



Review

Kinetics and mechanism of formation and destruction of *N*-nitrosodimethylamine in water – A review

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ARTICLE INFO

Article history:

Received 16 July 2011

Received in revised form 20 November 2011

Accepted 22 November 2011

Available online 30 November 2011

Keywords:

Amines

Rates

Oxygen-transfer

Remediation

Ferrate

ABSTRACT

This paper presents an overview on the current knowledge of the mechanism of formation of *N*-nitrosodimethylamine (NDMA) in water. The kinetics of the reactions of NDMA precursors (amines and dimethylsulfamide) with disinfectants (ClO_2 , O_3 , $\cdot\text{OH}$, and Fe(VI)) is presented. The second-order rate constants were determined as 10^{-2} – 10^8 , 10^{-1} – 10^9 , 10^{-1} – 10^6 , and 10^8 – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for reactions with ClO_2 , O_3 , $\cdot\text{OH}$, and Fe(VI) , respectively, at pH 7.0. The rate constants for reactions with most of the secondary and tertiary amines were of the order of 10^2 – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which suggest that the moieties of dimethylamine (DMA) and tertiary amine in nitrogen-containing precursors may largely be the sources of the NDMA formation potentials (NDMA-FPs) in treated water. The proposed mechanisms of the reactions involve one-electron transfers in the initial step in the case of ClO_2 , O_3 , and $\cdot\text{OH}$ as oxidants while Fe(VI) prefers a two-electron transfer (oxygen atom transfer) step. NDMA destruction methods include biodegradation, reduction, and oxidation (photolytic, photocatalytic, chemical, and electrochemical). Current concepts of the proposed mechanisms of NDMA transformations are briefly described.

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Table 1
Concentrations of NDMA in water and wastewater samples.

Source	ng L ⁻¹	Reference
<i>Drinking Water</i>		
Ohsweken, Ontario, Canada	nd-52	[16]
Water Factory 21, California, USA	nd-200	[17]
Alberta, Canada	nd-100	[8]
United Kingdom	≤5.8	[20]
Supply Systems, United Kingdom	<0.9–15.6	[10]
Germany ^a	≤100	[11]
Japan	≤10	[19]
River water, Japan	<0.5–5.2	[13]
Groundwater, Japan	<0.5–3.4	[13]
<i>Wastewater</i>		
Primary sludge supernatant, USA	≤1000	[15]
WWTPs, USA	≤3000	[14]
WWTPs, USA	80–790	[12]
WWTPs, Switzerland	5–25	[18]
Secondary effluents, Switzerland	<10	[18]

WWTPs – wastewater treatment plants.

^a After ozonation.

1. Introduction

N-nitrosodimethylamine (NDMA) has been found in air, beverage and food products, soil, and water and is of considerable concern as an environmental contaminant [1–5]. Studies on animal species have shown that NDMA can initiate cancer through methylation of DNA and it is classified as a “probable human carcinogen” by the International Agency for Research on Cancer [6]. NDMA exhibits a 10⁻⁶ cancer risk level at concentrations as low as 0.7 ng/l [7]. The governments of Ontario, Canada and California, USA have thus established tolerable limits of 9 and 10 ng/l, of NDMA in drinking water, respectively [4].

NDMA has been detected above established limits in treated drinking water and wastewater [8,9]. A summary of levels of NDMA in different regions of the world is given in Table 1 [8,10–20]. More than 100 ng/l of NDMA has been found in drinking water; however, mean concentrations were generally low (3–7 ng/l) [4]. High values were determined in effluents of WWTPs (Table 1). A recent study found low levels of NDMA in river water and groundwater of Japan (Table 1). Levels of NDMA in both drinking water and wastewater samples are related to water quality parameters such as pH, temperature, alkalinity, total organic carbon, and inorganic and organic nitrogen as well as the method of disinfection used [10,21–23]. Several studies have shown chloramination and chlorination processes produce NDMA [24–29]. More recently, ozonation has also been shown to cause the generation of NDMA [22].

This paper summarizes mechanisms of the formation of NDMA in water, followed by an overview of studies conducted on the destruction of NDMA in the aquatic environment.

2. Formation of NDMA

Amines, amine based polymers, and humic substances all have been suggested to be precursors of NDMA due to their reactions with water treatment disinfectants. Commonly used treatment chemicals, chlorine and chloramines play significant role in the formation of NDMA [30]. More recently, the reaction of *N,N*-dimethylsulfamide with O₃ has also been found to result in NDMA production. The formation of NDMA in water was initially associated with reactions including chloramines and chlorination [24,29]. Dimethylamine (DMA) was shown to be a precursor, which can react with chloramines and chlorine to result in NDMA [29]. Based on kinetic and reaction products studies of DMA and chloramines, different reaction pathways for the reaction were proposed (Fig. 1) [24]. Significantly, one of the nitrogen atoms in the nitroso group of NDMA was proposed to transfer from monochloramine. The pathways consist of three reactions: (i) the reaction of DMA with monochloramine to result in 1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH), (ii) the oxidation of UDMH by monochloramine to form NDMA, and (iii) the reversible chlorine transfer between DMA and monochloramine, which is parallel to reaction (i). However, recent work showed that the scheme depicted in Fig. 1 may not be valid, and formation of NDMA may occur through the reaction of DMA with dichloramine to result in chlorinated UDMH, which on subsequent oxidation by O₂ forms NDMA [31,32].

2.1. Amines

The kinetics of the reactions of amine precursors of NDMA formation with other potential disinfectants has also been investigated during the last few years [33]. The structures of studied amines are given in Fig. S1. The second-order rate constants of the reactions are summarized in Table 2 [34–38]. ClO₂, O₃, and Fe(VI) are selective oxidants and their rate constants varied over several orders of magnitude, from 10⁻² to 10⁸, 10⁻¹ to 10⁹, and 10⁻¹ to >10⁶ M⁻¹ s⁻¹ [33]. A similar trend of the rate constants of reactions of NDMA precursors with ClO₂ and O₃ was observed [39]. Dimethylaminobenzene (DMAB), 3-dimethylaminomethyl indole (DMAI), and 4-dimethylaminoantipyrine (DMAP) contain electron-donating groups and hence reacted faster with selective oxidants. Comparatively, molecules with electron-withdrawing groups, such as dimethylformamide (DMFA), had much lower reactivity with ClO₂, O₃, and Fe(VI). The

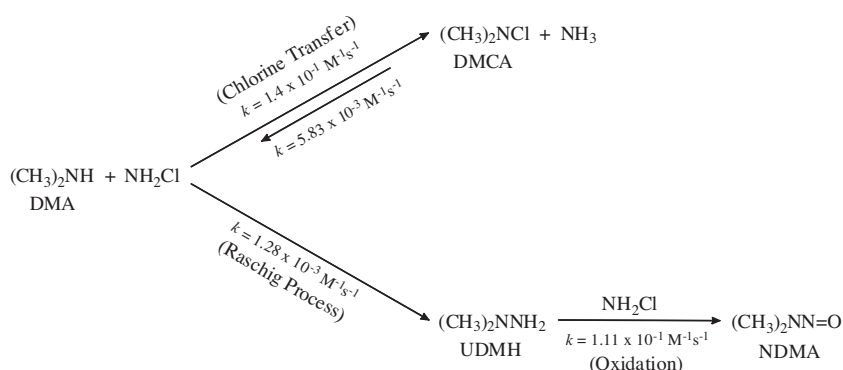


Fig. 1. Proposed reaction scheme for the formation of NDMA from the reaction of monochloramine with DMA. Rate constants are at pH 7.0 and 25 °C (reproduced from [24] with the permission of Elsevier Inc.).

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