Environ. Sci. Technol. **2002**, *36,* 884−890

Chlorination of Phenols: Kinetics and Formation of Chloroform

HERVÉ GALLARD[£] AND
URS VON GUNTEN[*]
Swiss Federal Institute for Environmental Science
and Technology (EAWAG), Überlandstrasse 133,
CH-8600 Dübendorf, Switzerland

The kinetics of chlorination of several phenolic compounds and the corresponding formation of chloroform were investigated at room temperature. For the chlorination of phenolic compounds, second-order kinetics was observed, first-order in chlorine, and first-order in the phenolic compound. The rate constants of the reactions of HOCl with phenol and phenolate anion and the rate constant of the acid-catalyzed reaction were determined in the pH range 1−11. The second-order rate constants for the reaction HOCl + phenol varied between 0.02 and 0.52 $M^{-1}\ s^{-1}$, for the reaction HOCl and phenolate between 8.46×10^1 and 2.71×10^4 $M^{-1}\ s^{-1}$. The rate constant for the acid-catalyzed reaction varied between 0.37 $M^{-2}\ s^{-1}$ to 6.4×10^3 $M^{-2}\ s^{-1}$. Hammett-type correlations were obtained for the reaction of HOCl with phenolate ($\log(k) = 4.15 - 3.00 \times \Sigma\sigma$) and the acid-catalyzed reaction of HOCl with phenol ($\log(k) = 2.37 - 4.26 \times \Sigma\sigma$). The formation of chloroform could be interpreted with a second-order model, first-order in chlorine, and first-order in chloroform precursors. The corresponding rate constants varied between $k > 100$ $M^{-1}\ s^{-1}$ for resorcinol to 0.026 $M^{-1}\ s^{-1}$ for *p*-nitrophenol at pH 8.0. It was found that the rate-limiting step of chloroform formation is the chlorination of the chlorinated ketones. Yields of chloroform formation depend on the type and position of the substituents and varied between 2 and 95% based on the concentration of the phenol.

Introduction

Since the work of Rook in 1974 (*1*), it is well documented that chlorinated byproducts detected in drinking water are produced through the reactions of chlorine with natural organic matter (NOM) in the presence or absence of bromide. Chlorinated byproducts are mainly trihalomethanes (THM), haloacetic acids (i.e. di- or trichloroacetic acids (*2*)), and haloacetonitriles (*3*). In the last 30 years, the formation of volatile THM, i.e., chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$) has been intensively investigated to explain their formation from chlorination of NOM. Because of the complexity of natural organic matter, the mechanisms of THM formation were studied in synthetic waters with model organic compounds. In many studies, 1,3-dihydroxybenzenes (resorcinol) were shown to form chloroform with high yields (*4*−*9*). The mechanism of THM formation from resorcinols was originally studied by Rook (*4*) and was later completed by Boyce and Hornig (*8*) and Tretyakova et al. (*12*). The importance of dihydroxybenzene structures in the formation of THM from humic acid was confirmed because 3,5-dihydroxybenzoic acid was found as chemical degradation byproducts of humic acids (*10*). However, we showed in a previous paper that the rate of THM formation from resorcinol is too fast to account for all THM precursors contained in natural organic matter (*11*). Therefore, THM formation from monohydroxybenzenes can be an explanation for the kinetics of slowly reacting THM precursors, which can account for 70% of the whole THM precursors (*11*). Monohydroxybenzenes give lower yield, *R*, of THM than resorcinols ($0.004 < R < 0.7$ mole of $CHCl_3$ per mole of phenol at pH 7 (*7, 9*)) but they are more concentrated in humic materials than dihydroxybenzene moieties (*10*). Therefore, they could be responsible for a large part of the slowly reacting THM precursors.

The first step of the chlorination of phenol is the chlorination of the aromatic ring. Successive chlorination leads to the formation of mono-, di-, and 2,4,6-trichlorophenols for phenols (*13*) and 2,4,6-trichlororesorcinols for resorcinols (*14*), respectively. The formation of chloro-substituted phenols is relevant for drinking water treatment since these compounds can be responsible for taste and odor problems (*13*).

Kinetics of the initial chlorination of phenolic compounds and chlorine-substituted phenolic compounds was studied previously for both phenols (*15, 16*) and resorcinols (*17*). The reaction is second-order, first-order in chlorine, and first-order in the organic compound. The second-order rate constant showed a pH-dependence with a maximum in slightly alkaline media and a minimum in acidic pH range (*17*). The pH-dependence was explained by considering the speciation of both chlorine (reaction 1) and phenol (reaction 2) species, the acid-catalyzed reaction of HOCl with nondissociated phenol (reaction 3), and the reactions of HOCl with nondissociated phenol (reaction 4) and with phenolate anion (reaction 5).

$$\mathrm{HOCl} \rightleftarrows \mathrm{ClO^-} + \mathrm{H^+} \quad K_{a1} \tag{1}$$

$$\text{phenol} \rightleftarrows \text{phenolate} + \mathrm{H^+} \quad K_{a2} \tag{2}$$

$$\text{phenol} + \mathrm{HOCl} + \mathrm{H^+} \rightarrow \text{products} \quad k_3 \tag{3}$$

$$\text{phenol} + \mathrm{HOCl} \rightarrow \text{products} \quad k_4 \tag{4}$$

$$\text{phenolate} + \mathrm{HOCl} \rightarrow \text{products} \quad k_5 \tag{5}$$

For phenol and some chlorophenols, rate constants of the reaction of HOCl with phenolate anions were first determined by Soper and Smith (*15*). Later studies by Lee and Morris showed considerably lower values (*16*). Using Hammett-type correlation, Rebenne (*17*) showed that the values of Soper and Smith (*15*) correlated well with the rate constants of chlorination of substituted dihydroxybenzenes but Lee and Morris's values did not. To resolve this controversy further kinetic investigations were carried out in the present study.

A previous kinetic study on chloroform formation from monohydroxybenzenes was conducted by de Laat et al. (*7*). Yields of chloroform formed after 15 h of reaction time at pH

---

[*] Corresponding author phone: +41 1 823 5270; fax: +41 1 823 5210; e-mail: vongunten@eawag.ch.

[£] Present address: Laboratoire de Chimie de l'Eau et de l'Environnement UMR CNRS 6008. Ecole Supérieure d'Ingénieurs de Poitiers, 40, avenue du Recteur Pineau, F-86 022 Poitiers Cedex, France.

10.1021/es010076a CCC: $22.00

7.5 depended on the type and position of the substituent. Kinetics of chloroform formation from phenols were interpreted assuming second-order kinetics, first-order in chlorine, and first-order in the phenolic compound. The rate constant for the formation of chloroform from 3,5-dichlorophenol was determined as 0.5 M^{-1} s^{-1} at pH 7.5. Except for this study, THM formation from monohydroxybenzenes has not been investigated in detail so far.

The purpose of the present study was to investigate the kinetics of chlorination and of chloroform formation when phenols are chlorinated. In the first part, the kinetics of initial chlorination of several substituted phenols was conducted between pH 1 and 11. The rate constants of chlorination were compared to the rate constants obtained previously for chlorine substituted phenols and for resorcinols (*15*−*17*). In the second part, the kinetics of chloroform formation was investigated to elucidate reaction pathways for the formation of trihalomethanes from phenols.

Experimental Procedures

All chemicals were of the purest available quality. Solutions of organic compounds and of chlorine were prepared with Nanopure water from a Barnstead B-pure purification system. Stock solutions of chlorine were prepared by diluting a commercial solution of sodium hypochlorite (NaOCl, 4% active chlorine, Aldrich). Sodium hypochlorite was standardized by iodometry. All experiments were performed at room temperature (23 ± 2 °C). pH measurements were carried out with a Ross electrode (ATI Orion, Boston, MA) and a Metrohm 632 pH-meter (Metrohm, Herisau, Switzerland), which was calibrated with standard buffers (pH 4, 7, and 9 Merck). Spectrophotometric measurements were performed on a Uvikon 940 spectrophotometer (Kontron Instruments, Eching, Germany).

All glassware was cleaned with a concentrated solution of chlorine (1 mM) and was kept under chlorine before the experiments.

Consumption of Chlorine by Phenolic Compounds. Chlorination experiments were performed in batch reactors under conditions for pseudo-first-order kinetics ($[\text{phenolic compound}]_o \gg 10 \times [HOCl]_T$). The batch reactor consisted of a 500-mL bottle equipped with a dispenser (*18*). The initial concentration of total chlorine ($[HOCl]_T = [HOCl] + [ClO^-]$) was between 3 and 6 μM. pH was controlled with H_2SO_4 and NaOH for pH < 3 and pH > 10, respectively. For 3 < pH < 10, solutions were buffered using phosphate buffer (2−5 mM). Experiments were initiated by adding an aliquot of a concentrated chlorine solution to the phenol-containing aqueous solution. At different reaction times, 25 mL of solution was rapidly transferred into a 10 cm-spectrophotometer cell previously filled with 5 mL of KI (1 M). Reaction between chlorine and iodide is fast and quantitative according to the eq 6.

$$HOCl + 3I^- + H^+ \rightarrow I_3^- + H_2O + Cl^- \qquad (6)$$

Chlorine residual was analyzed spectrophotometrically as I_3^- (ϵ at 351 nm = 25 700 M^{-1} cm^{-1} (*19*)).

Formation of THMs from Phenolic Compounds. Experiments were conducted with an excess of chlorine relative to the chlorine demand of the solution. Concentrations of phenolic compounds were 2 or 4 μM. Concentrations of chlorine were 90 μM (6.4 mg L^{-1}) or 140 μM (10 mg L^{-1}). After adding chlorine to the phenol-containing solution (250 mL or 500 mL phosphate-buffered solution) it was immediately transferred to 25 mL vials and sealed with TFE-lined screw caps. A blank with buffered Nanopure water was prepared under the same conditions. Through this procedure, volatilization of trihalomethanes during the reaction time could be avoided because of the lack of headspace. For each desired reaction time, the solution of one vial was analyzed for chlorine and THM concentrations.

Free chlorine was determined spectrophotometrically by the ABTS (2,2-azinobis(3-ethylbenzothiazoline)-6-sulfonic acid diammonium salt, Aldrich)) method (*20*). THM concentrations were determined with the headspace technique (GC8000 Fisons gas chromatography) and ECD detection. Headspace vials (10 mL) were filled with 5 mL of the chlorinated sample. The excess of chlorine was then quenched with Na_2SO_3 (100 μL of 100 g L^{-1} Na_2SO_3 solution), and the vials were heated for 15 min at 60 °C. One milliliter of the headspace was withdrawn and injected on a DB-5 column. Detection limits (S/N = 3) was 2.5 nM (0.3 μg/L) for $CHCl_3$.

Results and Discussion

Consumption of Chlorine by Phenols. The kinetics of initial chlorination of phenol and four para-substituted phenols (4-chlorophenol, 4-iodophenol, 4-methylphenol, 4-cyanophenol) were studied between pH 1 and 11 and with $[\text{phenol}] \gg [HOCl]_T$. For all compounds, the reaction between chlorine and phenols could be described by second-order kinetics, first-order in chlorine, and first-order in phenol. The observed second-order rate constant, k_{app}, is given by the eq 7

$$k_{app} = f_{Cl}\cdot((k_3\cdot[H^+] + k_4)\cdot(1 - f_{ph}) + k_5\cdot f_{ph}) \qquad (7)$$

where

$$f_{Cl} = \frac{1}{(1 + 10^{pH-pKa1})} \quad \text{and} \quad f_{ph} = \frac{1}{(1 + 10^{pKa2-pH})}$$

The rate constants of reactions 3−5 and the standard errors were determined by a nonlinear least-squares regression of our experimental data using the fit curve function of SigmaPlot 2000 software (*21*). Values of pK_{a2} are given in Table 1 and $pK_{a1} = 7.54$. To better estimate the rate constants of reaction 4, regression was first conducted at pH < 5 where reaction 4 appreciably contributes to the overall rate constant. The rate constants for reaction 5 were also calculated from experimental data from Lee and Morris (*16*) (phenol and five chlorinated phenols pH > 7).

Figure 1a depicts the profile of the apparent second-order rate constants vs pH for 4-methylphenol, 4-iodophenol, and 4-cyanophenol. Figure 1b shows the pH-dependence of the apparent second-order rate constants of chlorination of phenol and 4-chlorophenol. Experimental values obtained by Lee and Morris (*16*) for the same compounds are also plotted in Figure 1b (full symbols). The apparent rate constants show a minimum at acidic pH (3 < pH < 5) and a maximum in the pH range 8−9. A similar behavior was observed for chlorination of resorcinols (*17*) and the iodination of phenols (*22*). The pH-dependence of the apparent rate constant can be explained by reactions 1−5. For pH < 7, Figure 1b shows that our apparent second-order rate constants are lower than the rate constants determined by Lee and Morris (*16*), whereas for pH > 7, both data sets are similar. In Lee and Morris's study, experiments were conducted in the presence of 1 mM Cl^-, and it can be suspected that Cl_2 explains the higher rate constants obtained by Lee and Morris at pH 5−6. However, with the hydrolysis constant of 4.0×10^{-4} for Cl_2 and a 1 mM concentration of Cl^-, the molar fractions of Cl_2 are only 2.49×10^{-5} and 2.42×10^{-6} at pH 5 and 6, respectively. These molar fractions are too low to find reasonable rate constants fitting Lee and Morris's data. Therefore, the presence of Cl_2 species cannot explain the differences observed between both studies for pH 5−6.

TABLE 1. Rate Constants for the Initial Chlorination of Mono- and Dihydroxybenzenes in Aqueous Media

no.	derivatives of phenol	pK_a	$\Sigma\sigma_{o,m,p}$[f]	rate constants k_3 ($M^{-2}\ s^{-1}$)	k_4 ($M^{-1}\ s^{-1}$)	k_5 ($M^{-1}\ s^{-1}$)	reference
				Monohydroxybenzenes			
1	4-methyl (*p*-cresol)	10.26[a]	−0.17	1.69 (±0.49) × 10^3	0.09 (±0.05)	2.71 (±0.49) × 10^4	this study[g]
2	unsubstituted	9.99[a]	0	2.49 (±0.98) × 10^2	0.36 (±0.28)	2.19 (±0.08) × 10^4	this study[g]
3	4-iodo	9.20[a]	0.18	6.39 (±0.34) × 10^3	0.52 (±0.28)	2.01 (±0.43) × 10^3	this study[g]
4	4-chloro	9.43[a]	0.23	1.6 (±0.4) × 10^1	0.02 (±0.005)	2.17 (±0.33) × 10^3	this study[g]
5	4-cyano	7.86[b]	0.66	0.37 (±0.12)	0.03 (±0.01)	8.46 (±0.38) × 10^1	this study[g]
6	unsubstituted	9.99[a]	0	nd[h]	nd[h]	3.52 (±0.19) × 10^4	(*16*) 25 °C
7	4-chloro	9.43[a]	0.23	nd[h]	nd[h]	3.16 (±0.22) × 10^3	(*16*) 25 °C
8	2-chloro	8.56[c]	0.23	nd[h]	nd[h]	2.42 (±0.08) × 10^3	(*16*) 25 °C
9	2,4-dichloro	7.85[d]	0.60	nd[h]	nd[h]	3.03 (±0.09) × 10^2	(*16*) 25 °C
10	2,6-dichloro	6.97[c]	0.74	nd[h]	nd[h]	1.94 (±0.11) × 10^2	(*16*) 25 °C
11	2,4,6-trichloro	6.15[d]	0.97	nd[h]	nd[h]	12.84 (±0.69)	(*16*) 25 °C
				Meta-dihydroxybenzenes			
12	3-hydroxy (resorcinol)	9.43[e]	0.12	8.5 (±1.8) × 10^6	<330	1.36 (±0.26) × 10^6	(*17*) 22 °C
13	3-oxido (resorcinol monophenolate)	11.21[e]	−0.47			1.15 (±0.10) × 10^8	(*17*) 22 °C
14	3-hydroxy-4-chloro	8.09[e]	0.35	1.19 (±0.15) × 10^6	<65	1.43 (±0.16) × 10^5	(*17*) 22 °C
15	3-oxido-4-chloro	10.75[e]	−0.24			6.37 (±0.53) × 10^7	(*17*) 22 °C
16	3-hydroxy-4,6-dichloro	7.53[e]	0.72	2.6 (±1.2) × 10^4	47 (±17)	3.21 (±0.76) × 10^4	(*17*) 22 °C
17	3-oxido-4,6-dichloro	10.35[e]	0.11			5.91 (±0.81) × 10^7	(*17*) 22 °C
18	3-hydroxy-5-methyl (resorcinol)	9.35[e]	0.05	9.8 (±1.1) × 10^6	1250 (±160)	5.18 (±0.34) × 10^6	(*17*) 22 °C
19	3-oxido-5-methyl (resorcinol monophenolate)	11.5[e]	−0.54			4.20 (±0.04) × 10^8	(*17*) 22 °C

[a] From ref *30*. [b] From ref *22*. [c] From ref *31*. [d] From ref *32*. [e] From ref *17*. [f] Calculated from ref *23*. [g] Chlorine 3−6 μM, phenol 30 μM−5 mM, phosphate buffer 2 mM, 22 (±2) °C. [h] nd, not determined.

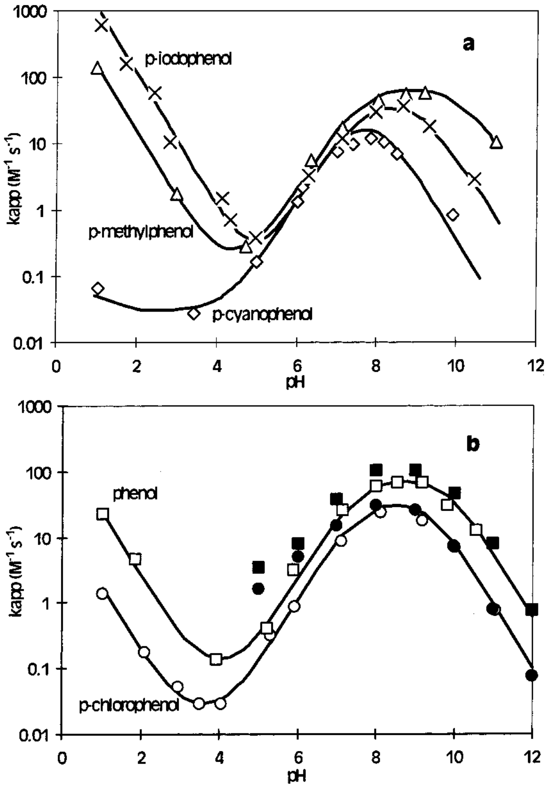

FIGURE 1. pH-dependence of the apparent rate constants of the reaction of HOCl with phenolic compounds: (a) 4-cyanophenol (open diamond), 4-iodophenol (cross), and 4-methylphenol (open triangle) and (b) Lee and Morris's study (*16*): full symbol, our study: open symbol, phenol (square), 4-chlorophenol (circle). The lines are calculated according to the reactions 1−5 and k_3, k_4, k_5, and pK_a in Table 1.

Table 1 shows the rate constants of HOCl with monohydroxybenzenes for both studies (nos. 1−5 our study, nos. 6−11 Lee and Morris's study (*16*)). To further discuss the results, the rate constants of meta-dihydroxybenzenes (*17*) were also included in Table 1 (nos. 12−19). For each model compound, Table 1 shows also the pK_a and the sum of Hammett constant for ortho, meta, and para substituents ($\Sigma\sigma_{o,m,p}$). The sum $\Sigma\sigma_{o,m,p}$ was calculated for all substituted phenols from the database of Hansch et al. (*23*).

Reaction rate constants for the acid-catalyzed reaction 3 of HOCl with substituted phenols vary between 0.37 $M^{-2}\ s^{-1}$ for 4-cyanophenol (Table 1, no. 5) to 6.39 × 10^3 $M^{-2}\ s^{-1}$ for 4-iodophenol (Table 1, no. 4). For reaction 3, an alternate mechanism was suggested involving the reaction of H_2OCl^+ with phenols (*17*). The pK_a of H_2OCl^+ is only roughly known ($-4 <$ pK_a < -3 (*24*)). For p$K_a = -3$ and for the values in Table 1 rate constants of H_2OCl^+ with substituted phenols would be between 3.7 × 10^2 $M^{-1}\ s^{-1}$ (4-cyanophenol, no. 5) and 6.39 × 10^6 $M^{-1}\ s^{-1}$ (4-iodophenol, no. 3). The rate constants would be 10^4−10^8-fold higher than the corresponding rate constants with HOCl. This can be explained by the higher electrophilicity of H_2OCl^+.

The rate constants for the reaction of HOCl with the undissociated form of substituted monohydroxybenzenes (k_4 reaction 4) are between 0.02 $M^{-1}\ s^{-1}$ for 4-chlorophenol (Table 1, no. 4) and 0.52 $M^{-1}\ s^{-1}$ for 4-iodophenol (Table 1, no. 3). The rate constants for the reaction of HOCl with substituted phenolates (k_5) are between 12.84 $M^{-1}\ s^{-1}$ for 2,4,6-trichlorophenol (no. 11) to 2.19−3.52 × 10^4 $M^{-1}\ s^{-1}$ for both phenol and 4-methylphenol (nos. 1, 2, and 6). Hence, k_5 is 10^3−10^5-fold greater than k_4. These differences are explained by the higher activating effect of $-O^-$ compared to $-OH$ upon electrophilic substitution (*17*). Consequently, the reaction of HOCl with phenolate (reaction 5) controls the overall reaction for pH ≥ 5. Reaction 4 is only important in a small pH range below 5 ($k_4 \leq 0.52\ M^{-1}\ s^{-1}$). Values of k_4 were obtained with high standard errors because reaction 4 is relatively unimportant compared to reactions 3 and 5.

The rate constants in Table 1 show that the values of k_3, k_4, and k_5 for monohydroxybenzenes (Table 1, nos. 1−5) are 10^2−10^4-fold smaller than for meta-dihydroxybenzenes (nos. 12−19). This indicates that resorcinol type structures are important for the fast initial consumption of HOCl of natural waters, whereas phenol type structures are more important during the secondary phase.

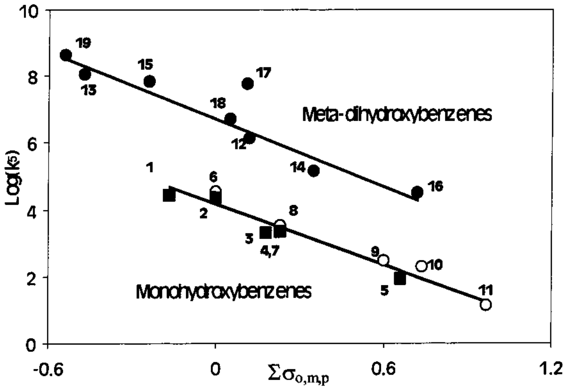

FIGURE 2. Correlations between the second-order rate constants of the reactions of substituted phenolate anions with HOCl vs the Hammett constants (our study: full squares, Lee and Morris (*16*): open circles, Rebenne et al. (*17*): full circles). The numbers correspond to those in Table 1.

Linear Free Energy Relationships. To predict the effect of substituents on both pK_a and rate constants of substituted phenols, Hammett substituent constants ($\Sigma\sigma_{o,m,p}$) can be used. Hammett constants reflect the effects of substituents on the electron density of the aromatic ring by inductive and resonance effects. For $\sigma > 0$, substituents have an electron-withdrawing effect (e.g. $-CN$), whereas for $\sigma < 0$ substituents exert an electron-donating effect (e.g. $-CH_3$). The nondissociated phenol was used as a reference compound ($\Sigma\sigma_{o,m,p} = 0$). Values of $\Sigma\sigma_{o,m,p}$ are shown in Table 1.

Figure 2 shows the Hammett-type correlation for the rate constants of HOCl with substituted phenolate anion (k_5) obtained in our study (Table 1, nos. 1−5) and by Lee and Morris (*16*) (Table 1, nos. 6−11). For comparison, Figure 2 also shows a Hammett correlation for the rate constants (k_5) of the HOCl reaction with meta-dihydroxybenzene phenoxide anions and dianions (k_5 Table 1, nos. 12−19). The data from both sources for monohydroxybenzenes can be well correlated together, whereas meta-dihydroxybenzenes show a different linear regression. For the same values of $\Sigma\sigma_{o,m,p}$ rate constants of resorcinol compounds are more than an order of magnitude greater than rate constants of monohydroxybenzenes. The linear regressions for both types of phenols are

$$\text{monohydroxybenzenes: } \log(k_5) = 4.15-3.00\ (\pm 0.22) \times \Sigma\sigma_{o,m,p} \quad r^2 = 0.951,\ n = 11 \quad (8)$$

$$\text{meta-dihydroxybenzenes: } \log(k_5) = 6.71-3.36\ (\pm 0.25) \times \Sigma\sigma_{o,m,p} \quad r^2 = 0.971,\ n = 7 \quad (9)$$

The negative Hammett slope (ρ) is expected for electrophilic substitution. The magnitude of ρ value reflects the sensitivity of the reaction to substituent effect (*25*). Therefore, the reaction of HOCl with resorcinols is more sensitive to substituent effect than with monohydroxybenzenes.

In contrast to ClO_2 where both mono- and dihydroxybenzenes gave the same linear regression (*25*), HOCl lead to two distinct curves. The effect of the hydroxyl substituent in meta position is too strong to be correlated by a unique Hammett correlation. The different behavior of ClO_2 and HOCl are probably due to the difference between electron-transfer reactions for ClO_2 and transfer of chlorine for HOCl.

To compare the reactivity of different oxidants with phenolate anions, Figure 3 shows Hammett-type correlations for HOCl (data from Figure 2), HOI (calculated from (*22*)), ClO_2 (*25*), and for O_3 (calculated from (*26*)). For active bromine a Hammett-type correlation is only available for the Br_2 species (*27*). This correlation was not introduced in Figure 3. Since in neutral aqueous solutions the dominant bromine species are HOBr and BrO^-. For most of substituted phenols, the rate constants for O_3, HOI, and ClO_2 are several orders of magnitude higher than rate constants for HOCl. These results explain why iodinated-organic compounds can be formed when iodide-containing waters are chlorinated (*22*) and that mixtures of HOCl and ClO_2 lower the concentrations of trihalomethanes when disinfecting drinking waters (*28*).

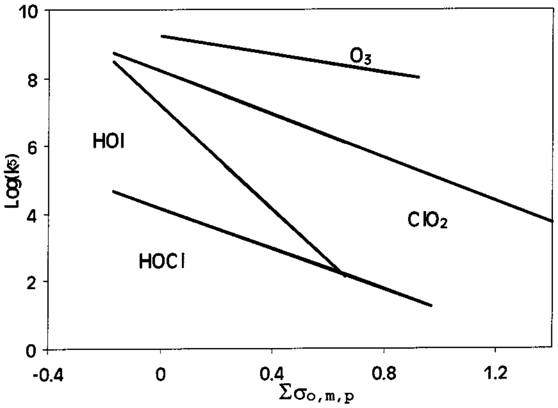

FIGURE 3. Comparison of the correlations between the second-order rate constants of the reactions of substituted phenolate anions with HOCl, O_3, HOI, and ClO_2 vs the Hammett constants. Correlation for O_3, HOI, and ClO_2 were taken from refs *26*, *22*, and *25*, respectively.

The Hammett slope for HOCl ($\rho = -3.00\ (\pm 0.22)$) is similar to the value found for ClO_2 ($\rho = -3.2\ (\pm 0.4)$ (*25*)) but lower than for HOI ($\rho = -7.64\ (\pm 1.1)$) and higher to the value obtained for O_3 ($\rho = -2.1\ (\pm 0.7)$). Therefore, the sensitivity of oxidants to substitution effects for their reaction with phenolate anions decreases in the following order: HOI > $ClO_2 \approx$ HOCl > O_3. The low value of ρ for ozone can be explained by the fact that measured rate constants approached the diffusion controlled limit.

Attempts to correlate the rate constants of undissociated monohydroxybenzenes (reaction 4) with Hammett constants did not give a good fit ($r^2 = 0.452$). Similar observations were made for the reactions of phenols with chlorine dioxide (*25*) and could be explained by the great uncertainty in the determination of k_4.

Except for 4-iodophenol, a linear regression was found between the apparent rate constants k_3 for the acid-catalyzed chlorination of para-substituted phenols (Table 1, nos. 1−5) vs $\Sigma\sigma_{o,m,p}$: $\log(k_3) = 2.37-4.26\ (\pm 0.29) \times \Sigma\sigma_{o,m,p}$, $r^2 = 0.99$, $n = 4$. 4-Iodophenol shows an unexpected high reactivity. Also, in this case, a different linear regression was obtained for resorcinols (Table 1, nos. 12−19): $\log(k_3) = 7.32-3.95\ (\pm 0.29)\ \Sigma\sigma_{o,m,p}$, $r^2 = 0.989$, $n = 4$.

Formation of Chloroform from Phenols. Both formation of chloroform and chlorine consumption were followed when solutions of phenol, resorcinol, 4 *para*-substituted phenols, and 7 chlorophenols were chlorinated at pH 8.0 ([phenol] = 4 μM, $[HOCl]_{T_0}$ = 140 μM). Figure 4a shows the formation kinetics of $CHCl_3$ for phenol, 4-methylphenol, 3-chlorophenol, 2,4,6-trichlorophenol, and 2,3,4,6-tetrachlorophenol. Figure 4b shows the plot of $CHCl_3$ vs chlorine demand for the same compounds.

Figure 4a depicts that chloroform increases during 10−20 h of reaction time until a plateau is reached. The concentration of chloroform depends on the type of phenolic compound. The rate of formation of chloroform for both phenol and 2,4,6-trichlorophenol was identical. A very low chloroform formation was obtained from 4-methylphenol (≅0.02 mol/mol), whereas 3-chlorophenol, 2,4,5-trichlorophenol, and 2,3,4,6-tetrachlorophenol had the highest chloroform yield (>0.25 mol/mol). A linear relationship exists

TABLE 2. Molar Yields and Rate Constants of Chloroform Formation from Chlorination of Phenols and Resorcinol at pH 8.0

no.	phenolic compounds	initial Cl_2 demand (mol/mol phenol)	total Cl_2 demand (mol/mol phenol)	molar yields of $CHCl_3$ (mol/mol phenol)	% of chlorine incorporated into chloroform	rate constant k (M^{-1} s^{-1})
1	resorcinol	nd	nd	0.95	nd	>100
2	phenol	3.1	9.5	0.11	3.5	0.24 (±0.02)
3	4-methylphenol	5.0	10.5	0.02	0.6	0.043 (±0.004)
4	4-iodophenol	4.1	12.5	0.05	1.2	0.09 (±0.01)
5	4-cyanophenol	2.2	11.0	0.07	1.9	0.030 (±0.004)
6	4-nitrophenol	1.5	8.2	0.05	1.8	0.026 (±0.002)
7	2-chlorophenol	4.0	9.4	0.10	3.2	0.22 (±0.02)
8	3-chlorophenol	3.9	9.5	0.32	10.1	0.29 (±0.04)
9	4-chlorophenol	3.8	9.8	0.11	3.4	0.24 (±0.03)
10	2,4-dichlorophenol	3.0	8.0	0.10	3.7	0.23 (±0.04)
11	2,4,6-trichlorophenol	2.0	8.0	0.10	3.7	0.24 (±0.01)
12	2,4,5-trichlorophenol	2.9	8.5	0.28	9.9	0.25 (±0.03)
13	2,3,4,6-tetrachlorophenol	1.0	7.2	0.29	12.0	0.24 (±0.03)

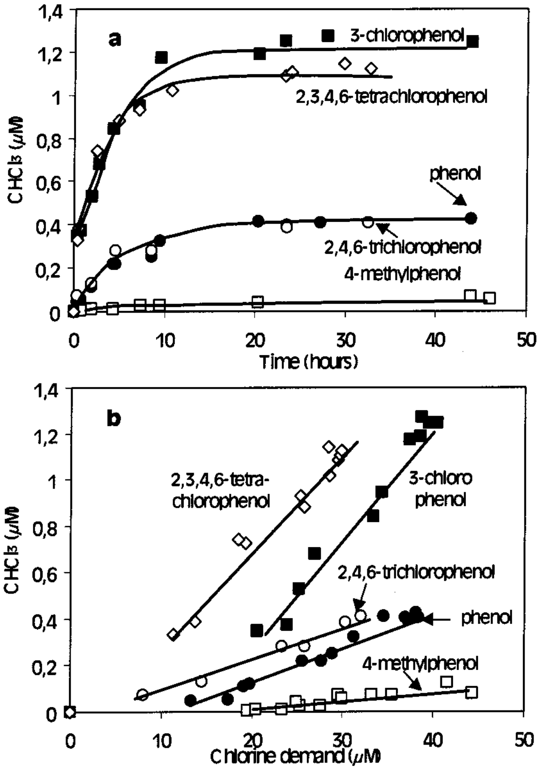

FIGURE 4. (a) Chloroform formation vs time and (b) chloroform formation vs chlorine demand for solutions of phenol (full circles), 2,4,6-trichlorophenol (open circles), 4-methylphenol (open squares), 3-chlorophenol (full squares), 2,3,4,6-tetrachlorophenol (full diamonds) ([phenol]$_o$ = 4 μM, [Cl_2]$_o$ = 140 μM, pH 8.0, 5 mM phosphate buffer).

between the concentration of $CHCl_3$ and chlorine demand (Figure 4b). The linear regression lines do not go through the origin. The slopes and intercepts of the linear regression lines depend on the nature of the phenolic compound. Phenol and natural organic matter showed similar slopes at pH 8.0 (*11*). The initial rapid consumption of chlorine without formation of chloroform is attributed to the fast chlorination of the aromatic ring. The initial chlorine demand corresponds to 5 mol per mole for 4-methylphenol and only 1 mol per mole for 2,3,4,6-tetrachlorophenol and 2 mol for 2,4,6-trichlorophenol. Table 2 depicts the molar yields of chloroform, the initial and total chlorine demand, and the percentage of chlorine consumed incorporated into chloroform. Chlorine incorporated into chloroform was calculated from the molar yields of chloroform and the chlorine demand.

Long-term formation of THMs from natural waters presents a similar behavior and was predicted using a second-order model (*11*). To compare THM precursors of natural water with model organic compounds, a second-order model, first-order in reactive sites, and first-order in chlorine was used in this study:

$$Cl_2 + \text{reactive sites} \rightarrow \text{THM} \qquad (10)$$

The initial concentration of reactive sites (or the THM formation potential [THMFP]) is given by the concentration of THM at the plateau. According to reaction (*10*) the rate of THM formation is formulated as follows:

$$\frac{d[\text{THM}]}{dt} = k \cdot [Cl_2] \cdot ([\text{THMFP}] - [\text{THM}]) \qquad (11)$$

[THM] and [Cl_2] are the concentration of THM and chlorine at time t, respectively, and k is the apparent rate constant of THM formation. Integrating (*11*) yields

$$\frac{1}{[Cl_2]_i - [\text{THMFP}]} \cdot \ln\left(\frac{[\text{THMFP}] \cdot [Cl_2]}{[Cl_2]_i \cdot ([\text{THMFP}] - [\text{THM}])}\right) = k \cdot t \qquad (12)$$

[Cl_2]$_i$ is the concentration of chlorine after the fast initial consumption of chlorine. [Cl_2]$_i$ was estimated by plotting [$CHCl_3$] vs the chlorine demand (Figure 4b) and by subtracting the initial chlorine demand ([$CHCl_3$] = 0) from [Cl_2]$_o$. [Cl_2] and [THM] (i.e $CHCl_3$) were analyzed at different time intervals. The plot of the left-hand side of eq 12 vs time should result in a straight line with a slope of k. Figure 5 shows that eq 12 is verified for phenol and 4-methylphenol. This indicates that only one rate-limiting step exists for the formation of chloroform or that the different rate-limiting steps have similar rate constant (i.e. a similar nature of reactants). Comparable results were obtained for phenols substituted in para and ortho position only. For chlorinated phenols substituted in meta position such as 2,3,4,6-tetrachlorophenol (Figure 5) eq 12 is verified only after an initial fast phase during the first 2 h. For these compounds, only a rate constant was calculated for the secondary phase. The apparent rate constants of chloroform formation (k) for phenolic compounds at pH 8.0 are presented in Table 2.

For resorcinol (Table 2, nos. 1) yield and rate constant of chloroform formation are dramatically higher than for monohydroxybenzenes; its molar yield of chloroform is 0.95, and the rate constant was estimated > 100 M^{-1} s^{-1}. The molar yield of chloroform is consistent with previous studies (*4*−*8*) and was explained by the activating effect of both hydroxyl

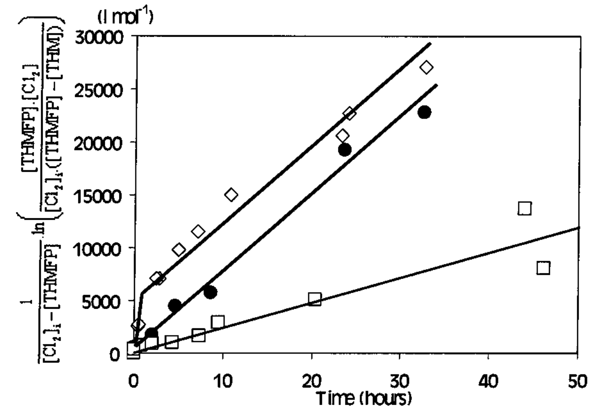

FIGURE 5. Applications of the second-order model for the formation of chloroform from phenol (full circles), 4-methylphenol (open squares), and 2,3,4,6-tetrachlorophenol (open diamond) ([phenol]$_0$ = 4 μM, [Cl$_2$]$_0$ = 140 μM, pH 8.0, 5 mM phosphate buffer).

groups on the ortho position. The rate constant for $CHCl_3$ formation is 500–5000-fold higher than for monohydroxybenzenes.

For monohydroxybenzenes, Table 2 shows that the total chlorine demand decreases with increasing the degree of substitution of the aromatic ring. For monosubstituted phenols (Table 2, nos. 3–9), the chlorine demand is around 10 mol/mole, whereas for tetrachlorophenol (Table 2, nos. 13) chlorine demand is only 7.5 mol/mole. Phenol and chlorophenols substituted in ortho and para position show similar rate constants (k around 0.24 M^{-1} s^{-1}) and similar yields of chloroform (around 0.1 mol per mole of parent compound). As shown for phenol and 2,4,6-trichlorophenol in Figure 4a, these compounds have the same kinetics of formation of chloroform. This is consistent with the observation that chlorination of phenol leads to the formation of 2,4,6-trichlorophenol as a crucial intermediate (*13*).

Results in Table 2 also show that both molar yields of chloroform and percentages of chlorine incorporated into chloroform are greater for chlorinated phenols substituted in meta position than for phenols substituted only in ortho and para position (see also Figure 4a). Molar yields of chloroform are around 0.3 mol/mol for meta-substituted chlorophenols and in the range of 0.02–0.11 mol/mol for the other monohydroxybenzenes. Percentage incorporation of chlorine into chloroform was calculated in the range 0.6–3.5% for para- and ortho-substituted phenols, whereas it is equal to 10% for meta-substituted chlorophenols. Meta-substituted phenols differ also from others monohydroxybenzenes by a fast initial phase with a rate constant > 100 M^{-1} s^{-1}. Two pathways with different rate-determining steps leading to chloroform seem to be present in case of meta-substituted chlorophenols. Kinetic results suggest that the first pathway might be similar to resorcinols, and the second pathway would involve similar byproducts to the others chlorophenols because their rate constants are identical.

In addition, the rate constants of chloroform formation for phenol and para-substituted phenols (Table 2, nos. 2–6) depend on the nature of the substituent. Rate constants range between 0.24 M^{-1} s^{-1} for phenol to 0.026 M^{-1} s^{-1} for *p*-nitrophenol. For natural waters, rate constants were found between 0.124 and 0.008 M^{-1} s^{-1} (*11*). Intermediate products that are responsible of the rate-determining step of chloroform formation depend strongly on the type of the para-substituent of the parent compound. For deactivating substituents, rate constants of chloroform formation decrease with increasing the withdrawing effect of substituent in the order −H > −I > −CN > $-NO_2$ (Table 2). This would suggest that the rate-limiting reactions involve byproducts varying mainly by the nature of the para-substituent of phenolic compounds. *p*-Methylphenol (Table 2, no. 3) that exhibits an activating substituent in para position exhibits lower yield of chloroform formation and rate constant than phenol and presents higher initial chlorine demand than the other phenolic compounds (Table 2 and Figure 4). Because of both hydroxyl and methyl activating groups, chlorination of the aromatic ring occurs probably in all meta and ortho positions leading to 2,3,5,6-tetrachloro-4-methylphenol as intermediate byproduct. In addition, compared to phenols with deactivating groups the activating methyl group might modify the position of the ring openings, which would affect the reactivity of byproducts toward formation of chloroform.

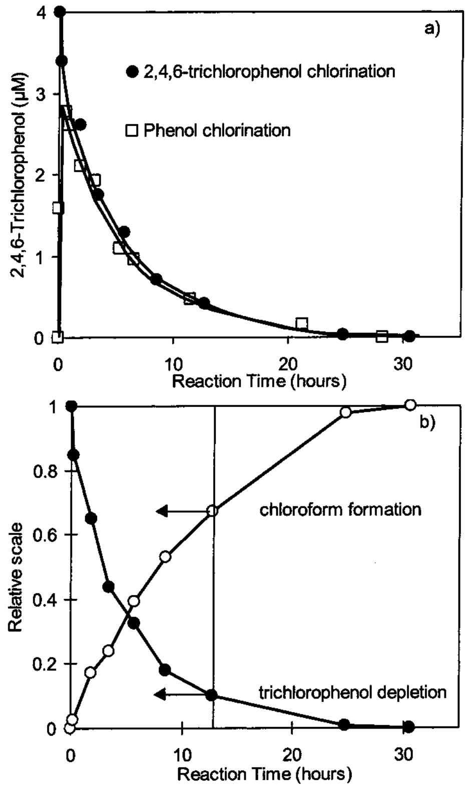

FIGURE 6. Chlorination of solutions of phenol and 2,4,6-trichlorophenol (a) 2,4,6-trichlorophenol vs time (b) relative decrease of 2,4,6-trichlorophenol and increase of $CHCl_3$ ([phenolic compound]$_0$ 4 μM, [Cl$_2$]$_0$ 90 μM, pH 8.0, 5 mM phosphate buffer).

To further investigate the rate-limiting step for the formation of chloroform, both phenol and 2,4,6-trichlorophenol were chlorinated at pH 8.0. Concentrations of chlorine and phenolic compounds were 90 μM and 4 μM, respectively. The concentration of 2,4,6-trichlorophenol was measured as a function of reaction time. Figure 6a depicts the concentration time-profile of 2,4,6-trichlorophenol. In Figure 6b the depletion of 2,4,6-trichlorophenol and the formation of chloroform are shown for chlorination of 2,4,6-trichlorophenol.

Figure 6a shows that 2,4,6-trichlorophenol is rapidly and quantitatively produced from the chlorination of phenol. Therefore, chlorination of the aromatic ring is not the rate-determining step. When 2,4,6-trichlorophenol is chlorinated, the depletion of the parent compound and the formation of chloroform occur within a similar time frame (Figure 6b). However, Figure 6b shows that 2,4,6-trichlorophenol was depleted faster than chloroform was produced. For example for a reaction time of 13 h (vertical line), 90% of 2,4,6-trichlorophenol was consumed, and only 65% of chloroform was formed. Therefore, chlorination of 2,4,6-trichlorophenol cannot be the rate-determining step for the formation of chloroform. Moreover, since the formation of chloroform was quenched when the excess of chlorine was reduced by sodium sulfite, both ring cleavage and hydrolysis of trichloromethyl compounds into chloroform cannot be rate determining either. Hence, chlorination of the chlorinated ketones resulting from the ring cleavage can be responsible for the rate-determining step for the chloroform formation. This was postulated before for chloroform formation from resorcinol (*6*). As a consequence, the differences for phenols and resorcinols with respect to chloroform formation cannot be only explained by the higher reactivity of resorcinol compounds with chlorine. For resorcinols, ring cleavage leads to chlorinated keto-carboxylic acids (*8*), whereas for monohydroxybenzenes ring cleavage leads to chlorinated ketones only. Keto-carboxylic acids, whose enol can be stabilized by the carboxylate groups, show a high reactivity with chlorine and high yields of chloroform formation (*29*). In case of chlorinated ketones produced from monohydroxybenzenes such stabilization is not possible. Therefore, their rate of chlorination would be slower than the corresponding rate of chlorination of keto-acids. This hypothesis may explain the slower formation of chloroform from monohydroxybenzenes compared to meta-dihydroxybenzenes and their respective contribution to long-term (secondary phase) and short-term (primary) effects. However, it does not explain the initial fast formation of chloroform from meta chlorinated phenols.

In literature, meta-dihydroxybenzenes have been considered as THM precursors of NOM because of their high yield of chloroform. However, their kinetics of initial chlorination and THM formation are too fast to explain the results observed when drinking waters are chlorinated. Monohydroxybenzenes, that show much slower initial chlorination and chloroform formation, can be responsible for the slow formation of THM during chlorination.

Acknowledgments

The authors gratefully thank Wasserversorgung Zürich for the financial Support. Lisa Salhi is acknowledged for her help in the laboratory. The authors also thank Silvio Canonica for his review of the manuscript.

Literature Cited

(1) Rook, J. J. *Water Treat. Exam.* **1974**, *2*, 234−243.
(2) Christman, R. F.; Norwood, D. L.; Millington, D. S.; Johnson, J. D. *Environ. Sci. Technol.* **1983**, *17*, 625−628.
(3) Oliver, B. G. *Environ. Sci. Technol.* **1983**, *17*, 80.
(4) Rook, J. J. In *Water chlorination: Environmental impact and health effects*; Jolley R. L., et al., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; Vol. 3, p 85.
(5) Morris, J. C.; Baum, B. In *Water chlorination: Environmental impact and health effects*; Jolley R. L., et al., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1978; Vol. 2, pp 29−48.
(6) Christman, R. F.; Johnson, J. D.; Hass, J. R.; Pfaender, F. K.; Liao, W. T.; Norwood, D. L.; Alexander, H. J. In *Water chlorination: Environmental impact and health effects*; Jolley R. L., et al., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1978; Vol. 2, pp 15−27.
(7) De Laat, J.; Merlet, M.; Doré, M. *Water Res.* **1982**, *16*, 1437−1450.
(8) Boyce, S. D.; Hornig, J. F. *Environ. Sci. Technol.* **1983**, *17*, 4, 202−211.
(9) Reckhow, D. A.; Singer, P. C. In *Water Chlorination: Environmental impact and health effects*; Jolley R. L., et al., Eds.; Ann Arbor Science: Ann Arbor, M, 1985; Vol. 5, pp 1229−1257.
(10) Norwood, D. L.; Christman, R. F.; Hatcher, P. G. *Environ. Sci. Technol.* **1987**, *21*, 8, 791−798.
(11) Gallard, H.; von Gunten, U. *Water Res.* **2002**, *36*, 65−74.
(12) Tretyakova, N. Y.; Lebedev, A. T.; Petrosyan, V. S. *Environ. Sci. Technol.* **1994**, *28*, 4, 606−613.
(13) Burttschell, R. H.; Rosen, A. A.; Middleton, F. M.; Ettinger, M. B. *J. Am. Water Works Assoc.* **1959**, *51*, 205−214.
(14) Heasley, V. L.; Anderson, M. E.; Combes, D. S.; Elias, D. S.; Gardner, J. T.; Hernandez, M. L.; Moreland, R. J.; Shellhamer, D. F. *Environ. Toxicol. Chem.* **1993**, *12*, 1653−1659.
(15) Soper, F. G.; Smith, G. F. *J. Chem. Soc.* **1926**, 1582−1591.
(16) Lee, G. F.; Morris, J. C. *Int. J. Air−Water Pollut.* **1962**, *6*, 419.
(17) Rebenne, L. M.; Gonzalez, A. C.; Olson, T. M. *Environ. Sci. Technol.* **1996**, *30*, 2235−2242.
(18) Hoigné J.; Bader H. *Ozone Sci. Eng.* **1994**, *16*, 121.
(19) Bichsel, Y.; von Gunten, U. *Anal. Chem.* **1999**, *71*, 1, 34−38.
(20) Pinkernell, U.; Nowack, B.; Gallard, H.; von Gunten, U. *Water Res.* **2000**, *34*, 4343−4350.
(21) SigmaPlot 2000 User's Guide SPSS Science Software UK, Birmingham.
(22) Bichsel, Y.; von Gunten, U. *Environ Sci. Technol.* **2000**, *34*, 2784−2791.
(23) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.
(24) Arotsky, J.; Symons, M. R. C. Q. *Rev. Chem. Soc.* **1962**, *16*, 282−297.
(25) Tratnyek, P. G.; Hoigné, J. *Water Res.* **1994**, *28*, 1, 57−66.
(26) Hoigné J.; Bader H. *Water Res.* **1983**, *17*, 185−194.
(27) Tee O. S., Iyengar N. R., Kraus B. *J. Org. Chem.* **1985**, *50*, 973−976.
(28) Li, J. W.; Yu, Z.; Cai, X.; Gao, M.; Chao, F. *Water Res.* **1996**, *30*, 10, 2371−2376.
(29) Larson, R. A.; Rockwell, A. L. *Environ. Sci. Technol.* **1979**, *13*, 3, 325−329.
(30) Dean, J. A. *Lange's Handbook of Chemistry;* McGraw-Hill: New York, 1985.
(31) Lipnick, R. L.; Bickings, C. K.; Johnson, D. E.; Eastmond, D. A. *Aquat. Toxicol. Hazard Assess.* **1985**, 8th Symp., 153−176.
(32) Schellenberg, K.; Leuenberger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1984**, *18*, 652−657.

Received for review March 14, 2001. Revised manuscript received October 10, 2001. Accepted October 30, 2001.

ES010076A