Journal of Hazardous Materials 321 (2017) 362–370

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Comparison of *N*-nitrosodimethylamine formation mechanisms from dimethylamine during chloramination and ozonation: A computational study

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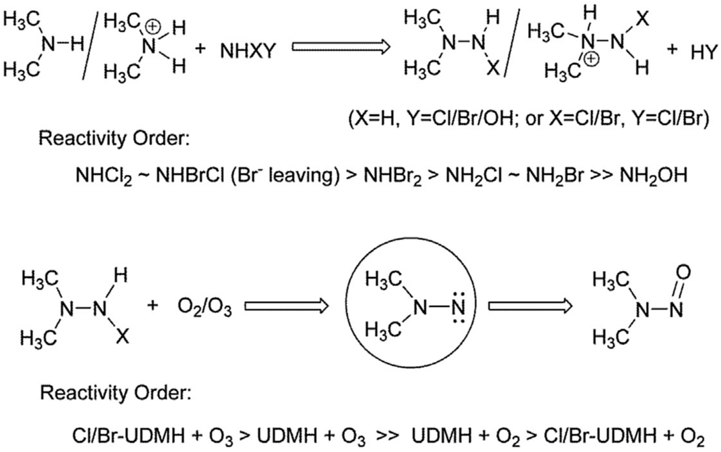
HIGHLIGHTS

- NDMA formation mechanisms from dimethylamine in chloramination/ozonation were reinvestigated by G4 method.
- The reactivity order of halo-/hydroxyl-amines reacting with dimethylamine is $NHCl_2 \sim NHBrCl > NH_2Cl \gg NH_2OH$.
- Nitrene compound is an important intermediate to form NDMA in oxidation reaction.
- Oxidation of unsymmetrical dimethylhydrazine by O_2 is significantly less feasible compared to that by O_3.
- The amines containing the second nitrogen source are potential NDMA precursors in ozonation.

GRAPHICAL ABSTRACT



(X=H, Y=Cl/Br/OH; or X=Cl/Br, Y=Cl/Br)

Reactivity Order:

$NHCl_2 \sim NHBrCl\ (Br^-\ leaving) > NHBr_2 > NH_2Cl \sim NH_2Br >> NH_2OH$

Reactivity Order:

$Cl/Br\text{-}UDMH + O_3 > UDMH + O_3 >> UDMH + O_2 > Cl/Br\text{-}UDMH + O_2$

ARTICLE INFO

Article history:
Received 23 May 2016
Received in revised form 27 August 2016
Accepted 11 September 2016
Available online 12 September 2016

Keywords:
N-nitrosodimethylamine
Chloramination
Ozonation
G4 method
Dimethylamine

ABSTRACT

N-nitrosodimethylamine (NDMA) as a disinfection by-product has recently become the focus of considerable research interest due to its unusually high carcinogenicity. In this study, the formation mechanisms of NDMA from dimethylamine (DMA) during chloramination and ozonation were investigated by using the quantum chemical G4 method. The reactivity of haloamines and hydroxylamine reacting with DMA was found in the order: $NHCl_2 \sim NHBrCl\ (Br^-leaving) > NHBr_2 > NH_2Cl \sim NH_2Br \gg NH_2OH$. This offers a theoretical support for the experimentally proposed mechanism that dimethylamine reacts with $NHCl_2$ rather than NH_2Cl to form chlorinated unsymmetrical dimethylhydrazine intermediate and the existence of bromochloramine in the presence of bromide during chloramination, and explains the observation that NDMA yield during ozonation is much lower than that during chloramination. Importantly, an *N,N*-dimethylaminonitrene was found to be a significant intermediate to form NDMA in oxidation reactions by molecular oxygen and ozone. Additionally, results suggest that the amines containing the second nitrogen source directly connecting or close to the N-$(CH_3)_2$ moiety are potential significant NDMA precursors upon ozonation. The findings of this study are helpful for expanding the knowledge of NDMA formation mechanism, and predicting potential NDMA precursors during disinfection.

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http://dx.doi.org/10.1016/j.jhazmat.2016.09.023
0304-3894/

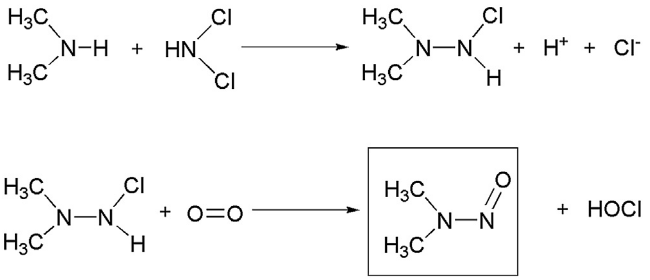
1. Introduction

As unusually powerful carcinogenic, mutagenic and teratogenic agents, *N*-nitrosamines have attracted extensive attention and especially there has been great interest in the investigation of *N*-nitrosamines formation in water treatment and disinfection during the last decades [1–6]. There are also an amount of studies focused on *N*-nitrosamines analysis and removal [7–9]. *N*-nitrosodimethylamine (NDMA), which has the simplest structure and is the most widely detected *N*-nitrosamine, has been demonstrated to be a probable human carcinogen [10,11]. In the Integrated Risk Information Service (IRIS) database of the United States Environmental Protection Agency (USEPA), NDMA has been identified to have an estimated 10^{-6} lifetime cancer risk level at a concentration of 0.7 ng/L in drinking water [11].

Dimethylamine (DMA) is often used as the model NDMA precursor. To date, several NDMA formation mechanisms from DMA during chloramination have been proposed [1–4,12–15]. Among them, the revised NDMA formation pathway as shown in Scheme 1 proposed by Schreiber and Mitch [15] is the commonly accepted mechanism upon chloramination of DMA. It demonstrates the critical importance of dichloramine and dissolved oxygen, and emphasizes the formation of chlorinated unsymmetrical dimethylhydrazine (Cl-UDMH) intermediate instead of the firstly proposed unsymmetrical dimethylhydrazine (UDMH) intermediate for the formation of NDMA.

However, Nawrocki and Andrzejewski [1] pointed out that there is a weak side of this hypothetical mechanism. It is the formation of hypochlorous acid (HOCl) in the oxidation reaction, which is a stronger oxidant compared to the reactant molecular oxygen (O_2). Therefore, although the formation mechanisms of Cl-UDMH intermediate are generally accepted, the oxidation reaction mechanism to form NDMA is still ambiguous. Additionally, bromide ion as a constituent of natural water was reported to have the ability to enhance NDMA formation in the monochloramination of DMA at the relatively high pH values [16,17]. Bromoamines were initially suggested to be formed in the present of bromide during chloramination by researchers [16], however, recent results [17,18] demonstrated that only bromochloramine (NHBrCl) was suspected to be responsible for the enhanced NDMA yield. Unfortunately, the mechanism in this reaction remains unclear. Additionally, some tertiary amines were also found to be important precursors in NDMA formation during chloramination [19–23], however, few formation mechanisms have been known [24,25].

Except chloramination is the main source of NDMA formation in wastewater and drinking water disinfection, recent studies reported that ozonation is also associated with the formation of NDMA [26–36]. NDMA formation mechanism during ozonation was first suspected to involve the direct nitrosation of DMA by the oxidized products from the reaction of DMA with O_3 [26]. Later, Yang et al. [27] proposed the importance of hydroxylamine. According to Yang et al.'s hypothesis displayed as the dotted-line arrows in Scheme 2, DMA first reacts with ozone to generate hydroxylamine through *N*-dimethylhydroxylamine (DMHA) and *N*-methylhydroxylamine (MHA) intermediates, and then a nucleophilic substitution between hydroxylamine and DMA occurs, finally the result of which, UDMH, is oxidized by oxygen molecule to form NDMA.



Scheme 1. Schreiber and Mitch [15] modified NDMA formation mechanisms of DMA during chloramination.

Nonetheless Andrzejewski et al. [28] found that only addition of hydroxylamine to the DMA solution increases the NDMA yield, whereas addition of DMHA or MHA does not enhance the yield of NDMA. More recently, Zhang et al. [29] set forward the significance of ammonia as an intermediate rather than DMHA and MHA to generate hydroxylamine in the reaction of DMA with ozone (see the reactions with solid-line arrows in Scheme 2) by using DFT calculation method, which supported results of Andrzejewski et al. [28]. They also proved the hydroxylamine mechanism for NDMA formation from DMA during ozonation and proposed UDMH intermediate can be oxidized by ozone and oxygen molecules to form NDMA through 4-step and 2-step processes, respectively.

However, in Zhang et al.'s calculation results [29], the activation free energies of oxidation reactions of UDMH by ozone and oxygen molecules are about 30 and 40 kcal/mol, respectively. Such high activation free energy of UDMH reacting with molecular ozone disagrees with the relatively high molar NDMA yield upon ozonation of UDMH in the range of 16–80% [30,31]. In addition, Marti et al. [30] reported that bromide concentration plays an important role in enhancing NDMA formation in the ozonation of UDMH and the catalytic effect of bromide was also reported for *N*,*N*-dimethylsulfamide (DMS) [31,32]. Very recently, Trogolo et al. [33] reported NDMA formation mechanisms from DMS during ozonation. However, to date, questions on how the oxidation reactions of UDMH and DMA by molecular ozone proceed and why bromide can enhance NDMA yields in the ozonation of DMA have not been elucidated yet.

To date computational quantum chemistry, as an application of quantum mechanical principles and equations to explore molecules, has become a tool for scientists from many research fields. Especially with the increasement of computing power and improvement of algorithms over the last decades, it is now possible to accurately predict many significant properties. In the environmental research field, some very recent computational results [25,33,34] provide a good complement to the experiment.

To address the above questions, herein, we used the computational quantum chemistry method to investigate the formation mechanisms of NDMA from dimethylamine (DMA) during chloramination and ozonation. A comparison of NDMA formation mechanisms upon the two different disinfectants was made and mechanisms of NDMA yields enhanced by bromide ion were also investigated. The results are expected to expand our understanding of NDMA formation mechanisms, and help for developing efficient strategies to control the carcinogenic NDMA formation.

2. Theoretical methods

All quantum chemical computations were carried out with the GAUSSIAN-09 program package [35] and the corresponding parameters and convergence criteria used in the calculation were assigned default values. The geometry optimizations and vibrational frequencies of all complexes involved in this study were firstly calculated using the B3LYP (Becke's three-parameter functional [36] with the correlation functional of Lee et al. [37]), in conjunction with the 6-311G(d) [38] basis set. To obtain more accurate energies, the composite Gaussian-4 (G4) method was used [39]. Since no transition states for *N*,*N*-dimethylaminonitrene (DMAN) formation from Br-UDMH were found with G4 method, a more theoretically rigorous CCSD [40] method along with the 6-