

N-nitrosodimethylamine formation during treatment with strong oxidants of dimethylamine containing water

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Abstract The aim of the paper is the evaluation of the possibility of NDMA formation, as a result of strong oxidants reacting with DMA. Summarized results of investigations on N-nitrosodimethylamine formation as a result of dimethylamine reactions with chlorine dioxide, ozone and hydrogen peroxide are presented. Preliminary results of experiments on NDMA formation as a result of DMA reactions with permanganate are also shown.

The experiments on dimethylamine reactions with chlorine dioxide, hydrogen peroxide and permanganate were carried out at room temperature under static conditions. Ozonation experiments were carried out at room temperature in a semi-continuous mode. Water samples from all experiments described above were collected during the experiment itself and subsequently analyzed with HPLC-IE with UV-Vis detector at 230 nm. NDMA formation was also confirmed by GC-LRMS.

NDMA forms as a result of chlorine dioxide, ozone, hydrogen peroxide or permanganate reactions with dimethylamine, both in the presence as well as in the absence of ammonia ions. The presence of nitrites and nitrates in a post-reaction mixture suggests that NDMA are formed as the result of DMA reactions with nitrites. Thus the mechanism of NDMA formation with these oxidants is different than that described by Mitch *et al.* and Choi *et al.*

The results also showed a conversion ratio of DMA to NDMA of even up to a single percent (with relation to amines), a simultaneous decrease of NDMA formation potential with a decrease of pH, however, in the case of chlorine dioxide application, a maximum conversion ratio was observed, as well the NDMA formation potential is strongly dependent on the oxidant/DMA ratio.

Keywords Chlorine dioxide; disinfection; hydrogen peroxide; NDMA; N-nitrosodimethylamine; ozone; permanganate; strong oxidants; water treatment

Introduction

Secondary nitrosamines, mainly short chain ones, like N-nitrosodimethylamine (NDMA), N-nitrosomethylethylamine (NMEA) and N-nitrosodiethylamine (NDEA), are highly mutagenic compounds, suspected of carcinogenic activity to the human body.

In 2002, Mitch and Sedlak (2002) and Choi and Valentine (2002) reported that NDMA is formed during the disinfection with chlorine of water or wastewater treatment plant effluents containing dimethylamine (DMA) and ammonia. The mechanism proposed by Choi and Valentine (2002) and Mitch and Sedlak (2002) is based on chlorination, leading to the formation of 1,1-dimethylhydrazine, known as unsymmetrical dimethylhydrazine (UDMH). Furthermore, 1,1-dimethylhydrazine undergoes oxidation to yield many different by-products, including NDMA. The proposed mechanism was subsequently modified by Schreiber *et al.* The authors emphasized the role of dichloroamine and dissolved oxygen in NDMA formation, due to the reaction of DMA with chlorine in the presence of ammonia ions (Schreiber and Mitch, 2006).

The problem of NDMA formation, due to the reaction of DMA with nitrite ions, was analyzed by Keefer and Roller (1973) and Lv *et al.* (2007). Keefer *et al.* have shown that

formaldehyde may catalyze the reaction of secondary amines with nitrites, leading to NDMA formation even at $7 < \text{pH} < 11$. The yield of this reaction, however, decreases with increased pH (Keefer and Roller, 1973). The reactivity of DMA with nitrite ions was also theoretically assessed by Chun Lin Lv *et al.* The reaction of DMA with nitrite ions was demonstrated, but only in the presence of carbon dioxide, which may catalyze the reaction (Lv *et al.*, 2007). The direct nitrosation reaction was also discussed previously by Choi and Valentine (2002) and Mitch and Sedlak (2002). Mitch *et al.* rejected the possibility of NDMA formation in the reaction of DMA with nitrite ions, due to a low reaction rate constant, which would lead to the formation of less than $10^{-21} \text{ g l}^{-1}$ of NDMA after 24 h of reaction time at $\text{pH} = 7$, for $100 \mu\text{M}$ of DMA and $100 \mu\text{M}$ of nitrite ions as the initial concentrations of substrates (Mitch and Sedlak, 2002). However, Choi *et al.* found out that the yield of the NDMA formation during reaction of DMA with chloramine is barely 6 times higher than that for reaction of DMA with nitrite ions at $\text{pH} = 7$ and 24 contact time (Choi and Valentine, 2002). In 2003, Choi *et al.* proposed another mechanism of NDMA formation, during the reaction of dimethylamine with chlorine. According to the proposed mechanism, HOCl reacts with nitrites present in water, to form a very reactive nitrosating intermediate, i.e. dinitrogen tetroxide (N_2O_4), which subsequently reacts with dimethylamine to form NDMA (Choi and Valentine, 2003).

Andrzejewski *et al.* (2005) indicated the possibility of NMEA and NDEA formation as a result of respective amine reactions with chlorine in the presence of ammonia ions. During further investigations, Andrzejewski *et al.* proved that NDMA could be formed during reaction of DMA with chlorine dioxide (Andrzejewski *et al.*, 2005), ozone (Andrzejewski *et al.*, 2007) and hydrogen peroxide (Andrzejewski and Kulik, 2007). The mechanism of NDMA formation with chlorine dioxide, ozone and hydrogen peroxide reaction with DMA is different from that postulated by Choi and Valentine (2002) and Mitch and Sedlak (2002). Based on the nitrosamine formation pathway proposed by Keefer and Roller (1973), Andrzejewski *et al.* assume that NDMA, a product of ozone reaction with DMA, is formed as a result of a multi-step reaction. In the first stage, formaldehyde and nitrites are formed, which subsequently react with DMA, forming NDMA (Andrzejewski *et al.*, 2007).

Oxidation of selected secondary and tertiary amines with ozone and chlorine dioxide was also investigated by Lee *et al.* (2007). Compounds that contribute to the formation of NDMA are mainly: monochloramine and organic compounds, containing nitrogen such as DMA, or tertiary amines, containing dimethyl functional groups. The other N-compounds, such as proteins and aminoacids, do not form significant concentrations of NDMA (Mitch *et al.*, 2003). Gerecke *et al.* reported that natural organic matter, which is also a precursor of NDMA, has a significant influence on NDMA formation (Gerecke and Sedlak, 2003).

The aim of the paper is the evaluation of the possibility of NDMA formation, as the result of strong oxidants reacting with DMA. Summarized results of investigations on N-nitrosodimethylamine formation as a result of dimethylamine reactions with chlorine dioxide, ozone and hydrogen peroxide are presented. Preliminary results of experiments on NDMA formation as the result of DMA reactions with permanganate are also shown.

Materials and methods

Materials and chemicals

All chemicals used, obtained from Fluka, were of reagent grade or analytical grade, when available, and were used without further purification. Stock solutions were prepared in high quality pure deionized water (Millipore). Reaction solutions were prepared by spiking of high quality pure deionized water (Millipore) or nearly iron-free ground water

with DMA (40%). The removal of iron from the natural ground water was done by aeration and filtration through an active sand filter. As a result, the average concentration of Fe in the ground water did not exceed 0.05 mg l^{-1} . The initial concentration of DMA in reaction solutions were from 5 to 400 mg l^{-1} .

Tert-Butyl alcohol (*t*BuOH, >99.8%) was used as a hydroxyl radical scavenger in some experiments. The pure water samples spiked with DMA were buffered, before oxidation, at desired pH by adding Na_2HPO_4 and/or NaH_2PO_4 aqueous solutions. The natural ground water samples spiked with respective secondary amine were treated without buffering of solution. The pH of reaction solutions was adjusted using aqueous solutions of H_3PO_4 and NaOH.

Experimental procedures

The ozonation of DMA experiments were carried out at room temperature (20°C) in a semi-continuous mode. 400 ml of model solution was transferred to the contact column, recirculated and continuously treated with ozone for 1 h. Ozone was generated from pure oxygen and introduced to the reactor through a ceramic sparger. Total doses of ozone ranged from 30 to $200 \text{ mg O}_3 \text{ l}^{-1}$ while O_3/DMA ratio ranged from 0.01 to 4.3 (M/M). The pH of the buffered DMA solution ranged from 7 to 11. Samples of the reaction solution were collected every 15 minutes and quenched with $0.025 \text{ M Na}_2\text{SO}_3$ (>98%, Fluka) in order to dissipate any residual ozone (Andrzejewski *et al.*, 2007).

Experiments on DMA oxidation by chlorine dioxide as well as catalyzed and non-catalyzed hydrogen peroxide were carried out under batch conditions at ambient temperature ($20 \pm 1^\circ\text{C}$). 0.51 l (hydrogen peroxide application) or 0.25 l (chlorine dioxide application) of reaction solution were treated in glass reactors with continuous agitation for a period of 24–720 hours. During these experiments, the oxidant/DMA ratios were ranged from 0.46 to 2.6 [M/M] and initial DMA concentration from ranged from 0.11 mM to 1.18 mM (for chlorine dioxide) and oxidant/DMA ratios were ranged from 5.0 to 100 (M/M) initial DMA concentration ranged from 0.05 mM to 2.21 mM (for hydrogen peroxide), respectively. The pH of the buffered DMA solution ranged from 5.5 to 9.5 for the chlorine dioxide application and from 5.5 to 11 for hydrogen peroxide application, respectively. Samples of oxidized solution were withdrawn at regular interval times and reaction was terminated by addition of anhydrous sodium sulfite (Na_2SO_3 , > 98%) (Andrzejewski *et al.*, 2005; Andrzejewski and Kulik, 2007).

Preliminary experiments on DMA oxidation with permanganate were also conducted. The main aim of this preliminary research stage was to verify whether NDMA is formed as a result of permanganate reactions with DMA. Quantitative analysis was also carried out to assess the concentration of NDMA and other important by-products formed, such as formic acid and nitrites. The experiments were performed according to the following procedure, similar to one developed for oxidation of secondary amines by chlorine dioxide together with catalyzed and non-catalyzed hydrogen peroxide (Andrzejewski *et al.*, 2005; Andrzejewski and Kulik, 2007). 0.25 l of reaction solution was treated in glass reactors with permanent agitation for period of 168 hours. The buffered DMA solution was added first and the reaction was subsequently initiated by addition of a potassium permanganate solution. The initial DMA concentrations varied from 0.14 mM to 1.1 mM and molar ratios of KMnO_4/DMA varied from 1 to 8 [M/M]. The pH of the DMA solution samples was adjusted to 8. Samples of oxidized solution were withdrawn at regular interval times and the reaction was terminated by adding drops of concentrated sodium sulfite solution until the disappearance of the violet solution color. Sodium sulfite solution addition to the post-reaction mixture additionally resulted in the precipitation of manganese dioxide, formed as a result of potassium permanganate reduction. Precipitated manganese dioxide

was removed from the post-reaction mixture by means of 15 min centrifugation and subsequent filtration by filter paper (pore size: 20–25 μm).

Analytical methods

The presence of as well as changes in concentrations of the following compounds were investigated: NDMA (by the HPLC-IE-UV-Vis technique), aldehydes (by the GC-ECD technique developed by Yamada and Somiya (1989)), nitrites and nitrates (by the HPLC-CD technique).

All analytical methods concerning the above-shown compounds as well as apparatus used in these experiments were described in detail in previous papers (Andrzejewski *et al.*, 2005a, b; Andrzejewski and Kulik, 2007; Andrzejewski *et al.*, 2007).

Results and discussion

NDMA as a product of strong oxidants reacting with DMA

Analytical data obtained through the HPLC-IE-UV technique and confirmed by the GC-MS technique clearly show that NDMA is formed as a result of strong oxidants like ozone, chlorine dioxide, hydrogen peroxide and permanganate reacting with DMA. These reactions run both in the presence of as well as in the absence of ammonia ions. No NDMA are formed during the Fenton/Fenton-like oxidation of DMA (Andrzejewski and Kulik, 2007). Formic acid, formaldehyde, nitrites and nitrates are other products identified in post-reaction mixtures of strong oxidants with DMA (Andrzejewski and Kulik, 2007; Andrzejewski *et al.* 2007). Formation of NDMA during ozone and chlorine dioxide reaction with DMA was confirmed by Lee *et al.* (2007).

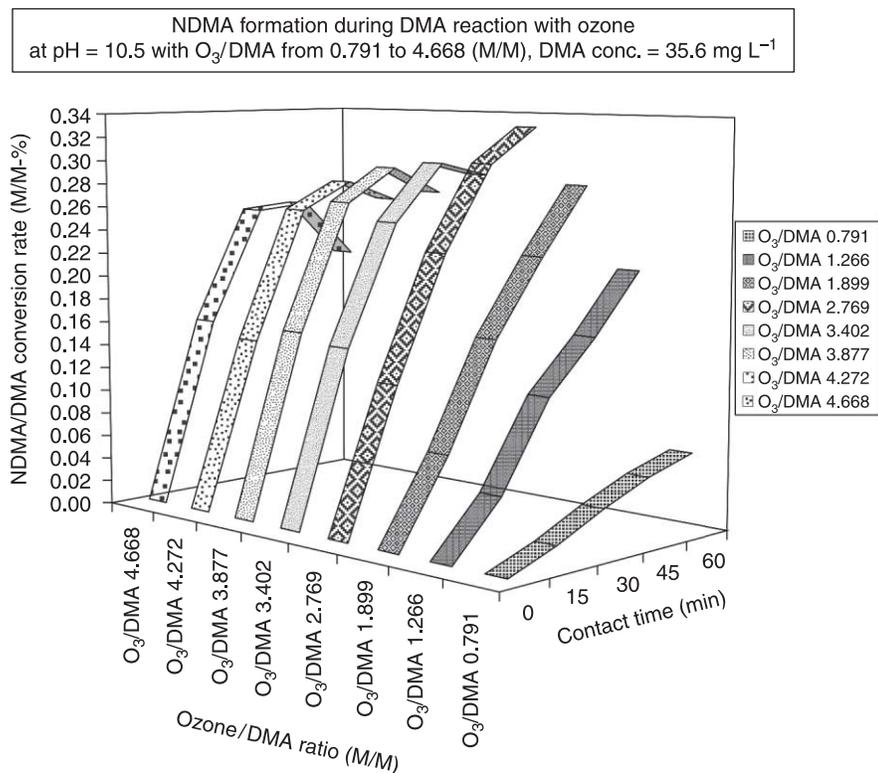


Figure 1 Influence of oxidant/DMA ratio on NDMA formation during DMA ozonation

Influence of pH, oxidant/DMA ratio and contact time on NDMA formation

The results also showed a conversion ratio of DMA to NDMA of even up to a single percent (with relation to amine), and a simultaneous increase of NDMA formation potential with increased pH; in the case of chlorine dioxide application, however, a maximum conversion ratio was observed. Moreover, in the case of hydrogen peroxide application, NDMA formation, as a result of hydrogen peroxide reaction with DMA, was observed only at a pH above 10 (Andrzejewski and Kulik, 2007). The NDMA formation potential is strongly dependent on the oxidant/DMA ratio; influence of the oxidant/DMA ratio on NDMA formation, however, depends on the oxidant applied. Results of the influence of oxidant/DMA ratio on NDMA formation for ozone, chlorine dioxide and hydrogen peroxide, respectively, are presented in Figures 1–3.

In the case of ozone or chlorine dioxide application, maximum conversion ratio was observed, as opposed to hydrogen peroxide application where the NDMA/DMA conversion ratio increases with an increased oxygenate/DMA ratio, up to an oxygenate/DMA ratio of at least one hundred (Andrzejewski and Kulik, 2007).

The mechanism of NDMA formation

The presence of nitrites and nitrates in a post-reaction mixture as well as the fact that reactions run both in the presence and in the absence of ammonia ions, suggests that NDMA are formed as a result of DMA reactions with nitrites. Thus, the mechanism of NDMA formation with these oxygenates is different from that described by Mitch and Sedlak (2002) and Choi and Valentine (2002). Nitrites are formed during the first reaction

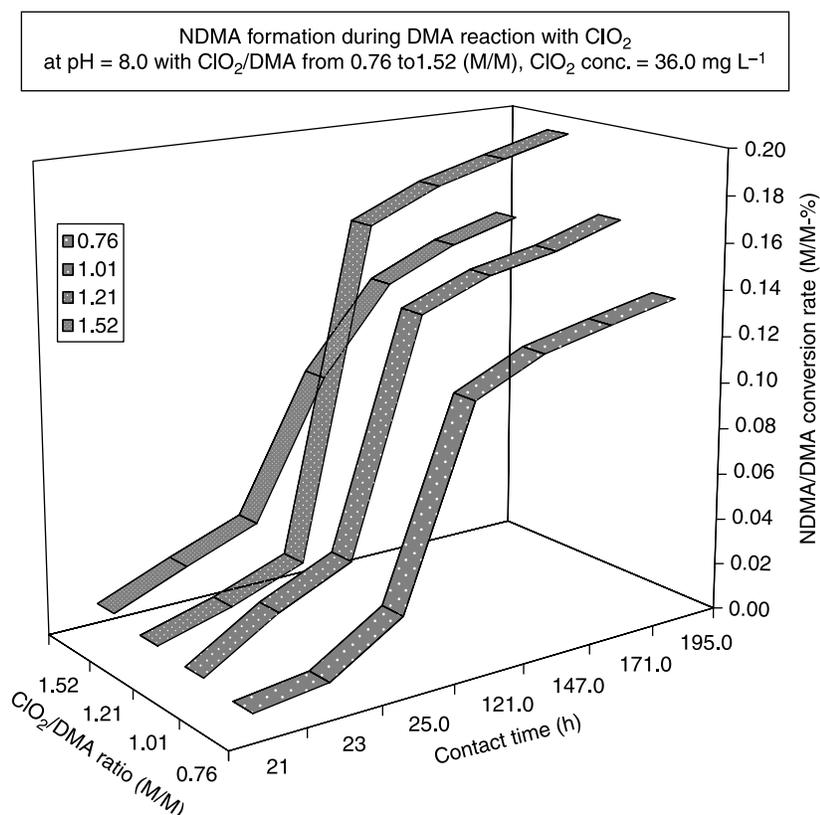


Figure 2 Influence of oxidant/DMA ratio on NDMA formation during DMA reaction with chlorine dioxide

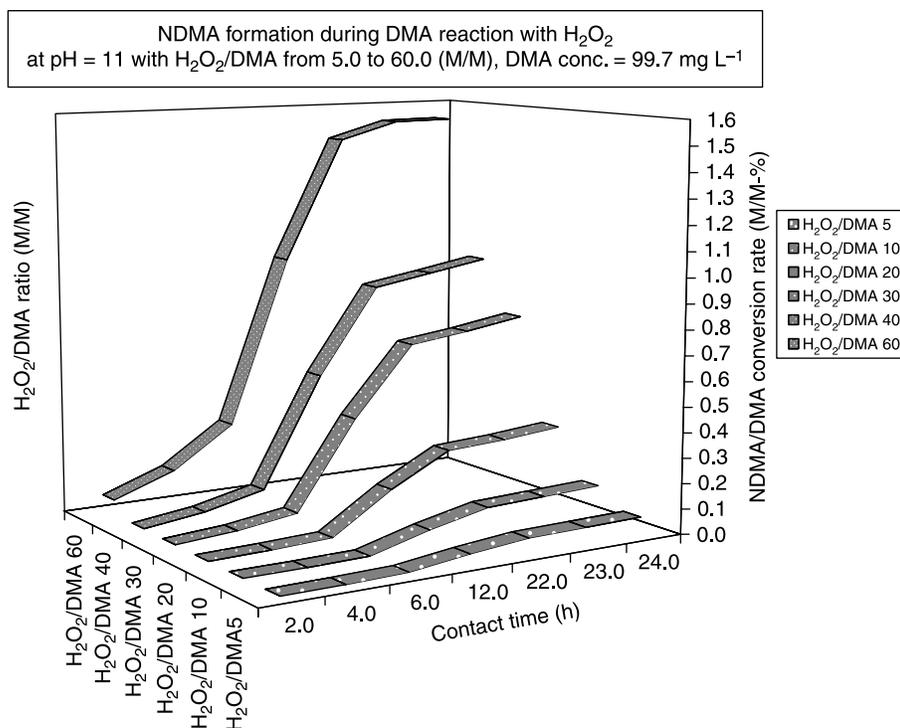


Figure 3 Influence of oxidant/DMA ratio on NDMA formation during DMA reaction with hydrogen peroxide

step, i.e. oxidation of DMA by strong oxidants, both according to a radical mechanism (ozone) as well as a molecular mechanism (hydrogen peroxide). In the second stage of the reaction, nitrites subsequently react with DMA, forming NDMA.

Conclusions

1. The reaction of strong oxidants, such as ozone, chlorine dioxide, hydrogen peroxide and permanganate, with DMA leads to the formation of N-nitrosodimethylamine.
2. The results showed a relatively low conversion ratio of DMA to NDMA. A simultaneous decrease of NDMA formation potential with decreased pH, however, as in the case of chlorine dioxide application, demonstrated a maximum conversion ratio. As well, the NDMA formation potential is strongly dependent on the oxygenate/DMA ratio.
3. NDMA is formed as a result of a multi-step reaction. In the first stage, nitrites are formed. These subsequently react with DMA, forming NDMA.

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