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UV-A induced photochemical formation of *N*-nitrosodimethylamine (NDMA) in the presence of nitrite and dimethylamine

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Abstract

The photochemical nitrosation of dimethylamine (DMA) has been suggested as a possible pathway for the occurrence of *N*-nitrosodimethylamine (NDMA) in aquatic environments. The aim of this study was to investigate the formation of NDMA from the nitrosation of DMA during nitrite (NO_2^-) photolysis in aqueous solution by varying several of the experimental parameters. NDMA was formed at neutral pH, in the presence of DMA and NO_2^- under UV-A irradiation, and exhibited an increase in concentration with irradiation time. Increasing the concentrations of DMA and NO_2^- led to enhanced NDMA formation. Through experiments employing $^{\bullet}OH$ scavenger (*t*-BuOH), $^{\bullet}OH$ was found to play an important role in the production of nitrosating agents during the photolysis of NO_2^-. The optimum pH for the formation of NDMA was around 10. This pH dependence was explained by the dual role of deprotonated DMA as a nucleophile, which enhances the nitrosation reaction between nitrosating agents and DMA, and a hydroxyl radical ($^{\bullet}OH$) scavenger, which reduces the production of nitrosating agents. A higher concentration of NDMA was obtained under N_2 condition due to the lower quantum yield for NDMA photolysis in the absence of oxygen. Various anions, including phosphate ions in the buffer solution, retarded the formation of NDMA, possibly due to degradation of the nitrosating agents.
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Keywords: *N*-Nitrosodimethylamine (NDMA); Dimethylamine; Nitrite; Photolysis; Ultraviolet (UV) irradiation

1. Introduction

N-Nitrosamines have been known as mutagenic, carcinogenic and teratogenic compounds since the 1960s. In recent years, *N*-nitrosodimethylamine (NDMA) has been recognized as an emerging contaminant in drinking water and wastewater [1,2], as trace levels have been detected, with the help of the advanced analytical technologies, in surface and drinking waters in North America. The US EPA classifies NDMA as a probable human carcinogen, with a 10^{-6} cancer risk level of 0.7 ng/L. The California Department of Health Services and the Ontario Ministry of the Environment have established interim drinking water levels for NDMA at 10 and 9 ng/L, respectively.

A number of studies have attempted to elucidate the mechanisms of NDMA formation in water. Recently, several research groups found that NDMA can be formed as a disinfection byproduct from chloramination [3,4]. According to one study, chloramination of secondary wastewater and surface water was found to form 100 and 10 ng/L NDMA, respectively [5]. The mechanism responsible for the formation of NDMA by chloramination has been suggested to involve the formation of 1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH) by the reaction of dimethylamine (DMA) with monochloramine, with the subsequent oxidation to NDMA [3,4].

Another pathway for the formation of NDMA in aqueous solution is the reaction of DMA with nitrous acid (HNO_2), which is traditionally the best known mechanism for the nitrosation of DMA [6]. Nitrous acid (HNO_2) in aqueous acidic solution ($pH < 5$) is known to form nitrosating agents of the type $NO^{\delta+}–Y^{\delta-}$, which is a complex of the nitrosonium ion (NO^+) with stable anions. These nitrosating agents transfer the NO^+ entity to DMA through nucleophilic (S_N2) displacement to yield NDMA, as described in reaction (1). The formation of NDMA from the reaction of DMA with HNO_2 is known to have an optimum around pH 3.

(1)

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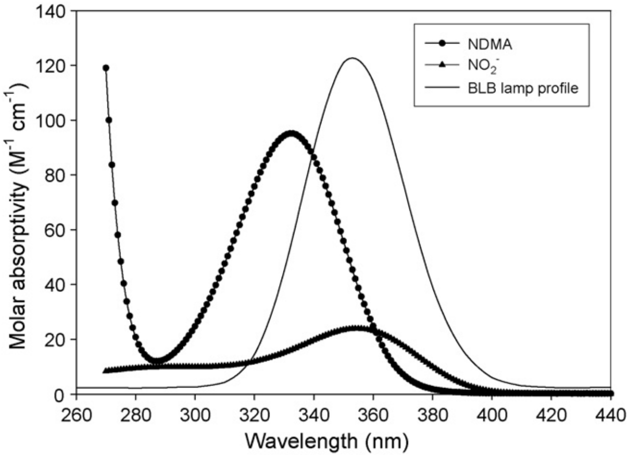

Fig. 1. Molar absorption coefficients of NDMA and nitrite, and the BLB lamp profile as a function of the wavelength.

In neutral or alkaline aqueous solutions, the reaction of DMA with HNO_2 produces insignificant amounts of NDMA, as no nitrosating agents can be formed from the nitrite ion (NO_2^-) (pK_a of $HNO_2 = 3.37$). However, UV irradiation on NO_2^- solution can produce nitrosating agents. The photolysis of NO_2^- is known to produce various nitric oxide species, of which N_2O_3 and N_2O_4 can act as nitrosating agents [7]. Significant photochemical nitrosation of DMA by the nitrosating agents produced from the photolysis of NO_2^- due to sunlight can occur in natural aquatic environments, since NO_2^- absorbs light at wavelengths up to 400 nm (Fig. 1).

One previous study has experimentally shown that NDMA can be photochemically formed from DMA during the photolysis of NO_2^- under light irradiation from both medium-pressure Hg lamp with a Pyrex UV cut-off filter ($\lambda > 300$ nm) and sunlight [8], with yields up to 35%, depending on UV irradiation time, concentration of NO_2^- and solution pH. This observation suggests that the photolysis of NO_2^- can be a major source of NDMA formation in aquatic environments, when considering the yield of NDMA from chloramination is only <3% [3,4]. However, the high yield of NDMA by the photolysis of NO_2^- needs to be reexamined, since NDMA is known to be highly photolabile, with quantum yields around 0.31 [9,10], which are much higher than those of NO_2^-; e.g. 0.046 at 351 nm [7]. Significant NDMA photolysis can occur simultaneously with its formation. Moreover, the study only provided limited information on the influences of water parameters on the formation of NDMA.

In the present work, attempts were made to reinvestigate the photochemical formation of NDMA from DMA in the presence of NO_2^-. Various parameters, such as the concentrations of DMA and NO_2^-, solution pH, dissolved oxygen and the presence of a hydroxyl radical ($^{\bullet}OH$) scavenger or (in)organic anions were tested, with the results discussed in relation to the reactions of radical species and nitrosating agents produced during the photolysis of NO_2^-.

2. Experimental

2.1. Reagents

NDMA, DMA and sodium nitrite ($NaNO_2$) were obtained from Sigma–Aldrich, with purity higher than 99%. All chemicals used for making the solutions (buffer, eluents, etc.) were of reagent grade, and used without further purification. All stock solutions were prepared in distilled and deionized water (Barnstead NANO Pure, USA). Fifty millimolars aqueous stock solutions of NDMA, DMA and $NaNO_2$ were prepared and stored at room temperature, in the dark by covering with aluminum foil. The concentration of the NDMA stock solution was spectrophotometrically checked for variance prior to use.

2.2. Experimental apparatus and procedure

All experiments were performed in a 50 mL cylindrical Pyrex reactor, with an optical path length of 2 cm, with the solution exposed to UV supplied by four equivalent BLB lamps (Black Light Blue, Philips Co., USA.) emitting UV-A light of 300–400 nm (Fig. 1). The optical path length was chemically determined by photolysis kinetics of 2-nitrobenzaldehyde [11]. Most experiments were carried out open to atmosphere without gas purging (dissolved oxygen concentration $\approx 10\ \mathrm{mg\ L^{-1}}$). For the experiments using gas purging, the upside of the reactor was sealed with a rubber septum, with O_2 or N_2 gas sparged through a needle-type diffuser. The solution pH was controlled to be constant (±0.2) during the reaction time by 2 mM phosphate buffer for pH 7 and 8.2, and by the continuous addition of an appropriate amount of 0.1 M NaOH solution for pH 9–11. The solution was vigorously mixed using a magnetic stirrer. The lamps were stabilized for about 30 min prior to their use for illumination. The incident photon flow (Einstein $L^{-1}\ s^{-1}$) was measured using ferrioxalate actinometry [12]. The photolytic production of Fe(II) was maintained at <10% of the initial amount of Fe(III) to insure complete light absorption by the ferrioxalate actinometer. An overall quantum yield of 1.2 was used in the calculation pertaining to the ferrioxalate photolysis reaction [13]. The measured incident photon intensity in this system was 1.4×10^{-5} Einstein $L^{-1}\ s^{-1}$.

The general experimental procedure was as follows: reaction solutions with specific concentrations of DMA and NO_2^-, or NDMA (for determining quantum yields in Table 1) were prepared by the addition of calculated aliquots of the stock solutions to distilled water; the pH was then adjusted to the desired value.

Table 1
Determined quantum yields for NDMA photolysis as a function of the pH under both O_2 and N_2 conditions: $[NDMA]_0 = 0.1$ mM, 310–370 nm

pH	O_2 condition	N_2 condition
7.0	0.314 ± 0.0021	0.318 ± 0.0141
8.2	0.309 ± 0.0105	0.317 ± 0.0108
9.0	0.206 ± 0.0124	0.043 ± 0.0037
10.0	0.166 ± 0.0152	0.025 ± 0.0014
11.0	0.184 ± 0.0149	0.015 ± 0.0006

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