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# Aqueous Chlorination Kinetics and Mechanism of Substituted Dihydroxybenzenes

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The initial chlorination kinetics of several substituted dihydroxybenzenes, including chlorinated resorcinol compounds, was studied over the pH range of 2−12 at 22 °C. For each of the resorcinol substrates, the apparent chlorination rates are a minimum in the pH range of 3−6 and a maximum at pH values between 8−11. A mechanism that involves the reaction of HOCl with $ArX(OH)_2$, $ArX(OH)O^-$, and $ArX(O^-)_2$, and an acid-catalyzed pathway at pH < 4 was proposed to explain this pH dependence. Over natural water pH conditions, the reactions of HOCl with the anion and dianion forms of resorcinol groups are the most important. Although the intrinsic reactivity of HOCl with resorcinol substrates decreases with the extent of chlorine substitution on aromatic ring, the apparent reactivity of HOCl increases for more chlorinated resorcinols. In the presence of excess HOCl, monochloro- and dichloro resorcinol intermediates, therefore, should not accumulate when resorcinol groups undergo chlorine substitution. Linear free energy relationships for the reactivity of HOCl with resorcinols and phenols were developed. The sequential chlorination kinetics of resorcinol up to trichlororesorcinol can now be modeled.

## Introduction

The formation mechanisms of chlorination byproducts have been extensively investigated since humic substances were first identified as precursors for trihalomethanes in natural water disinfection processes (*1*). The majority of these studies have focused on the identification of stable intermediates and products with humic and fulvic acids (*2*−*7*) or model compounds (*8*−*13*) as substrates. Dihydroxybenzene moieties in humic matter were hypothesized by Rook (*9*) to be responsible for the formation of chloroform. Later studies by de Leer et al. (*5*) corroborated this theory. Norwood and Christman (*14*) have also demonstrated the importance of phenol groups as reactive centers for chlorination byproducts.

**TABLE 1**

**Rate Constants for Chlorination of Substituted Phenolates**

| substrate | $k_2$ ($M^{-1}$ $s^{-1}$)[a] | ref |
|---|---|---|
| phenolate | $3.05 \times 10^4$ | 16 |
| | $3.3 \times 10^5$ | 15 |
| 2-chlorophenolate | 2150 | 16 |
| | $5.9 \times 10^4$ | 15 |
| 4-chlorophenolate | 2680 | 16 |
| | $4.9 \times 10^4$ | 15 |

[a] Corresponds to the rate constant for the reaction of HOCl + substrate. Values from ref *16* were obtained by fitting the reported pH profiles of apparent rate constants (*17*).

Early kinetic studies of the chlorination of phenol and chlorine-substituted phenols by Soper and Smith (*15*) and later by Lee (*16*) have shown that the overall reaction is second-order and proportional to the concentration of aqueous chlorine and phenol at pH > 6. Both investigators also observed that the rate was highly pH-dependent and observed a maximum in the neutral or slightly alkaline pH range. The mechanism over this pH range was found to involve the reaction of the hypochlorous acid species with the phenolate ion:

$$HOCl + C_6H_5O^- \xrightarrow{k_2} C_6H_4Cl(O^-) + H_2O \qquad (1)$$

Similar findings were reported by Brittain and de la Mare (*18*).

Substantial differences exist, however, between the rate constants for the reaction of HOCl with substituted phenolates, as reported by Soper and Smith (*15*), and those that can be obtained from Lee's kinetic data (*16*). In the latter study, only the apparent rate constants, $k_{app}$, were reported as a function of pH where

$$\frac{d[\text{phenol}]}{dt} = k_{app}[\text{phenol}]_{TOT}[\text{chlorine}]_{TOT} \qquad (2)$$

Using Lee's data over the range pH > 6 to determine $k_2$, the values shown in Table 1 are obtained. Soper and Smith's estimates of $k_2$ for the same substituted phenols are considerably larger (see Table 1).

In addition to the large uncertainty that exists between the reported chlorination rates of phenols in neutral or alkaline solutions, the mechanism of phenol chlorination in acidic solution (pH < 6) has not been determined. The two existing kinetic studies were conducted in the presence of high chloride ion concentrations (*15*, *16*). When the solution was acidified with HCl, the reaction was found to be independent of phenol and proportional to the square of the HCl concentration (*15*). It was proposed that the reaction was limited by the formation rate of $Cl_2$. The reversible formation of molecular chlorine from chloride and hypochlorous acid is shifted to the right in the presence of chloride:

$$H^+ + Cl^- + HOCl \rightleftharpoons Cl_2 + H_2O \qquad (3)$$

Detailed kinetic studies of the bromination of phenols have also been conducted in the presence of high concentrations of bromide (>0.1 M) (*19*). Under these conditions, the rate of phenol bromination was governed by the

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reactions of molecular bromine with phenol and the phenoxide ion over the pH range between 0 and 7. In the absence of bromide, however, the rate of bromination of aromatic compounds by molecular hypobromous acid is proportional to the acidity at low concentrations of acid (*20*). It was hypothesized that the reaction pathway involves either (1) the pre-equilibrium protonation of hypobromous acid followed by the rate-limiting reaction of the positive bromine species with the substrate or (2) HOBr and the substrate are first brought together, protonated, and the rate-determining step is the decomposition of the protonated transition state. Given that the chlorination kinetics of phenols in acidic solution have only been characterized in the presence of high chloride concentrations and that phenol bromination is apparently catalyzed by acid in the absence of bromide, additional kinetic studies of phenol chlorination at $pH < 6$ are needed to determine whether acid catalysis is observed in the absence or presence of only small chloride concentrations.

Few detailed quantitative studies of the chlorination kinetics of dihydroxybenzene compounds are available. Heasley et al. (*21*, *22*) determined through the identification of intermediates that successive electrophilic chlorination of resorcinol from monochloro-, to dichloro-, to 2,4,6-trichlororesorcinol occurs before ring-opening. They hypothesized that a pentachloro intermediate was involved in the ring-opening step. In these studies, only relative chlorination rates of resorcinol and chlorine-substituted resorcinols were determined at pH 7 however. It is expected that the completely deprotonated resorcinol species (dianion) would be even more reactive than the singly deprotonated species. The contribution of the dianion form to the chlorination reaction at natural water pH conditions, however, cannot yet be predicted.

In this study, the chlorination kinetics of several substituted resorcinols were studied over a wide range of pH conditions. A series of chlorine-substituted resorcinol substrates were selected to obtain a stepwise evaluation of the successive chlorination of resorcinol through dichlororesorcinol. Free energy correlations and structure−reactivity relationships were also examined. The results are useful for predicting the extent of accumulation of chlorinated phenols and resorcinols under varying HOCl:phenol ratios and for comparing the relative reaction rates of chlorine with phenolic compounds and other substrates.

## Experimental Procedures

**Materials**. Reagents including resorcinol (99% Baker), orcinol or 5-methylresorcinol (ACS reagent grade, Fisher Scientific), 4-chlororesorcinol (98% Aldrich), 4,6-dichlororesorcinol (97% Aldrich), NaOCl (5% solution, Baker), $Na_2S_2O_3$ (Fisher), $H_2SO_4$ (Fisher), KOH (Fisher), and $NaClO_4$ (99% Aldrich) were used without further purification. Stock solutions (0.2 M) of the dihydroxybenzene compounds were prepared in HPLC grade methanol. All other solutions were prepared with deionized water from a Millipore purification system.

The commercial NaOCl reagent contained equimolar amounts of $OCl^-$ and $Cl^-$ ions. Based on reported values of the equilibrium constant for the hydrolysis of $Cl_2$ (*23*), the maximum concentration of $Cl_2$ (at pH 2) in our study was approximately $2.5 \times 10^{-8}$ M, since the reactions were conducted with $[HOCl]_{TOT} = [Cl^-] \leq 3.5 \times 10^{-5}$ M.

**Methods.** All kinetic experiments were conducted in a batch reactor at room temperature (22 °C). The pH of the solution was kept constant by additions of $H_2SO_4$ and KOH with a Radiometer pH-stat apparatus. Aluminum foil was used to shield the reactor from extraneous photochemical reactions. Reagents were added to the reactor with micropipets.

Chlorination experiments were conducted under pseudo-first-order conditions where HOCl was in excess. The molar chlorine to substrate ratio varied from 20 to 50. In a typical experiment, a 250-mL volume of HOCl solution was prepared in a batch reactor, and the pH was adjusted to the desired value. The dihydroxybenzene was added to the rapidly stirred chlorine solution, and at fixed time intervals the reaction was quenched with an excess of sodium thiosulfate. Half-lives for the substituted resorcinols ranged from 7 min to 5 s, and the uncertainty in measuring the reaction times was estimated to be 1 s. The stirring rate of the reactor was set by increasing the mixing speed until the reaction rate was independent of the stirring rate. Although no rate constant is available for the reaction of chlorine with $S_2O_3^-$, thiosulfate is typically used as a titrant in chlorine determinations on the basis of its rapid reaction rate. The reaction rate of thiosulfate with molecular iodine is also known to be diffusion-limited (*24*). Given the excess thiosulfate that was added and the high reactivity of thiosulfate with chlorine, quenching of HOCl by $S_2O_3^-$ is expected to be significantly faster than the reaction of resorcinol and HOCl.

Analyses for the resorcinol substrates were performed by HPLC with a Dionex Series 4000i chromatograph equipped with a Supelcosil LC-18 column and a Dionex variable UV/Vis wavelength detector. Samples were eluted with a methanol/water/acetic acid mobile phase at a flow rate of 1.5 mL/min. Chromatographic peaks for the substituted resorcinols were well-resolved, and hence the chlorinated products did not interfere with substrate concentration measurements.

Final concentrations of HOCl were measured in parallel experiments, in which potassium iodide was used to quench the reaction. The $I_2$ was quantitatively titrated with a standard sodium thiosulfate solution in the presence of a starch indicator, after acidifying the solution with acetic acid to the pH range of 3−4 (*25*).

Acid dissociation constants $K_{a1}$ and $K_{a2}$ for orcinol, 4-chlororesorcinol, and 4,6-dichlororesorcinol were determined by potentiometric titration according to the method of Albert and Serjeant (*26*).

## Results and Discussion

The measured acid dissociation constants for each of the resorcinol substrates and several reported $pK_a$ values for resorcinol are tabulated in Table 2. A relatively wide range of published $pK_{a1}$ values are available for resorcinol and hence the average of three reported values, 9.43, was used in modeling the proposed mechanism herein. The average literature value is also relatively consistent with the value of $pK_{a1} = 9.33$ obtained from available Hammett correlations for the acidity of phenols, i.e., $pK_a = 9.92 - 2.23\Sigma\sigma$ (*29*). With the exception of the second $pK_a$ for 4,6-dichlororesorcinol, all of the measured $pK_a$ values in Table 2 agree closely with the published Hammett correlations of phenol acid dissociation constants (see Figure 1).

**TABLE 2**

**Acid Dissociation Constants for Substituted Resorcinols**[a]

| substrate | p$K_{a1}$ ($\pm\sigma$) | p$K_{a2}$ ($\pm\sigma$) |
|---|---|---|
| resorcinol | 9.43 (0.34)[b] | 11.21 (0.16)[c] |
| 4-chlororesorcinol | 8.09 (0.08) | 10.75 (0.15) |
| 4,6-dichlororesorcinol | 7.53 (0.09) | 10.35 (0.11) |
| orcinol | 9.35 (0.03) | 11.50 (0.02) |

[a] Values determined experimentally in this study unless specified otherwise. [b] Value is the average of three reported values, 9.15 (*27*), 9.32 (*26*), and 9.81 (*28*). [c] Value is the average of two reported values, 11.1 (*26*) and 11.32 (*27*).

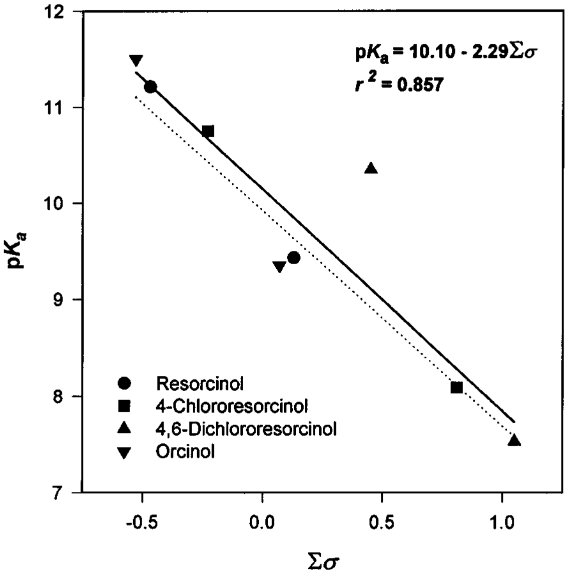


**FIGURE 1. Hammett correlation for resorcinol acid dissociation constants, p$K_{a1}$ and p$K_{a2}$. The solid line is a linear least-squares fit to the data, corresponding to the equation in the graph. Dashed line is a reported Hammett correlation for phenols (*29*).**

**Reaction Rate Orders.** Chlorination experiments, which were conducted at pH 4 with a large excess of HOCl relative to the dihydroxybenzene, exhibited a pseudo-first-order dependence on the substituted resorcinol ($ArX(OH)_2$), as demonstrated by the linear plot of ln($[ArX(OH)_2]/[ArX(OH_2)]_0$) vs time in Figure 2. These plots were linear ($r^2 > 0.99$) for reaction extents of at least 87%. The reaction order with respect to chlorine was examined at pH 5 by varying the chlorine concentration and monitoring the disappearance of resorcinol. These experiments were limited to the range of $[HOCl]_T < 3.5 \times 10^{-5}$ M, since the reaction was too rapid to monitor at higher chlorine concentrations. Plots of the pseudo-first-order rate constant were linear ($r^2 > 0.99$) with respect to $[HOCl]_T$. The rate of resorcinol disappearance, therefore, is first-order in the concentrations of chlorine and resorcinol:

$$\frac{d[ArH(OH)_2]_T}{dt} = -k_{app}[ArH(OH)_2]_T[HOCl]_T \qquad (4)$$

where $k_{app} = k_{obs}/[HOCl]_T$ is an apparent second-order constant, and $k_{obs}$ is the observed pseudo-first-order rate constant. Similar rate laws were found to describe the disappearance of 4-chlororesorcinol, 4,6-dichlororesorcinol, and orcinol.

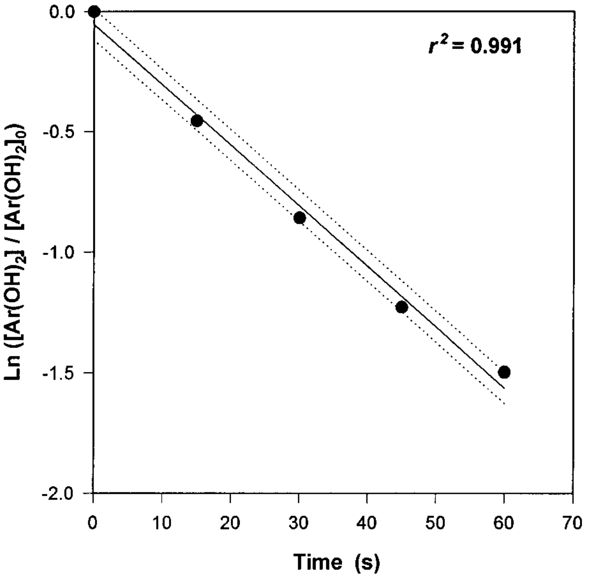


**FIGURE 2. Psuedo-first-order kinetic plot of the chlorination of resorcinol at pH 4. Initial concentrations of resorcinol and HOCl were 2.0 × $10^{-7}$ and 2.0 × $10^{-5}$ M, respectively. The solid line is a linear least-squares regression of the data. Dotted lines show intervals of 1 SD.**

At all other pH conditions, the pseudo-first-order rate constants were calculated from a single determination of the resorcinol concentration as follows:

$$k_{obs} = \frac{\ln\left(\frac{[ArH(OH)_2]_{T,0}}{[ArH(OH)_2]_{T,t}}\right)}{\Delta t} \qquad (5)$$

where $\Delta t$ was the time period of reaction before quenching. At least three determinations of $k_{obs}$ were performed at each pH. Only reaction extents, $\xi = 1 - ([ArH(OH)_2]/[ArH(OH)_2]_0)$, less than 0.8 were considered in calculating $k_{obs}$ values.

No temperature dependence of $k_{app}$ for resorcinol chlorination was observed at pH 5. Based on the standard error of $k_{app}$ measurements made between 4 and 25 °C, an upper limit activation energy for the reaction is therefore ≤2.5 kJ/mol. All other experiments were performed at room temperature, 22 °C.

**pH Dependence and Mechanism.** The pH dependence of $k_{app}$ is shown in Figures 3–6 for each of the resorcinol substrates. In each pH profile, the second-order apparent rate constant exhibits a minimum between pH 3 and pH 6 and a maximum between pH 8 and pH 11. The minimum rate constant for the reaction is also displaced to higher pH values as the substrate is more extensively chlorinated. The shape of the rate profile could be partially explained in terms of the reactivity of the ionized and un-ionized forms of the resorcinol substrates. Upon deprotonation, the $O^-$ substituent is more activating than OH toward electrophilic substitution. The shift of the minimum to lower pH values with successive chlorination would be consistent with this explanation, since p$K_a^{resorcinol}$ > p$K_a^{monochlororesorcinol}$ > p$K_a^{dichlororesorcinol}$. In addition, the maxima in the rate constant profiles might be explained if HOCl is the only active electrophile and the reactivity of $OCl^-$ is negligible. The increase in reaction rate in acidic solutions (pH < 4) suggests that the reaction is subject to acid catalysis.

One mechanism that incorporates the above features is proposed as follows:

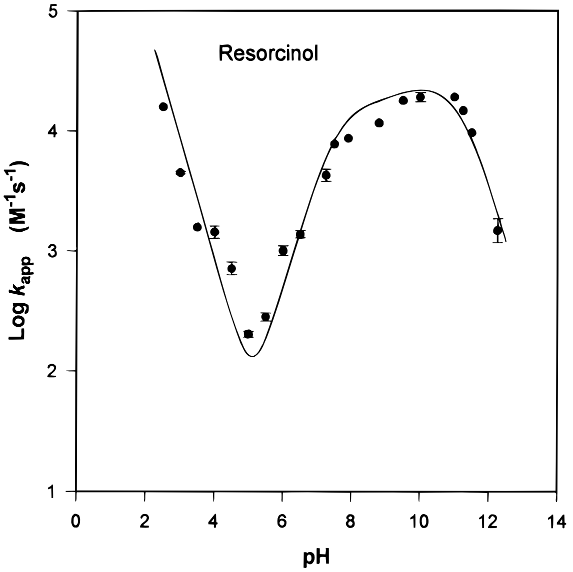


**FIGURE 3. Apparent rate constant–pH dependence for the attack of HOCl on resorcinol at 22 °C. The solid line is a non-linear least-squares regression fit of $k_2$, $k_3$, and $k_4$ to the data.**

$$\mathrm{HOCl} \overset{K_{a2}^{\mathrm{Cl}}}{\rightleftharpoons} \mathrm{OCl}^- + \mathrm{H}^+ \quad \text{(fast)} \quad (6)$$

$$\mathrm{ArX(OH)_2} \overset{K_{a1}^{\mathrm{R}}}{\rightleftharpoons} \mathrm{ArX(OH)O}^- + \mathrm{H}^+ \quad \text{(fast)} \quad (7)$$

$$\mathrm{ArX(OH)O}^- \overset{K_{a2}^{\mathrm{R}}}{\rightleftharpoons} \mathrm{ArX(O^-)_2} + \mathrm{H}^+ \quad \text{(fast)} \quad (8)$$

$$\mathrm{ArX(OH)_2} + \mathrm{HOCl} \xrightarrow{k_1} \text{products} \quad \text{(slow)} \quad (9)$$

$$\mathrm{ArX(OH)O}^- + \mathrm{HOCl} \xrightarrow{k_2} \text{products} \quad \text{(slow)} \quad (10)$$

$$\mathrm{ArX(O^-)_2} + \mathrm{HOCl} \xrightarrow{k_3} \text{products} \quad \text{(slow)} \quad (11)$$

$$\mathrm{ArX(OH)_2} + \mathrm{HOCl} + \mathrm{H_3O^+} \xrightarrow{k_4} \text{products} \quad \text{(slow)} \quad (12)$$

and the resulting general rate expression for the above reaction mechanism is

$$\begin{aligned} v &= -\frac{d[\mathrm{ArX(OH)_2}]_T}{dt} \\ &= k_1[\mathrm{ArX(OH)_2}][\mathrm{HOCl}] + k_2[\mathrm{ArX(OH)O^-}][\mathrm{HOCl}] + \\ &\quad k_3[\mathrm{ArX(O^-)_2}][\mathrm{HOCl}] + k_4[\mathrm{ArX(OH)_2}][\mathrm{HOCl}][\mathrm{H^+}] \quad (13) \end{aligned}$$

By introducing the following notation

$$[\mathrm{ArX(OH)_2}]_T = [\mathrm{ArX(OH)_2}] + [\mathrm{ArX(OH)O^-}] + [\mathrm{ArX(O^-)_2}] \quad (14)$$

$$[\mathrm{HOCl}]_T = [\mathrm{HOCl}] + [\mathrm{OCl^-}] \quad (15)$$

where $\alpha_i^{\mathrm{Cl}}$ is the ionization fraction of hypochlorous acid species, with $i = 0$ or 1, for HOCl and $\mathrm{OCl^-}$, respectively, and $\alpha_i^{\mathrm{R}}$ is the ionization fraction of resorcinol substrate species, with $i = 0$, 1, or 2, for $\mathrm{ArX(OH)_2}$, $\mathrm{ArX(OH)O^-}$, and $\mathrm{ArX(O^-)_2}$, respectively, the rate expression can be rewritten as follows:

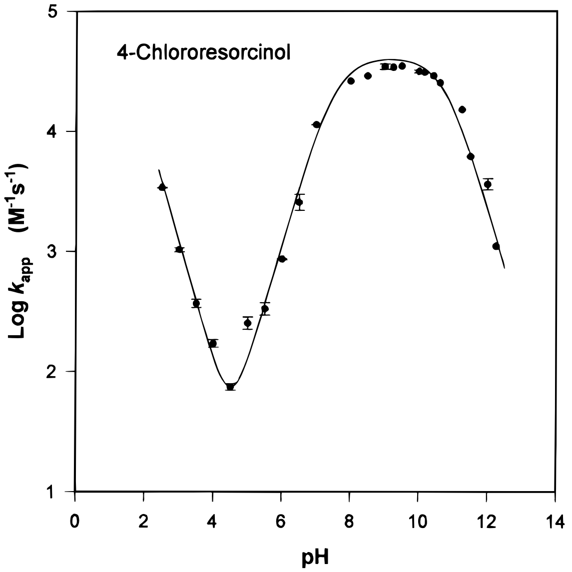


**FIGURE 4. Apparent rate constant–pH profile for the attack of HOCl on 4-chlororesorcinol at 22 °C. The solid line is a non-linear least-squares regression fit of $k_2$, $k_3$, and $k_4$ to the data.**

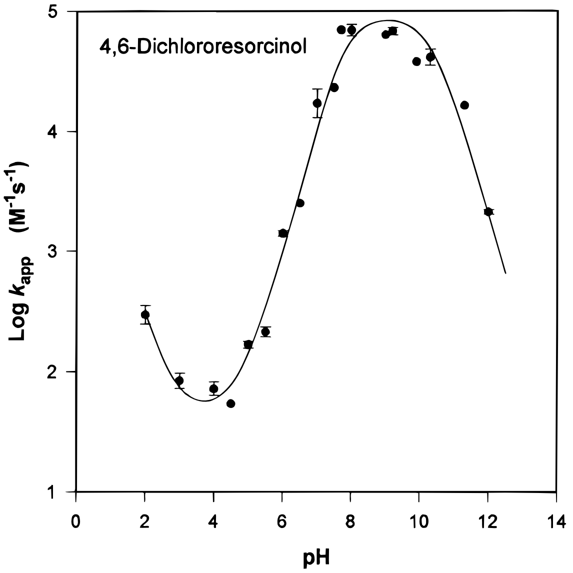


**FIGURE 5. Apparent rate constant–pH dependence for the attack of HOCl on 4,6-dichlororesorcinol at 22 °C. The solid line is a non-linear least-squares regression fit of $k_1$, $k_2$, $k_3$, and $k_4$ to the data.**

$$v = (k_1\alpha_o^{\mathrm{R}} + k_2\alpha_1^{\mathrm{R}} + k_3\alpha_2^{\mathrm{R}} + k_4\alpha_0^{\mathrm{R}}[\mathrm{H^+}])\alpha_1^{\mathrm{Cl}} \times [\mathrm{ArX(OH)_2}]_T[\mathrm{HOCl}]_T \quad (16)$$

and based on eq 16, the $k_{app}$ term in eq 4 can be rewritten as

$$k_{app} = \left[ (k_1\{\mathrm{H^+}\}^2 + k_2K_{a1}^{\mathrm{R}}\{\mathrm{H^+}\} + k_3K_{a1}^{\mathrm{R}}K_{a2}^{\mathrm{R}} + k_4\{\mathrm{H^+}\}^3)\left(\frac{\{\mathrm{H^+}\}}{\{\mathrm{H^+}\} + K_{a2}^{\mathrm{Cl}}}\right)\right] \Big/ [\{\mathrm{H^+}\}^2 + K_{a1}^{\mathrm{R}}\{\mathrm{H^+}\} + K_{a1}^{\mathrm{R}}K_{12}^{\mathrm{R}}] \quad (17)$$

The intrinsic constants $k_1$, $k_2$, $k_3$, and $k_4$ were fit to the data in Figures 3–6 with a non-linear least-squares regression and Marquardt–Levenberg algorithm solution method.

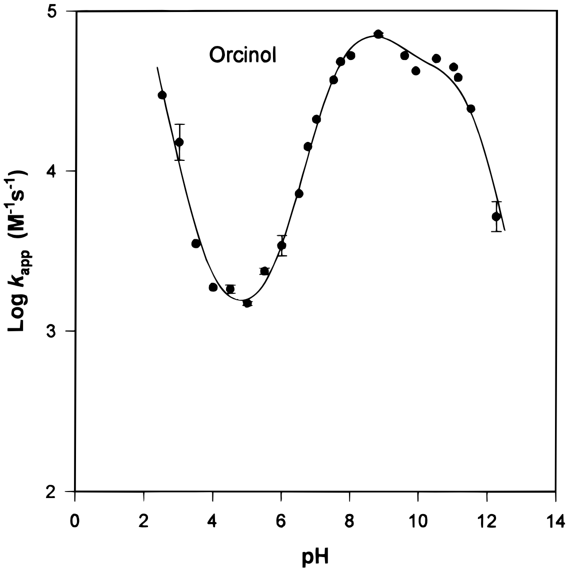


**FIGURE 6. Apparent rate constant−pH profile for the attack of HOCl on orcinol at 22 °C. The solid line is a non-linear least-squares regression fit of $k_1$, $k_2$, $k_3$, and $k_4$ to the data.**

Acid dissociation constants were held fixed at the values given in Table 2 for the resorcinol substrates, and $pK_{a2}^{Cl} = 7.54$ (*26*). Fitted values of all of the intrinsic rate constants are presented in Table 3. Reasonably close fits were obtained for each of the substrates, as shown by the solid lines in Figures 3−6, and hence the postulated mechanism is consistent with the data.

Given the large difference between the measured $pK_{a2}$ for 4,6-dichlororesorcinol and the value predicted by published LFERs (see Figure 1), a non-linear regression analysis of the data in Figure 5 was also performed wherein $K_{a2}$ was fixed at its "predicted" value. Very poor fits for $k_{app}$, however, were obtained in this case. The reaction rate pH dependence, therefore, is further evidence that the $pK_{a2}$ value of 4,6-dichlororesorcinol is much closer to our measured value of 10.35 than the 9.1 value predicted by the regression in Figure 1.

Since the chlorination rate−pH dependence of resorcinol and 4-chlororesorcinol could be fit satisfactorily with or without the $k_1$ step of the mechanism, the solid lines in Figures 3 and 4 correspond to the fit obtained with only the $k_2$, $k_3$, and $k_4$ steps. While the magnitude of $k_1$ cannot be determined for resorcinol and 4-chlororesorcinol, upper-limit estimates of $k_1 \leq 330\ M^{-1}\ s^{-1}$ for resorcinol and $k_1 \leq 65\ M^{-1}\ s^{-1}$ for 4-chlororesorcinol were obtained as $k_1 + \sigma$, when the $k_1$ step was included in the regression analysis. Modeling the rate constant−pH profiles for the chlorination of 4,6-dichlororesorcinol and orcinol required the inclusion of the $k_1$ step to fit the data, as might be expected from the broader shape of the minima in Figures 5 and 6.

One explanation for the differences in the importance of eq 9 among these substrates is the apparent variability in the ratio $k_4/k_1$. These ratios are smaller for dichlororesorcinol and orcinol than the other substrates when the upper-limit estimates of $k_1$ for resorcinol and 4-chlororesorcinol are assumed. The variability in these ratios also appears to be driven by differences in the sensitivity of the reaction to acid catalysis. It is hypothesized that the simultaneous reaction of HOCl and $H_3O^+$ with orcinol and 4,6-dichlororesorcinol is sterically hindered, since the reaction centers of these substrates have ortho substituents on either side.

The proposed mechanism of eqs 6−12 invokes a termolecular reaction to describe the increased chlorination rates of resorcinols at pH < 4. Similar acid-catalyzed reactions of HOCl with other nucleophiles have been proposed (*23, 30, 31*). An alternative mechanism, however, can also explain the acid-catalyzed reaction rate at pH < 4 if the $k_4$ step is replaced with the following reaction:

$$\mathrm{ArX(OH)_2} + \mathrm{ClOH_2}^+ \xrightarrow{k_4'} \text{products} \qquad \text{(slow)} \quad (18)$$

which in turn requires an additional equilibrium:

$$\mathrm{HOCl} + \mathrm{H}^+ \xrightleftharpoons{1/K_{a1}^{Cl}} \mathrm{ClOH_2}^+ \qquad \text{(fast)} \quad (19)$$

The magnitude of $K_{a1}^{Cl}$ is not known, although Arotsky and Symons (*32*) have estimated that $-4 < pK_{a1}^{Cl} < -3$. Over the range of pH studied here $K_{a1}^{Cl} \gg \{H^+\}$, so consequently the ionization fraction corresponding to $ClOH_2^+$ can be approximated as $\alpha_0^{Cl} \approx \{H^+\}/K_{a1}^{Cl}$ when pH $\leq pK_{a2}^{Cl}$. An "alternate" kinetically equivalent rate expression is obtained by replacing the $k_4\alpha_0^R\alpha_0^{Cl}$ term in eq 16 by $k_4'\alpha_0^R\{H^+\}/K_{a1}^{Cl}$ when pH $\leq pK_{a2}^{Cl}$. The constant $k_4$ obtained previously in Table 3 is related to $k_4'$ by $k_4 = k_4'/K_{a1}^{Cl}$. Given that the largest value of $k_4'/K_{a1}^{Cl}$ in Table 3 is $9.8 \times 10^6\ M^{-2}\ s^{-1}$, $pK_{a1}^{Cl}$ values smaller than approximately −3 would require that the $k_4'$ step be faster than diffusion-controlled. This alternate mechanism is possible, therefore, only if the value of $pK_{a1}^{Cl}$ is close to the high end of the range estimated by Arotsky and Symons. Thus, there is insufficient evidence to rule out the alternate $k_4'$ reaction pathway.

Based on the earlier chlorination studies of phenols by other investigators (*15*, *16*), it is unlikely that the above mechanism would be valid in acidic solution if high concentrations of chloride ions were present. Since $Cl_2$ is more electrophilic than HOCl and $Cl_2$ formation is favored under acidic conditions, the chlorination of phenol becomes rate-limited by the reaction shown in eq 3 and independent of the phenol concentration at low pH. The commercial hypochlorite reagent used in our study contained equimolar concentrations of HOCl and $Cl^-$, and hence the maximum chloride concentration was $3.5 \times 10^{-5}$ M. This $Cl^-$ concentration, however, did not apparently affect the rate of resorcinol decay since the reaction rates were first-order

**TABLE 3**

## Rate Constants for Proposed Reaction Mechanism (eqs 9−12) at 22 °C

| substrate | $k_1$ ($\pm\sigma$) ($M^{-1}\ s^{-1}$) | $k_2$ ($\pm\sigma$) ($M^{-1}\ s^{-1}$) | $k_3$ ($\pm\sigma$) ($M^{-1}\ s^{-1}$) | $k_4$ ($\pm\sigma$) ($M^{-2}\ s^{-1}$) |
|---|---|---|---|---|
| resorcinol | <330 | $1.36 (0.26) \times 10^6$ | $1.15 (0.10) \times 10^8$ | $8.5 (1.8) \times 10^6$ |
| 4-chlororesorcinol | <65 | $1.43 (0.16) \times 10^5$ | $6.73 (0.53) \times 10^7$ | $1.19 (0.15) \times 10^6$ |
| 4,6-dichlororesorcinol | 47 (17) | $3.21 (0.76) \times 10^4$ | $5.91 (0.81) \times 10^7$ | $2.6 (1.2) \times 10^4$ |
| orcinol | 1250 (160) | $5.18 (0.34) \times 10^6$ | $4.20 (0.04) \times 10^8$ | $9.8 (1.1) \times 10^6$ |

with respect to each of the substituted resorcinols, even at pH 2.

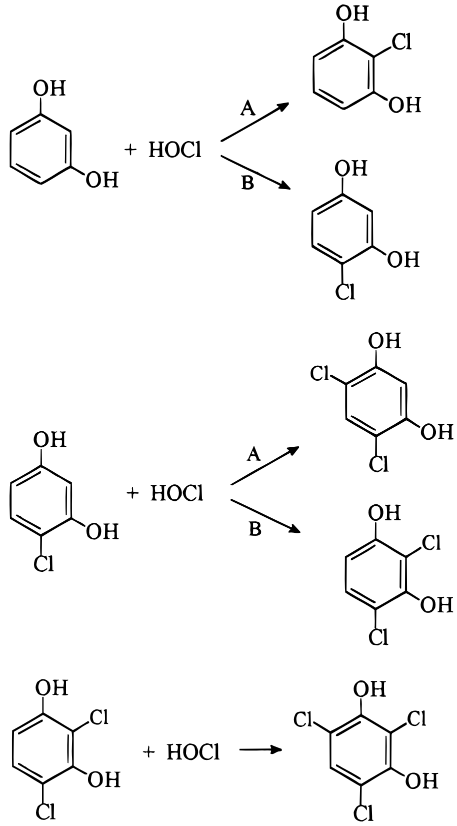
The rate-limiting steps in eqs 9−12 do not involve reactions of more than one charged species, and hence the intrinsic rate constants $k_1$, $k_2$, $k_3$, and $k_4$ should not vary with ionic strength according to classical Debye−Hückel theory (*33*). The apparent rate constant, $k_{app}$, on the other hand is expected to vary with ionic strength since it is a complex function of equilibrium constants (see eq 17). However, at pH 2 and pH 12 where the ionic strength was a maximum (0.01 M), the correction to $k_{app}$ is estimated to be at most 10%, which is within the error of measurement. The ionic strength was varied using sodium perchlorate up to 0.1 M at pH 5 with resorcinol, although little variation in $k_{app}$ was observed. According to the proposed mechanism, the $k_2$ and $k_4$ steps contribute primarily to $k_{app}$ at pH 5, and using the Davies equation to calculate activity corrections, the expected change in $k_{app}$ between 0 and 0.1 M ionic strengths is only between 10 and 11%. The chlorination rate of phenol at pH > 6 has also been reported to be independent of ionic strength, although the salt concentration range used was not given (*16*).

While the relative order of the intrinsic reactivities of chlorine with the four substrates in Table 3 is as expected, the order of apparent reactivity, as indicated in Figures 3−6, is reversed between pH 6 and pH 10, with the most apparently reactive substrate being 4,6-dichlororesorcinol. This reversal can be explained in terms of the relative acidity of the substrates. Chlorine-substituted resorcinols are more acidic, and the deprotonated forms are more activated for electrophilic attack. An important implication of this result is that chlorinated resorcinol intermediates up to dichlororesorcinols should not accumulate at natural water pH conditions when HOCl is in excess. Comparisons of the chlorination kinetics of dihydroxybenzene-type groups with other competing reactant centers in natural organic matter, therefore, are best made on the basis of the initial reactivity with these moieties.

**Reaction Products.** The initial reaction products were identified by performing chlorination experiments under pseudo-first-order conditions in the substrate at pH 5. Chlorination of resorcinol gave two products that were discernible by HPLC. One was 4-chlororesorcinol, as demonstrated by matching its retention time with a pure standard. The second product eluted immediately after 4-chlororesorcinol and before 4,6-dichlororesorcinol. While a positive identification of this compound against a standard was not performed, it is likely to be 2-chlororesorcinol, in accordance with a study conducted under similar conditions (*21*).

Two chlorination products of 4-chlororesorcinol were also observed by HPLC, and one of the chromatogram peaks matched the retention time of 4,6-dichlororesorcinol. The second product was not identified; however, it is probably 2,4-dichlororesorcinol, as previously reported by Heasley (*21*).

Preferred sites for chlorine substitution on the benzene ring depend usually on the combined resonance and inductive effects of the ring substitutents. For phenolic compounds, OH and O$^-$ substituents are activating and ortho- and para-directing. A Cl substitutent on the other hand deactivates the ring. The immediate expected products upon electrophilic substitution of chlorine onto resorcinol, 4-chlororesorcinol, and 4,6-dichlororesorcinol are as follows:



The rate constants in Table 3 for resorcinol, 4-chlororesorcinol, and orcinol therefore correspond to the sum of rate constants for the A and B pathways shown above. The orientation of resorcinol OH groups renders the 2, 4, and 6 positions equivalent in terms of reactivity and their reaction-directing effect. Consequently, the proportion of each of the products can be estimated on the basis of a statistical distribution. In the absence of steric hindrance, the product distribution for the chlorination of resorcinol should be approximately 33% 2-chlororesorcinol and 66% 4-chlororesorcinol. Heasley et al. (*21*) found a product ratio of 2- and 4-chlororesorcinol of approximately 1:3, respectively, for resorcinol chlorination over the pH range of 2−12. The reduced reactivity measured by Heasley at the ortho position may be due to steric hindrance or to deactivation caused by inductive effects of the neighboring OH group. In Heasley's study, however, significant fractions of the resorcinol were already converted to dichloro- and trichlororesorcinol when the products were determined. Therefore, the actual product formation rate ratio may be closer to the statistically predicted ratio of 1:2. Nevertheless, Heasley's study is evidence that the three ring positions are similarly reactive toward HOCl.

Chlorine substitution rates at either the 2 or 6 ring position of 4-chlororesorcinol should also be similar, and hence equal fractions of the products 2,4- and 4,6-dichlororesorcinol are expected. Deviations from this statistical distribution are possible if steric hindrance effects are important. Such effects would likely favor 4,6-dichlororesorcinol.

The introduction of a methyl group to resorcinol at the $C_5$ position serves to weakly activate meta positions, which are already occupied by OH substitutents. Similar product isomer distributions should therefore be expected for resorcinol and orcinol.

**Linear Free Energy Relationships.** Substituent effects on the second-order rate constants in Table 3 appear to follow expected trends. Chlorination rates increase by almost 5 orders of magnitude, for example, when both OH groups are replaced with $O^-$ ($k_1$ vs $k_3$). The rates also decrease in the following order: orcinol > resorcinol > 4-chlororesorcinol > 4,6-dichlororesorcinol, as the weakly deactivating Cl group is added to the benzene ring. Rate constants reported by Soper and Smith (*15*) for the reaction of HOCl with substituted phenolates similarly decrease as chlorine substituents are added to the ring.

Hammett-type linear free energy relationships (LFER) are often used to correlate effects of substituent groups for aromatic compounds. Using the rate constants $k_1$, $k_2$, and $k_3$ determined in this study and the reported rate constants for the chlorination of substituted phenolate compounds (*15*), a Hammett-type correlation was tested. For substrates in which electrophilic attack by HOCl occurs at more than one site on the ring, an assumption of approximately equal reactivity was made for each of the reaction centers in estimating Hammett $\sigma$ parameters. When the chlorination reactions occur at $n$ positions on the ring, the measured rate constant is

$$k = \sum_{i=1}^{n} k_i$$

where $k_i$ values correspond to the rate constants of the reaction pathways A, B, etc., described above. Furthermore, if all the $k_i$ are nearly equal so they can be approximated by $k_{i,\mathrm{av}}$ and the rates are well-correlated with the Hammett $\sigma$ parameter, then

$$\log k = \log\left(\sum_{i=1}^{n} k_i\right) \approx \log(n k_{i,\mathrm{av}}) \qquad (20)$$

$$\log\frac{k}{n} = \log k_{i,\mathrm{av}} \qquad (21)$$

$$\log\frac{k}{n} = \log k^0 + \rho(\Sigma\sigma)_{\mathrm{av}} \qquad (22)$$

where $k^0$ is the rate constant for the reaction of HOCl with benzene, $\rho$ is the Hammett slope, and $(\Sigma\sigma)_{\mathrm{av}}$ is the average of the $(\Sigma\sigma)_i$ constants for the $n$ sites of attack. As shown in Figure 7, a relatively linear plot of $\log(k/n)$ vs $(\Sigma\sigma)_{\mathrm{av}}$ is obtained for substituted resorcinols and phenols, using the substituent Hammett $\sigma$ parameters tabulated by Perrin et al. (*29*). The magnitude and sign of the slope reflect the sensitivity of the reaction to the electron density. Negative values of $\rho$ are typical of electrophilic substitution reactions.

While the rate constants obtained by Soper and Smith (*15*) for substituted phenolates are consistent with the Hammett correlation for the resorcinol compounds studied here, rate constants obtained from an analysis of Lee's phenol chlorination study are not (*16*). In the latter kinetic study, the pH dependence of phenol chlorination was examined over the range of pH 5−12. While a mechanism was not fit to the data, it can be shown that the observed chlorination rates can be modeled by the following rate determining steps (*17*):

$$\mathrm{HOCl} + \mathrm{C_6H_4X(OH)} \xrightarrow{k_1} \text{products} \qquad (23)$$

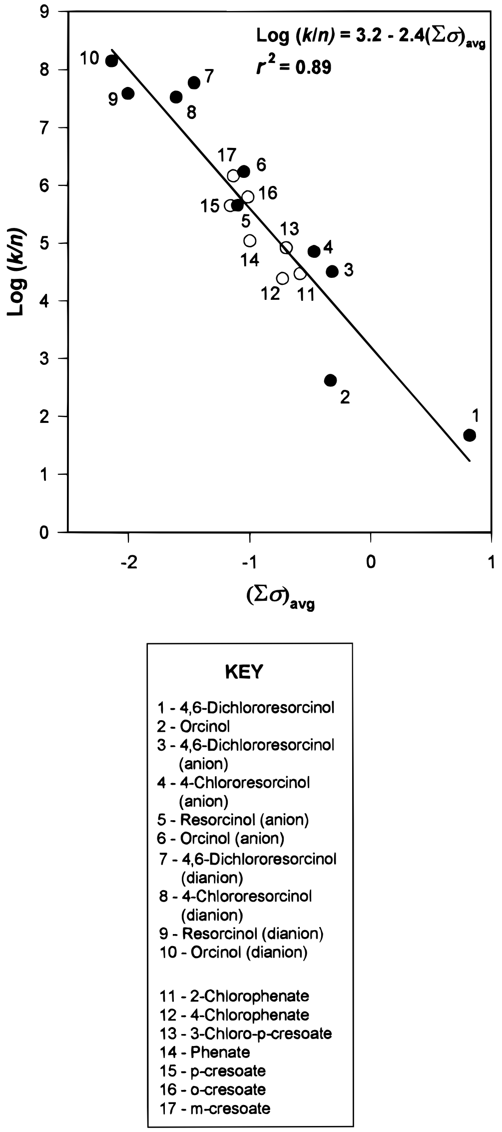


**FIGURE 7. Hammett-type correlation of log (*k/n*) vs $(\Sigma\sigma)_{\mathrm{av}}$ for the reaction of substituted resorcinols and phenols with HOCl. Filled circles correspond to the rate constants for substituted resorcinols determined in this study. Open circles correspond to previously determined rate constants for substituted phenols (*15*). The solid line is a linear least-squares fit to all of the data.**

$$\mathrm{HOCl} + \mathrm{C_6H_4X(O^-)} \xrightarrow{k_2} \text{products} \qquad (24)$$

The resulting values of $k_2$ for phenolate, 2-chlorophenolate, and 4-chlorophenolate, however, are more than an order of magnitude smaller than those reported by Soper and Smith (*15*). The reason for these differences is not clear, but the rate constants obtained by Soper and Smith seem more reasonable given the agreement of their rate constants with our Hammett correlation for resorcinols.

Relatively close correlations of the chlorination rates of phenolates ($k_2$) with the p$K_a$ of the phenol group have also been demonstrated using Soper and Smith's data (*34*), where $\log k_2 = -3.86 + 0.95\,\mathrm{p}K_a$. As shown in Figure 8, the analogous LFER for resorcinol rate constants $k_2$ and $k_3$ yields a very strong correlation with a slope that is similar to the LFER slope obtained for phenols but a different intercept. This LFER suggests that an even higher degree of correlation exists between chlorination rate constants and thermodynamic acid dissociation constants than between chlo-

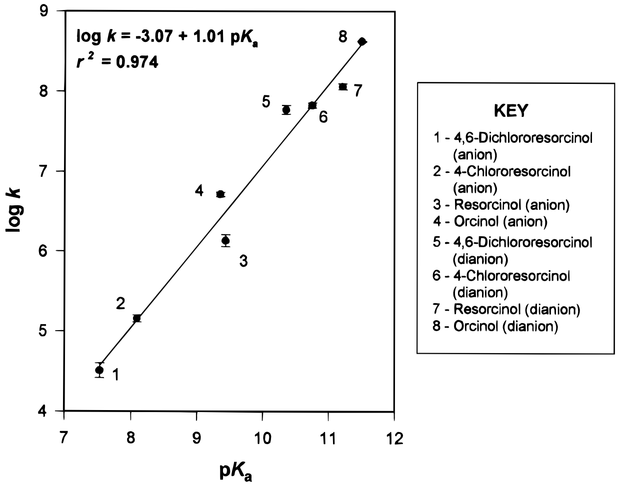


**FIGURE 8. LFER correlation of log $k_2$ and log $k_3$ with p$K_{a1}$ and p$K_{a2}$, respectively, for the chlorination of substituted resorcinols. The solid line is a linear least-squares fit to all the data.**

rination rates and the Hammett $\sigma$ parameter. Where p$K_a$ values for substituted resorcinols or phenols are available, these LFERs are likely to give better predictions of the rate constants. Since the correlation in Figure 8 spans more than a 4-order of magnitude range in rate constants, however, significant errors may still be associated with estimates obtained using this LFER.

In the pH range of most natural waters, the contribution of the ArX(OH)O$^-$ + HOCl and ArX(O$^-$)$_2$ + HOCl pathways are typically the most important. Rate constants for these steps of some isomer intermediates formed during the chlorination of resorcinol have not been experimentally determined, such as 2-chlororesorcinol and 2,4-dichlororesorcinol. Using the LFERs developed in this study, however, it is now possible to estimate their reactivity and thus to completely model the chlorination sequence of resorcinol up to the formation of 2,4,6-trichlororesorcinol for the pH range of most aquatic systems.

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