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PolyDADMAC and Dimethylamine as Precursors of *N*-Nitrosodimethylamine during Ozonation: Reaction Kinetics and Mechanisms

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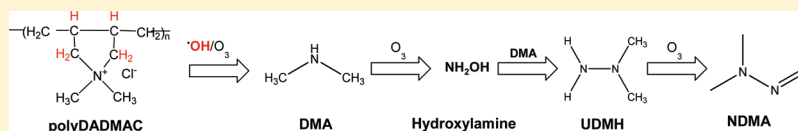
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S Supporting Information

ABSTRACT:



Interactions of ozone with organic precursors during water treatment may generate carcinogenic *N*-nitrosodimethylamine (NDMA) byproduct. This study investigates the reaction mechanisms responsible for NDMA formation from ozonation of the commonly used poly(diallyldimethylammonium chloride) (polyDADMAC) coagulant. Upon ozonation, polyDADMAC yields the highest amount of NDMA among several water treatment polymers, including polyamines and cationic polyacrylamides. Ozonation transforms polyDADMAC to dimethylamine (DMA) and NDMA formation is correlated to polyDADMAC degradation and DMA release. Hydroxyl radicals generated from ozone play an important role in the degradation of polyDADMAC's quaternary ammonium ring groups and subsequent release of secondary amine. Although nitrite and formaldehyde are detected as ozonation products of DMA and polyDADMAC, contribution of formaldehyde-enhanced nitrosation pathway is determined to be insignificant in NDMA formation. In contrast, reaction of hydroxylamine, another ozonation product of DMA, with DMA in the presence of ozone is deemed critical in the formation of NDMA during ozonation. The study results show that that contact of polyDADMAC with ozone will lead to release of the more potent NDMA precursor DMA but may not generate a significant amount of NDMA under typical drinking water treatment conditions due to low yield. The mechanistic understanding from this study can help develop source control strategies for minimization of NDMA formation risk at water and wastewater utilities.

INTRODUCTION

N-Nitrosamines constitute an emerging group of disinfection byproducts¹ that exhibit unusually high carcinogenic risk [e.g., 10^{−6} cancer risk level at concentration as low as 0.7 ng/L for *N*-nitrosodimethylamine (NDMA)].² However, these compounds are frequently detected in treated drinking waters and wastewater at levels higher than their advisory guidelines in the United States^{3–5} and other parts of the world.⁶ Of all the nitrosamines, NDMA has been most commonly detected, with concentrations ranging from 0 to 630 ng/L with an average of 9 ng/L in treated drinking waters⁷ and up to 1000 ng/L in wastewater effluents.³ Recent NDMA occurrence data showed the presence of NDMA above the method reporting limit (MRL) of 2 ng/L at nearly 25% of public water utilities screened for nitrosamines.⁷ Past studies on NDMA formation mechanisms^{8,9} have shown dimethylamine (DMA) as a precursor for NDMA formation during chemical disinfection.^{10,11} However, DMA alone cannot account for the entire mass of NDMA formed.^{3,12–14} Hence, efforts to identify other potential NDMA precursors and formation pathways are critical to develop proper strategies to minimize NDMA formation during water and wastewater treatment.¹⁵

Among potential NDMA precursors, cationic amine-based water treatment polymers containing DMA moieties have been reported to form NDMA upon chlorination or chloramination.^{16–18} Accordingly, nitrosamines have been frequently detected in treatment plants employing quaternary amine-based polymers such as poly(diallyldimethylammonium chloride) (polyDADMACs).^{19,20} Mechanisms of NDMA formation from chloramination of polyDADMACs and polyamines, amine-based polymers most commonly used in potable water treatment, have been also reported.¹⁷ However, there exists a knowledge gap in the literature on the behavior of these polymers when reacted with different disinfectants other than chlorine or chloramines.

Ozone is increasingly used as a disinfectant of choice in water treatment, since it is much more effective in inactivating various pathogenic microorganisms of public health concern, including

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Cryptosporidium parvum oocysts and *Giardia lamblia* cysts, compared to chlorine-based disinfectants.²¹ Recent studies have indicated that ozonation of DMA²² as well as the fungicide tolylfluand and its metabolites *N,N*-dimethyl-*N'*-(4-methylphenyl)sulfamide (DMST) and *N,N*-dimethylsulfamide (DMS)^{23,24} can result in the formation of NDMA. Andrzejewski et al.²² proposed formaldehyde-catalyzed nitrosation²⁵ as a possible pathway for NDMA formation from ozonation of DMA based on the observation of nitrite formation as one of reaction products. However, products other than NDMA were not quantified, and the formaldehyde-catalyzed nitrosation pathway was unable to explain the observed increase in NDMA yield with pH increase. Hence, Yang et al.²⁶ proposed an alternative mechanism involving reaction of hydroxylamine, an ozonation product of DMA, with DMA to explain NDMA formation via unsymmetrical dimethylhydrazine (UDMH) pathway in neutral and alkaline pH. However, the above reaction pathway was not verified during ozonation experiments, and mechanisms for NDMA formation from ozonation of DMA are still uncertain.

This study examined the reactions of ozone with common amine-based water treatment polymers and DMA with particular emphasis on assessing their potential for NDMA formation as well as formation mechanisms. Among the tested polymers, polyDADMACs exhibited the highest potential to release DMA and consequently form the greatest amount of NDMA during ozone treatment. Hence, polyDADMACs were focused on in the detailed mechanistic study. On the basis of the study results, suggestions were made to water treatment utilities employing ozonation to reduce NDMA formation risks associated with the use of polyDADMACs.

MATERIALS AND METHODS

Experimental Protocol. Details of chemicals used in this study are provided in the Supporting Information (Text S1). All glassware was cleaned with a laboratory detergent, rinsed with acetone and DI water, and baked at 300 °C for 3 h prior to use. All batch experiments, unless mentioned otherwise, were conducted using pH 7.6 buffer solution containing 5 mM phosphate and 1 mM carbonate, prepared using ultrapure water (18.2 MΩ cm at 25 °C) from a Millipore Milli-Q water purification system. Reaction solutions were contained in amber borosilicate bottles with Teflon-lined caps to which polymer was added at dosage ranging from 5 to 10 mg/L as the amount of active ingredient. Note that all polymer concentrations mentioned in this paper are concentrations as active ingredient. For comparative experiments, 2.25 mg/L (0.05 mM) DMA was added instead of polyDADMAC. A stock solution of dissolved ozone with concentrations ranging from 16 to 20 mg/L (0.33–0.42 mM) was prepared in a 500-mL gas-washing cylinder at 4 °C, by bubbling gaseous ozone produced from extra dry grade (minimum purity of 99.8%) oxygen using a PCI-Wedeco Model GSO 10 ozone generator (Herford, Germany) through DI water. This freshly prepared ozone stock was used to achieve initial ozone concentrations ranging from 1 mg/L (0.02 mM) to 10 mg/L (0.21 mM). Experiments were conducted at room temperature (23 ± 1 °C) under mild agitation using a stir bar and each bottle represented a single data point. All experiments were in triplicate, unless mentioned otherwise. Selected experiments were performed using Fenton's reagent, which was prepared by adding ferrous ammonium sulfate (FAS) and hydrogen peroxide (H₂O₂) in a 1:5 molar ratio. Solution pH was adjusted to 4.6 by HCl and NaOH for optimum production of •OH.²⁷ The solution

containing either 5 mg/L polyDADMAC, 2.25 mg/L DMA, or 6.3 mg/L DADMAC was allowed to react with the Fenton's reagent for 30 min at room temperature.

Analytical Methods. Procedures for DMA and NDMA extraction and analysis were based on previously established methods¹⁵ and are described in detail in the Supporting Information (Text S2). Analytical methods for other compounds including ozone, DADMAC monomer, bromide, nitrite, nitrate, formaldehyde, and dimethylformamide (DMF) are also described in Supporting Information (Text S3). PolyDADMAC degradation was monitored through a Fourier transform infrared spectrometer using an attenuated total reflection mode (FT-IR/ATR). IR-ATR spectra were recorded from 4000 to 400 cm⁻¹ using a Bruker Equinox 55 Fourier transform (FT-IR) spectrometer (Bruker Optics Inc., Billerica, MA). The spectrometer was equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector (Infrared Associates, Stuart, FL) and an in-compartment horizontal ATR unit (Gateway, Specac Inc., Woodstock, GA) with trough top plate and six-reflection trapezoidal ZnSe ($n_D = 2.43$ at $\lambda = 5 \mu\text{m}$) ATR crystal (MacroOptica, Moscow, Russia).

RESULTS AND DISCUSSION

NDMA Formation from Ozonation of PolyDADMAC and Other Polymers. Preliminary ozonation experiments were conducted on three common water treatment polymers, polyDADMAC, polyamine, and cationic polyacrylamide (PAM). The polymer structures and ozonation results are discussed in detail in Text S4 and Figures S1 and S2 of the Supporting Information. Overall, ozonation of polyDADMAC yielded 3 and 4 times more NDMA compared to PAM and polyamine, respectively. PolyDADMAC also showed considerably more DMA released upon ozonation, suggesting that polyDADMAC is more susceptible to oxidation by ozone than the other two polymers. On the basis of the highest risk to form NDMA among tested polymers, polyDADMAC was chosen for further mechanistic evaluation on NDMA formation upon ozonation.

Effect of pH on Ozonation of PolyDADMAC and DMA. Effects of pH on NDMA formation and DMA release (indicated by the measured [DMA]_{final} at the end of ozonation) during ozonation of polyDADMAC are shown in Figure 1A,B. Comparative pH-effect studies were also conducted for DMA, as shown in Figure 1C,D. Note that, since the experiments were carried out in batch reactors and ozone decayed more rapidly at higher pH, the CT (i.e., ozone concentration × contact time) values²⁸ were different at different pHs, even for the same exposure time. For example, Figure S3 of the Supporting Information compares the kinetics of ozone decay at pH 5 and 9 in solutions containing polyDADMAC. The CT values (Table S1, Supporting Information) were calculated by integrating the area under each curve of the CT plot. Then, the experimental results of NDMA and DMA concentrations measured at each pH were normalized by the corresponding CT value and plotted in Figure 1. Similar data treatment was conducted for the results of ozonation of DMA (ozone decay curves not shown). For the ozonation of polyDADMAC, NDMA formation and DMA release after ozonation both increased as pH was increased. For the ozonation of DMA, NDMA formation also increased as pH was increased (Figure 1C). Figure 1D shows that consumption of DMA by ozone increased with increasing pH; this is expected since ozone reacts predominantly with the unprotonated form of DMA²⁸ and thus more DMA is consumed at higher pH. Taking this into account, it is likely that the [DMA]_{final} values in Figure 1B underestimated

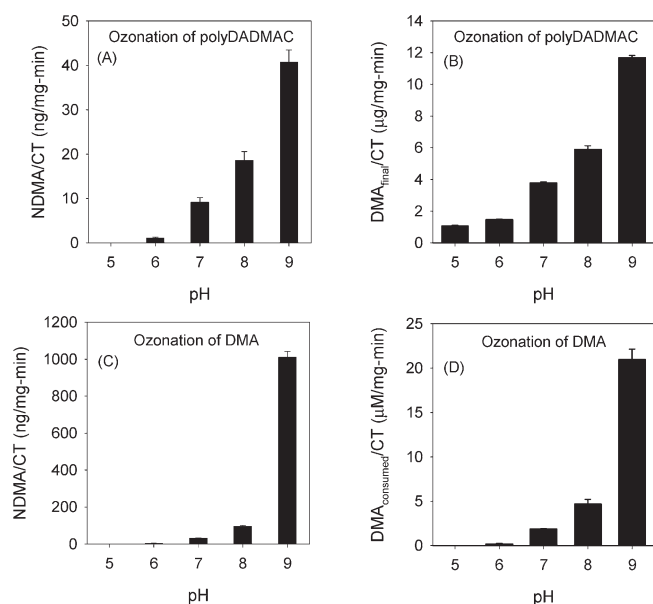


Figure 1. Effect of pH on (A) NDMA formed for 5 mg/L polyDADMAC solution, (B) final DMA remaining for 5 mg/L polyDADMAC solution, (C) NDMA formed for 50 μM (2.25 mg/L) DMA solution, and (D) DMA consumed for 50 μM (2.25 mg/L) DMA solution upon ozonation. Initial ozone concentration was 0.1 mM (4.8 mg/L). (Error bars represent one standard deviation of the means.)

the actual amount of DMA released from polyDADMAC, especially at higher pHs.

Significance of Hydroxyl Radicals in Degradation of PolyDADMAC. Ozone decomposes in water to produce a range of radical species including highly reactive hydroxyl radicals ($\cdot\text{OH}$)²⁹ that can also react with the polymers. When 0.1 mM of the well-known $\cdot\text{OH}$ scavenger *tert*-butanol (TBA)²⁸ was added to the polyDADMAC solution for ozonation, the amount of $[\text{DMA}]_{\text{final}}$ after ozonation was decreased by more than 40% and the NDMA formation was decreased by more than 70% (Figure S4, Supporting Information). These results imply that $\cdot\text{OH}$ play an important role in polyDADMAC degradation to release DMA and subsequent NDMA formation. These results are also consistent with results shown in Figure 1, since at higher pH more $\cdot\text{OH}$ are formed due to faster ozone decay.

To further verify the role of $\cdot\text{OH}$, reactions were conducted with Fenton's reagent, an alternative way to induce $\cdot\text{OH}$ exposure. Consistently, both polyDADMAC and DADMAC monomer showed a significant decrease in DADMAC concentration and release of a large amount of DMA after reaction with Fenton's reagent (Figure S5, Supporting Information). PolyDADMAC solution initially contained only a small amount (0.07 μM) of residual DADMAC, and no significant amount of DADMAC was found after the reaction with Fenton's reagent (Figure S5A, Supporting Information). In a control experiment performed with hydrogen peroxide alone or with ferrous ammonium sulfate alone, degradation of DADMAC or polyDADMAC or release of DMA from either source was not observed. Also, no detectable amount of NDMA was found when DADMAC and polyDADMAC were exposed to Fenton's reagent. Since DADMAC and polyDADMAC share the same quaternary ammonium ring moiety, the above results suggest that $\cdot\text{OH}$ attack the quaternary ammonium site of polyDADMAC to release DMA.

Effect of Initial Ozone Concentration. The amount of NDMA formed and DMA measured after ozonation with varying initial ozone concentrations is shown in Figure 2 for polyDADMAC and

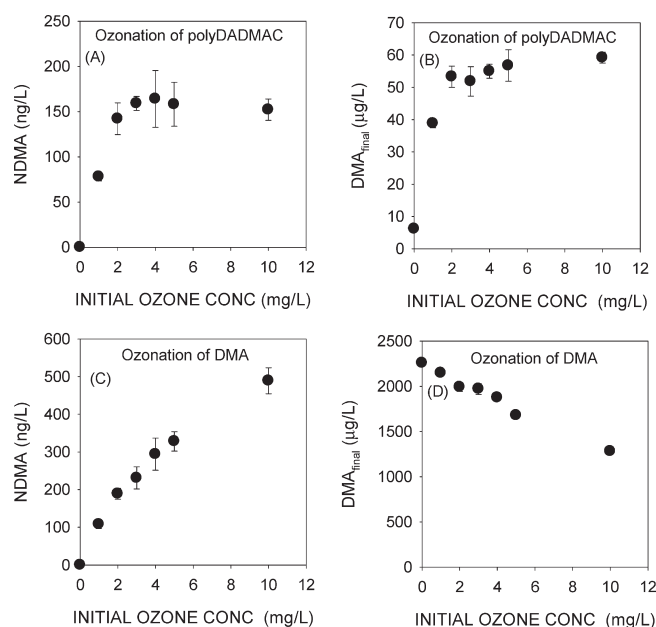


Figure 2. Effect of initial ozone concentrations on (A) NDMA formed for 5 mg/L polyDADMAC solution, (B) final DMA remaining for 5 mg/L polyDADMAC solution, (C) NDMA formed for 50 μM (2.25 mg/L) DMA solution, and (D) final DMA remaining for 50 μM (2.25 mg/L) DMA solution upon ozonation. Initial ozone concentrations varied from 1 to 10 mg/L (0.02–0.21 mM) at pH 7.6 in batch reactors. (Error bars represent one standard deviation of the means.)

DMA. NDMA formation from polyDADMAC increased sharply up to 2 mg/L of initial ozone concentration after which the formation plateaued (Figure 2A). Similar trend was observed for $[\text{DMA}]_{\text{final}}$ for which higher initial ozone concentrations resulted in only small increase in $[\text{DMA}]_{\text{final}}$; $[\text{DMA}]_{\text{final}}$ plateaued at 55–60 μg/L (Figure 2B). In contrast, during ozonation of DMA, NDMA formation continuously increased (Figure 2C) and $[\text{DMA}]_{\text{final}}$ continuously decreased (Figure 2D) with increasing initial ozone concentration.

When polyDADMAC was exposed to different initial concentrations of Fenton's reagent ($[\text{FAS}]:[\text{H}_2\text{O}_2] = 10:50, 20:100, 40:200, 100:500, \text{ or } 200:1000 \mu\text{M}/\mu\text{M}$), $[\text{DMA}]_{\text{final}}$ also plateaued near 50 μg/L (i.e., 1.1 μM) at higher $\cdot\text{OH}$ exposure (Figure S6, Supporting Information). Note that the initial concentration of polyDADMAC at 5 mg/L as active ingredient contained approximately 30 μM of monomeric unit and, hence, could release a maximum of 30 μM (1.35 mg/L) of DMA. This large difference implies that only a small fraction (approximately 4%) of DMA was observed from polyDADMAC after oxidation by ozone and Fenton's reagent. This might have resulted because some of the DMA moieties on polyDADMAC were not accessible to oxidants such as $\cdot\text{OH}$ and ozone due to polymer folding (see further discussion below). The low $[\text{DMA}]_{\text{final}}$ value may also partly be due to the fact that some of the DMA released was oxidized to form other products or even mineralized, especially under excessive oxidant exposure condition,²² since $[\text{DMA}]_{\text{final}}$ is the overall result of $[\text{DMA}]_{\text{initial}} + [\text{DMA}]_{\text{released}} - [\text{DMA}]_{\text{consumption by oxidant}}$. It is therefore noteworthy that the initial ozone to DMA ratio at higher ozone dosage was 20–50 times higher for polyDADMAC ozonation (Figure 2B) than for DMA ozonation (Figure 2D), and thus, there was possibly greater consumption of released DMA in the former case.

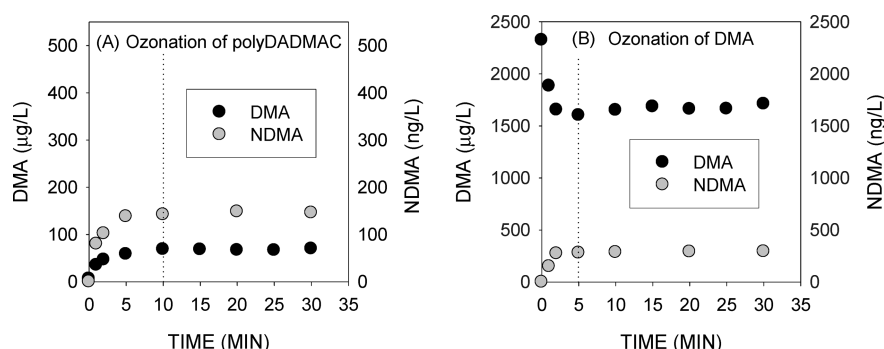


Figure 3. (A) Kinetics of NDMA formation and final DMA remaining for 5 mg/L polyDADMAC solution upon ozonation at pH 7.6 and (B) kinetics of NDMA formation and final DMA remaining for 50 μ M (2.25 mg/L) DMA solution upon ozonation at pH 7.6. The initial ozone concentration was 0.1 mM (4.8 mg/L). The dotted line represents depletion of ozone under the experimental conditions.

Kinetics of NDMA Formation and DMA Release from Ozonation of PolyDADMAC. As shown in Figure 3A, both $[DMA]_{final}$ and NDMA formation increased until about 10 min and then plateaued during the course of polyDADMAC ozonation. The 10 min time correlated well with the ozone depletion time in polyDADMAC solution (Figure S7A, Supporting Information). Hence, the presence of ozone is termed responsible not only for DMA release, but also for the majority of the NDMA formation. These results were similar to those observed during ozonation of DMA (Figure 3B), which ozone depleted within 5 min (Figure S7B, Supporting Information). Most of the DMA degradation and NDMA formation also occurred during the period of ozone depletion. These results indicate that the presence of ozone is essential, not only for DMA release from polyDADMAC but also for the formation of NDMA from DMA. To understand the reaction of NDMA with ozone under conditions employed in this study, an experiment was performed with 300 ng/L of NDMA exposed to 0.1 mM of ozone for 30 min in a batch mode at pH 7.6. After the end of the reaction, no significant degradation of NDMA (278 ± 6 ng/L) was observed, confirming its low reactivity with ozone.³⁰

Polymer Structural Change and Ozonation Product Characterization. Results of FT-IR analysis on polyDADMAC prior to and after ozonation provided insights on the structural changes in the polymer's backbone (Figure 4). Note that a higher polymer dose was employed in these experiments to obtain clear distinction of signals on FT-IR, and the CT value was adjusted higher accordingly. After ozonation, FT-IR spectra displayed decreased C–N stretching (1137 cm^{-1}) (Figures 4 and S8, Supporting Information), which is characteristic of quaternary amine group, suggesting ring-opening.¹⁷ The formation of DMA after ozonation was also evident with the appearance of N–H stretch ($3000\text{--}3200\text{ cm}^{-1}$) representative of secondary amine.²¹ The appearance of formaldehyde was clearly seen in the polyDADMAC spectra after ozonation as C=O stretch at 1750 cm^{-1} .²¹ Additionally, the appearance of DMF could be attributed to a strong absorption at 1650 cm^{-1} , representative of C=O and C–N stretches at $1000\text{--}1350\text{ cm}^{-1}$.²¹ Moreover, an increase in CH_3 deformations in the $1300\text{--}1400\text{ cm}^{-1}$ region further confirmed the presence of secondary and tertiary amines.³¹

The amounts of reaction products including NDMA, DMA, DMF, formaldehyde, DADMAC, nitrite, and nitrate formed in the ozonation of polyDADMAC, DADMAC and DMA at different pHs (5.0, 7.6, and 9.0) are presented in Table 1. Significant amounts of nitrite and formaldehyde were detected. The nitrite concentration increased significantly as the solution pH was increased, confirming that nitrite was one of the major ozonation products of unprotonated

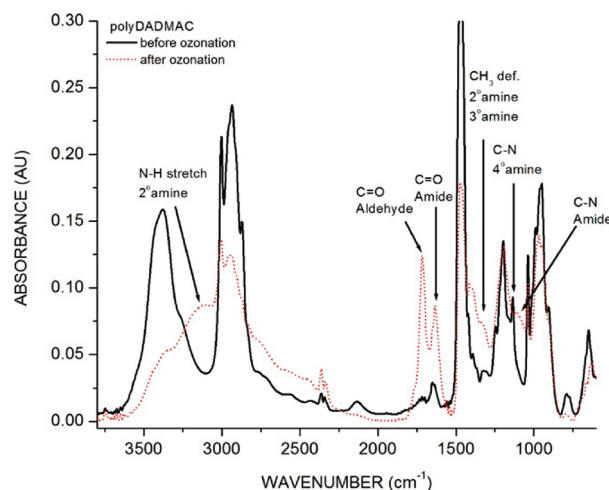


Figure 4. FT-IR spectra for 50 mg/L polyDADMAC solution before and after ozonation ($CT = 150\text{ mg min/L}$) at pH 7.6.

DMA. Among the products quantified, formaldehyde was present at significantly higher concentrations than DMF, nitrite, and NDMA. In contrast, DADMAC was not observed to be a product of ozonation of polyDADMAC. When NDMA yields were compared on the mass basis for polyDADMAC and on the molar basis for DMA and DADMAC, NDMA showed increase in yields with increase in pH. In studies of ozonation of DMA by Andrzejewski et al.,²² the observed NDMA yield was 0.008% for 15 min contact time at pH 7.67 and an O_3/DMA molar ratio of 1.978, while Yang et al.²⁶ observed NDMA/DMA yield of 0.003% with a much smaller O_3/DMA ratio of 0.03. NDMA yield of 0.009% (Table 1) from ozonation of DMA in this study is comparable to the above studies, especially considering that higher NDMA yield is associated with higher O_3/DMA ratio²² (Figure 3C). Other possible ozonation intermediates, such as hydroxylamine,²⁶ were not quantified in this study.

POSSIBLE REACTION MECHANISMS

Mechanism of DMA Release from PolyDADMAC. The above results collectively suggest that $\cdot\text{OH}$ plays a critical role in the degradation of polyDADMAC and release of DMA during ozonation. One of the predominant modes of $\cdot\text{OH}$ attack is H-atom abstraction from a C–H bond.³² For organic macromolecules, it has been shown that H-atom abstraction by $\cdot\text{OH}$ from C–H bonds in

Table 1. Ozonation Products for 5 mg/L polyDADMAC, 50 μ M (6.3 mg/L) DADMAC, and 50 μ M (2.25 mg/L) DMA at pH 5.0, 7.6, and 9.0 with Initial Ozone Dose of 0.1 mM^a

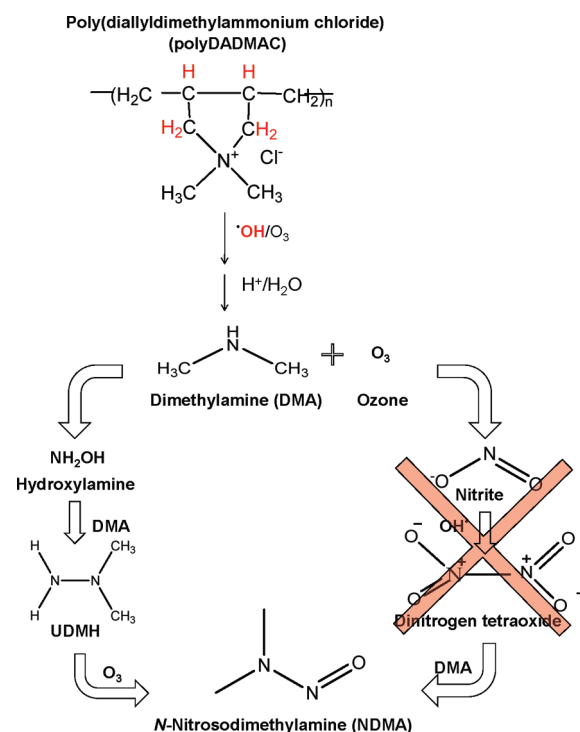
sample	DMA conc (μ M)		DMC conc (μ M)		DMF conc (μ M)	nitrite conc (μ M)	FAlD conc (μ M)	NDMA	
	initial	final	initial	final				conc (ng/L)	yield (%)
pDAD									
pH 5.0	0.10	1.71	0.07	0.00	0.05	0.01	4.99	ND	0.000
pH 7.6	0.10	1.44	0.07	0.00	0.04	0.09	6.00	152	0.003
pH 9.0	0.10	0.77	0.07	0.00	0.04	0.18	4.05	225	0.005
DMC									
pH 5.0	0.04	0.19	50	12.35	0.05	0.01	25.46	ND	0.000
pH 7.6	0.04	0.94	50	13.50	0.04	0.08	41.56	167	0.004
pH 9.0	0.04	1.42	50	16.30	0.04	0.16	16.53	237	0.006
DMA									
pH 5.0	50.00	40.72	NA	NA	0.03	0.05	12.43	ND	0.000
pH 7.6	50.00	34.87	NA	NA	0.04	0.20	5.35	354	0.009
pH 9.0	50.00	29.99	NA	NA	0.04	0.80	11.77	1480	0.040

^apDAD- polyDADMAC; DMC- DADMAC; DMF- dimethylformamide; FAlD- formaldehyde; NA- not applicable; ND- nondetectable. Initial refers to the initial concentration before ozonation and final to the final concentration after ozonation. Method detection limit for NDMA = 20 ng/L. NDMA yield is calculated on mass basis for initial concentration (5 mg/L) of polyDADMAC and on molar basis for initial concentration of DADMAC and DMA (50 μ M).

the backbone is a rare event compared to reaction with the side chains.³² Hence, the quaternary ammonium rings in the pendent position in polyDADMAC would be the primary sites for the radical attacks. Comparative ozonation experiments with different molecular weights of polyDADMAC found no significant difference in NDMA formation or DMA release (Text S5 and Figure S9, Supporting Information). This result further supports that the backbone and chain ends of polyDADMAC did not play an important role in the polymer degradation to release DMA. It is hypothesized that \cdot OH preferentially attacks the β -carbon of quaternary ammonium ring, resulting in H-abstraction and subsequent C–N bond cleavage and formation of tertiary amine. Additional H-abstraction at β -carbon of tertiary amine would result in the release of secondary amine (Figure 5). The presence of electron-donating alkyl groups (i.e., polymer backbone) is believed to render H-abstraction from β -carbon of quaternary amine rings in polyDADMAC more feasible.

Mechanism of NDMA Formation from PolyDADMAC and DMA. Results from this study show that NDMA formation from polyDADMAC was strongly correlated to DMA release during ozonation, indicating that NDMA formation may be the result of ozonation of released DMA from polyDADMAC. Andrzejewski et al.²² proposed that the presence of nitrite and formaldehyde (both are ozonation products of DMA) can catalyze NDMA formation at circumneutral pH during ozonation of DMA. However, this pathway cannot explain the observed increased yield on NDMA with increasing pH (Table 1) since such reaction would have lower NDMA yield at higher pH.²⁵ Furthermore, our kinetic study results along with ozonation product characterization contradict this hypothesis. After ozone depletion, formaldehyde, nitrite, and DMA all remained in the solution (Table 1), but NDMA formation ceased (Figures 3 and S7, Supporting Information).

It has been suggested that enhanced nitrosation may contribute to NDMA formation during ozonation of DMA because of transformation of nitrite to the more potent nitrosating agent dinitrogen tetroxide under the oxidation conditions.²⁶ To evaluate this pathway, experiments were performed with 20 mM nitrite and 20 mM DMA at pH 4.6. A twice higher amount of NDMA (3.54 \pm 0.06 μ M) was formed with the addition of Fenton's reagent (50 μ M FAS and 200 μ M H₂O₂) compared to nitrite and DMA only (1.62 \pm 0.03 μ M NDMA formed). Since

**Figure 5.** Proposed reaction mechanism for NDMA formation from ozonation of polyDADMAC and DMA.

the acidic pH 4.6 is favorable for nitrosation, the higher yield of NDMA in the presence of Fenton's reagent seems to indicate a role of \cdot OH in transforming nitrite to a stronger nitrosating agent such as N₂O₄. However, no increase in NDMA formation was observed when nitrite was added during ozonation of DMA (at pH 7.6, Table 2), indicating that contribution of the nitrosation pathway is minimal and cannot explain the observed NDMA yield for the conditions employed in this study.

There may be the possibility of other ozonation products of DMA not quantified in this study, such as hydroxylamine,²⁶ reacting with DMA to form NDMA. When 50 μ M hydroxylamine and 50 μ M DMA were reacted at pH 7.6 for 30 min in the

Table 2. Assessing NDMA Formation Pathways from DMA during Ozonation^a

samples	NDMA (ng/L)	¹⁵ N-NDMA (ng/L)	¹⁵ N, ¹⁵ N-NDMA (ng/L)
DMA + ozone	240 ± 29	ND	ND
DMA + NH ₂ OH	ND	ND	ND
DMA + NH ₂ OH + ozone	660 ± 27	ND	ND
¹⁵ N-DMA + ozone	ND	ND	194 ± 6
¹⁵ N-DMA + NH ₂ OH + ozone	ND	500 ± 13	106 ± 4
DMA + NO ₂ ⁻ + ozone	190 ± 15	ND	ND
DMA + ¹⁵ N-NO ₂ ⁻ + ozone	191 ± 6	ND	ND
UDMH + dissolved oxygen	5,200 ± 850	ND	ND
UDMH + ozone	1,500,000 ± 80,000	ND	ND

^a Conditions: 50 μM DMA, 10 μM NO₂⁻, 10 μM NH₂OH, 100 μM UDMH, 100 μM ozone, pH 7.6 with a reaction time of 30 minutes. ND, nondetectable. Method detection limit for NDMA = 20 ng/L. Values are mean ± standard deviation (*n* = 2).

absence of ozone, NDMA formation was below the method detection limit of 20 ng/L (Table 2), indicating that this pathway is insignificant without ozone. Yet, when 10 μM hydroxylamine was added externally during ozonation of 50 μM DMA, NDMA yield was tripled (Table 2), indicating that the presence of ozone or ROS species generated by ozone was critical. When the isotope-labeled ¹⁵N-DMA was reacted with hydroxylamine in the presence of ozone, significant formation of ¹⁵N-NDMA was observed (Table 2), suggesting that hydroxylamine contributes one nitrogen atom in forming NDMA. In contrast, when labeled nitrite was added additionally during ozonation of DMA, no labeled NDMA was formed. When ¹⁵N-DMA was ozonated, NDMA with both nitrogens labeled was formed, suggesting that ¹⁵N-hydroxylamine intermediate may be formed and then participates in NDMA formation by reacting with another ¹⁵N-DMA molecule. Furthermore, when UDMH, a proposed intermediate of reaction between hydroxylamine and DMA,²⁶ was ozonated, it formed 3 orders of magnitude more NDMA than in the absence of ozone (Table 2). The above results coupled with the kinetic study results presented earlier indicate that the presence of ozone is critical during reaction of hydroxylamine with DMA to yield NDMA. Figure 5 shows the proposed mechanism of NDMA formation from ozonation of polyDADMAC and DMA.

Environmental Significance. The concentrations used in this study were significantly higher than the optimum dosages of polymer required for coagulation (~1 mg/L as active ingredient)³³ and recommended ozone dosage for disinfection (*CT* = ~ 2–10 mg min/L at 20 °C for 0.5–3 log inactivation of *C. parvum* oocysts)³⁴ to ensure that any NDMA formation that occurred would be detectable. It has to be noted that only trace levels of polyDADMAC will persist in water after coagulation/flocculation, sedimentation, and filtration processes and is unlikely to come in contact with disinfectant at concentrations tested in this study. Also, dissolved organic carbon and common radical quenchers²⁸ found in real water matrices are expected to consume ozone much faster than its reaction with polyDADMAC alone. On the basis of the above factors, the risk of NDMA formation from ozonation of polyDADMAC in drinking water treatment plants appears minimal. However, a significant issue from the use of polyDADMAC and ozonation could be the release of DMA, which could react with chloramines to form substantially more NDMA than would be formed by chloramines's reaction with polyDADMAC alone. In addition, in wastewater treatment plants, where an order of magnitude higher dosage of polyDADMAC for

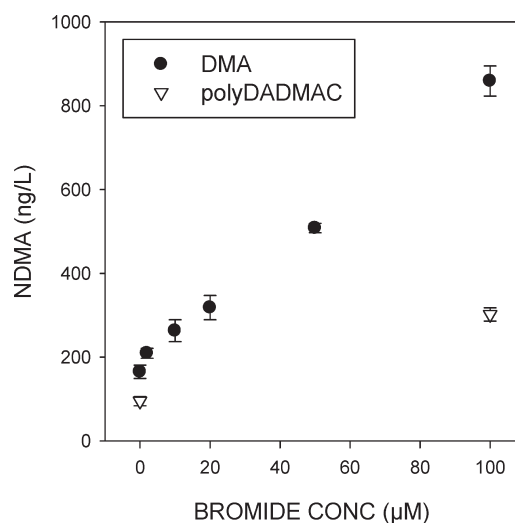


Figure 6. Effect of bromide on NDMA formation from ozonation of DMA and polyDADMAC. DMA (50 μM) or polyDADMAC (5 mg/L) were reacted with 4.8 mg/L (100 μM) of ozone at pH 7.6 for 30 min. (Error bars represent one standard deviation of the means.)

sludge thickening operations is not uncommon, practicing tertiary treatment of ozone disinfection can potentially form significant amounts of NDMA.

Though DMA concentrations used in this study were higher than its typical detection (1–3 μg/L) in surface water,³⁵ the risk of NDMA formation from ozonation of polyDADMAC and DMA present in water could potentially be enhanced by constituents such as hydroxylamine or bromide in real water matrices, as shown by this study. Our preliminary experiments indicate that bromide may significantly increase the yield of NDMA formation during ozonation of polyDADMAC and DMA (Figure 6); for example, three times more NDMA was formed when 100 μM of bromide was added during ozonation of 50 μM DMA and 5 mg/L polyDADMAC. It may be possible that HOBr, resulting from the reaction of bromide with ozone, may be responsible for this observed enhancement effect;²⁴ however, the bromide effect is not important in the results presented in this paper, since bromide concentration in polyDADMAC solutions was found to be below the detection limit (2 μM). However, the bromide enhancement effect will be relevant in certain real water matrices and merits further investigation.

In brief, avoiding direct contact of ozone with polyDADMAC will reduce the risk of NDMA formation during water and wastewater treatment. In addition, suppressing solution pH will help reduce DMA release from polyDADMAC. Lowering pH will also reduce NDMA formation risk, because ozone and hydroxylamine react only with unprotonated DMA. Treatment plants employing advanced oxidation processes (AOPs), such as Fenton's reagent, can also be at increased risk of NDMA formation due to generation of •OH. To minimize NDMA formation risk at such treatment processes, it is advised to remove NDMA precursors such as polyDADMAC and DMA as much as possible before the oxidation step.

■ ASSOCIATED CONTENT

S Supporting Information. Texts S1–S4, Figures S1–S9, and Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ DISCLOSURE

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the Georgia Tech or National Science Foundation.

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