol and hypoiodous acid (1) or the phenoxide ion and positive iodine (2).

$$dx/dt = k_0(C_6H_5OH)(HOI) + k_{cat}(C_6H_5O^-)(AcOI) \quad (1)$$

$$dx/dt = k_0(C_6H_5O^-)(I^+) + k_{cat}(C_6H_5O^-)(AcOI) \quad (2)$$

In addition, there is for both cases a general acid-catalyzed reaction of phenoxide ion and hypoiodous acid which the authors formulated as indicating reaction between acyl hypoiodite and the phenoxide ion. A distinction between these two possibilities (1 and 2) could not be made on kinetic grounds, but the authors preferred the latter of the two. The present study was undertaken in order to add further evidence in favor of a reaction involving the phenoxide ion. Since the kinetics alone do not lead to a single answer, it seemed necessary to introduce non-kinetic considerations, but even then, as will be seen, the results are not unambiguous. A possible distinction between the two mechanisms was suggested through the following considerations: the electronic theory demands that the order of activation by different substituents on the benzene ring toward an electrophilic reagent should be $-O^- > -NH_2 > -OH$.[2] Since the kinetics of the iodination of aniline have recently been reported,[3] it should be possible to arrive at a decision simply by establishing the relative order of the two reactions. Because the actual species used in the iodinations is the undissociated phenol, the rate for the phenoxide ion reaction must be calculated from the known concentration of the phenoxide ion at every *p*H. There are, therefore, obtained two sets of rate constants, an observed rate constant (which is possibly a true rate constant for phenol) and one calculated for the phenoxide ion, and these have to be compared with the data for aniline. If the rate constants calculated for the phenoxide ion reaction should be faster than those for the aniline reaction, the evidence can be used as a further support for reaction (2), though not as a proof. If they are slower a reaction involving the phenoxide ion is unlikely. If the reacting species is phenol, the aniline reaction should be faster, except for the unlikely possibility that phenol reacts faster than aniline because HOI is a more powerful iodinating agent than positive iodine.

**The Catalytic Constants.**—A complication arises from the different catalytic characteristics of the two reactions. According to Painter and Soper,[1] the observed rate constants for the iodination of phenol can be expressed as the sum of the catalytic constants as shown in (3).

$$k_{obsd} = \frac{k_0}{(H^+)} + \frac{k_{cat}}{(H^+)^2}(\text{acid}) \quad (3)$$

There is an "uncatalyzed" reaction[4] whose rate varies inversely with the hydrogen ion concentration and an acid-catalyzed reaction whose rate is inversely proportional to the square of the hydrogen ion concentration. This relationship can be rewritten in the form (4). If expressed in this

$$k_{obsd} = k_0(HO^-) + k_{cat}(HO^-)(\text{base}) \quad (4)$$

form, the equation becomes very similar to that found for the aniline reaction (5), except that a hy-

$$k_{obsd} = k_0 + k_{cat}(\text{base}) \quad (5)$$

droxide ion catalysis is superimposed on both the catalyzed and uncatalyzed reactions. The catalytic form of the phenol reaction (4) is rather unusual; while there are many reactions which show specific hydroxide ion and general base catalysis,[5] in the above case the hydroxide ions appear in both terms. This kinetic form indicates the possibility that the hydroxide ions serve a specific purpose, not connected with the substitution process, namely the formation of the phenoxide ion.

In order to obtain all the data required for the comparison some of the work of Painter and Soper had to be repeated under conditions identical with those maintained in the aniline reaction. The iodinations were carried out at 25° with an 0.008 *M* phenol concentration and a 0.002 *M* concentration of iodine. The iodide ion concentration, as in the reactions with aniline, was 0.12 *M* and the total ionic strength was 0.3 (NaCl). Almost all reactions were carried out with phosphate buffers where both secondary and primary phosphate are catalytically active, although the latter much less. Five different buffer ratios were used (*p*H 5.71–6.61). If the observed rate constants are plotted against the primary phosphate ion concentration, lines as shown in Fig. 1 are obtained. The observed rate constants can be expressed by equation (6). If the intercepts at different *p*H's are plotted

$$k_{obsd} = \frac{k_0}{(H^+)} + \frac{k'_{cat}}{(H^+)}(\text{base}') + \frac{k''_{cat}}{(H^+)}(\text{base}'') \quad (6)$$

against the inverse hydrogen ion concentration, the line, whose slope is equal to $k_0$, goes through the origin so that the phenol reaction apparently does not

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[1] B. S. Painter and F. G. Soper, *J. Chem. Soc.*, 342 (1947); F. G. Soper and G. F. Smith, *ibid.*, 2757 (1927).

[2] C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934); *Rec. trav. chim.*, **48**, 797 (1929).

[3] E. Berliner, THIS JOURNAL, **72**, 4003 (1950).

[4] The reaction referred to in the following as the uncatalyzed reaction is actually an inverse hydrogen ion catalyzed reaction.

[5] See for instance, L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 215 ff.

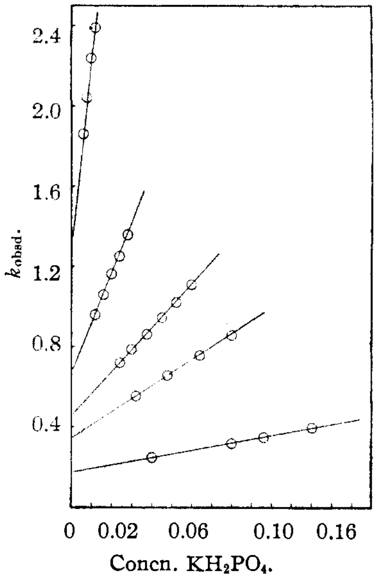

Fig. 1.—The influence of buffers on the iodination of phenol. The lines correspond, from left to right, to the following *p*H's: 6.61, 6.31, 6.13, 6.01, 5.71.

have a water reaction. It seemed preferable to plot $k_{obs}(H^+)$ instead of $k_{obs}$ (7). In that case all

$$k_{obsd}(H^+) = k_0 + k'_{cat}(\text{base}') + k''_{cat}(\text{base}'') \quad (7)$$

the lines converge in one point (Fig. 2). The intercept is equal to $k_0$ and from the slopes of all the lines the two catalytic constants can be calculated by the method used for aniline. The catalytic constants thus obtained are $k_0 = 3.34 \pm 0.06 \times 10^{-7}$; $k_{Na_2HPO_4} = 22.5 \times 10^{-6}$; $k_{KH_2PO_4} \cong 0.7 \times 10^{-6}$. The corresponding constants for aniline are $k_0 = 0.123$; $k_{Na_2HPO_4} = 29.3$; $k_{KH_2PO_4} \cong 0.3$. These two sets of data are clearly not comparable, because the aniline reaction lacks the inverse hydrogen ion catalysis (or direct hydroxide ion catalysis) in all terms. A comparison of the numerical data in terms of reactivities would therefore be quite meaningless and misleading. This shows the need for exercising caution in evaluating relative reactivities, even when the experimental conditions are the same. For instance, relative activating powers deduced from the direction of substitution in compounds such as *p*-aminophenol are very doubtful and the results fortuitous.[6]

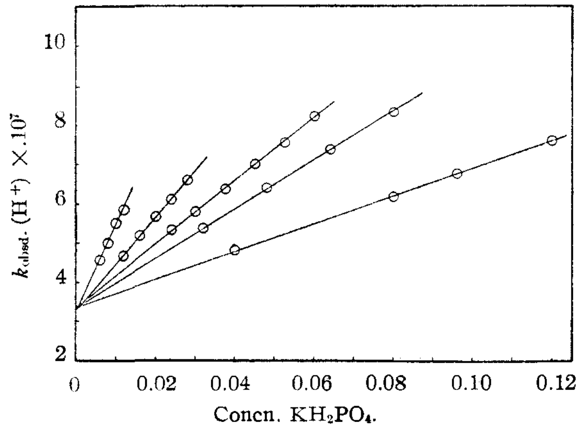

Fig. 2.—The influence of buffers on the iodination of phenol: a plot of $k_{obsd.}(H^+)$ against the concentration of $KH_2PO_4$.

In order to obtain the rate constants for the iodination of the phenoxide ion one can use, for each experimental run, expression (8), where *K* is the

$k_{obsd}(C_6H_5OH)(I_2) = k_{C_6H_5O^-}(C_6H_5O^-)(I_2)$ and

$$k_{C_6H_5O^-} = \frac{k_{obsd}(H^+)}{K} \quad (8)$$

dissociation constant of phenol. The observed rate constants for the phenoxide ion reaction can be expressed by an equation of the type (9). This re-

$$k_{obsd} = k_0 + k_{cat}(\text{base}) \quad (9)$$

action has the same catalytic characteristics as the aniline reaction, and the respective data can be compared, because in both reactions the catalytic constants are independent of the hydrogen ion concentration. From Fig. 3, in which the rate constants for the phenoxide ion reaction are plotted against the concentration of primary phosphate, the rate constants are found to be $k_0 = 3.06 \pm 0.05 \times 10^3$; $k_{Na_2HPO_4} = 20.8 \times 10^4$; $k_{KH_2PO_4} \cong 0.6 \times 10^4$. Table I shows the observed rate constants and those calculated assuming equation (10).

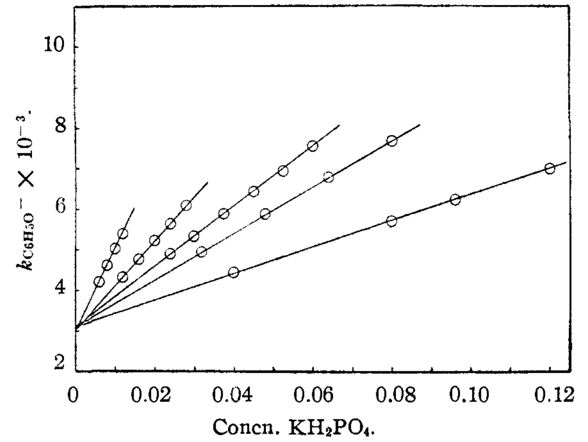

Fig. 3.—The influence of buffers on the iodination of phenol: a plot of $k_{C_6H_5O^-}$ against the concentration of $KH_2PO_4$.

$$k_{obsd} = 3.06 \times 10^3 + 20.8 \times 10^4[Na_2HPO_4] + 0.6 \times 10^4[KH_2PO_4] \quad (10)$$

A comparison with the aniline reaction shows that the uncatalyzed reaction of phenoxide ion is 25,000 times faster than the uncatalyzed reaction of aniline, and the catalytic constant $k_{Na_2HPO_4}$ is 7,100 times greater than the corresponding constant for aniline. Not only is the assumption of phenoxide ion as the reacting species in agreement with the data, but the numerical differences are reasonable on chemical grounds. The charged phenoxide ion and the uncharged aniline should differ in reactivity by an appreciable factor.

**The Energies of Activation.**—Another comparison is possible through the energies of activation, but here again two sets of data are obtained. A clear-cut decision cannot be made and it can only be decided whether or not the data are in agreement with the assumption of the phenoxide

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[6] W. Theilacker, *Ber.*, **71**, 2065 (1938); W. Fuchs, *Monatsh.*, **38**, 331 (1917).

TABLE I

THE RATES OF IODINATION OF PHENOL AT VARYING BUFFER CONCENTRATIONS[a]

KI 0.12 $M$, $\mu = 0.3$, $T = 25°$

| $p$H | Concn. $KH_2$-$PO_4$ | Concn. $Na_2$-$HPO_4$ | $k_{obsd}$ | $k_{obsd}$ ($H^+$) $\times 10^7$ | $k_{obsd}$ ($H^+$) $\times 10^7$ (calcd.)[b] | $k_{C_6H_5O^-}$ $\times 10^{-3}$ | $k_{C_6H_5O^-}$ $\times 10^{-3}$ (calcd.)[c] |
|---|---|---|---|---|---|---|---|
| 6.13 | 0.024 | 0.008 | 0.719 | 5.33 | 5.31 | 4.89 | 4.87 |
| | .03 | .01 | .783 | 5.80 | 5.80 | 5.32 | 5.32 |
| | .0375 | .0125 | .862 | 6.39 | 6.41 | 5.86 | 5.87 |
| | .045 | .015 | .944 | 7.00 | 7.03 | 6.42 | 6.45 |
| | .0525 | .0175 | 1.02 | 7.56 | 7.64 | 6.94 | 7.01 |
| | .06 | .02 | 1.11 | 8.23 | 8.26 | 7.55 | 7.58 |
| 6.01 | 0.032 | 0.008 | 0.550 | 5.38 | 5.36 | 4.93 | 4.92 |
| | .048 | .012 | .655 | 6.40 | 6.38 | 5.87 | 5.84 |
| | .064 | .016 | .755 | 7.38 | 7.39 | 6.77 | 6.77 |
| | .08 | .02 | .854 | 8.35 | 8.40 | 7.66 | 7 70 |
| | | | $T = 35°$ | | | | |
| 6.01 | 0.032 | 0.008 | 2.27 | 22.2 | 22.4[d] | 14.8 | 14.9[e] |
| | .048 | .012 | 2.74 | 26.8 | 26.9 | 17.9 | 17.9 |
| | .064 | .016 | 3.22 | 31.5 | 31.4 | 21.0 | 21.0 |
| | .08 | .02 | 3.64 | 35.6 | 35.9 | 23.7 | 24.0 |
| 5.61 | 0.05 | 0.005 | 0.843 | 20.7 | 20.6 | 13.8 | 13.8 |
| | .06 | .006 | .903 | 22.2 | 22.0 | 14.8 | 14.7 |
| | .08 | .008 | 1.02 | 25.0 | 25.0 | 16.7 | 16.7 |
| | .10 | .01 | 1.12 | 27.5 | 27.9 | 18.3 | 18.7 |
| | | | $T = 25°$ | | | | |
| | Concn. HAc | Concn. NaAc | | | | | |
| 5.60 | 0.01 | 0.1 | 0.665 | | | 1.53 | 1.54[f] |
| | .012 | .12 | .736 | | | 1.70 | 1.71 |
| | .014 | .14 | .815 | | | 1.88 | 1.87 |
| | .016 | .16 | .888 | | | 2.05 | 2.04 |

[a] All rate constants are in liters moles$^{-1}$ min.$^{-1}$. [b] Calculated from $k_{obsd}$ ($H^+$) = $3.34 \times 10^{-7} + 22.5 \times 10^{-6}$ [$Na_2HPO_4$] + $0.7 \times 10^{-6}$ [$KH_2PO_4$]. [c] Calculated from $k_{C_6H_5O^-} = 3.06 \times 10^3 + 20.8 \times 10^4$ [$Na_2HPO_4$] + $0.6 \times 10^4$ [$KH_2PO_4$]. [d] Calculated from $k_{obsd}$ ($H^+$) = $1.33 \times 10^{-6} + 91.7 \times 10^{-6}$ [$Na_2HPO_4$] + $5.4 \times 10^{-6}$ [$KH_2PO_4$]. [e] Calculated from $k_{C_6H_5O^-} = 8.88 \times 10^3 + 60.7 \times 10^4$ [$Na_2HPO_4$] + $3.7 \times 10^4$ ($KH_2PO_4$]. [f] Calculated from $k_{C_6H_5O^-} = 0.71 \times 10^4 + 8.3 \times 10^4$ [$CH_3COONa$].

ion reaction.[7] From the plot of $k_{obsd.}(H^+)$ at 35° against primary phosphate at five different buffer ratios ($p$H 6.01–5.61), similar to the one represented by Fig. 2 and equation (7) $k_0$ is calculated to be $1.33 \pm 0.01 \times 10^{-6}$. From this value and the value at 25° the experimental energy of activation for the observed uncatalyzed reaction is 25.2 kcal. Aniline was iodinated at 35° using four different phosphate buffer ratios ($p$H 7.23–5.61). At 35° $k_0$ for aniline is $0.455 \pm 0.005$ from which in conjunction with $k_0$ at 25° the activation energy of the uncatalyzed aniline reaction is calculated to be $23.9 \pm 0.5$ kcal. To calculate the energy of activation of the phenoxide reaction it is necessary to know the dissociation constant of phenol at two different temperatures. The only data in the literature are those of Lunden,[8] and from his data the value for $K$ at 35° ($1.50 \times 10^{-10}$) was obtained by extrapolation. In order to use a consistent set of data Lunden's value of $1.09 \times 10^{-10}$ was used for $K$ at 25°. With this value for $K_{35}$, $k_0$ for the phenoxide ion reaction at 35° is $8.88 \pm 0.06 \times 10^3$ and the activation energy is $19.4 \pm 0.4$ kcal. This is less by 4.5 kcal. than the value for aniline and constitutes again a reasonable difference between the phenoxide ion reaction and that of aniline.

The values for the activation energies of the catalyzed reactions could not be found with the same accuracy as those for the uncatalyzed reactions. This is partly due to the uncertainty with which the catalytic constants for primary phosphate are determined,[9] because they only constitute a few per cent. of the constants for secondary phosphate (the former being a much weaker base), and partly because the phenol reaction could not be studied over a wide enough range of $p$H on account of the great variations in reactivity. The data for secondary phosphate are recorded in Table II together with other relevant data. The energy of activation for the catalyzed reaction of phenoxide ion ($E_{Na_2HPO_4}$) is less than that for aniline, as expected, but the difference is rather small and not very significant. The difference is decidedly smaller than that for the uncatalyzed reactions for reasons which are not at all clear. Included in the table are also some data obtained in acetate buffers. Here again the uncatalyzed phenoxide ion reaction proceeds with a lower activation energy than the uncatalyzed aniline reaction. The energies of activation as given in Table II are not true activation energies for the iodinations; they are composite values and include the heats of reaction involved in the formation of the iodinating species as well as the heats of dissociation of the buffers. However, a comparison of the activation energies of the phenoxide ion and the aniline reaction is meaningful if, as is assumed here, the iodinating species for the two reactions are identical.

**The Iodinating Agent.**—The kinetic data so far presented make it seem probable that the iodination of phenol actually takes place on the phenoxide ion. The following argument is based on another analogy with the aniline reaction. The kinetics of the iodination of aniline are in agreement with a reaction between aniline and $I^+$ and a general base-catalyzed reaction between the same two species (11).[3] The function of the

$$dx/dt = k_0(C_6H_5NH_2)(I^+) + k_{cat}(C_6H_5NH_2)(I^+)(\text{base}) \qquad (11)$$

base could be visualized as being concerned with the removal of the proton from the benzene ring. However, good arguments have been advanced to the effect that the proton loss in aromatic substitution is kinetically insignificant and takes place after the rate-determining step.[10] If this also applies to iodination the base may not have this function and a second possibility, kinetically indistin-

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[7] There is a point to be considered when the reaction is conducted at two temperatures. The hydrogen ion concentration of a buffer is practically independent of the temperature (D. I. Hitchcock and A. C. Taylor, THIS JOURNAL, **60**, 2710 (1938); D. A. MacInnes, D. Belcher and T. Shedlovsky, *ibid.*, **60**, 1094 (1938)) but since $Kw$ has a strong temperature dependence the hydroxide ion concentration changes and is almost doubled between 25 and 35°. The two equations (3) and (4) are therefore not equivalent any more, and the energy of activation for the observed reaction is quite different (almost by a factor of two) depending on whether a hydroxide or inverse hydrogen ion catalysis is assumed to take place. Since in the present case both equilibria in question, namely, that of hypoiodous acid and that of phenol, involve stoichiometrically the hydrogen ions rather than the hydroxide ions the expression containing hydrogen ions was used in calculating $E$ for the observed reaction. This difficulty is absent in the phenoxide ion reaction.

[8] H. Lunden, *Z. physik. Chem.*, **70**, 249 (1910).

[9] The recorded values for the catalytic constants of primary phosphate are very approximate.

[10] L. Melander, *Acta Chem. Scand.*, **3**, 95 (1949); *Arkiv för Kemi*, **2**, 213 (1950); E. D. Hughes, C. K. Ingold and R. I. Reed, *J. Chem. Soc.*, 2400 (1950).

TABLE II

THE CATALYTIC CONSTANTS AND ENERGIES OF ACTIVATION OF THE IODINATION OF PHENOL AND ANILINE[a]

| | $k_0^{25}$ | $k_0^{35}$ | $E_0$ (kcal.) | $k^{25}_{\text{Na}_2\text{HPO}_4}$ | $k^{35}_{\text{Na}_2\text{HPO}_4}$ | $E_{\text{Na}_2\text{HPO}_4}$ | ${}^{c}k_0^{25}$ | ${}^{c}k_0^{35}$ | $E_0{}^{c}$ |
|---|---|---|---|---|---|---|---|---|---|
| $C_6H_5OH$[b] | $3.34 \pm 0.06 \times 10^{-7}$ | $1.33 \pm 0.01 \times 10^{-6}$ | $25.2 \pm 0.5$ | $22.5 \times 10^{-6}$ | $91.7 \times 10^{-6}$ | 25.6 | | | |
| $C_6H_5O$ | $3.06 \pm 0.05 \times 10^{3}$ | $8.88 \pm 0.06 \times 10^{3}$ | $19.4 \pm 0.4$ | $20.8 \times 10^{4}$ | $60.7 \times 10^{4}$ | 19.5 | $0.71 \times 10^{4}$ | $2.08 \times 10^{4}$ | 19.6 |
| $C_6H_5NH_2$ | $0.123 \pm 0.002$ | | $0.455 \pm 0.005$ | $23.9 \pm 0.5$ | 29.3 | 88.8 | 20.2 | 0.121 | 0.435 | 23.3 |

[a] All rate constants are in liters moles$^{-1}$ minutes$^{-1}$. [b] These are the values for the observed reaction. The rate constants for the "uncatalyzed" and the catalyzed reactions are inversely proportional to the hydrogen ion concentration. See equation (7) and footnote 4. [c] In acetate buffers.

guishable from the first, involves a hydrogen ion or general acid-catalyzed reaction of aniline and hypoiodous acid[3] (12). The complex of hypoiodous

$$dx/dt = k_0(C_6H_5NH_2)(HOI)(H^+) + k_{cat}(C_6H_5NH_2)(HOI)(\text{acid}) \quad (12)$$

acid and an acid can be represented as a hydrated $I^+$ or as the conjugate acid of hypoiodous acid $(H_2OI)^+$, and in either case the function of the acid would be to weaken the oxygen–iodine link either at the moment of or prior to the attack on the benzene ring. This possibility seems a rather plausible one, but when applied to the iodination of phenol it fits, kinetically, only a reaction involving the phenoxide ion (13); the undissociated phenol

$$dx/dt = k_0(C_6H_5O^-)(HOI)(H^+) + k_{cat}(C_6H_5O^-)(HOI)(HA) \quad (13)$$

cannot react with HOI by a reaction involving acid catalysis.[11] The second term in (13) is identical with that of Painter and Soper, except that the latter assumed the direct formation of an iodinating species between hypoiodous acid and the buffer acid, which in the present interpretation does not seem necessary.

There have recently been described a number of halogenation reactions in water which show the kinetic form of reactions (12) and (13). Wilson and Soper[12] have observed acid catalysis in the bromination of *o*-nitroanisole and of benzene with hypobromous acid, and Derbyshire and Waters[13] have noted the same in the bromination of ω-toluenesulfonic acid. The appearance of the term $(HOBr)(H^+)$, noted earlier by Schilov and Naniaev,[14] has independently been interpreted by these authors as indicating bromination by either $Br^+$ or the conjugate acid of hypobromous acid. As in the iodination, kinetically no distinction between the two can be made. Furthermore, De La Mare, Hughes and Vernon[15] found that the kinetics of chlorination with hypochlorous acid followed a similar expression. Under their experimental conditions the formation of $Cl^+$ is more surely established, because the reactions are of zeroth order with respect to the aromatic compound (if the latter is sufficiently reactive) and the kinetically important step, according to these authors, involves the formation of $Cl^+$, similar to zeroth order nitration.[16] Under favorable conditions these authors also visualize a second order reaction with $(H_2OCl)^+$,[17] and the difficulty to distinguish between the two possibilities in some cases has recently been emphasized.[18] In the present work the reactions are first order with respect to aromatic compound, probably because the equilibria leading to the formation of hypoiodous acid as well as the breaking of the iodine–oxygen bond are easier energetically than the breaking of the chlorine–oxygen bond, and the former must be comparable with the energy required for substitution. If chlorination proceeds through $Cl^+$, bromination and certainly iodination should be much more likely to proceed through the positive halogen itself,[19] but the kinetics of iodination (as of bromination) do not allow that conclusion, although they do not rule it out. The iodination is at the present time best pictured as involving either a preliminary formation of $I^+$ from HOI and $H^+$ (or a general acid), and an attack by the equilibrium $I^+$ on the aromatic compound, or an attack by the conjugate acid of HOI.

The striking similarity between the kinetics of chlorination, bromination and iodination speaks very much in favor of mechanism (13) for which the phenoxide ion has to be assumed to be the reacting species. That substitution takes place on phenoxide ion has recently been postulated even for nitration,[20] where the concentration of the phenoxide ion is much smaller than in the above experiments. It was also quite convincingly established for chlorination with hypochlorous acid[21] and for diazo coupling.[22]

## Experimental

**Materials.**—Two samples of phenol were tested. One was obtained by hydrolysis of twice recrystallized phenylbenzoate (Eastman Kodak Co., m.p. 68.3–68.9°) and two distillations, b.p. 180.2–180.4° (753 mm.). The other was Merck Reagent Grade Phenol which was twice distilled at atmospheric pressure (b.p. 181.4° (763–764 mm.)); it was then heated for four hours at 50° over Drierite and for 30 minutes over calcium chloride, and distilled *in vacuo*. Since both samples gave the same kinetic results in test runs, the second sample was used in subsequent runs. The aniline was the sample used in previous experiments[3] and was redistilled *in vacuo* before use. All other reagents were best commercial reagent grade chemicals and were used without further purification.

**Kinetic Runs.**—All stock solutions were prepared as described before except that the phenol was made up so as to give a 0.008 *M* solution rather than 0.004 *M*. At the lower phenol concentration the rate constants had a tendency to rise during the later parts of the reaction which may have been due to some precipitation of the product. These difficulties were not encountered with the higher concentrations of phenol. The kinetic runs were carried out as described

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[11] It can, however, react in a hydrogen ion or acid-catalyzed reaction with hypoiodite ion, although this is unlikely on chemical grounds.

[12] W. J. Wilson and F. G. Soper, *J. Chem. Soc.*, 3376 (1949).

[13] D. H. Derbyshire and W. A. Waters, *ibid.*, 564, 574 (1950).

[14] E. A. Schilov and N. P. Naniaev, *Compt. rend. acad. Sci. U. R. S. S.*, **24**, 890 (1939) [*C. A.*, **34**, 4062 (1940)].

[15] De La Mare, E. D. Hughes and C. A. Vernon, *Research*, **3**, 192 (1950).

[16] E. D. Hughes, C. K. Ingold and R. I. Reed, reference 10.

[17] P. B. D. De La Mare, E. D. Hughes and C. A. Vernon, *Research*, **3**, 242 (1950).

[18] D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 73 (1951).

[19] See J. Weiss, *Ann. Repts.*, **44**, 79 (1947).

[20] C. A. Bunton, E. D. Hughes, C. K. Ingold, D. I. H. Jacobs, M. H. Jones, G. I. Minkoff and R. I. Reed, *J. Chem. Soc.*, 2628 (1950).

[21] F. G. Soper and G. F. Smith, *ibid.*, 1582 (1926).

[22] R. Wister and P. D. Bartlett, THIS JOURNAL, **63**, 413 (1941).

before for aniline. At 35° in some buffers reaction was so fast that a blank was determined in order to establish the initial iodine titer. All runs were conducted at least in duplicate and agreed usually within 1–2%.

DATA FOR SOME TYPICAL RUNS

THE IODINATION OF PHENOL IN WATER

phenol 0.007948 *M*, KI 0.12 *M*, $KH_2PO_4$ 0.016 *M*, $Na_2HPO_4$ 0.008 *M*, NaCl 0.14 *M*, $\mu = 0.3$, $T = 25°$

| Time, min. | 0.02 Thiosulfate, ml. | $k$ (liters mole$^{-1}$ min.$^{-1}$) | Time, min. | 0.02 *M* thiosulfate, ml. | $k$ (liters mole$^{-1}$ min.$^{-1}$) |
|---|---|---|---|---|---|
| 0 | 1.966 | | 0 | 1.966 | |
| 13 | 1.762 | (1.074) | 12 | 1.778 | 1.067 |
| 23 | 1.630 | 1.048 | 24 | 1.613 | 1.062 |
| 37 | 1.454 | 1.062 | 35 | 1.476 | 1.065 |
| 47 | 1.342 | 1.067 | 46 | 1.350 | 1.073 |
| 57 | 1.244 | 1.063 | 56 | 1.250 | 1.070 |
| 68 | 1.152 | 1.048 | 67 | 1.156 | 1.057 |
| 84 | 1.020 | 1.054 | 77 | 1.072 | 1.058 |
| 94 | 0.946 | 1.057 | 91 | 0.966 | 1.058 |
| | Av. | 1.057 | | Av. | 1.064 |

The catalytic constants for secondary phosphate were obtained by the method of least squares with the omission of one point which fell obviously too far from the line.

Since in acetate buffers the reactions were very slow the iodide ion concentration was changed from 0.12 to 0.08 *M*. Recalculated to 0.12 *M* (*i.e.*, multiplied by 0.0064/0.0144) $k_0^{25}$ for phenoxide ion becomes $3.15 \times 10^3$ and $k_0^{35}$ $9.2 \times 10^3$, which agrees well with the constants for the uncatalyzed phenoxide ion reaction in phosphate buffers. Only a few acetate buffer ratios were used and the data for acetate buffer are less accurate than those for phosphate, particularly since difficulties were encountered in reproducing exactly the *p*H of the buffer. The values for $k_{Ac^-}$ at 25° and 35° are approximately $8.3 \times 10^4$ and $29 \times 10^4$ for phenoxide ion. The approximate activation energy ($E_{Ac^-}$) is therefore 22.8 kcal.

In Table III are listed the rate constants obtained when the initial concentrations are varied; they show the second order nature of the reaction. Table IV records some data which show that an increase in ionic strength from $\mu$ 0.3 to 0.5 decreases the rate by about 20%.

TABLE III

THE IODINATION OF PHENOL WITH DIFFERENT CONCENTRATIONS OF REACTANTS AT 25°

KI 0.12 *M*, $KH_2PO_4$ 0.06 *M*, $Na_2HPO_4$ 0.01 *M*, NaCl 0.09 $\mu = 0.3$

| Molarity of phenol $\times 10^3$ | Molarity of iodine $\times 10^3$ | $k$(liters moles$^{-1}$ min.$^{-1}$) |
|---|---|---|
| 3.99 | 1.99 | 4.45[a] |
| 7.99 | 1.96 | 4.05 |
| 12.0 | 1.97 | 4.15 |
| 16.0 | 1.97 | 4.03 |
| 7.99 | 1.00 | 4.07 |
| 7.99 | 3.96 | 4.36[a] |
| 16.0 | 3.96 | 4.06 |

[a] The product precipitated during the reaction.

TABLE IV

THE EFFECT OF IONIC STRENGTH ON THE RATES OF IODINATION OF PHENOL

Phenol 0.008 *M*, Iodine 0.002 *M*, KI 0.12 *M*

| $KH_2PO_4$ 0.08 *M*, $Na_2HPO_4$ 0.01 *M* | | $KH_2PO_4$ 0.03 *M*, $Na_2HPO_4$ 0.01 *M* | |
|---|---|---|---|
| $\mu$ | $k$(liter moles$^{-1}$ min.$^{-1}$) | $\mu$ | $k$(liter moles$^{-1}$ min.$^{-1}$) |
| 0.3 | 0.324 | 0.3 | 0.786 |
| .4 | .292 | .4 | .706 |
| .5 | .265 | .5 | .646 |

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# Sensitized Catalysts. II. The Ascorbic Acid Method

BY HUGO J. KAUFFMANN

Ascorbic acid accelerates the catalytic oxidation of dyes with hydrogen peroxide in acidic solution. Dyes of different kinds show this effect, methyl orange being especially suitable and applicable under various conditions. Efficient catalysts are cupric and ferric salts. Hydrogen peroxide can be replaced by potassium persulfate. Oxygen is an inhibitor. Ethers and alcohols in the presence of ascorbic acid act as sensitizers. In the absence of ascorbic acid, they are inhibitors. The efficiency of a sensitizer increases with its concentration. The sensitization is due to the reduction of the catalyst and, presumably, to subsequent formation of free hydroxyl. The sensitization can be interpreted as an activation of the sensitizer brought about by free hydroxyl.

As shown in the first communication,[1] the catalytic oxidation of acid indigo carmine solutions by hydrogen peroxide or a persulfate can be greatly accelerated by many organic substances. Organic compounds, such as benzene or its sulfonates, which do not reduce ferric ions and which accelerate with ferric as well as with cupric salts as catalyst, have been called sensitizers.

Because with other dyes or other colored substrates, benzene, and the various sensitizers, act as regular inhibitors, the sensitizing effect seems to be connected with the particular constitution of the indigo. The kinetics of the process has been found to be complicated, but one essential fact can be stated: The described sensitization is an autoxidation of the indigo solution induced by the percompound and highly accelerated by the sensitizer.

As to the organic compounds which reduce ferric salts, an exceptional behavior of ascorbic acid was observed, best demonstrated by comparing it with phloroglucinol. The latter is an inhibitor, retarding the indigo oxidation, especially at high hydrogen ion concentration. Ascorbic acid, on the contrary, is an excellent accelerator for other dyes also. However, what is more significant, dyes such as methyl orange are in the presence of ascorbic acid not only easily oxidizable, *they now respond to sensitizers.* Another substance, which like ascorbic acid stimulates sensitization, is pyrogallol, but its stimulating effect is less drastic and very limited.

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[1] H. Kauffmann THIS JOURNAL, 69, 899 (1947).