

KINETICS OF CHLORINATION OF PHENOL — CHLOROPHENOLIC TASTES AND ODORS*

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ONE of the major problems associated with the disinfection of water supplies by chlorination is that the organoleptic properties of the chlorinated water may be increased. This malodorous water is often produced by a reaction between the added chlorine and trace concentrations of organic compounds present in the water. By far the most notorious of the organic compounds found in water which increase the taste and odors in the water upon chlorination are phenol and some of its homologs.

The nature of the compound or compounds which give rise to "chlorophenolic" tastes and odors resulting from the reaction between aqueous chlorine and phenolic compounds, has been repeatedly investigated (ADAMS, 1931; ETTINGER, 1951; ETTINGER and RUCHOFT, 1951; INGOLS and RIDENOUR, 1948; TODD, 1947). However, very little was known with certainty about the chemical reactions involved in the production or destruction of chlorophenolic tastes and odor until recent appearances of a significant paper by BURTTSCHELL, ROSEN, MIDDLETON and ETTINGER (1959).

In their important study, the chlorophenols that are formed from the chlorination of phenol in dilute aqueous solutions were for the time isolated and identified. From a knowledge of the chlorophenols formed, they were able to propose a reaction scheme, FIG. 1, to account for the production and subsequent elimination of "chlorophenolic" tastes and odors in water supplies arising from the chlorination of phenol.

According to BURTTSCHELL et al., the chlorination of phenol proceeds by the step-wise substitution of the 2, 4 and 6 positions of the aromatic ring. Initially, phenol is chlorinated to form either 2- or 4-chlorophenol. Then 2-chlorophenol is chlorinated to form either 2,4- or 2,6-dichlorophenol, while 4-chlorophenol to form 2,4-dichlorophenol. Both 2,4- and 2,6-dichlorophenol are chlorinated to form 2,4,6-trichlorophenol. The 2,4,6-trichlorophenol reacts with aqueous chlorine to form a mixture of non-phenolic oxidation products.

BURTTSCHELL et al. also determined the threshold odor concentration, i.e., the maximum dilution at which odor can be detected by any individual with an average olfactory sensitivity, for the chlorophenols formed from the chlorination of phenol. These threshold odor concentrations are listed below each of the compounds in BURTTSCHELL'S et al. reaction scheme presented in FIG. 1. The compounds found to have the strongest organoleptic properties were 2-chlorophenol, 2,4-dichlorophenol, and 2,6-dichlorophenol; these were detectable at concentration of 2 to 3 µg/L. In contrast, phenol, 4-chlorophenol, 2,4,6-trichlorophenol were detectable only at much higher concentrations. Consequently, it appears from their study that 2-chlorophenol, 2,4- and 2,6-dichlorophenol are the compounds primarily responsible for the "chlorophenolic" tastes and odors in water supplies arising from the chlorination of phenol.

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Although the investigation by BURTTSCHELL et al. has contributed valuable and badly needed information about the products formed from the chlorination of phenol, it does not provide a complete picture of the way in which these products may change with time of reaction, proportions of reactants, pH, temperature and other conditions of reaction. What is needed for this purpose is a thorough kinetic study of the individual reactions forming the overall pattern of chlorination. Knowledge of the changing relative importance of individual reactions as the conditions of chlorination vary, will provide the data needed for prediction of differences in overall characteristics and for

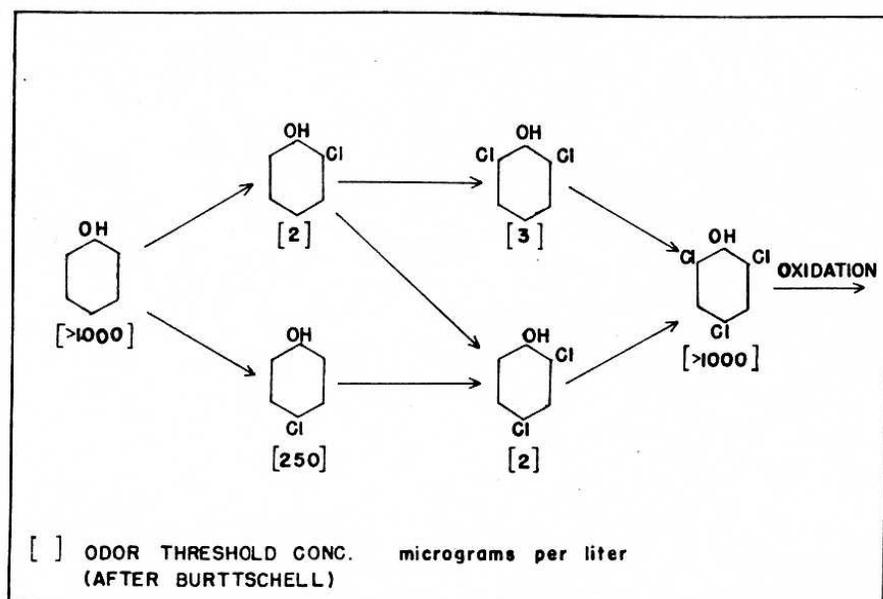


FIG. 1. Reaction scheme for the chlorination of phenol.

specification of optimum conditions of chlorination to minimize "chlorophenolic" taste and odor production. Consequently, determination of the kinetic properties of potential individual reactions occurring during the chlorination of phenol comprises the experimental portion of this paper.

These data have been used to compute the expected concentration of the individual chlorinated phenols as a function of time and other variables to give a detailed picture of the progress of the overall reaction between chlorine and phenol for the range of conditions likely to be encountered in the treatment of phenol-bearing waters and wastes.

Furthermore, this information has been combined with the data on the organoleptic properties of the individual chlorophenols to compute anticipated threshold odors of chlorinated phenol-containing waters as a function of time and solution conditions. These final data provide a basis for prediction and selection of optimum procedures for minimizing taste and odor problems caused by the presence of phenol in water subject to chlorination.

EXPERIMENTAL TECHNIQUES

Reagents

Stock solutions of aqueous chlorine approximately 0.05 M were prepared by bubbling chlorine gas (Matheson lecture bottle) into chlorine-demand-free, double distilled water. These solutions were stored in "low actinic" Pyrex vessels at 5° C. Fresh solutions were prepared weekly. These aqueous chlorine solutions were standardized by

iodine-thiosulfate titration using starch as indicator (STANDARD METHODS, 1955). The concentration of aqueous chlorine remaining as a function of time of reaction was determined by the o-tolidine method (STANDARD METHODS, 1955), absorbance measurements were made on a Beckman D U Spectrophotometer.

Stock solutions of phenol and each of the chlorophenols were prepared by weighing the dried compounds, purified by fractional distillation, and dissolving this amount in distilled water.

The pH of the reaction solution was maintained at a constant value during the course of the reaction by addition of pH buffers. The buffers used were as follows: pH 4–6, acetic acid-acetate, pH 6–8, mono- and dibasic phosphate, pH 8–10, bicarbonate-carbonate, pH 10–12, hydroxide. All pH measurements were made on a Beckman Model G pH Meter.

The reaction was carried out in the presence of added chloride, and at known ionic strength by addition of sodium perchlorate to the reaction solution.

Procedure of kinetic runs

All reactions were carried in a thermostat-controlled waterbath to 0.2 C° in diffuse light. The procedure for each experiment run was as follows: (1) To one 500 ml volumetric flask was added the desired amount of aqueous chlorine, pH buffer and chloride, to another 500 ml volumetric flask was added phenol or chlorophenol and perchlorate. Both flasks were placed in a water bath and allowed to come to the desired temperature. After temperature equilibrium, the contents of each flask were poured simultaneously into the reaction vessel (1 liter Pyrex reagent bottle). A stopwatch was started at the beginning of pouring. The reaction vessel was placed in water bath and at desired time intervals an aliquot of the reaction solution was withdrawn and an analysis was made of aqueous chlorine content. At the start of each run an aliquot of the reaction solution was placed in a spectrophotometric absorption cells and a continuous record of the ultraviolet spectra was obtained on a Beckman DK-2 Ratio Recording Spectrophotometer. The infrared spectra of the reaction products were obtained for some of the reaction solutions. The chlorophenolic products were extracted by ethyl ether following the procedure described by BURTTSCHELL et al. (1959). The infrared spectra was obtained on a Perkin Elmer Model 21 Infrared Spectrophotometer using carbon disulfide as the solvent.

EXPERIMENTAL RESULTS

The chlorination of phenol and each of the chlorophenols studied conforms to a second-order rate expression in which the rate of change of chlorine or phenolic compound is proportional to the product of the formal concentrations of aqueous chlorine and phenolic compound. This expression in terms of the quantities analytically measured is

$$-\frac{dF_{Cl}}{dt} = k_{ob}F_{Cl}F_{PhOH} \quad (1)$$

This equation may be integrated to yield

$$\frac{1}{F_{PhOH}^{\circ} - F_{Cl}^{\circ}} \ln \frac{F_{Cl}^{\circ} F_{PhOH}}{F_{PhOH} F_{Cl}^{\circ}} = k_{ob}t \quad (2)$$

- where F°_{PhOH} is the initial formal concentration of phenolic compound;
 F_{PhOH}^* is the formal concentration of phenolic compound at time, t ;
 F°_{Cl} is the initial formal concentration of chlorine;
 F_{Cl}^{\dagger} is the formal concentration of chlorine in an oxidation state of plus 1 at time, t ;
 k_{ob} is the second-order rate constant in liters per mol, minute

The rate constant, k_{ob} , was evaluated from the slope of a plot of the left side of Equation (2) as a function of time for each experimental run. The constants for the chlorination of phenol and each of chlorophenols formed are presented in TABLE 1 and plotted in FIG. 2.

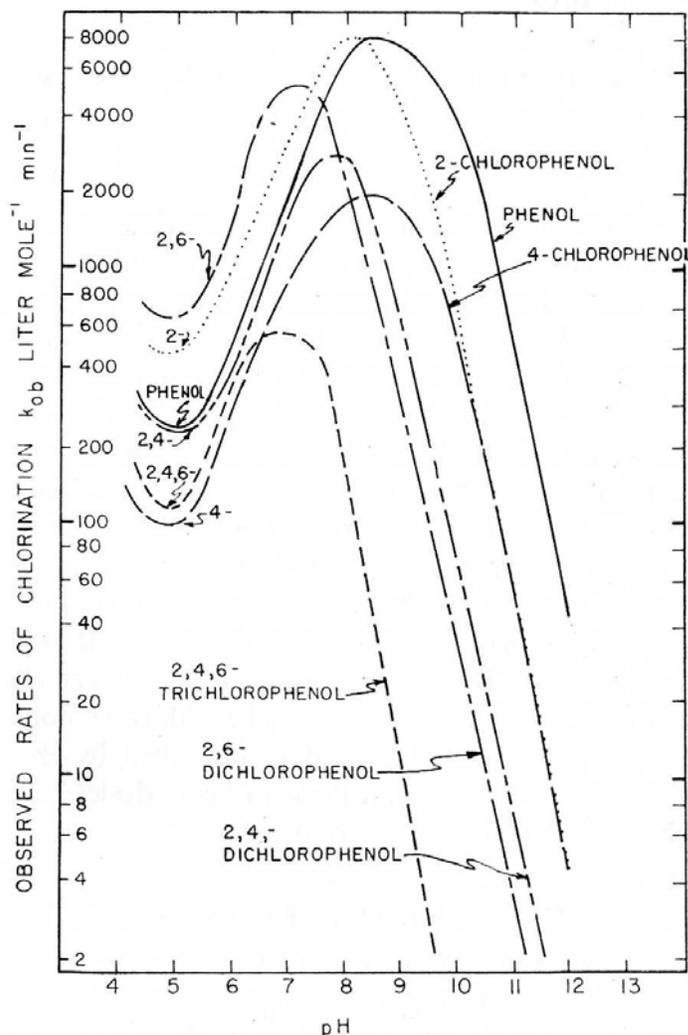


FIG. 2. Observed rates of chlorination.

The rates of chlorination of phenol in the neutral pH range are of similar magnitude to those of the chlorophenols. Therefore, the chlorophenols formed when phenol is chlorinated compete for the remaining aqueous chlorine in the reaction solution. This

* Formal concentration of phenol is the molar sum of phenol or chlorophenol and phenolate or chlorophenolate.

† Formal concentration of aqueous chlorine is the molar sum of molecular chlorine, hypochlorous acid, and hypochlorite ion.

competition causes deviation from the second-order rate expression, Equation (1). To reduce this deviation and to isolate the desired reaction, it was necessary to study the chlorination of phenol and each of the phenolic compounds, and then to use only the initial periods of reaction to evaluate k_{ob} .

The rate constants presented in FIG. 2 were obtained with initial concentration of aqueous chlorine of approximately 5×10^{-5} M and 5×10^{-4} M phenolic compound. A hundred-fold dilution of these concentrations obey the same rate expression, Equation (1); however, great care must be exercised to remove traces of ammonia to obtain reliable results.

Table 1. Observed Rate Constants of Chlorination of Phenolic Compounds

| Temperature 25° C, $Cl^- = 10^{-3}$ M. Ionic strength = 0.02 | | | | | | |
|--------------------------------------------------------------|--------------------|--------------------|--------------------|-----------------------|-----------------------|------------------------|
| pH | Phenol | 2-Chloro-phenol | 4-Chloro-phenol | 2,4-Dichloro-phenol | 2,6-Dichloro-phenol | 2,4,6-Tri-chlorophenol |
| 5 | 2.09×10^2 | 9.60×10^1 | 4.30×10^2 | 2.38×10^2 | 6.32×10^2 | 1.17×10^2 |
| 6 | 4.82×10^2 | 2.98×10^2 | 1.04×10^3 | 4.02×10^2 | 1.34×10^3 | 3.46×10^2 |
| 7 | 2.23×10^2 | 8.93×10^2 | 3.16×10^3 | 1.76×10^3 | 4.95×10^2 | 5.16×10^2 |
| 8 | 6.15×10^3 | 1.84×10^3 | 8.15×10^3 | 2.72×10^3 | 2.19×10^3 | 1.45×10^2 |
| 9 | 6.14×10^3 | 1.54×10^3 | 3.21×10^3 | 5.48×10^2 | 2.96×10^2 | 1.34×10^1 |
| 10 | 2.84×10^3 | 4.15×10^2 | 4.30×10^2 | 6.32×10^1 | 3.09×10^1 | 9.05×10^{-1} |
| 11 | 4.73×10^2 | 4.74×10^1 | 4.60×10^1 | 6.37 | 3.12 | 5.44×10^{-2} |
| 12 | 4.50×10^1 | 4.54 | 4.60 | 6.36×10^{-1} | 3.15×10^{-1} | 1.81×10^{-3} |

Examination of FIG. 2 shows that chlorination of each phenolic investigated has a maximum value of k_{ob} , corresponding to a maximum rate of chlorination, occurs in the pH 7–9. The position of the maxima shifts to lower pH values with increasing acidity of the chlorophenols. In addition, when chloride is present in the reaction solution, each system exhibits a minimum in k_{ob} near pH 5. In the presence of chloride, the rates of chlorination increase rapidly with decreasing pH below pH 5. It is of interest to compare the rates chlorination of the chlorophenols at pH 9. At this pH the dichlorophenols are chlorinated about 10 to 20 times slower than the monochlorophenols. Therefore, the chlorination of phenol in the alkaline pH range, e.g., pH 9 or greater, will result in the build-up in the reaction solution of the odorous dichlorophenols. While at pH 7–8, the odorous dichlorophenols are chlorinated at the same or at a greater rate than phenol or the monochlorophenols. The effect of pH of chlorination on the distribution of chlorophenolic products and as a result the threshold odor of the reaction solution will be discussed more fully under application of the kinetic results to the chlorination of phenol-bearing water.

INTERPRETATION OF KINETIC DATA

The rates of reaction of aqueous chlorine with phenol and the chlorophenols investigated vary enormously with pH largely because of the effect of pH on acid-base equilibria which determine the concentration of the various species of hydrolyzed chlorine and of phenolic compound in the reaction solution.

SOPER and SMITH (1926) found the variation in the rate of chlorination of phenol with pH could be explained by the hypothesis that the rate was proportional to the

product of hypochlorous acid and phenolate ion concentration. If Equation (1) is expressed in terms of the activities of hypochlorous acid, HOCl, and phenolate, PhO^- , rather than the formal concentrations of chlorine and phenolic compound, a rate expression

$$-\frac{dF_{\text{Cl}}}{dt} = k_2 (\text{HOCl}) (\text{PhO}^-) \quad (3)$$

is obtained in which the rate constant, k_2 , is independent of pH for pH range 6–12 except for a minor acid catalysis. The data obtained in this investigation conform to, and confirm in part the mechanism of SOPER and SMITH, namely that in the neutral or alkaline pH range, the chlorination of phenol and the chlorophenols investigated proceeds by the reaction of hypochlorous acid with the phenolate or chlorophenolate. The minor deviation from the SOPER and SMITH mechanism found in this investigation can be attributed to an acid catalysis of this reaction.

It is of interest at this point to compare the rates of chlorination of phenol and each of the chlorophenols investigated. As was previously pointed out, the pH of the maximum rate of chlorination of the phenolic compounds studied is related to the acidity of the phenolic compound; the more acidic compounds show a shift in the position of the maximum toward more acid pH values, see FIG. 2. It was found that the product of the rate constant, k_2 , times the acid dissociation constant for the compound being chlorinated, is a constant equal to approximately 10^{-4} . This same relationship was found by SOPER and SMITH (1926) for the chlorination of a variety of phenolic compounds. This observation may be interpreted as: those substitute groups on phenol which tend to make the substituted phenol more acidic also tend to decrease the rate of reaction of aqueous chlorine with this compound.

The rate constants, k_2 , for the chlorination of phenol were found to be independent of ionic strength, concentration of pH buffering materials, and chloride concentration at pH values greater than pH 6. An activation energy of 14 K cal per mole deg K was obtained, for the temperature range 5–35° C, for the uncatalyzed reaction between chlorine and phenol. This value is in the same range as commonly found for a majority of chemical reactions. An activation energy of this order of magnitude means that in the pH range 7–12, the rate of chlorination decreases by a factor of 2 for each 10 C° decrease in temperature.

Below pH 6, with chloride present in the reaction solution, the equilibrium



is displaced far enough to the right so that a significant reaction occurs between molecular chlorine and the phenolic compound.

In reacting with aqueous chlorine, phenol and each of the chlorophenols studied display some tendency to undergo oxidative rupture of the benzene ring rather than substitution as was noted in the infrared spectra of the reacted solutions. No attempt was made quantitatively to determine the respective fractions of oxidative rupture and substitutions, but qualitatively it was found that the degree of oxidation is greater the more highly chlorinated the phenolic reactant. The infrared data clearly show that an appreciable fraction of the reaction between aqueous chlorine and the dichlorophenols may proceed by direct oxidation rather than substitution to the trichlorophenol and followed by oxidation. The exact nature of these oxidation products is of little interest

in this investigation since BURTTSCHELL et al. (1959) found that these products do not contribute to the organoleptic properties of the reaction solution.

Measurement of the ultraviolet absorption spectra of the reaction solution yielded only qualitative or, in some cases, semi-quantitative results because of the similarity of the spectra of phenol and the chlorophenols. However, differences in the resulting absorption spectra were observed, particularly between reactions carried out in the alkaline pH range and those conducted in the acid pH range, which allow some discriminatory conclusions to be drawn.

The ultraviolet spectra of reacting solutions in the pH range 4 to 7 during the course of the reaction exhibit marked departures from typical chlorophenolic spectra obtained in the alkaline pH range.

Atypical chlorophenolic absorption bands were obtained if the pH of chlorination was below pH 7. The maximum absorption due to these bands coincides with the disappearance of aqueous chlorine from the reaction solution. After this time, the absorption due to these bands slowly decreases, and after an extended period of time, several weeks to a month, a stable absorption spectra was obtained which was very similar to that obtained if the chlorination had been carried out in more alkaline solutions. The atypical chlorophenolic absorption bands have been attributed to a long-lived reaction intermediate of undetermined structure. The formation of this intermediate may account for the reason why BURTTSCHELL et al. (1959) found that atypical chlorophenolic tastes and odors were developed if the pH of chlorination was less than pH 7.

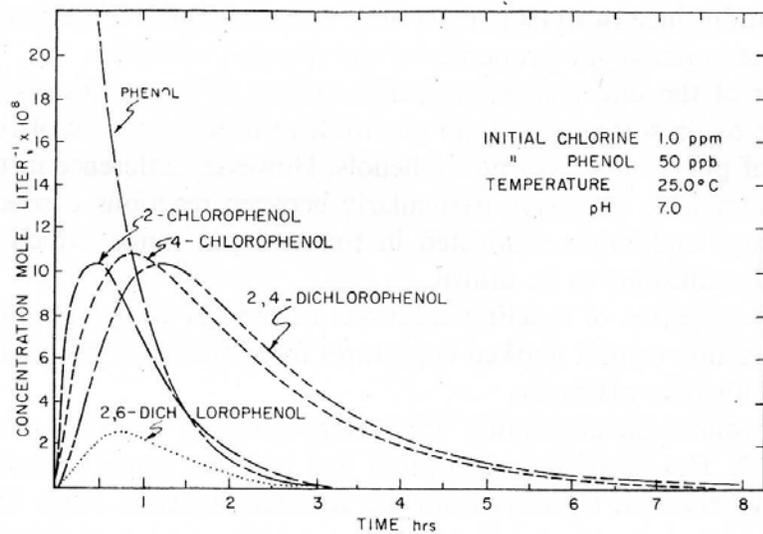
CHLORINATION OF PHENOL IN THE PRESENCE OF AMMONIA

An important constituent of natural waters which has been reported to alter the kinetics of the chlorination of phenol is ammonia. Therefore, it is of interest to compare the rates of chlorination of ammonia and phenol. Calculations based upon rates of chlorination of ammonia reported by WEIL and MORRIS (1945) indicate that for equal initial molar concentrations of ammonia and phenol, pH 8, temperature 25° C, the ammonia is chlorinated to form NH_2Cl about 1000 times faster than phenol is chlorinated to form a monochlorophenol. Therefore, little chlorophenol would be expected from the chlorination of phenol in the presence of excess ammonia.

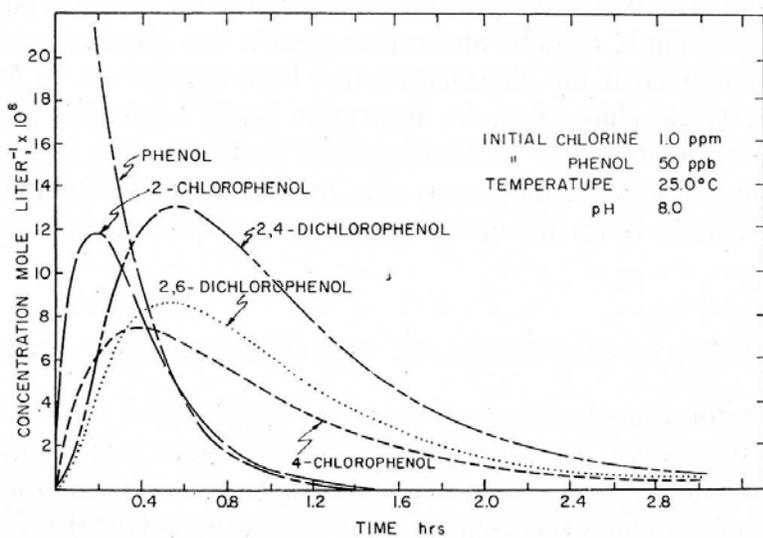
However, BURTTSCHELL et al. (1959) found that if sufficient time was allowed for the reaction to proceed (several days to a week at water supply concentrations) the same chlorophenols are formed when chloramine reacts with phenol as were found in a considerably shorter period of time when chlorination of phenol was carried out in the absence of ammonia.

The effect of ammonia on the rate of chlorophenol formation in chlorinating very dilute phenol solutions may account for the enormous concentration effects that have been reported by some workers for this reaction. The difficulty of preparing water free from traces of ammonia means that in experiments with extremely dilute chlorine solutions chloramine is likely to be inadvertently formed.

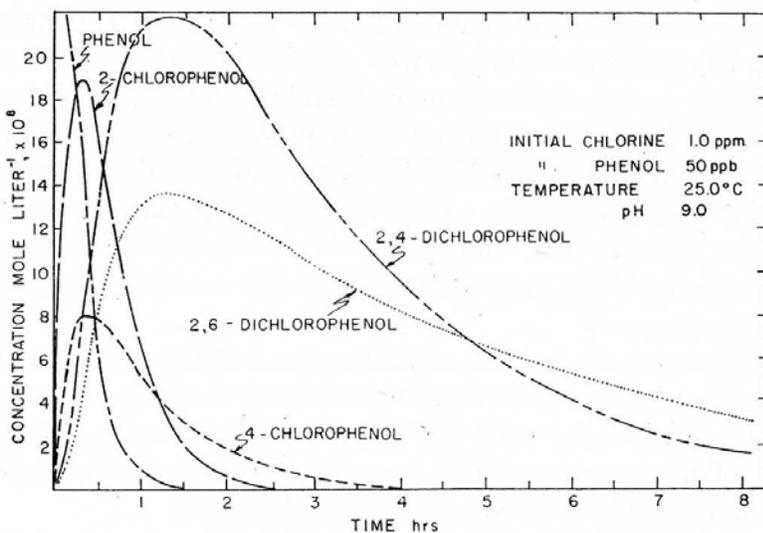
This extremely slow formation of the chlorophenols in the presence of ammonia may account for some of the problems found in water supply practice with taste and odors' development after the water has left the treatment plant particularly in the dead ends of the distribution systems.



3a.



3b.



3c.

FIG. 3a. Chlorination of phenol and the chlorophenols formed at pH 7.
 FIG. 3b. Chlorination of phenol and the chlorophenols formed at pH 8.
 FIG. 3c. Chlorination of phenol and the chlorophenols formed at pH 9.

APPLICATION OF RESULTS TO WATER TREATMENT

If the concentrations of each of the chlorophenols resulting from the chlorination of phenol is known, for a given initial condition, as a function of time and if the organoleptic intensity of each of them is also known, then the expected taste and odor characteristics of chlorinated phenol-containing waters can be computed on the assumption that the individual organoleptic intensities of the chlorophenolic substances are additive to give overall taste and odor intensity. These taste and odor intensities can be expressed as threshold odor. Computations of the expected threshold odor for varying experimental conditions, time of contact, relative concentrations of chlorine to phenol, pH, temperature, permits delineation of conditions for maximal and minimal development of objectionable organoleptic conditions and specification of conditions for chlorination phenol-containing waters to lessen production of noxious tastes and odors.

Examination of reaction scheme, FIG. 1, shows that a short time after mixing chlorine and phenol, there are 8 interdependent reactions occurring simultaneously. The rates of each of these reactions have been determined in this investigation. To compute the concentration of each of the compounds in the reaction scheme requires the integration and simultaneous solution of 8 second-order differential equations. These computations were made by Univac I digital computer.

Computations were performed for initial aqueous concentrations of 1.0 mg/L and 0.2 mg/L each acting on initial phenol concentration of 50 $\mu\text{g/L}$ and 5 $\mu\text{g/L}$; these values were chosen as typical of the concentrations encountered in the treatment of water supplies. Reaction paths at pH values 7, 8 and 9 were evaluated for each pair of reactant concentrations.

All of the sets of concentrations gave similar results at a given pH value, the major difference being the scales for concentration and time. Only the results for 1.0 mg/L chlorine and 50 $\mu\text{g/L}$ are presented graphically in FIG. 3, for pH 7, 8 and 9 respectively. Curves are shown for the formation and reaction of phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 2,6-dichlorophenol. Neither the concentrations of 2,4,6-trichlorophenol nor the build-up of oxidation products is shown since they do not contribute to the "chlorophenolic" tastes and odors at the concentrations formed during the course of the reaction.

At pH 7 the maximum concentrations of 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol are all about the same, each amounting to about 20 percent of the initial phenol concentration. For the plotted reactant concentrations, the maximum 2-chlorophenol occurs after about 30 min, maximum 4-chlorophenol after about 50 min and maximum 2,4-dichlorophenol after about 80 min because it is formed from the first two. At this pH the concentration of 2,6-dichlorophenol always remains low.

Reactions at pH 8 are more rapid, as can be seen by comparing the time scale of FIG. 3a with that of 3b. The maximum steady state concentration of 4-chlorophenol has become much less than that of 2-chlorophenol and that of 2,6-dichlorophenol has increased greatly so that it is now greater than the maximum concentration of 4-chlorophenol. The maximum concentration of 2,4-dichlorophenol which now occurs after about 35 minutes is about 30 percent greater than at pH 7.

Further changes in the reaction pattern are exhibited at pH 9, as shown in FIG. 3c. The overall rate of reaction is again slower but the peaks for the monochlorophenols are much sharper as a result of relative acceleration of the rate of the dichlorophenols.

The peak concentration of 2-chlorophenol has increased sharply, being about twice as great as at pH 7. Peak concentrations of the dichlorophenols are also greater. That of 2,4-dichlorophenol is more than twice as great as at pH 7 and over 50 percent greater than at pH 8. The maximum concentration of 2,6-dichlorophenol is also about 50 percent greater than at pH 7.

These changing concentrations and relative proportions of chlorinated phenols as a function of time and pH will be exhibited in changes in the intensity of the tastes and odors produced during the process of chlorination. Since, as previously described, the compounds producing the strongest tastes and odors are 2-chlorophenol, 2,4-dichlorophenol, and 2,6-dichlorophenol, it may be expected qualitatively that the production of tastes and odors will be greatest for those conditions leading to maximum total formation of these substances.

Expected threshold odor

The threshold odor of a water is defined as the dilution ratio at which the odor is just detectable (STANDARD METHODS, 1955). In other words, the threshold odor is the dilution of the water necessary to reduce its odor to a mean perceptible level.

The threshold odor contribution of each compound of the reaction solution was evaluated by multiplying the reciprocal of the threshold odor concentration, listed in FIG. 1, times the computed concentration of the odorous compound. The total threshold odor of the reaction solution at any time during the course of the reaction was obtained by adding the individual contributions of each compound.

The assumption that the chlorophenols contribute additively to the total organoleptic sensation and that each has the same type of odor appears reasonable for the conditions encountered in water treatment. Even if the odors are not strictly additive, they certainly reinforce each other, resulting in the same general relationship between threshold odor and time as presented in FIG. 4.

Examination of FIG. 4a, with an initial chlorine concentration of 1 mg/L and 50 µg/L of phenol, shows that the maximum threshold odors are developed at pH 9, and the water is still malodorous some 8 hours after the addition of chlorine. For the same reaction carried out pH 8, the threshold odors are only 80 percent at the maximum of those at pH 9, also malodorous water is present for only about 3.5 hr. At pH 7, chlorophenolic odors develop more slowly with the maximum occurring after about 1 hr, and are about 50 percent, at this point, of those developed at pH 9. However, malodorous water persists for a longer period of time, 5.5 hr at pH 7 as compared to 3.5 hr at pH 8.

FIG. 4b, with an initial concentration of chlorine 0.2 mg/L and phenol 50 µg/L, and 4c, 0.2 mg/L chlorine and 5.0 µg/L phenol, show the same general relationships of threshold odor and time of reaction as a function of pH of chlorination. Comparison of the results presented in FIGS. 4a and 4b, where the only difference is the initial concentration of chlorine has been reduced from 1.0 mg/L to 0.2 mg/L in 4b, shows that malodorous water persists for a much greater period of time when small amounts of chlorine are used. It was found from these and other calculations, that an increase in chlorine dose by 5-fold (0.2 to 1.0 mg/L) reduces the time necessary to obtain an odorless water by about 8-fold. This conclusion is in accordance with water treatment practice of using the maximum free chlorine (super-chlorination) to carry the reaction to the odorless trichlorophenol and thereby obtain an odorless water.

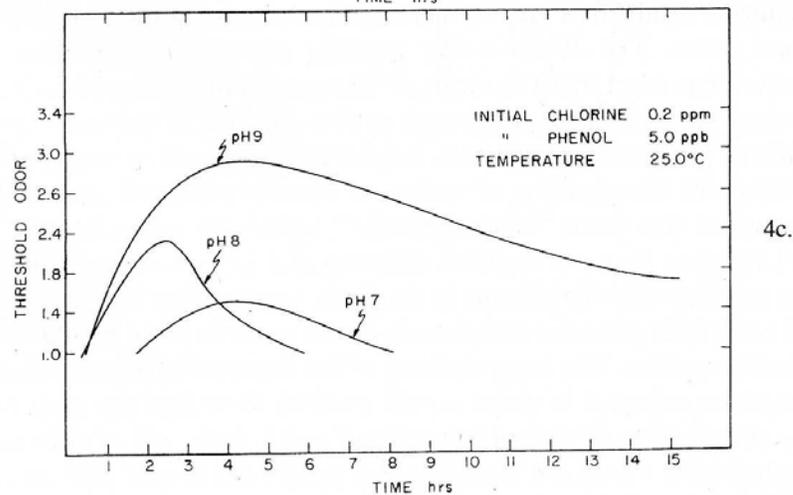
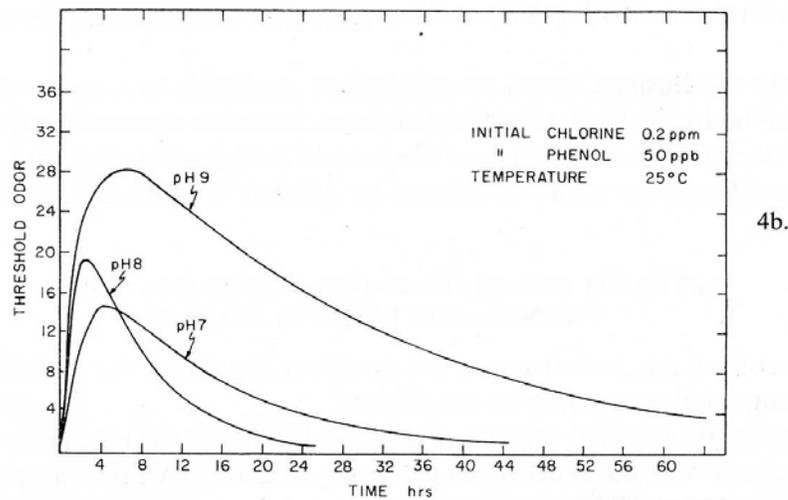
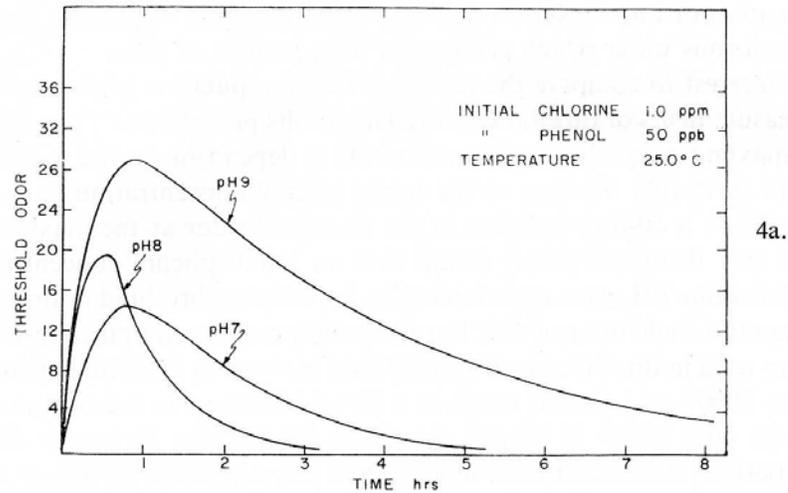


Fig. 4a. Threshold odor from chlorination of phenol. Initial chlorine, 1.0 ppm. Initial phenol, 50 ppb. Temperature 25C.

Fig. 4b. Threshold odor from chlorination of phenol. Initial chlorine, 0.2 ppm. Initial phenol, 50 ppb. Temperature 25C.

Fig. 4c. Threshold odor from chlorination of phenol. Initial chlorine, 0.2 ppm. Initial phenol, 5.0 ppb. Temperature 25C.

Examination of FIG. 4c shows that very small amounts of phenol, 5 $\mu\text{g/L}$, may produce malodorous water which persists for long periods of time.

It is of interest to compare the results of this computation of threshold odors with actual measurements of threshold odor. The results presented in FIGS. 4b and 4c show that the maximum threshold odor at any pH is dependent on the initial phenol concentration. A 10-fold increase in the initial phenol concentration (5 to 50 $\mu\text{g/L}$), at pH 8 results in a 10-fold increase in the threshold odor at the maximum (2 to 20). ETTINGER and RUCHOFT (1951) found that an initial phenol concentration of 1000 $\mu\text{g/L}$, at this same pH, gave experimentally, by making threshold odor measurements, a maximum threshold odor of 400. By extrapolation of the computed results to the concentrations used in this investigation, a 20-fold increase in the initial phenol concentration (50 to 1000 $\mu\text{g/L}$) should result in a 20-fold increase in the maximum threshold odor (20 to 400) which is exactly the value obtained by ETTINGER and RUCHOFT. This comparison shows that three independent investigations, ETTINGER and RUCHOFT (1951), BURTSCHHELL et al. (1959), and the present investigation, all show good agreement.

All of the conclusions, based on calculations applicable to a temperature of 25° C should also be applicable to lower temperatures. It is reasonable to assume, based upon the temperature dependence of the rates of chlorination of phenol, that the rate of the overall reaction would be reduced by a factor of 2 for each 10 C° decrease in temperature.

OPTIMUM CONDITIONS FOR CHLORINATION OF PHENOL-CONTAINING WATERS

As a result of this investigation, the optimum conditions for the chlorination of phenol-containing waters may be established.

The commonly accepted Water-works practice of using the maximum free chlorine is in agreement with the conclusions of this investigation. An incremental increase in the free chlorine results in a greater incremental decrease in the time of persistence of malodorous water. The Water-works practice of super-chlorination followed by dechlorination has great merit in terms of elimination of "chlorophenolic" tastes and odors in water supplies. The large excess of free chlorine in the water insures a rapid chlorination of phenol to the odorless, 2,4,6-trichlorophenol or oxidation products.

The breakpoint chlorination of water, as usually practiced, may not necessarily render the water free from "chlorophenolic" tastes and odors because of the slow (24–60 hr) reaction between aqueous chlorine and phenol at low concentrations of each. Free residual chlorine present in the water supply after breakpoint chlorination could still react with phenolic compounds in the water to form malodorous waters in the distribution system. The computations of the expected threshold odors for several initial conditions expected in water supply practice show that the most advantageous pH for the chlorination of phenol is between 7 and 8. If the pH of chlorination is near pH 9, much greater odors are formed which persist for longer periods of time.

The purposeful addition of ammonia to phenol-containing waters to prevent the development of malodorous water can now be explained by the relative rates of chlorination of ammonia and phenol. Ammonia is chlorinated several orders of magnitude faster than phenol; therefore, little or no chlorophenol is formed initially when a phenol-containing water is chlorinated in the presence of excess ammonia.

Some of the difficulties encountered with chloramine treatment may be accounted for on the basis of the slow reactions between the chloramines and phenol to form chlorophenols, particularly in dead ends of the distribution system.

These results, conclusions and recommendations apply pacifically to the chlorination of phenol-bearing waters and are not intended to be directly applicable to the chlorination of waters which contain a variety of phenolic compounds which may give rise to "chlorophenolic" tastes and odors in chlorinated water supplies.

From an operational point of view, the primary contribution of this investigation is to define and show the interplay of the important parameters which may alter the development of "chlorophenolic" tastes and odors in water supplies.

SUMMARY AND CONCLUSIONS

The chlorination of phenol proceeds by the stepwise substitution of the 2, 4 and 6 positions of the aromatic ring leading to the formation of non-phenolic oxidation products. The rate of reaction of aqueous chlorine and phenol or the chlorophenols formed obey a second-order rate expression where the rate of reaction is proportional to the product of the formal concentrations of aqueous chlorine and phenolic compound. The rates of these reactions is highly pH dependent with the maximum rate occurring, dependent on the compound being chlorinated, in the neutral or slightly alkaline pH range. As a result of this investigation, the chlorination of phenol-bearing waters should be conducted with the maximum possible free chlorine in the pH range 7–8.

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