A kinetic model of N-nitrosodimethylamine (NDMA) formation during water chlorination/chloramination

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Abstract Experiments were conducted to investigate the hypothesis that N-nitrosodimethylamine (NDMA) is a potential disinfection by-product. NDMA was formed by the reaction of dimethylamine (DMA) with monochloramine and also with free chlorine in the presence of ammonia. We proposed a mechanism for NDMA formation which does not require the presence of nitrite as in N-nitrosation. The critical NDMA formation reactions consist of i) the formation of monochloramine by combination of free chlorine with ammonia, ii) the formation of 1,1-dimethylhydrazine (UDMH) intermediate from the reaction of DMA with monochloramine followed by, iii) the oxidation of UDMH by monochloramine to NDMA, and iv) the reversible chlorine transfer reaction between free chlorine/monochloramine and DMA which is parallel with i) and ii). A kinetic model was developed to validate the proposed mechanism.

Keywords Chlorine; chlorine transfer; dimethylamine (DMA); 1,1-dimethylhydrazine (UDMH); disinfection by-product (DBP); monochloramine; N-nitrosodimethylamine (NDMA)

Introduction

NDMA, a probable human carcinogen (US EPA, 1997), has been found in highly purified wastewaters intended for recycle as well as some treated drinking waters while absent in the influent streams (California Department of Health Services, 2000; Najm and Trussel, 2001). The current investigations suggest there might be a possible link between NDMA formation and treatment practices.

The most common and studied NDMA formation mechanism involves N-nitrosation, the reaction of a precursor amine with nitrite (Williams, 1988). In most environmentally related NDMA formation studies, researchers have therefore added nitrite and/or a nitrosatable nitrogen precursor such as dimethylamine (DMA) into the water samples to evaluate NDMA formation potential (Mills and Alexander, 1976; Jobb *et al*., 1992; Graham *et al*., 1995).

Our studies were conducted as part of a more comprehensive study of alternative formation pathways. In this paper we report on studies aimed at investigating the hypothesis that NDMA is also a disinfection by-product specifically produced by the reaction of monochloramine with DMA in the absence of nitrite. We selected DMA as a potential precursor because it is ubiquitous in surface and wastewater (Sacher *et al*., 1997; Smith, 1971). A series of experiments were conducted to investigate factors influencing the formation of NDMA from monochloramine and DMA. Unlike N-nitrosation, which requires nitrite, we propose a new NDMA formation mechanism that involves monochloramine as a key reactant or intermediate. A kinetic model was then developed and used to validate the proposed mechanism.

Methods

Chemicals

N-nitrosodimethylamine (NDMA, 100 μg/mL in methanol) was obtained from Chem Service. Deuterated N-nitrosodimethylamine (d_6-NDMA, 1,000 μg/mL in methanol) was

obtained from Protocol Analytical Supplies. ^{15}N isotope labeled ammonium sulfate ($^{15}N_2$, 98%+) was obtained from Cambridge Isotope Lab, Inc. Sodium nitrite, 1,1-dimethylamine hydrochloride, and ammonium sulfate were obtained from Aldrich. Sodium hypochlorite solution was obtained from Fisher Scientific. All other chemicals used in these experiments were analytical laboratory grade.

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Experimental

Batch experiments were conducted in 1 L sealed bottles using deionized water with chemical resistivity greater than 18 MΩ·cm. The pH was adjusted at 7.0 ± 0.1 with 4 mM bicarbonate buffer by addition of H_2SO_4. All reaction solutions were reacted for 24 hours in the dark at 25°C. Preformed monochloramine was reacted with solution containing DMA. Both preformed monochloramine and DMA concentrations were varied from 0.005 to 2.0 mM. Instead of preformed monochloramine, free chlorine was added to solutions containing DMA and ammonia. Monochloramine stock solutions were preformed by adding a predetermined amount of sodium hypochlorite solution into pH adjusted ammonium sulfate solution. The final concentration of monochloramine in the stock was measured using the DPD-FAS method (APHA *et al.*, 1992). Cl/N molar ratio was approximately 0.7 (mole/mole).

NDMA analysis

NDMA was determined by isotope dilution gas chromatography/mass spectrometer (GC/MS) method (Taguchi *et al.*, 1994). Prior to extraction, all 1 L samples are dosed with the isotopically labeled d_6-NDMA as an internal standard. 1 L sample is added with 200 mg of carbonaceous adsorbent (Ambersorb 572, Aldrich) and extracted by shaking the solution for 1 hour at 200 rpm. Ambersorb beads are vacuum filtered onto a glass fiber filter, and dried in air for 30 minutes. Beads are transferred to a 2 mL amber vial where beads are soaked with 0.5 mL of methylene chloride for 20 minutes before analysis. A 95 µL aliquot of methylene chloride extract is injected into GC/MS (Finnigan MAT) equipped with Large Volume Injector (Optic2). NDMA is quantified based on the mass detection of the characteristic molecular ion (m/z = 74.048) of NDMA and molecular ion of d_6-NDMA (m/z = 80.086). The MDL at the 99% confidence level was determined to be 2.4 ng/L.

Results and discussion

NDMA formation studies

Initial experiments compared NDMA formation by the reaction of DMA with nitrite to that from the reaction of DMA with monochloramine, free chlorine, and free chlorine in the presence of ammonia (Table 1). The concentration of each compound is 0.1 mM. NDMA was not found as a contaminant in any of the individual reactant solutions. All mixtures were reacted in the dark at pH 7 for 24 hours.

NDMA formed from the reaction of DMA with nitrite is 2.1 µg/L. On the other hand, the reaction of DMA with monochloramine produced about 12.3 µg/L of NDMA. In the absence of nitrite, the formation of NDMA is attributed to monochloramine with the reaction of DMA. Nitrite was not measured as an intermediate product with detection limit of

Table 1 NDMA formation studies

Batch No.	DMA, mM	NO_2^-, mM	NH_2Cl, mM	HOCl, mM	NH_3, mM	NDMA, µg/L
1	0.1	0.1	–	–	–	2.1
2	0.1	–	0.1	–	–	12.3
3	0.1	–	–	0.1	–	0.5
4	0.1	–	–	0.1	0.1	10.5

0.01 mM. About 0.5 µg/L of NDMA was produced by the addition of HOCl to a solution of DMA, however, addition of ammonia into this solution produced 10.5 µg/L of NDMA.

NDMA formation was studied as a function of preformed monochloramine concentration at a fixed DMA concentration of 0.1 mM (Figure 1). NDMA formation increased with increasing monochloramine concentration from 0.01 mM to 2 mM. The formation appeared to reach an apparent plateau with addition of approximately 2 mM of monochloramine. The lines in this figure and the following figures are the predicted NDMA concentration obtained from the model.

The NDMA formation showed a maximum in yield when DMA was varied from 0.005 mM to 2.0 mM at fixed preformed monochloramine concentrations of 0.1 mM (Figure 2). The maximum occurred when the ratio of DMA to monochloramine was near 1.0 and then decreased as this ratio was increased by addition of DMA.

Free chlorine (0.1 mM) was added to mixtures of DMA (0.2 mM) and variable ammonia concentration. Increasing ammonia concentration increased the formation of NDMA (Figure 3).

Proposed mechanism and model results

We propose a mechanism for NDMA formation in chlorinated water (Table 2 and Figure 4) containing NDMA and ammonia. The key reactions include the formation of monochloramine from the initially added HOCl (Reaction 1). DMA also combines with HOCl to form dimethylchloramine (DMCA) (Reaction 2), however, its rate is slower than the rate of monochloramine formation. The transfer of chlorine occurs from monochloramine to DMA to form DMCA accounting for a gradual depletion of monochloramine (Reaction 3). NDMA Formation is initiated by the formation of UDMH from the reaction of DMA with monochloramine (Reaction 4), followed by the oxidation of UDMH by monochloramine to NDMA (Reaction 5).

Reaction 1, 2, and 3 are based on chlorine chemistry and chlorine transfer reactions (Isaac and Morris, 1983; Ferriol *et al*., 1989, 1991; Yoon and Jensen, 1993). Reaction 4 is based on Raschig synthesis where it has been shown that monochloramine reacts with DMA in aqueous solution to produce UDMH (Audrieth *et al*., 1954; Cahn and Powell, 1954; Rowe and Audrieth, 1956; Jones *et al*., 1992). The oxidation of UDMH has also been
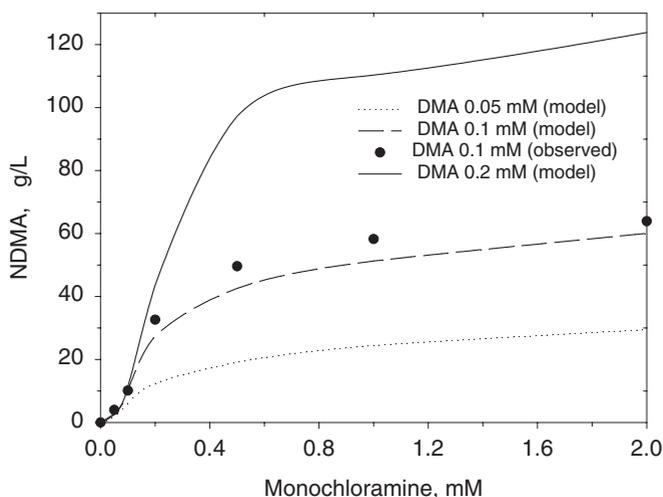
Figure 1 Measured and predicted NDMA formation as a function of preformed monochloramine concentration. DMA concentration was fixed at 0.1 mM (observed). The lines are predicted NDMA formation from model with DMA concentration fixed at 0.05 mM, 0.1 mM, and 0.2 mM. The pH was adjusted to 7.0 ± 0.1 using 4 mM bicarbonate buffer. Solutions were reacted for 24 hours in the dark at 25°C
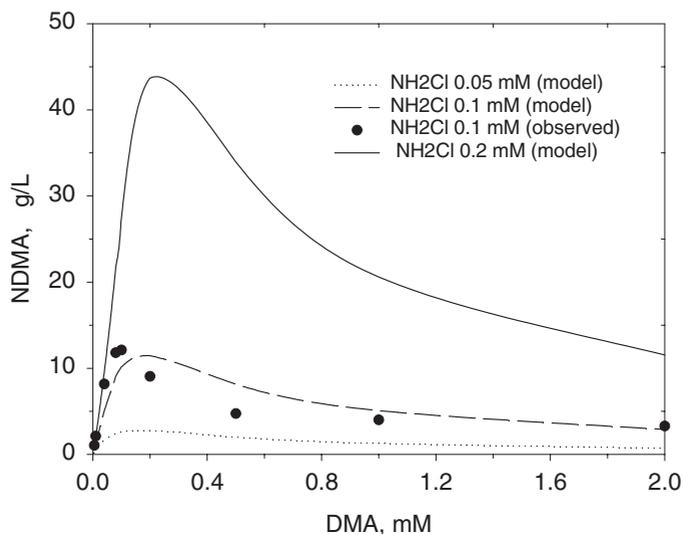
Figure 2 Measured and predicted NDMA formation from reaction of preformed monochloramine as a function of DMA concentration. Preformed monochloramine concentration was fixed at 0.1 mM (observed). The lines are predicted NDMA formation from model with monochloramine concentration fixed at 0.05 mM, 0.1 mM, and 0.2 mM. The pH was adjusted at 7.0 ± 0.1 with 4 mM bicarbonate buffer. Solutions were reacted for 24 hours in the dark at 25°C
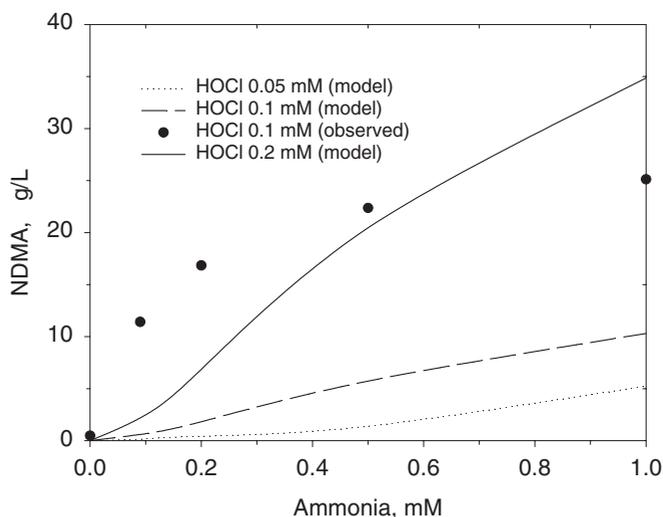

Figure 3 Measured and predicted NDMA formation from free chlorination of ammonia and DMA containing water. 0.1 mM of HOCl was added into solutions containing 0.2 mM of DMA and ammonia (observed). Ammonia concentration was varied at 0, 0.1, 0.2, 0.5 and 1.0 mM. The lines are predicted NDMA formation from model with HOCl concentration of 0.05 mM, 0.1 mM, and 0.2 mM. The pH was adjusted to 7.0 ± 0.1 with 4 mM bicarbonate buffer. Solutions were reacted for 24 hours in the dark at 25°C

studied because UDMH is widely used in rocket propellant fuels. NDMA was found when UDMH was deliberately exposed to the atmosphere (Lunn *et al*., 1991; Lunn and Sansone, 1994) and oxidized by sodium hypochlorite (Castegnaro *et al*., 1986). In chloraminated or chlorinated water with ammonia, we hypothesize that UDMH would be preferentially oxidized by monochloramine. However, oxidation of UDMH by HOCl (Castegnaro *et al*., 1986) cannot be excluded because the hydrolysis of chloramine in the presence of

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excess ammonia produces HOCl in equilibrium. The oxidation of UDMH may form other products including nitrogen gas and several other organic compounds such as tetramethyl-tetrazene (TMT), formaldehyde dimethylhydrazone (FDMH), and methylenedimethylhy-drazine (Sisler *et al.*, 1969).

The reactions shown in Table 2 and corresponding rate expressions were used to develop the set of differential rate expressions describing the reaction mechanism. We assumed that reactions 1–4 were elementary and could be described by simple second order reactions. Reaction 5 is clearly not elementary. We assumed, however, that the rate limiting reaction is first order in both DMA and monochloramine. Presumably any intermediates would be rapidly oxidized to NDMA.

The rate constants in Table 2 were obtained either from the literature or estimated from the data. The rate constant characterizing DMCA hydrolysis (k_{-2}) and chlorine transfer from DMCA to ammonia (k_{-3}) were estimated using the value for methylamine and a corre-lation between rate constants and the basicity (Isaac and Morris, 1983; Yoon and Jensen, 1993). The rate constants characterizing chlorine transfer from HOCl to DMA (k_2), the for-mation of UDMH (k_4), and its oxidation to NDMA (k_5) were estimated simultaneously by minimizing the errors between measured and predicted NDMA concentrations on the data sets. Finally, the set of differential equations was solved using Scientist™.

The model predicted a plateau in NDMA formation with monochloramine concentration (Figure 1), which is consistent with the expected limitation of DMA concentration due to DMCA formation. It also captured the maximum in NDMA formation occurring near the ratio of DMA to monochloramine of approximately one (Figure 2). The maximum is hypothesized to occur because when the DMA to monochloramine ratio becomes approxi-mately greater than one, the amount of monochloramine available to oxidize UDMH is rap-idly exhausted with increasing DMA due to chlorine transfer. However, the model underestimated an increase in the NDMA formation with increasing ammonia by addition of HOCl into DMA and ammonia mixture solutions (Figure 3). This may be due to an artifact caused by poor initial mixing or possibly other reactions involving free chlorine, which is not included in the current model.

Further model results indicate that NDMA formation should be approximately pro-portional to organic N precursor concentration in the presence of excess monochloramine. Increasing monochloramine or free chlorine at a fixed precursor and ammonia con-centration will also increase NDMA but in a non linear manner.

Table 2 Proposed mechanism of NDMA formation mechanism

Reaction	Rate constant at pH 7 (25°C)	Reference
(1) $HOCl + NH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NH_2Cl + H_2O$	$k_1 = 4.17 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ $k_{-1} = 2.11 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$	Morris and Isaac, 1981 Morris and Isaac, 1981
(2) $HOCl + (CH_3)_2NH \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} (CH_3)_2NCl + H_2O$	$k_2 = 4.22 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ $k_{-2} = 1.60 \times 10^{-6} \text{ M}^{-1}\text{s}^{-1}$ [a]	This model Yoon and Jensen, 1993
(3) $NH_2Cl + (CH_3)_2NH \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} (CH_3)_2NCl + NH_3$	$k_3 = 1.40 \times 10^{-1} \text{ M}^{-1}\text{s}^{-1}$ $k_{-3} = 5.83 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ [a]	Isaac and Morris, 1983; Yoon and Jensen, 1993
(4) $NH_2Cl + (CH_3)_2NH \overset{k_4}{\rightarrow} (CH_3)_2NNH_2 + H^+ + Cl^-$	$k_4 = 1.56 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$	This model
(5) $(CH_3)_2NNH_2 + 2NH_2Cl + H_2O \overset{k_5}{\rightarrow}$ $(CH_3)_2NNO + 2NH_3 + 2H^+ + 2Cl^-$	$k_5 = 2.38 \times 10^{-1} \text{ M}^{-1}\text{s}^{-1}$	This model

[a] Estimated using the value for methylamine and a correlation between rate constants and the basicity
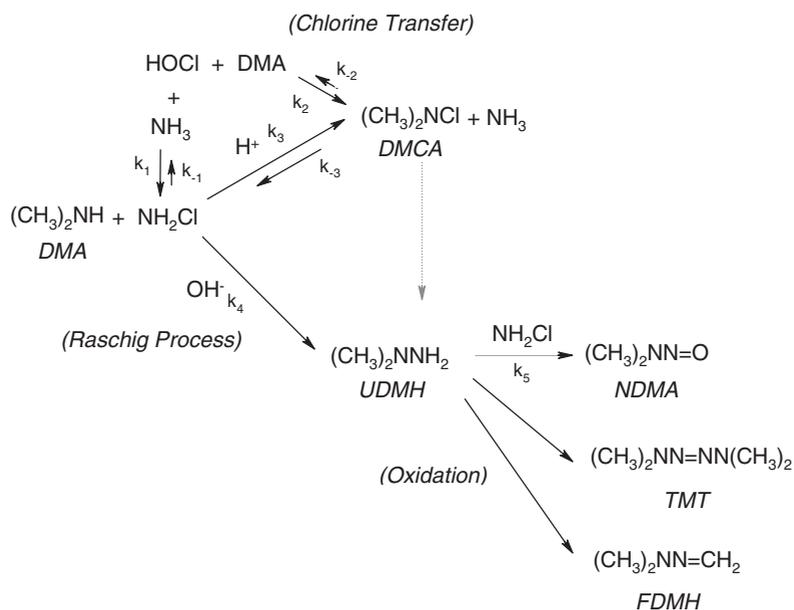
Figure 4 The proposed mechanism of NDMA formation in chlorinated water containing DMA and ammonia

Conclusions

NDMA should be considered a disinfection by-product. Our work shows that it can be potentially formed wherever monochloramine could form. The capability of the model to predict NDMA formation suggests that key reactions have been accounted for. The model, however, is certainly a simplification of a much more complicated process. Other mechanisms and reactions may also contribute to NDMA formation under reaction conditions not evaluated in this work.

Acknowledgements

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