



HAL
open science

Monochloramination of Resorcinol: Mechanism and Kinetic Modeling

Nicolas Cimetiere, Florence Dossier-Berne, Joseph de Laat

► **To cite this version:**

Nicolas Cimetiere, Florence Dossier-Berne, Joseph de Laat. Monochloramination of Resorcinol: Mechanism and Kinetic Modeling. *Environmental Science and Technology*, 2009, 43, pp.9380. 10.1021/es901425n . hal-01367727

HAL Id: hal-01367727

<https://univ-rennes.hal.science/hal-01367727>

Submitted on 27 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL
open science

Effect of some parameters on the formation of chloroform during chloramination of aqueous solutions of resorcinol

Nicolas Cimetiere, Florence Dossier-Berne, Joseph de Laat

► **To cite this version:**

Nicolas Cimetiere, Florence Dossier-Berne, Joseph de Laat. Effect of some parameters on the formation of chloroform during chloramination of aqueous solutions of resorcinol. *Water Research*, 2010, 44 (15), pp.4497-4504. 10.1016/j.watres.2010.06.010 . hal-00920252

HAL Id: hal-00920252

<https://hal.science/hal-00920252>

Submitted on 27 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Monochloramination of Resorcinol: Mechanism and Kinetic Modeling

Journal:	<i>Environmental Science & Technology</i>
Manuscript ID:	es-2009-01425n.R1
Manuscript Type:	Article
Date Submitted by the Author:	21-Sep-2009
Complete List of Authors:	Cimetiere, Nicolas; Université de Poitiers, Laboratoire de Chimie et Microbiologie de l'Eau (UMR 6008) Dossier-Berne, Florence; Université de Poitiers, Laboratoire de Chimie et Microbiologie de l'Eau (UMR 6008) De Laat, Joseph; Université de Poitiers, Laboratoire de Chimie et Microbiologie de l'Eau (UMR 6008)



Monochloramination of Resorcinol: Mechanism and Kinetic Modeling

NICOLAS CIMETIERE, FLORENCE DOSSIER-BERNE AND JOSEPH DE LAAT*

Université de Poitiers, Laboratoire de Chimie et Microbiologie de l'Eau (UMR CNRS 6008),

Ecole Supérieure d'Ingénieurs de Poitiers, 40, Avenue du Recteur Pineau, 86022 Poitiers Cedex, France

*Corresponding author. Tel.: +33 5 49 45 39 21; fax: +33 5 49 45 37 68. E-mail address: joseph.delaat@esip.univ-poitiers.fr

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

ABSTRACT

The kinetics of monochloramination of resorcinol, 4-chlororesorcinol and 4,6-dichlororesorcinol have been investigated over the pH range of 5 - 12, at 23 ± 2 °C. Monochloramine solutions were prepared with ammonia-to-chlorine ratios (N/Cl) ranging from 1.08 to 31 mol/mol. Under conditions that minimize free chlorine reactions (N/Cl > 2 mol/mol), the apparent second-order rate constants of monochloramination of resorcinol compounds show a maximum at pH values between 8.6 and 10.2. The intrinsic second-order rate constants for the reaction of monochloramine with the acid-base forms of the dihydroxybenzenes ($\text{Ar}(\text{OH})_2$, $\text{Ar}(\text{OH})\text{O}^-$ and $\text{Ar}(\text{O}^-)_2$) were calculated from the apparent second-order rate constants. The stoichiometric coefficients for the formation of 4-chlororesorcinol by monochloramination of resorcinol and 4,6-dichlororesorcinol by monochloramination of 4-chlororesorcinol were found to be equal to 0.66 ± 0.05 and 0.25 ± 0.02 mol/mol, respectively at pH 8.6. A kinetic model that incorporates reactions of free chlorine and monochloramine with the different acid-base forms of resorcinol compounds simulated well the initial rates of degradation of resorcinol compounds and was useful in order to evaluate the contribution of free chlorine reactions to the overall rates of degradation of resorcinol at low N/Cl ratios.

KEYWORDS: Monochloramine, Resorcinol, Rate constants, Chlorine.

Introduction

1 26 Chlorination is the most widely used method for drinking water disinfection and has proven highly
2
3 27 effective in preventing waterborne diseases caused by pathogenic microorganisms. However, reactions
4
5 28 of chlorine with natural organic matter (NOM) also lead to the formation of many disinfection by-
6
7 29 products (DBPs) which can have adverse effects for human health. Since the pioneering works of Bellar
8
9
10 30 et al. (1) and Rook (2), who demonstrated the formation of trihalomethanes (THMs), more than 600
11
12 31 DBPs have been identified in chlorinated drinking water (3). Many utilities have adopted the use of
13
14 32 monochloramine as a secondary disinfectant in order to comply with the current or future regulations
15
16
17 33 concerning the concentrations of DBPs in drinking water (4).
18

19 34 Monochloramine is produced by the reaction of hypochlorous acid with ammonia and is quantitatively
20
21 35 formed at ammonia-to-chlorine ratio (N/Cl) higher than 1 mol/mol at $\text{pH} \approx 8$. In the practice of
22
23
24 36 monochloramination, monochloramine is prepared with a small excess of ammonia (N/Cl $\approx 1.1 - 1.2$
25
26 37 mol/mol) in order to minimize the formation of dichloramine and trichloramine and to prevent the
27
28
29 38 breakpoint reactions (5). As compared to free chlorine, monochloramine is a weaker disinfectant and
30
31 39 produces less DBPs (6). Monochloramine is also used as a secondary disinfectant in order to obtain a
32
33 40 long lasting residual of disinfectant in the distribution systems because monochloramine is less reactive
34
35
36 41 with NOM than free chlorine. The decay of monochloramine in drinking water can be attributed to
37
38 42 autodecomposition reactions, direct reactions of monochloramine with NOM and indirect reactions with
39
40 43 NOM involving free chlorine formed from monochloramine hydrolysis (7).
41
42

43 44 The reactivity of monochloramine with simple organic compounds is not well-documented. Only a
44
45 45 few second-order rate constants for the reaction of monochloramine have been published (8-10). The
46
47 46 objective of this research was to determine the rate constant for the reaction of monochloramine with
48
49
50 47 resorcinol. It is well-known that chlorination of resorcinol leads to the formation of 0.9-0.95 mole of
51
52 48 chloroform per mole of resorcinol (11) and that polyhydroxybenzenic functional groups of NOM
53
54 49 contribute to the formation of THMs (12-14). The rate and the mechanism of chlorination of phenolic
55
56
57 50 compounds have been investigated by several researchers (15-16). In a detailed kinetic study of the
58
59 51 chlorination of dihydroxybenzenes (resorcinol, 4-chlororesorcinol and 4,6-dichlororesorcinol), Rebenne
60

52 et al. (15) showed that the pH-dependence of the apparent-second-order rate could be attributed to an
53 acid-catalyzed reaction at $\text{pH} < 4$ and to a mechanism involving the reactions of hypochlorous acid
54 (HOCl) with the un-ionized and the ionized forms of resorcinol compounds.

55 The mechanism of monochloramination of resorcinol and of its chlorinated derivatives in water has
56 been thoroughly investigated by Heasley et al. (17), but the reaction rate constants are unknown.
57 Therefore, this work was undertaken to determine intrinsic second-order rate constants for the reaction
58 of monochloramine with the un-ionized and ionized forms of resorcinol, 4-chlororesorcinol and 4,6-
59 dichlororesorcinol. The kinetic study of monochloramination of resorcinol and of its chlorinated
60 derivatives has been conducted within the pH range 5 to 12 and under conditions that minimize the
61 equilibrium concentration of free chlorine in solutions of monochloramine. A kinetic model has also
62 been tested in order to simulate the formation and the decay of 4-chlororesorcinol and of 4,6-
63 dichlororesorcinol and to evaluate the effect of the ammonia-to-chlorine ratio on the contribution of free
64 chlorine reactions to the degradation of resorcinol.

65 Experimental Section

66 **Chemicals and Preparation of solutions.** All solutions were prepared from reagent-grade chemicals
67 and purified water delivered by a Millipore system (Milli RX75/Synergy 185). Stock solutions of
68 resorcinol (R) (Sigma-Aldrich, ACS reagent, > 99 %), 4-chlororesorcinol (4-MCR) (Aldrich, 98 %), 4,6-
69 dichlororesorcinol (4,6-DCR) (Aldrich, 97 %), ammonium chloride (Fisher Scientific, > 99%) and free
70 chlorine (NaOCl , 13 %, Acros Organics) were stored in the dark at 4 °C.

71 Solutions of monochloramine (0.1 to 4 mM) were prepared daily by slowly adding free chlorine into
72 an ammonium chloride solution in a well-stirred reactor and using a nitrogen-to-chlorine ratio ranging
73 from 1.08 to 31 mol/mol. The pH of the sodium hypochlorite and ammonium chloride solutions were
74 preadjusted to 8.3 ± 0.1 . As carbonate and phosphate ions are known to catalyse the decomposition of
75 monochloramine in water (18), all kinetic experiments were carried out without pH buffer, pH being
76 possibly regulated during the reaction by addition of hydrochloric acid or sodium hydroxide. All

1 77 glassware was cleaned with a solution of monochloramine (≈ 1 mM) and was kept under
2
3 78 monochloramine before the experiments.
4

5 79
6
7 80 Free chlorine and total chlorine concentrations in the stock solutions of sodium hypochlorite and
8
9
10 81 monochloramine were determined iodometrically with sodium thiosulfate 0.01 M (Prolabo, > 99.9 %).
11
12 82 Monochloramine concentrations were determined spectrophotometrically using a molar extinction
13
14 83 coefficient of $446 \text{ M}^{-1} \text{ cm}^{-1}$ for NH_2Cl at 244 nm
15
16

17 84 Iodometric titrations and spectrophotometric analyses of freshly prepared solutions of NH_2Cl showed
18
19 85 that free chlorine introduced in the solution of ammonium chloride was quantitatively converted into
20
21 86 NH_2Cl at $\text{pH} \approx 8.3$. In addition, the concentration of NH_2Cl in organic-free solutions ($[\text{NH}_2\text{Cl}]_0 = 1$ - 4
22
23
24 87 mM at $\text{pH} = 8.6$ or ($[\text{NH}_2\text{Cl}]_0 = 0.1$ mM at $5 < \text{pH} < 12$) remained essentially constant during the total
25
26 88 reaction times in any of our kinetic experiments. This is in good agreement with the concentration-time
27
28 89 profiles of NH_2Cl predicted by the kinetic model of Jafvert and Valentine (1992). As shown the
29
30 90 experimental data and the model predictions in Section A of the Supporting Information, the
31
32
33 91 disproportionation reaction of NH_2Cl and the decay of NH_2Cl under experimental conditions can be
34
35
36 92 neglected.
37

38 93 **Experimental Procedures.** All experiments were conducted in batch reactors (125 – 1250 mL Pyrex
39
40 94 bottles with PTFE screw caps) and under constant stirring using a magnetic bar. All experiments,
41
42
43 95 excepted for activation energy determination, were performed at room temperature ($23 \pm 2^\circ\text{C}$).
44

45 96 To determine reaction rates, experiments were performed in the presence of a large excess of
46
47 97 dihydroxybenzene ($[\text{Ar}(\text{OH})_2]_0/[\text{NH}_2\text{Cl}]_0 = 50$ mol/mol) or monochloramine ($[\text{NH}_2\text{Cl}]_0/[\text{Ar}(\text{OH})_2]_0 >$
48
49
50 98 20 mol/mol) in order to obtain pseudo-first decays of monochloramine or dihydroxybenzene,
51
52 99 respectively. In the presence of a large excess of dihydroxybenzene ($[\text{Ar}(\text{OH})_2]_0/[\text{NH}_2\text{Cl}]_0 = 50$
53
54 100 mol/mol), the concentration of monochloramine ($[\text{NH}_2\text{Cl}]_0 = 100 \mu\text{M}$) was monitored at different
55
56
57 101 reaction times by reaction with iodide and subsequent spectroscopic quantification at 351 nm of the
58
59 102 liberated triiodide ion. Kinetic experiments of the consumption of monochloramine were initiated by
60

1 103 adding 5 mL of a stock solution of monochloramine, under vigorous magnetic stirring, to 95 mL of a
2
3 104 solution containing the dihydroxybenzene. At various time intervals, a 4 mL-sample of the solution was
4
5 105 rapidly transferred into a 10 mL vial containing 1 ml of KI 1 M (Acros Organics, > 99 % for analysis)
6
7 106 and 100 μL of acetic acid 1.7 M (Riedel-de Haën, 99 - 100 %). After a reaction time of 2 or 3 minutes,
8
9
10 107 the mixture was then transferred into a 1 cm-spectrophotometer quartz-cell and the concentration of
11
12 108 triiodide ion was determined by measuring the absorbance at 351 nm (Shimadzu UVmini 1240
13
14 109 spectrophotometer). The concentration of monochloramine was calculated using a molar extinction
15
16
17 110 coefficient of $2.69 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for I_3^- at 351 nm. This value which has been determined in the present
18
19 111 work from calibration curves obtained from various standard solutions of chlorine and of
20
21 112 monochloramine was consistent with values reported in literature (19-21).

22
23
24 113 It should be noted that the oxidation reaction of iodide ion by monochloramine is very fast, being
25
26 114 complete within a few seconds. Furthermore, the UV absorbance measured at 351 nm was stable
27
28 115 indicating that the liberated triiodide ion did not react with the organic solutes present in the solutions.

29
30
31 116 A few experiments were carried out at $\text{pH} = 8.6$ with a large excess of monochloramine
32
33 117 ($[\text{NH}_2\text{Cl}]_0/[\text{Ar}(\text{OH})_2]_0 = 20 - 100 \text{ mol/mol}$) and the reaction was followed by measuring the decay of the
34
35 118 concentrations of the dihydroxybenzene (R, 4-MCR or 4,6-DCR) by HPLC. The reaction was started by
36
37
38 119 introducing under vigorous magnetic stirring 5 mL of a solution of the dihydroxybenzene (10 mM) to
39
40 120 1000 mL of NH_2Cl solution (1 - 4 mM) at $\text{pH} 8.6$. At various reaction times, 4-mL samples were taken
41
42 121 from the reactor, spiked with 10 μL of a sodium sulfite solution (1 M) in order to neutralize
43
44
45 122 monochloramine. Then, concentrations of dihydroxybenzenes were determined by HPLC. Analyses
46
47 123 were performed with a Waters system (W600 controller; W717plus Autosampler) equipped with a C18
48
49
50 124 Uptisphere 5 HDO column and a photodiode array detector (Waters W996) for the UV-VIS spectra
51
52 125 acquisition. The organic compounds were eluted with a methanol/water mobile phase at a flow rate of
53
54 126 1.0 mL min^{-1} .

1 127 To determine elementary rate constants, kinetic data were treated with a non-linear regression program
 2
 3 128 (Sigma plot 2000). Model simulations were undertaken using the kinetic modeling software package
 4
 5 129 Copasi Version 4.4. (22).
 6

7 130 **Results and Discussion**

9
 10 131 **Determination of reaction rate constants.** The reactions of monochloramine with organic solutes are
 11
 12 132 assumed to follow second-order kinetics, first-order with respect to each reactant. In the case of a
 13
 14 133 dihydroxybenzenic compound ($\text{Ar}(\text{OH})_2$), the rate can be expressed as (eq 1):
 15

$$16 \quad - \frac{d[\text{Ar}(\text{OH})_2]_{\text{tot}}}{dt} = - \frac{d[\text{NH}_2\text{Cl}]}{dt} = k_{\text{app}} [\text{NH}_2\text{Cl}] [\text{Ar}(\text{OH})_2]_{\text{tot}} \quad (1)$$

17 134
 18
 19
 20
 21 135 where k_{app} represents the apparent second-order rate constant and $[\text{Ar}(\text{OH})_2]_{\text{tot}}$, the sum of the
 22
 23 136 concentrations of the three acid-base species of the dihydroxybenzene ($\text{Ar}(\text{OH})_2$, $\text{Ar}(\text{OH})\text{O}^-$, $\text{Ar}(\text{O}^-)_2$).
 24

25 137 Under conditions that minimize the contribution of free chlorine reactions to the oxidation of organic
 26
 27
 28 138 solutes ($\text{N}/\text{Cl} > 2$ mol/mol, see section B in Supporting Information), the rates of disappearance of
 29
 30 139 resorcinol, 4-chlororesorcinol and 4,6-dichlororesorcinol in the presence of a large excess of
 31
 32 140 monochloramine ($[\text{NH}_2\text{Cl}]_0 / [\text{Ar}(\text{OH})_2]_{\text{tot},0} > 20$ mol/mol) were first-order with respect to the organic
 33
 34
 35 141 compound :
 36

$$37 \quad - \frac{d[\text{Ar}(\text{OH})_2]_{\text{tot}}}{dt} = k_{\text{obs}} [(\text{Ar}(\text{OH})_2)]_{\text{tot}} \quad \text{with } k_{\text{obs}} = k_{\text{app}} [\text{NH}_2\text{Cl}]_0 \quad (2)$$

38 142
 39
 40
 41 143 The linear plots which could be drawn between the pseudo first-order rate constant (k_{obs}) and the
 42
 43 144 initial concentration of monochloramine confirm that the rate of oxidation of the dihydroxybenzenic
 44
 45
 46 145 compound was also first-order with respect to the concentration of monochloramine (Figures S3-S8 in
 47
 48 146 Supporting Information).
 49

50 147 As illustrated by the data presented in figure S9, the consumption rates of monochloramine in the
 51
 52
 53 148 presence of a large excess of dihydroxybenzene ($[\text{Ar}(\text{OH})_2]_{\text{tot},0} / [\text{NH}_2\text{Cl}]_0 = 50$ mol/mol) were first-
 54
 55 149 order with respect to monochloramine concentration (eq 3) :
 56

$$57 \quad - \frac{d[\text{NH}_2\text{Cl}]}{dt} = k'_{\text{obs}} [\text{NH}_2\text{Cl}] \quad \text{with } k'_{\text{obs}} = k_{\text{app}} [(\text{Ar}(\text{OH})_2)]_{\text{tot},0} \quad (3)$$

151

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

The pseudo first-order rate constants (k'_{obs}) were also found to be proportional to the initial concentration of the organic solute, thus confirming that the rates of monochloramination of the three dihydroxybenzenes follow a second-order kinetic law (eq 1).

All experimental conditions (pH, initial concentrations of reactants), apparent first-order kinetic constants (k_{obs} and k'_{obs}) and apparent second-order rate constants (k_{app}) have been reported in tables S1 and S2 in Supporting Information. It should be noted that the apparent second-order rate constants calculated from k_{obs} values were consistent with those calculated from k'_{obs} .

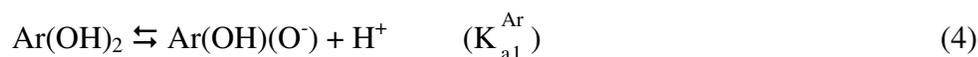
pH Dependency of k_{app} and Mechanism. Figures 1-3 show the experimental pH profiles of k_{app} for the monochloramination of resorcinol, 4-chlororesorcinol and 4,6-dichlororesorcinol, respectively. pH values lower than 5 have not been investigated in the present work because of the acid-catalyzed disproportionation reaction of monochloramine into dichloramine and ammonia.

As for chlorine (15), the pH dependency of the k_{app} values of monochloramination of resorcinol compounds exhibits a maximum in weak-alkaline media : pH $\approx 10.2 \pm 0.2$ for resorcinol, pH $\approx 9.4 \pm 0.2$ for 4-chloro-resorcinol and pH $\approx 8.6 \pm 0.2$ for 4,6-dichlororesorcinol. Unlike the data obtained by Rebenne et al. (15), the acid-catalyzed oxidation of the resorcinol compounds is not observed with monochloramine. Under the experimental conditions used in the present work ($5 < \text{pH} < 12$), spectrophotometric analyses which have been conducted with aqueous solutions of monochloramine indicate that NH_2Cl is the unique form of monochloramine. Therefore, the shape of the pH-rate profiles obtained in the present study can be attributed to the fact that the monoionized form ($\text{Ar}(\text{OH})\text{O}^-$) of a dihydroxybenzenic compound is more reactive with monochloramine than the unionized ($\text{Ar}(\text{OH})_2$) and the diionized ($\text{Ar}(\text{O}^-)_2$) forms. Hence, the highest value of the apparent second-order rate constant for the reaction of monochloramine with dihydroxybenzenes is obtained at pH equal to $\text{pH} = (\text{pK}_{\text{a}1}^{\text{Ar}} + \text{pK}_{\text{a}2}^{\text{Ar}})/2$,

In addition, it should be pointed out that trace amounts of dichloramine present in monochloramine solutions at pH 5 ($[\text{NH}_2\text{Cl}]_0 = 100 \mu\text{M}$; Figure S3 in Supporting Information) may also oxidize organic

176 solutes. The second-order rate constants for the reaction of NHCl_2 with resorcinol compounds are
 177 unknown. Nonetheless, the contribution of NHCl_2 to the degradation of resorcinol compounds under our
 178 conditions should be negligible because the concentrations of dichloramine are very low.

179 A simple kinetic model which incorporates the acid-base dissociation reactions of dihydroxybenzenes
 180 and the reactions of monochloramine with the three forms of dihydroxybenzenes is proposed as follows:



186 By assuming that the reaction rate of monochloramine with each acid-base form of dihydroxybenzene
 187 is second-order, the apparent second-order rate constant k_{app} can be expressed as follows:

$$188 k_{\text{app}} = \frac{k_1[\text{H}^+]^2 + k_2\text{K}_{\text{a1}}^{\text{Ar}}[\text{H}^+] + k_3\text{K}_{\text{a1}}^{\text{Ar}}\text{K}_{\text{a2}}^{\text{Ar}}}{\text{K}_{\text{a1}}^{\text{Ar}}[\text{H}^+] + [\text{H}^+]^2 + \text{K}_{\text{a1}}^{\text{Ar}}\text{K}_{\text{a2}}^{\text{Ar}}} \quad (9)$$

189 Additional information on this kinetic expression can be found in Section E of the Supporting
 190 Information.

191 The individual rate constants (k_1 , k_2 and k_3) for the reactions of monochloramine with
 192 dihydroxybenzenes were determined by a non-linear least-squares regression analysis of the
 193 experimental pH profiles of k_{app} by using SigmaPlot 2000 software. The values of the acid dissociation
 194 constants used in the present work and the fitted values of all the individual rate constants are reported
 195 in Table 1.

196 As shown by the solid lines in Figures 1-3, the pH dependency of the apparent second-order rate
 197 constant of monochloramination of resorcinol, 4-chlororesorcinol and 4,6-dichlororesorcinol could be
 198 fitted reasonably well. For resorcinol and 4-MCR, the good fit was obtained with the $\text{pK}_{\text{a1}}^{\text{Ar}}$ and $\text{pK}_{\text{a2}}^{\text{Ar}}$

199 values used by Rebenne et al. (1996). In the case of 4,6-dichlororesorcinol, a poor fit for the
200 monochloramination rate - pH dependency was obtained with the pK_{a2}^{Ar} value of 10.35 used by Rebenne
201 et al. (15), (Figure S16 in Supporting Information). Given the large difference between the experimental
202 and the calculated pH profiles of k_{app} , an acid-base titration has been performed to determine the pK_{a2}^{Ar}
203 value of 4,6-dichlororesorcinol. The acid-base titration (Figure S15) and the non-linear least-squares
204 regression analysis of the reaction rate pH dependency (Figure S16), indicates that the best fit is
205 obtained with a pK_{a2}^{Ar} value of 9.78 ± 0.05 for 4,6-dichlororesorcinol.

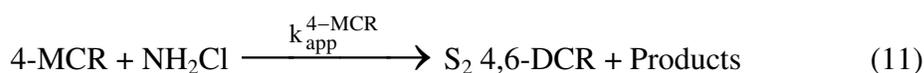
206 The individual reaction rate constants listed in Table 1 show that the $Ar(OH)O^-$ form of each
207 dihydroxybenzene is more reactive toward monochloramine than the $Ar(OH)_2$ and the $Ar(O^-)_2$ forms.
208 For the $Ar(OH)O^-$ form, the rate constant increases with increasing substitution of chlorine on the
209 aromatic ring: $k_2 \approx 9.3 \times 10^2$, 1.72×10^3 and $4.3 \times 10^3 \text{ M}^{-1} \text{ h}^{-1}$ for resorcinol, 4-chlororesorcinol and 4,6-
210 dichlororesorcinol, respectively.

211 Table 1 also reports the individual rate constants for the reaction of hypochlorous acid with
212 dihydroxybenzenes determined by Rebenne et al. (15). A comparison of the individual reaction rate
213 constants shows that resorcinol, monochloro and dichlororesorcinol are much more reactive with
214 hypochlorous acid than with monochloramine. The k^{HOCl}/k^{NH_2Cl} ratios are $> 6 \times 10^2$, $\approx (0.3-5.3) \times 10^6$
215 and $\approx (0.8 - 2.4) \times 10^9$ for the intrinsic rate constants k_1 , k_2 and k_3 respectively – Table 1). Apparent
216 second-order rate constants for the chlorination and for the monochloramination of resorcinol, 4-
217 chlororesorcinol and 4,6-dichlororesorcinol were also calculated from eq 9 and plotted in Figure 4. The
218 data shows that the apparent rate constant of chlorination is 3-4 orders of magnitude greater than the
219 apparent rate of monochloramination at any pH between 5 and 13, confirming that chlorine is much
220 more reactive than monochloramine with the resorcinol derivatives.

221 **Effect of temperature.** The effect of temperature on the rate of monochloramination has only been
222 examined for resorcinol at pH 9.0. Experiments were conducted at 15, 20, 25, 35, 45 and 55 °C and in
223 the presence of a large excess of resorcinol ($[Resorcinol]_0 = 5 \text{ mM}$; $[NH_2Cl]_0 = 100 \text{ } \mu\text{M}$; $N/Cl = 5$).

Figure S12 shows that the plot of $\ln(k_{app})$ versus $1/T$ gave a straight line, in agreement with the linearized form of the Arrhenius expression. From the slope of the straight line, a value $E_a = 40$ kJ/mol was calculated for the activation energy of the monochloramination reaction at pH = 9. For chlorine, no temperature dependency was observed at pH = 5 by Rebenne et al. (15), and only the upper limit of the activation energy was established ($E_a \leq 2.5$ kJ/mol).

Determination of stoichiometric coefficients. HPLC analyses showed that monochloramination of resorcinol leads to the formation of 4-chlororesorcinol and 4,6-dichlororesorcinol and that monochloramination of 4-chlororesorcinol leads to the formation of 4,6-dichlororesorcinol.



where S_1 and S_2 represent stoichiometric coefficients for the formation of 4-chlororesorcinol from resorcinol and of 4,6-dichlororesorcinol from 4-chlororesorcinol, respectively. The stoichiometric coefficients were determined from experiments which have been conducted with a large excess of monochloramine. Under these conditions, the reactions of monochloramine with the unidentified by-products would not affect the concentration-time profiles for resorcinol, 4-chlororesorcinol and 4,6-dichlororesorcinol.

Computer simulations show that the best fits of the concentration-time profiles at pH 8.6 were obtained for $S_1 = 0.66 \pm 0.05$ and $S_2 = 0.25 \pm 0.02$ (Figures S13 and S14). It should be noted that these stoichiometric coefficients at pH = 8.6 represent apparent values because the stoichiometric coefficients for the reactions of monochloramine with the three acid-base forms of a dihydroxybenzene might be different, and therefore, the stoichiometric constants might be pH dependent.

The stoichiometric coefficient for the formation of 4-chlororesorcinol from resorcinol obtained at pH 8.6 ($S_1 = 0.66 \pm 0.05$) suggests that 2-chlororesorcinol is formed with a yield of 0.34 mole per mole of

1 248 resorcinol. Thus, this distribution of by-products indicates that the three ortho positions to the hydroxyl
2
3 249 groups on the aromatic ring of resorcinol have the same reactivity toward monochloramine at pH 8.6. As
4
5 250 far as 4-chlororesorcinol is concerned, our study shows that monochloramination of 4-chlororesorcinol
6
7 251 leads to 4,6-dichlororesorcinol with a molar yield of 0.25 at pH 8.6 ($S_2 = 0.25 \pm 0.02$). In the absence of
8
9
10 252 steric hindrance and of selective attack, the theoretical distribution should be approximately 50% of 4,6-
11
12 253 dichlororesorcinol and 50% of 2,6-dichlororesorcinol. The data obtained in our work indicates that the
13
14
15 254 2-position is about three times more reactive than the 4-position toward monochloramine.

16
17 255 **Effect of the N/Cl ratio on the rate of oxidation of resorcinol.** The experimental data obtained in the
18
19 256 present work suggest that free chlorine formed from monochloramine hydrolysis contributes to the
20
21
22 257 oxidation of resorcinol when monochloramine was prepared by using low nitrogen-to-chlorine ratios
23
24 258 ($N/Cl < 1.5$ mol/mol, Section B in Supporting Information). The concentration of free chlorine in
25
26 259 solutions of monochloramine depends on various parameters such as the concentration of
27
28
29 260 monochloramine, the N/Cl ratio and pH (Section I in Supporting Information).

30
31 261 Since the individual rate constants for the reaction of resorcinol with monochloramine (this study) and
32
33 262 with free chlorine (15) are known, a kinetic model has been used to evaluate the contribution of free
34
35
36 263 chlorine reactions to the rate of disappearance of resorcinol during monochloramination. The kinetic
37
38 264 model incorporates acid dissociation reactions for ammonia, hypochlorous acid, resorcinol, 4-
39
40 265 chlororesorcinol and 4,6-dichlororesorcinol, formation and hydrolysis reactions of monochloramine and
41
42
43 266 the reactions of hypochlorous acid and monochloramine with all the acid-base forms of resorcinol, 4-
44
45 267 chlororesorcinol and 4,6-dichlororesorcinol. The reaction model and the rate constants have been
46
47 268 reported in table S3 in Supporting Information. It should be emphasized that our kinetic model cannot
48
49
50 269 be used to predict the rate of consumption of monochloramine because reactions of monochloramine
51
52 270 and chlorine with most of the oxidation intermediates of resorcinol are unknown. However, our model
53
54 271 can be used to simulate the disappearance rate of resorcinol in the presence of a large excess of
55
56
57 272 monochloramine ($[NH_2Cl]_0/[Resorcinol]_0 > 20$ mol/mol) because the concentrations of monochloramine
58
59 273 is quite constant during the early stage of the reaction. Figure 5 shows that our kinetic model simulates
60

1 274 reasonably well the disappearance rates of resorcinol obtained at various N/Cl values at pH 8.6, thus
2
3 275 validating the rate constants for the reactions of free chlorine and monochloramine with resorcinol listed
4
5 276 in table 1. Contribution of free chlorine reactions to the overall degradation of resorcinol could also be
6
7 277 estimated by kinetic modelling. Under the conditions used for the data presented in Figure 5, and for a
8
9
10 278 N/Cl ratio of 1.08, 52 % of the overall rate of degradation of resorcinol can be attributed to free chlorine
11
12 279 oxidation reactions. This contribution falls to 12 % when the N/Cl increases from 1.08 to 1.12. This
13
14 280 result shows that the oxidation rates of resorcinol by monochloramine is highly sensitive to the N/Cl
15
16
17 281 ratio when this ratio is close to unity.

18
19 282 Free chlorine concentration in monochloramine solutions is also pH-dependent (section I in supporting
20
21 283 information). For a given N/Cl ratio, the concentration of free chlorine in organic-free water is at a
22
23
24 284 minimum at $\text{pH} = (\text{pK}_{\text{aHOCl}} + \text{pK}_{\text{aammonia}}/2) \approx 8.4$ (Figure S17). The contributions of free chlorine
25
26 285 oxidation reactions to the degradation of resorcinol, 4-chlororesorcinol and 4,6-dichlororesorcinol were
27
28
29 286 also calculated with our kinetic model for all the experiments conducted in the pH range 5.5 -12
30
31 287 (examples are given in Figures S18 and S19). Computer calculations demonstrate that the contribution
32
33 288 of free chlorine reactions could be neglected for all the experimental conditions used for the
34
35
36 289 determination of the intrinsic rate constants for the reaction of monochloramine with the
37
38 290 dihydroxybenzenic compounds ($5 < \text{pH} < 12$; $\text{N/Cl} > 2$ or 5).

40 291 **Implications on water treatment**

41
42
43 292 The results obtained in the present work show that monochloramine is much less reactive than chlorine
44
45 293 toward dihydroxybenzenes. This study also confirms the reaction model proposed by the research group
46
47 294 of Valentine for the monochloramination of Natural Organic Matter (NOM) (7, 23). These authors have
48
49
50 295 demonstrated that the monochloramine hydrolysis reaction plays a key role in governing the overall rate
51
52 296 of decomposition of monochloramine in water in the presence of NOM. It has also been demonstrated
53
54 297 that free chlorine in equilibrium with monochloramine contributes to the oxidation of As(III) during
55
56
57 298 monochloramination of water containing As(III) (24).

299 During monochloramination of drinking water, the indirect reactions involving free chlorine can also
300 participate to DBP formation. Although the contribution of free chlorine to DBP formation should be of
301 little importance under conditions typical for drinking water treatment, further investigation is needed to
302 differentiate the role of monochloramine and of free chlorine on the formation of trihalomethanes and of
303 other DBPs.

Supporting Information Available

305 Tables and figures addressing to stability and purity of monochloramine solutions prepared in this work,
306 the determination of experimental conditions for minimizing the contribution of free chlorine reactions
307 to the overall rates of decomposition of resorcinol compounds, experimental data obtained for the
308 oxidation rate of resorcinol compounds in the presence of a large excess of monochloramine and for the
309 effect of pH on the rate of monochloramination of resorcinol compounds in the presence of a large
310 excess of organic solute, the effect of temperature on the rate of monochloramination of resorcinol, the
311 determination of an acid dissociation constant of 4,6-dichlororesorcinol, the description of the kinetic
312 model used in this work and computed data or model predictions obtained to determine stoichiometric
313 coefficients, free chlorine concentration in NH_2Cl solutions, the overall reaction rates and the
314 contribution of free chlorine reactions to the degradation of resorcinol compounds.

315 This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- 317 (1) Bellar, T. A.; Lichtenberg, J. J.; Kroner, R. C. Occurrence of organohalides in chlorinated
318 drinking waters. *J. Am. Water Works Assoc.* **1974**, 66, 703-706.
- 319 (2) Rook, J. J. Formation of haloforms during chlorination of natural waters. *Water Treat. Exam.*
320 **1974**, 23, 234-243.
- 321 (3) Richardson, S. D. Disinfection by-products and other emerging contaminants in drinking water.
322 *Trends Anal. Chem.* **2003**, 22, 666-684.
- 323 (4) EPA. *Alternative Disinfectants and Oxidants Guidance Manual*; EPA815R990014; 1999,
324 <http://www.epa.gov/safewater/mdbp/mdbptg.html#disinfect>
- 325 (5) Jafvert, C. T.; Valentine, R. L. Reaction scheme for the chlorination of ammoniacal water.
326 *Environ. Sci. Technol.* **1992**, 26, 577-586.

- 1 327 (6) Hua, G.; Reckhow, D. A. Comparison of disinfection byproduct formation from chlorine and
2
3 328 alternative disinfectants. *Water Res.* **2007**, 41, 1667-1678.
- 4
5 329 (7) Duirk, S. E.; Gombert, B.; Croue, J. P.; Valentine, R. L. Modeling monochloramine loss in the
6
7 330 presence of natural organic matter. *Water Res.* **2005**, 39, 3418-3431.
- 8
9
10 331 (8) Topudurti, K. V.; Haas, C. N. THM formation by the transfer of active chlorine from
11
12 332 monochloramine to phloroacetophenone. *J. Am. Water Works Assoc.* **1991**, 83, 62-66.
- 13
14 333 (9) Pedersen Iii, E. J.; Urbansky, E. T.; Marinas, B. J.; Margerum, D. W. Formation of cyanogen
15
16 334 chloride from the reaction of monochloramine with formaldehyde. *Environ. Sci. Technol.* **1999**, 33,
17
18 335 4239-4249.
- 19
20
21 336 (10) Greyshock, A. E.; Vikesland, P. J. Triclosan reactivity in chloraminated waters. *Environ. Sci.*
22
23 337 *Technol.* **2006**, 40, 2615-2622.
- 24
25
26 338 (11) De Laat, J.; Merlet, N.; Dore, M. Chlorine demand and reactivity in relationship to the
27
28 339 trihalomethane formation. Incidence of ammoniacal nitrogen. *Water Res.* **1982**, 16, 1437.
- 29
30
31 340 (12) Rook, J. J. Chlorination reactions of fulvic acids in natural waters. *Environ. Sci. Technol.* **1977**,
32
33 341 11, 478-482.
- 34
35
36 342 (13) De Leer, E. W. B.; Damsté, J. S. S.; Erkelens, C.; De Galan, L. Identification of intermediates
37
38 343 leading to chloroform and C-4 diacids in the chlorination of humic acid. *Environ. Sci. Technol.* **1985**,
39
40 344 19, 512-522.
- 41
42
43 345 (14) Arnold, W. A.; Bolotin, J.; Von Gunten, U.; Hofstetter, T. B. Evaluation of functional groups
44
45 346 responsible for chloroform formation during water chlorination using compound specific isotope
46
47 347 analysis. *Environ. Sci. Technol.* **2008**, 42, 7778-7785.
- 48
49
50 348 (15) Rebenne, L. M.; Gonzalez, A. C.; Olson, T. M. Aqueous Chlorination Kinetics and Mechanism
51
52 349 of Substituted Dihydroxybenzenes. *Environ. Sci. Technol.* **1996**, 30, 2235-2242.
- 53
54 350 (16) Gallard, H.; Von Gunten, U. Chlorination of phenols: Kinetics and formation of chloroform.
55
56 351 *Environ. Sci. Technol.* **2002**, 36, 884-890.
- 57
58
59
60

- 1 352 (17) Heasley, V. L.; Alexander, M. B.; Deboard, R. H.; Hanley Jr, J. C.; McKee, T. C.; Wadley, B.
2
3 353 D.; Shellhamer, D. F. Reactions of resorcinol and its chlorinated derivatives with monochloramine:
4
5 354 Identification of intermediates and products. *Environ. Toxicol. Chem.* **1999**, 18, 2406-2409.
6
7 355 (18) Valentine, R. L.; Jafvert, C. T. General acid catalysis of monochloramine disproportionation.
8
9
10 356 *Environ. Sci. Technol.* **1988**, 22, 691-696.
11
12 357 (19) Awtrey, A. D.; Connick, R. E. The absorption spectra of I_2 , I_3^- , I , IO_3^- , $S_4O_6^{=}$ and $S_2O_3^{=}$. Heat of
13
14 358 the reaction $I_3^- = I_2 + I$. *J. Am. Chem. Soc.* **1951**, 73, 1842-1843.
15
16
17 359 (20) Klassen, N. V.; Marchington, D.; McGowan, H. C. E. H_2O_2 determination by the I_3^- method and
18
19 360 by $KMnO_4$ titration. *Anal. Chem.* **1994**, 66, 2921-2925.
20
21 361 (21) Bichsel, Y.; Von Gunten, U. Determination of iodide and iodate by ion chromatography with
22
23 362 postcolumn reaction and UV/visible detection. *Analytical Chemistry* **1999**, 71, 34-38.
24
25
26 363 (22) Hoops, S.; Gauges, R.; Lee, C.; Pahle, J.; Simus, N.; Singhal, M.; Xu, L.; Mendes, P.; Kummer,
27
28 364 U. COPASI - A COMplex PATHway Simulator. *Bioinformatics* **2006**, 22, 3067-3074.
29
30
31 365 (23) Duirk, S. E.; Valentine, R. L. Modeling dichloroacetic acid formation from the reaction of
32
33 366 monochloramine with natural organic matter. *Water Res.* **2006**, 40, 2667-2674.
34
35
36 367 (24) Dodd, M.C.; Vu, N.D.; Amann, A.; Le, V.C.; Kissner, R.; Pham, H.V.; Cao, T.H.; Berg, M.;
37
38 368 Von Gunten, U. *Environ. Sci. Technol.* **2006**, 40, 3285-3292.
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

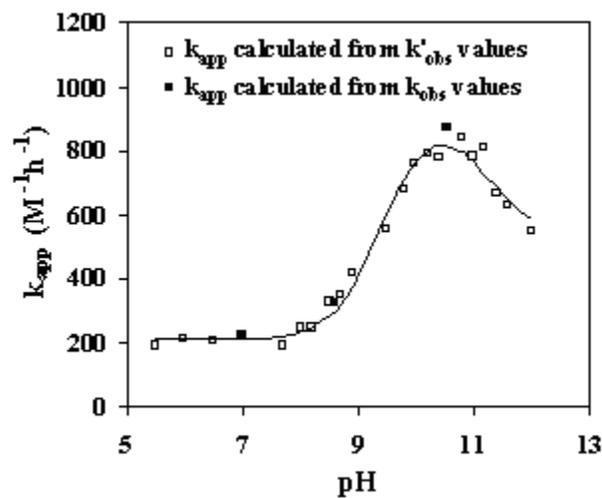


Figure 1. Experimental (symbol) and modeled (solid line) pH profile of the second-order apparent rate constant for the reaction of monochloramine with resorcinol. The modelled pH-profile was obtained with $k_1 = 207 M^{-1} h^{-1}$, $k_2 = 927 M^{-1} h^{-1}$ and $k_3 = 525 M^{-1} h^{-1}$.

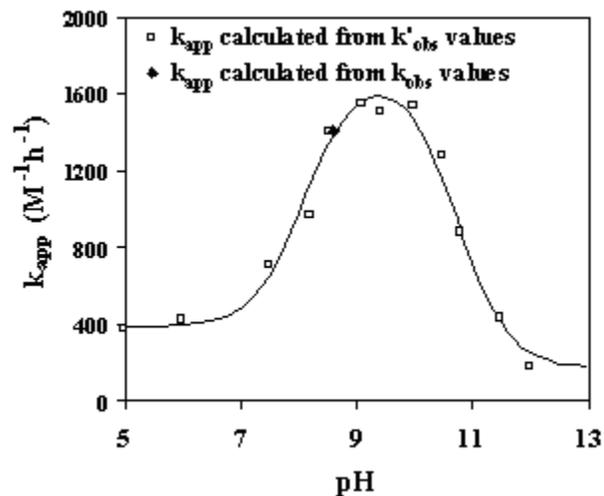
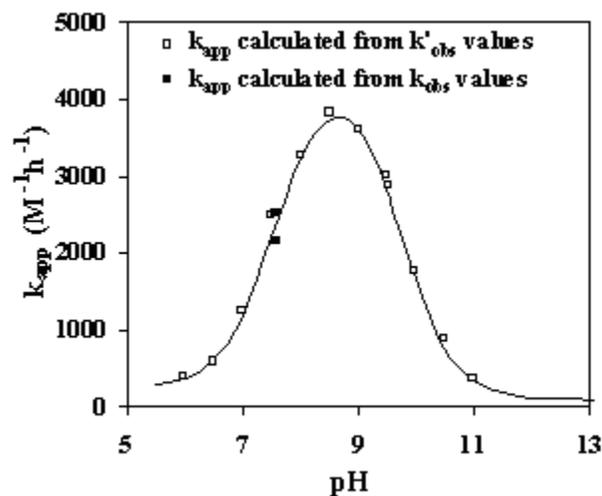


Figure 2. Experimental (symbol) and modeled (solid line) pH profile of the second-order apparent rate constant for the reaction of monochloramine with 4-chlororesorcinol. The modelled pH-profile was obtained with $k_1 = 380 M^{-1} h^{-1}$, $k_2 = 1720 M^{-1} h^{-1}$ and $k_3 = 170 M^{-1} h^{-1}$.



383
384
385 **Figure 3.** Experimental (symbol) and modeled (solid line) pH profile of the second-order apparent rate
386 constant for the reaction of monochloramine with 4,6-dichlororesorcinol. (The modelled pH-profile was
387 obtained with $k_1 = 245 \text{ M}^{-1} \text{ h}^{-1}$, $k_2 = 4305 \text{ M}^{-1} \text{ h}^{-1}$ and $k_3 = 90 \text{ M}^{-1} \text{ h}^{-1}$).

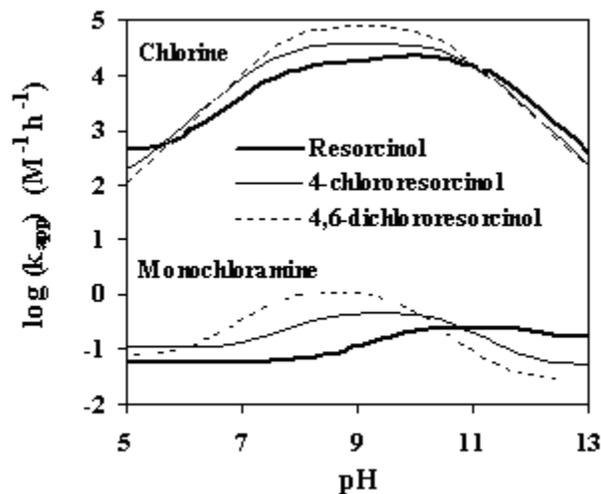


Figure 4. Apparent second-order reaction rate constants for the chlorination (upper curves) and for monochloramination (lower curves) of resorcinol, 4-chlororesorcinol and 4,6-dichlororesorcinol. (The k_{app} values were calculated from eq 9 by using the rate and acid-base equilibrium constants listed in Table 1).

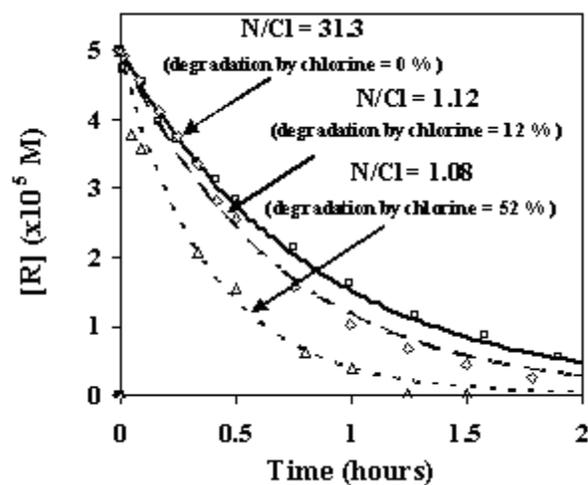


Figure 5. Effect of the N/Cl ratio (N/Cl = 1.08, 1.12 or 31.3) on the rate of disappearance of resorcinol (R). Symbols and solid and dotted lines refer to experimental data points and kinetic simulations respectively ($[R]_0 = 50 \mu\text{M}$; $[\text{NH}_2\text{Cl}]_0 = 4 \text{ mM}$).

400

Table 1. Acid dissociation constants and individual rate constants for the reactions of monochloramine (this work, at 23°C^a) and of hypochlorous acid (15) with resorcinol, 4-chlororesorcinol and 4,6-dichlororesorcinol.

Organic compound	Oxidant	pK _{a1} ^{Ar}	pK _{a2} ^{Ar}	k ₁ (±σ) (M ⁻¹ h ⁻¹)	k ₂ (±σ) (M ⁻¹ h ⁻¹)	k ₃ (±σ) (M ⁻¹ h ⁻¹)
Resorcinol	NH ₂ Cl	9.43 ^b	11.21 ^b	207 (13)	927 (21)	526 (28)
	HOCl	9.43 ^b	11.21 ^b	< 1.19 x 10 ^{6b}	4.90 x 10 ^{9b}	4.14 x 10 ^{11b}
		k ^{HOCl} /k ^{NH₂Cl}		> 5.7 x 10 ³	5.3 x 10 ⁶	7.9 x 10 ⁸
4-chlororesorcinol	NH ₂ Cl	8.09 ^b	10.75 ^b	383 (50)	1716 (45)	171(60)
	HOCl	8.09 ^b	10.75 ^b	< 2.34 x 10 ^{5b}	5.15 x 10 ^{8b}	2.42 x 10 ^{11b}
		k ^{HOCl} /k ^{NH₂Cl}		> 6.0 x 10 ²	3.0 x 10 ⁵	1.4 x 10 ⁹
4,6-dichlororesorcinol	NH ₂ Cl	7.53 ^b	9.78 ^a	244 (6)	4305 (7)	88 (7)
	HOCl	7.53 ^b	10.35 ^b	1.69 x 10 ^{5b}	1.16 x 10 ^{8b}	2.13 x 10 ¹¹
		k ^{HOCl} /k ^{NH₂Cl}		6.9 x 10 ²	2.7 x 10 ⁴	2.4 x 10 ⁹

^a Value determined experimentally in the present work unless specified otherwise. ^b From ref 15.

401

1 402

2

3 403

4

5 404 **Brief**

6

7 405

8

9

10 406 The apparent and the intrinsic rate constants for the reaction of monochloramine with resorcinol, 4-

11

12 407 chlororesorcinol and 4,6-dichlororesorcinol have been determined within the pH range 5 to 12.

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60