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Degradation of methiocarb by monochloramine in water treatment: Kinetics and pathways

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ABSTRACT

The micropollution of drinking water sources with pesticides has become a global concern. This work investigated the degradation of methiocarb (MC), a most commonly-used carbamate pesticide, by monochloramine (NH₂Cl) under simulated water treatment conditions. Results indicate that the reaction was of first-order in MC and varied orders in NH₂Cl depending on water pH. The observed rate constant of MC degradation decreased quickly with either a decrease in the molar ratio of chlorine to ammonia (Cl₂:N) or an increase in water pH. The apparent activation energy of the reaction was determined to be 34 kJ mol⁻¹. The MC degradation pathways also exhibited a strong pH dependence: at pH 6.5, MC was first oxidized by NH₂Cl to methiocarb sulfoxide (MCX), and then hydrolyzed to methiocarb sulfoxide phenol (MCXP); while at pH 8.5, MCX, MCXP and methiocarb sulfone phenol (MCNP) were formed successively through either oxidation or hydrolysis reactions. Based on the identified byproducts and their concentrations evolution, the proposed pathways of MC degradation in the presence of NH₂Cl were further validated through kinetic model simulations.

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1. Introduction

Methiocarb (mesurol, 3,5-dimethyl-4-(methylthio)phenyl methylcarbamate) (MC) is one of the most commonly-used carbamate pesticides worldwide (Keum et al., 2000; Gitahi et al., 2002; Altinok et al., 2006). It has been frequently detected in groundwater in various countries at concentrations ranging from 0.03 to 5.40 µg L⁻¹ (Barcelo et al., 1996; Garcia de Llasera and Bernal-Gonzalez, 2001; Squillace et al., 2002; APVMA, 2005). Although the detected concentrations of MC in natural waters are generally low, it poses a serious health threat to aquatic life and human considering

its high toxicity. The oral LD₅₀ in rats for MC is in the range of 13–130 mg kg⁻¹ body weight (bw) (Marrs, 1998). In aqueous environments, MC can be degraded to methiocarb sulfoxide (MCX) or lose its carbamate group to yield methiocarb phenol (MCP) (UNFAO and WHO, 1999; APVMA, 2005). The byproduct MCX is more toxic than MC, with an oral LD₅₀ in rats of 6–43 mg kg⁻¹ bw (Marrs, 1998). MCX is hence listed in the Priority List of Transformation Products in Great British Drinking Water Supplies as a result of comprehensive evaluations based on pesticide usage, toxicity, transformation products, mobility, and persistence (Sinclair et al., 2006).

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Nomenclature

MC	Methiocarb
MCN	Methiocarb sulfone
MCNP	Methiocarb sulfone phenol
MCP	Methiocarb phenol
MCX	Methiocarb sulfoxide
MCXP	Methiocarb sulfoxide phenol

Monochloramine (NH_2Cl) has been increasingly used as an alternative disinfectant to free chlorine or as a secondary disinfectant post chlorination because it is less reactive towards natural organic matter (NOM) and thus produces a lower level of regulated disinfection byproducts (DBPs) (Duirk et al., 2002; Greychock and Vikesland, 2006). Extensive researches have been conducted on the formation of DBPs during water monochloramination (Choi and Valentine, 2002; Qi et al., 2004). Though NH_2Cl has a low reactivity towards NOM, it can still react with many chemical contaminants with reaction rates dependent on water pH and the molar ratio of chlorine to ammonia ($\text{Cl}_2:\text{N}$) (Heasley et al., 2004; Sandín-España et al., 2005; Chamberlain and Adams, 2006; Greychock and Vikesland, 2006). In general, its reactivity towards a chemical contaminant increases as water pH decreases. It was also reported that the degradation of triclosan by NH_2Cl slowed down as the $\text{Cl}_2:\text{N}$ ratio decreased (Greychock and Vikesland, 2006).

Although water treatment processes can sometimes reduce the concentrations of many pesticides (Ormad et al., 2008), the formation of byproducts may increase the toxicity of treated water (Wu and Laird, 2003). Our previous study has found that the toxicity of MC solution increased after ClO_2 treatment (Tian et al., 2010). However, to date, little is known about the kinetics and mechanism of MC degradation by NH_2Cl , particularly in terms of degradation byproducts. Therefore, the aim of this study was to determine the reaction kinetics, identify major degradation byproducts, and elucidate the pathways of MC degradation in the presence of NH_2Cl . The results would clarify the fate and behavior of MC during water disinfection with NH_2Cl , thus help ensure the drinking water safety.

2. Materials and methods

2.1. Chemicals

MC (98.5%) was purchased from Dr. Ehrenstorfer GmbH, and MCX (98.2%), MCN (94.4%) and *N,O*-bis(trimethylsilyl)-tri-fluoroacetamide (BSTFA) containing 1% trimethylchlorosilane were from Sigma–Aldrich. Methanol, acetone, and acetonitrile of high performance liquid chromatography (HPLC) grade were obtained from Fisher Scientific, and methyl *tert*-butyl ether (MTBE, HPLC grade) was from Tedia. Other chemicals were of at least analytical grade and used without further purification.

The stock solutions of MC, MCX and MCN were prepared individually in methanol with a concentration of about

200–300 mg L^{-1} . The mixed calibration standards containing MC, MCX and MCN (0.25–10.0 μM) were prepared from their stock solutions and 0.1 M HCl was added to prevent hydrolysis. The standard solutions of MCP, MCXP and MCNP were prepared respectively by hydrolyzing a desired volume of the stock solutions of MC, MCX and MCN with 1 mL of 2.0 M NaOH for about 1 min, and then acidifying with 5 mL of 2.0 M HCl. The completeness of hydrolysis was confirmed by liquid chromatography/photodiode array/mass spectrometry (LC/PDA/MS, Alliance 2695 HPLC and ZQ4000 MSD, Waters) analysis. NH_2Cl was freshly prepared by mixing NaOCl and NH_4Cl solutions at a $\text{Cl}_2:\text{N}$ molar ratio of 0.8 at about pH 10 except otherwise stated. NH_4Cl was purposely applied in excess to achieve a 100% yield of NH_2Cl and suppress the spontaneous decomposition of the formed NH_2Cl as well (Qiang and Adams, 2004). All reaction solutions were prepared with ultrapure water produced by a Milli-Q system (Advantage A10, Millipore) and buffered with 10 mM phosphate in the pH range of 6.1–8.9.

2.2. Hydrolysis experiments

The hydrolysis kinetics of MC, MCX and MCN was studied separately in 60 mL brown glass reactors to exclude potential light influence. The reaction solution of a target compound was freshly prepared by diluting its stock solution with ultrapure water containing 10 mM KH_2PO_4 . The hydrolysis reaction was initiated by addition of a desired volume of 2.0 M NaOH solution and terminated by addition of 2.0 M HCl solution. Samples were withdrawn at pre-selected time intervals and analyzed for the residual MC concentrations with HPLC/PDA.

2.3. Degradation experiments

MC degradation by NH_2Cl was studied under pseudo-first-order conditions with at least 10-fold excess of NH_2Cl in a pH range of 6.1–8.9 and a temperature range of 6–33 °C. Experiments were conducted in 250 mL brown glass reactors to exclude potential light influence. To restrain MC from hydrolysis, the reaction solution of MC (10 μM) was freshly prepared by spiking a desired volume of its stock solution into 100 mL of ultrapure water buffered with 10 mM KH_2PO_4 . Note that the presence of methanol, at a level of below 1.0% (v/v), has negligible impact on the reaction of NH_2Cl towards an organic compound (Greychock and Vikesland, 2006). Our preliminary experiment had also confirmed that 0.8% (v/v) methanol exerted insignificant influence on MC degradation by NH_2Cl in this study.

After adjusting the reaction solution pH, a desired volume of NH_2Cl stock solution was spiked to initiate the reaction. Samples were withdrawn at pre-selected time intervals, and the residual oxidant was immediately quenched with pre-added Na_2SO_3 solution. Each sample was extracted with 2 mL of MTBE, and then analyzed with gas chromatography/mass spectrometry (GC/MS, 7890 GC and 5975 MSD, Agilent) to determine the residual MC concentration. The degradation experiments were conducted in duplicate, and the relative standard deviations of all measurement data were determined to be below 5%.

2.4. Analytical methods

MC was analyzed with GC/MS equipped with an HP-5 capillary column (30 m × 0.25 mm, 0.25 μm) in kinetic experiments. The injection temperature was 280 °C, and the column temperature was programmed as follows: started at 90 °C and held for 1 min, ramped at 20 °C min⁻¹ to 280 °C and then held for 2 min. High purity helium gas was used as the carrier gas at a flow rate of 1 mL min⁻¹. The MS quadrupole and source temperatures were set at 150 and 230 °C, respectively. The quantification and confirmation ions for MC adopted in the selective ion mode (SIM) were 168 and 153, respectively. NH₂Cl was measured with Hach Indophenol Method 10172 on a UV–Vis spectrophotometer (DR5000, Hach). Solution pH and temperature were measured simultaneously by using a Mettler Toledo Delta 320 pH meter.

Byproducts formed during MC degradation by NH₂Cl were identified with GC/MS and HPLC/PDA/MS. MCXP and MCNP were identified with GC/MS as follows: 1) transfer the sample to a glass tube of cusate bottom; 2) evaporate it under vacuum until dryness in a water bath of 40 °C; 3) add 100 μL BSTFA and 100 μL pyridine to the dry residue; 4) vortex for 20 s with the tube capped and heat in a water bath of 60 °C for 20 min; 5) cool the mixture down to room temperature, and blow off the residual BSTFA and pyridine under a gentle stream of nitrogen gas; and 6) dissolve the resulting derivatives in 1 mL acetone and analyze with GC/MS.

MCX was identified with HPLC/MS by comparing its retention time and MS spectrum with those of an authentic standard. An Atlantis C18 column (150 mm × 2.1 mm, 3 μm) was used for organic separation at a constant temperature of 40 °C and an acetonitrile/water eluent flow rate of 0.2 mL min⁻¹. The eluent gradient consisted of 3 min elution with 20% acetonitrile, linearly ramped to 60% acetonitrile over 5 min and held for 4 min, and then decreased to 20% acetonitrile over 3 min and held for 10 min. The MS system was operated in the positive ionization mode with an electrospray ionization source under the following conditions: capillary voltage 3.5 kV, cone voltage 20 V, source temperature 120 °C, and desolvation temperature 300 °C. High purity nitrogen gas was used as both cone and desolvation gases at a flow rate of 50 and 300 L h⁻¹, respectively.

After being identified, the three major byproducts (MCXP, MCNP and MCX) together with the parent compound (MC) were further quantified by HPLC/PDA in a wavelength range from 209 to 211 nm under the separation conditions mentioned above.

3. Results and discussion

3.1. Determination of reaction order

Previous studies have shown that the reaction between NH₂Cl and an organic compound is usually of first-order with respect to the organic compound (Greyshock and Vikesland, 2006; Chamberlain and Adams, 2006; Rodríguez et al., 2007). Fig. 1a shows the pseudo-first-order kinetic simulation (Eq. (1)) for MC degradation at pH 7.5 with various initial NH₂Cl

Fig. 1 – Determination of the reaction order for MC degradation by NH₂Cl: (a) plot of $\ln([MC]/[MC]_0)$ vs. reaction time at pH 7.5; (b) plot of $\lg k_h$ vs. pH for MC and MCX; and (c) plot of $\ln k_{ox,MC}$ vs. $\ln[NH_2Cl]$ at pHs 7.5 and 8.5. Experimental conditions: $[MC]_0 = [MCX]_0 = 10 \mu\text{M}$, $T = 26 \pm 2 \text{ }^\circ\text{C}$.

(Chamberlain and Adams, 2006; Qiang et al., 2006; Rodríguez et al., 2007). The degree of NH_2Cl hydrolysis increases with a decrease in the solution pH (Morris and Issac, 1983). The secondary HOCl may also contribute to the MC degradation. To clarify the role of HOCl in MC degradation, the effect of $\text{Cl}_2:\text{N}$ ratio was further examined.

3.3. Effect of $\text{Cl}_2:\text{N}$ ratio

In the pH range of 6.5–8.5, which is typical for drinking water treatment, NH_2Cl is predominantly produced at a $\text{Cl}_2:\text{N}$ ratio $\leq 5:1$ (by weight); otherwise, breakpoint chlorination will occur which reduces the residual chlorine. For chloramination, water utilities generally apply a $\text{Cl}_2:\text{N}$ weight ratio between 3 and 5 (i.e., molar ratio of 0.6–1.0) (USEPA, 1999). In the chloramination process, the hydrolysis of NH_2Cl will yield HOCl (Eq. (4)). Due to its high oxidation potential, HOCl cannot be neglected even though at a very low concentration. Therefore, MC degradation may be attributed to both the direct reaction with NH_2Cl and the simultaneous indirect reaction with HOCl .

To examine the contribution of HOCl to MC degradation, experiments were conducted at various molar ratios of $\text{Cl}_2:\text{N}$ (from 0.79 to 0.01) at pH 7.5. Table 1 indicates that the observed degradation rate of MC (k_{obs}) first decreased with a decreasing $\text{Cl}_2:\text{N}$ ratio from 0.79 to 0.35, and then approached nearly constant at molar ratios no more than 0.05. It is inferred that MC was also oxidized by HOCl besides NH_2Cl , and a higher $\text{Cl}_2:\text{N}$ ratio caused a more significant contribution of HOCl to MC degradation. This result is similar to the degradation of triclosan by NH_2Cl (Greyschok and Vikesland, 2006).

3.4. Effect of temperature

The effect of temperature on MC degradation was studied at pH 7.5 from 6 to 33 °C, which represents a typical temperature range for drinking water treatment. The results indicate that the k_{obs} increased rapidly with an increase in temperature at a constant pH (Fig. S1), as expressed by the Arrhenius equation:

$$k_{\text{obs}} = 5.37 \times 10^6 \exp(-4083.7/T) \quad (5)$$

The apparent activation energy was calculated to be 34 kJ mol⁻¹, which is considerably lower than 75 kJ mol⁻¹ for MC reaction with ClO_2 (Tian et al., 2010). According to this value, a 10 °C temperature increase will raise the reaction rate by 1.6 times.

Table 1 – The observed pseudo-first-order rate constant (k_{obs}) of MC degradation by NH_2Cl at various molar ratios of $\text{Cl}_2:\text{N}$ ($[\text{MC}]_0 = 10 \mu\text{M}$, pH = 7.5, $T = 25 \pm 2 \text{ }^\circ\text{C}$).

$\text{Cl}_2:\text{N}$	$[\text{NH}_2\text{Cl}]$ (mM)	k_{obs} (h ⁻¹)
0.79	0.507	6.065
0.65	0.430	4.449
0.51	0.401	3.928
0.35	0.408	2.669
0.05	0.451	2.024
0.01	0.514	2.074

3.5. Proposed degradation pathways

It was reported that MC could either be degraded to MCX or lose its carbamate group via hydrolysis to yield MCP in aqueous solution (UNFAO and WHO, 1999; APVMA, 2005). Since the solution pH greatly impacted MC degradation by NH_2Cl as mentioned above, it could also alter the degradation pathways and produce different byproducts.

The formation of byproducts along with MC degradation by NH_2Cl was studied at pH values of 6.5, 7.5 and 8.5, as shown in Fig. 3. Results indicate that at pH 6.5, MC was

Fig. 3 – Byproducts formation along with MC degradation by NH_2Cl at: (a) pH 6.5; (b) pH 7.5; and (c) pH 8.5.

Experimental conditions: $[\text{MC}]_0 = 9.3\text{--}10 \mu\text{M}$; $[\text{NH}_2\text{Cl}]_0 = 1.108 \text{ mM}$, $T = 26 \pm 2 \text{ }^\circ\text{C}$; mass balance was based on benzene ring; the relative standard deviations of all measurement data were below 10%.

oxidized quickly to MCX within 10 min, which was a major and fairly stable byproduct. A small amount of MCXP was also detected due to the further hydrolysis of MCX, which only accounted for about 3% of the initial MC concentration at the end of the reaction (i.e., 2 h). The good mass balance on the basis of benzene ring (i.e., including MC, MCX and MCXP) throughout the reaction course indicates that all major byproducts were identified at this pH. At pH 7.5, the MC degradation was retarded to some extent, but MCX was still a major byproduct; more MCXP was generated due to an enhanced hydrolysis of MCX at this elevated pH, which accounted for 22% of the initial MC concentration at 2 h. At pH 8.5, the concentration of MCX decreased greatly because of its rapid hydrolysis to MCXP under a basic condition, which accounted for 59% of the initial MC concentration at 2 h. Moreover, MCNP emerged as a new byproduct and accumulated with reaction time, implying that NH_2Cl could more easily oxidize MCXP than MCX. The mass balance based on benzene ring showed a deficiency of ca. 15% at the end of the reaction, most probably due to some unidentified byproducts. Because MCX is more toxic than MC and other identified byproducts (i.e., MCXP and MCNP), the MC solution would have a less toxicity after treatment by NH_2Cl at a higher pH (Fig. S2).

Fig. 4 – Proposed pathways of MC degradation in the presence of NH_2Cl .

Based on the identified byproducts and their concentrations evolution over the reaction course, the degradation pathways of MC in the presence of NH_2Cl were proposed (Fig. 4). Although NH_2Cl oxidation played a primary role in MC degradation, hydrolysis reactions occurred simultaneously. The initial attack of NH_2Cl on the sulfur of MC produced a major oxidation byproduct, MCX, which could hydrolyze easily to MCXP in aqueous solution. In the meanwhile, the hydrolysis of MC led to the formation of MCP, whose continuous oxidation by NH_2Cl yielded MCXP. The oxidation rate of MCP by NH_2Cl ($k_{ox,MCP}$) was experimentally determined to be 7.23 h^{-1} at pH 8.5 (Fig. 5a), which is much higher than its formation rate through the hydrolysis of MC (0.10 h^{-1} , experimentally determined, Table 2) at the same pH. As a consequence, MCP could not be detected in the reaction

Fig. 5 – (a) The degradation kinetics of MCP, MCXP and MCNP by NH_2Cl ($[\text{MCP}]_0 = [\text{MCXP}]_0 = [\text{MCNP}]_0 = 10 \mu\text{M}$); and (b) the model simulations of byproducts formation along with MC degradation by NH_2Cl ($[\text{MC}]_0 = 10 \mu\text{M}$). Experimental conditions: $[\text{NH}_2\text{Cl}]_0 = 0.486 \text{ mM}$, pH = 8.5, $T = 26 \pm 2^\circ\text{C}$; the symbols represent measurement data and the curves represent model-fitting; the relative standard deviations of all measurement data were below 10%.

Table 2 – Comparison of experimental and modeled rate constants of related reactions for MC degradation in the presence of NH_2Cl (pH = 8.5, $T = 26 \pm 2^\circ\text{C}$).

No.	Reactions	Rate constants (h^{-1})	
		Experimental data ^a	Modeled data
1	$\text{MC} + \text{NH}_2\text{Cl} + \text{H}_2\text{O} \xrightarrow{k_{\text{ox,MC}}} \text{MCX} + \text{NH}_4^+ + \text{Cl}^-$	$k_{\text{ox,MC}} = 1.07 \pm 0.03$	$k_{\text{ox,MC}} = 1.09$
2	$\text{MC} + \text{H}_2\text{O} \xrightarrow{k_{\text{h,MC}}} \text{MCP} + \text{CH}_3\text{NH}_2 + \text{CO}_2$	$k_{\text{h,MC}} = 0.10 \pm 0.01$	$k_{\text{h,MC}} = 0.11$
3	$\text{MCX} + \text{H}_2\text{O} \xrightarrow{k_{\text{h,MCX}}} \text{MCXP} + \text{CH}_3\text{NH}_2 + \text{CO}_2$	$k_{\text{h,MCX}} = 1.19 \pm 0.08$	$k_{\text{h,MCX}} = 1.07$
4	$\text{MCP} + \text{NH}_2\text{Cl} + \text{H}_2\text{O} \xrightarrow{k_{\text{ox,MCP}}} \text{MCXP} + \text{NH}_4^+ + \text{Cl}^-$	$k_{\text{ox,MCP}} = 7.23 \pm 0.02$	—
5	$\text{MCXP} + \text{NH}_2\text{Cl} + \text{H}_2\text{O} \xrightarrow{k_{\text{ox,MCXP}}} \text{MCNP} + \text{NH}_4^+ + \text{Cl}^-$	$k_{\text{ox,MCXP}} = 0.07 \pm 0.00$	$k_{\text{ox,MCXP}} = 0.07$
6	$\text{MCNP} + \text{NH}_2\text{Cl} + \text{H}_2\text{O} \xrightarrow{k_{\text{ox,MCNP}}} \text{other byproducts}$	$k_{\text{ox,MCNP}} = 0.03 \pm 0.01$	$k_{\text{ox,MCNP}} = 0.05$

^a Mean $\pm$ standard deviation ($n = 2$).

solution. A further attack on the $-(\text{S}=\text{O})-$ moiety of MCXP by NH_2Cl generated MCNP, and the reaction rate constant was measured to be 0.07 h^{-1} at pH 8.5 (Fig. 5a). MCNP was also reactive towards NH_2Cl , although with a notably lower rate constant (0.03 h^{-1} , Fig. 5a). It is seen that the reaction rates of the phenolic byproducts towards NH_2Cl decreased successively from MCP, MCXP, to MCNP. The proposed pathways suggest that a basic condition should favor the degradation of MC by NH_2Cl because MCXP and MCNP are much less toxic than MC and MCX (Fig. S2).

To verify the proposed pathways of MC degradation in the presence of NH_2Cl , Scientist[®] software (Micromath, Salt Lake, UT) was utilized to simulate the formation of byproducts along with the degradation of MC at pH 8.5 based upon the related reactions as listed in Table 2. Considering the fact that MCP was formed but could not be detected during the reaction course, in the model simulation process, the two-step pathways from MC to MCP (via hydrolysis) and further to MCXP (via oxidation) were simplified as one transformation step, i.e., directly from MC to MCXP with a rate constant of $k_{\text{h,MC}}$. This simplification is reasonable because the hydrolysis of MC to MCP ($k_{\text{h,MC}} = 0.10 \text{ h}^{-1}$) was the rate-limiting step in comparison to the oxidation of MCP to MCXP ($k_{\text{ox,MCP}} = 7.23 \text{ h}^{-1}$). The simulated curves are presented in Fig. 5b, and the simulated rate constants are given in Table 2. The good agreement between model predictions and experimental measurements well confirms the rationality of the proposed pathways for MC degradation in the presence of NH_2Cl .

4. Conclusions

This work investigated the kinetics and pathways of MC degradation by NH_2Cl under typical water treatment conditions. Based on the experimental results, the following conclusions can be drawn:

- The reaction between MC and NH_2Cl was of first-order in MC and varied orders in NH_2Cl . The observed pseudo-first-order rate constant of MC degradation was strongly pH dependent, which quickly decreased from 24.37 to 0.53 h^{-1} as the solution pH increased from 6.10 to 8.89 .
- MC degradation was attributed to both the direct reaction with NH_2Cl and the indirect reaction with HOCl produced from NH_2Cl hydrolysis. The apparent activation energy for MC reacting with NH_2Cl was determined as 34 kJ mol^{-1} .

- MCX and MCXP were two major byproducts identified in MC degradation by NH_2Cl at pHs 6.5 and 7.5, while MCNP emerged as a new byproduct at pH 8.5. Although NH_2Cl oxidation played a primary role in MC degradation, hydrolysis reactions occurred simultaneously, especially under basic conditions.
- The proposed pathways of MC degradation in the presence of NH_2Cl were substantiated through kinetic model simulations.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2013.12.011>.

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