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Mechanism of NDMA formation during ferrate or permanganate reactions with aqueous solutions of dimethylamine (DMA)

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ABSTRACT

Nitrosamines, mainly N-nitrosodimetylamine (NDMA), N-nitrosomethylethylamine (NMEA) and N-nitrosodiethylamine (NDEA) are mutagenic compounds and are suspected to be carcinogenic towards humans. American Environmental Protection Agency (US EPA) classified them into group B2 – i.e., compounds which are probably carcinogenic to humans. US-EPA also determined concentrations of these compounds in potable water (oral exposure) at the levels of 7 ng l^{-1} (NDMA), 20 ng l^{-1} (NMEA) and 2 ng l^{-1} (NDEA), associated with the risk of 10^{-5}. The reactions of permanganate ($KMnO_4$) or ferrate (K_2FeO_4) with dimethylamine, as possible paths of NDMA formation, have been investigated. The influence of nitrite (in the reaction mixture) on both, the efficiency of NDMA formation and determination of sources of nitroso group in an NDMA molecule, were aims of these experiments. The primary goal of these investigations was to check whether nitrosating mechanism of DMA, that occurs during the reaction of strong oxidants with DMA, is responsible for NDMA formation.The results of the permanganate-DMA reaction show that by adding nitrite to the reaction mixture the amount of NDMA formed significantly increases. On the other hand, no correlation between the nitrite concentration and the amount of NDMA formed was observed. The results obtained for ferrate differ from these for permanganate. The addition of nitrite to reaction mixture decreases the amount of NDMA formed. However, the addition of nitrite in the amount of up to 75% of the amount required to reduce ferrate to Fe_2O_3 has led to a negligible drop in NDMA formation rate. A significant decrease of NDMA formation rate (about 50% of reference sample, i.e. without nitrite addition) has been observed in the experiment, in which 100% of the amount of nitrite required for the reduction of ferrate was added. The addition of nitrite to the reaction mixture (for both oxidants) is not necessary for NDMA formation, since NDMA is also formed without an external source of nitrite. The formation of nitrite during DMA oxidation with both oxidants explains this phenomenon. The addition of labeled nitrite (^{15}N) to reaction mixtures containing DMA and permanganate or ferrate resulted in formation of higher amounts of NDMA with molecular mass of 75 Da (compared with the natural isotopic composition of nitrogen). The fragmentation analysis of the NDMA molecule has shown that the presence of isotope ^{15}N in nitroso group of NDMA is responsible for the molecular mass increase. This means that the presence of nitrite in the reaction is the source of nitrogen in the NDMA molecule. Thus the mechanism of nitrosation of DMA is responsible for NDMA formation during permanganate or ferrate reaction with aqueous solution of DMA.

Keywords: N-nitrosodimetylamine (NDMA); Disinfection by-product; Strong oxidants; Water treatment; Ferrate; Permanganate

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1. Introduction

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

American Environmental Protection Agency (US EPA) classified them into group B2—i.e. compounds which are probably carcinogenic to humans. US-EPA also determined concentrations of these compounds in potable water (oral exposure) at the levels of 7 ng l^{-1} (NDMA), 20 ng l^{-1} (NMEA) and 2 ng l^{-1} (NDEA), associated with the risk of 10^{-5} [1].

In 2002, Mitch and Sedlak [2] and Choi and Valentine [3] reported that NDMA is formed during the chloramines disinfection of water or in wastewater treatment plant effluents containing dimethylamine (DMA). The mechanism proposed by Choi and Valentine [3] and Mitch and Sedlak [2] is based on chloramination 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 and Mitch [4]. The authors emphasized the role of dichloroamine and dissolved oxygen in NDMA formation due to the reaction of chloramination of DMA [4]. In 2003, Choi and Valentine [5] proposed other model of mechanism of NDMA formation during reaction of dimethylamine with chlorine. According to the proposed mechanism, HOCl reacts with nitrite present in water to form very reactive nitrosating intermediate i.e. dinitrogen tetroxide (N_2O_4), which subsequently reacts with dimethylamie to form NDMA. Nevertheless, in that paper they stated that in chloraminated water NDMA is formed mainly by the reaction of HOCl with ammonia and subsequent formation of UDMH [5].

Schreiber and Mitch made an attempt to clarify doubts concerning mechanism of NDMA formation during DMA chloramination. They investigated the mechanism of this reaction under conditions, which occurred during chlorination near the breakpoint. The authors proposed two independent paths of NDMA formation: a relatively slow reaction of dichloramine with NDMA precursors in the presence of oxygen at molar ratio $Cl_2/NH_3 \leq 1{,}5$; and the fast reaction of reactive breakpoint chlorination intermediates which are involved in the direct nitrosation of DMA. The authors postulated, depending on pH, formation of peroxynitrous acid (O=N—O—OH; p*K*a = 6.8) or peroxynitrite ion ($O{=}N{-}O{-}O^-$), which subsequently release $^*NO_2$ and OH* or *NO and O_2^* radicals, respectively. The peroxynitrous acid-derived HO* could react with DMA to form an amine radical and then be nitrosated by nitric oxide (*NO), a one-electron transfer oxidation product of NO^- to form NDMA. Alternatively, peroxynitrite-derived *NO radical could react with DMA to form NDMA. The authors also pointed out the crucial role of dissolved oxygen in the peroxynitrous acid or peroxynitrite ion formation. However, they observed no differences in NDMA formation in the presence or absence of dissolved O_2 during breakpoint chlorination [6]. The above presented NDMA formation pathway via peroxynitrous acid or peroxynitrite ion could explain mechanisms of other oxidants reactions with DMA as well, because peroxynitrite can be formed also as a result of hydrogen peroxide reaction with nitrite [7].

Andrzejewski et al. proved the possibility of NDMA formation in water containing dimethylamine (DMA) disinfected with chlorine dioxide [8], ozone [9], hydrogen peroxide [10] and permanganate [11]. Provided that the reactions with chlorine dioxide, ozone, hydrogen peroxide and permanganate take place in the absence of ammonium ions, the mechanism of NDMA formation must be different from the one proposed by Choi and Valentine [3] and Mitch and Sedlak [2]. On the basis of the nitrosamine formation pathway, as proposed by Keefer and Roller [12] and Andrzejewski et al. [9], assuming that NDMA, which is a product of strong non-chlorine oxidants reaction with DMA, is formed as a result of a multi-step reaction. In the first stage, part of DMA is oxidized and formaldehyde, formic acid, nitrite and nitrate are formed. Subsequently, nitrite reacts with the remaining part of DMA to form NDMA.

If nitrosation mechanism is responsible for NDMA formation, nitrite (both added to reaction mixture as well as formed during DMA oxidation) should be a source of a nitrosation agent. Thus the nitrosation agent should be found as a part of the NDMA molecule (N=O group). The aim of this paper is to confirm this assumption by means of applying labeled nitrite (as $Na^{15}NO_2$) to the reaction mixture. Therefore, the attempt to explain the mechanism of NDMA formation was the main goal of this research.

2. Materials and methods

2.1. Model water

Experiments were carried out on the model water spiked with DMA. The model water was prepared by an addition of phosphate buffer (Na_2HPO_4, >99.5%, Fluka) and DMA solution (60%, Fluka) into high purity water (Millipore). Solution pH was adjusted by adding H_3PO_4 (>85%, Fluka) or NaOH (>98%, Fluka) to pH of 8.25.

2.2. DMA Oxidation with permanganate and ferrate

The reactivity of permanganate and ferrate with dimethylamine were evaluated at room temperature (20°C) in a reactor, with continuous stirring. Potassium permanganate stock solution was prepared by dissolving 1 g of potassium permanganate (>99.5%, Fluka) in 100 mL of ultra pure water (Millipore). Potassium ferrate stock solution was prepared by dissolving 0.8 g of potassium ferrate (97%, Aldrich) in 100 ml of ultra pure water (Millipore). The concentration of potassium permanganate in reaction mixture ranged from 0.63 to 1.27 mM $KMnO_4$. The molar ratio of $KMnO_4$/DMA was 0.29 (M/M). The concentration of potassium ferrate in reaction mixture ranged from 1.01 to 1.27 mM K_2FeO_4. The molar ratio of K_2FeO_4/DMA was 1.15 (M/M). The samples of reaction mixture were collected periodically, and dry Na_2SO_3 (>98%, Fluka) was added to remove the remaining permanganate or ferrate. The suspensions generated as a result of permanganate or ferrate reduction, were removed by centrifugation.

In order to find out whether nitrosation mechanism is responsible for NDMA formation in these reactions, the impact that the nitrite presence has on the efficiency of NDMA formation was evaluated. Thus the influence of the nitrite (as solution $NaNO_2$ >98%, Fluka or solution $Na^{15}NO_2$, 99%, of ^{15}N Fluka in the reaction mixture) on both, the efficiency of NDMA formation, as well as the source of nitroso group in the NDMA molecule was investigated. The amounts of nitrite added (in the form of labeled $Na^{15}NO_2$ solution) corresponded to 0%, 25%, 50%, 75% and 100% of the amount of nitrite required to reduce permanganate (or ferrate) to MnO_2 (or Fe_2O_3).

The following reaction parameters were examined: NDMA concentration (with HPLC-ion exclusion-UV technique), the oxidants concentrations (with spectrophotometrical method), DMA degradation rate and DMA degradation products (formic acid: with HPLC-ion exclusion-UV technique; nitrite and nitrate with HPLC-ion exchange-CD technique). In order to determine the source of nitroso group in the NDMA molecule, the presence of NDMA ($(CH_3)_2N^{14}–N^{14} = O$) and N-labeled NDMA ($(CH_3)_2N^{14}N^{15} = O$) in post-reaction mixture was checked with GC-MS technique.

2.3. Analytical methods

2.3.1. Potassium permanganate and ferrate concentration

Concentration of permanganate in the reaction mixture was measured spectrophotometrically at $\lambda = 525$ nm. Prior to spectrophotometric analysis, the MnO_2 suspension was removed from the collected samples by centrifugation. The method allows determination of 0.003 mM $KMnO_4$.

The authors also decided to apply spectrophotometric analysis to evaluate the ferrate concentration in the reaction mixture. However, a problem with evaluation of ferrate concentration has occurred. Ferrate is stable only in basic conditions and at relatively high concentrations, i.e. as stock solution. When ferrate concentration decreased after adding to the reaction mixture, ferrate concentration in the collected samples has changed even during centrifugation applied for the removal of Fe_2O_3 suspension. In the final stage of the ferrate's presence the purple color of the mixture originating from ferrate vanished.

2.3.2. NDMA Analytics

One of the principal goals of the study was to find out whether NDMA is formed as a reaction byproduct of permanganate or ferrate reactions with dimethylamine in the presence of nitrite. The GC-MS (full scan) technique, preceded by liquid-liquid extraction of post-reaction mixture with dichloromethane, was chosen for the identification of NDMA. This technique, though useful for qualitative purposes, was not fast enough to be used for quantitative ones. For that reason, in the quantitative analysis of nitrosamines, modified ion exclusion chromatography with UV-Vis detection was applied. This technique also enabled the analysis of other byproducts, such as formic acid. Both methods: GC-MS and HPLC-IE-UV have been described in our previous papers [11,10,13].

2.3.3. Analysis of formic acid

The presence of formic acid (the byproduct of DMA oxidation) in the reaction mixture was determined by means of the ion exclusion chromatography with UV-Vis (210 nm) detection. This method was also earlier described in details [11,9,10].

2.3.4. Analysis of inorganic reaction by products

Inorganic reaction byproducts were analyzed by ion exchange chromatography (IEC) with a conductometric detector.The method allows to quantify nitrate and nitrite at 50 µg l^{-1} and 30 µg l^{-1} respectively. Details are described elsewhere [11,9,10].

3. Results and discussion

3.1. NDMA as a reaction product of permanganate and ferrate with aqueous solutions of DMA in the presence of nitrite

Previous experiments have shown that NDMA is formed as a result of permanganate reaction with aqueous solution of DMA, both in the presence and in the absence of the external source of nitrite [11]. Preliminary experiments with ion-exclusion chromatography also showed that NDMA is a product of reaction of ferrate with aqueous solutions of DMA, both in the presence and in the absence of the external source of nitrite.

To ultimately confirm the presence of NDMA (as a product of ferrate reaction with DMA) in the post-reaction mixture, its dichloromethane extract was analyzed using GC-MS in a full scan mode. Because the highest reaction efficiency was observed for pH 8.08.5, the reaction of ferrate with aqueous DMA was repeated using a dose of DMA of 0.66 mM, with K_2FeO_4/DMA molar ratio of 1.93:1 and 24 h contact time of ferrate—DMA (see Fig. 1).

The GC-MS analysis unequivocally confirmed the formation of N-nitrosodimethylamine both in the presence and in the absence (see upper scan in Fig. 1.) of the external source of nitrite. Thus NDMA may now be considered a byproduct of the ferrate and DMA reaction.

3.2. *An influence of dose of nitrite on yield of NDMA formation in permanganate/ferrate reaction with aqueous solutions of DMA*

3.2.1. *Permanganate*

The influence of the nitrite presence and its concentration in the reaction mixture on the efficiency of NDMA formation was evaluated under the following experimental conditions: pH 8.25, permanganate concentration of 0.63 or 1.27 mM $KMnO_4$, the molar ratio of $KMnO_4$/DMA of 0.29:1

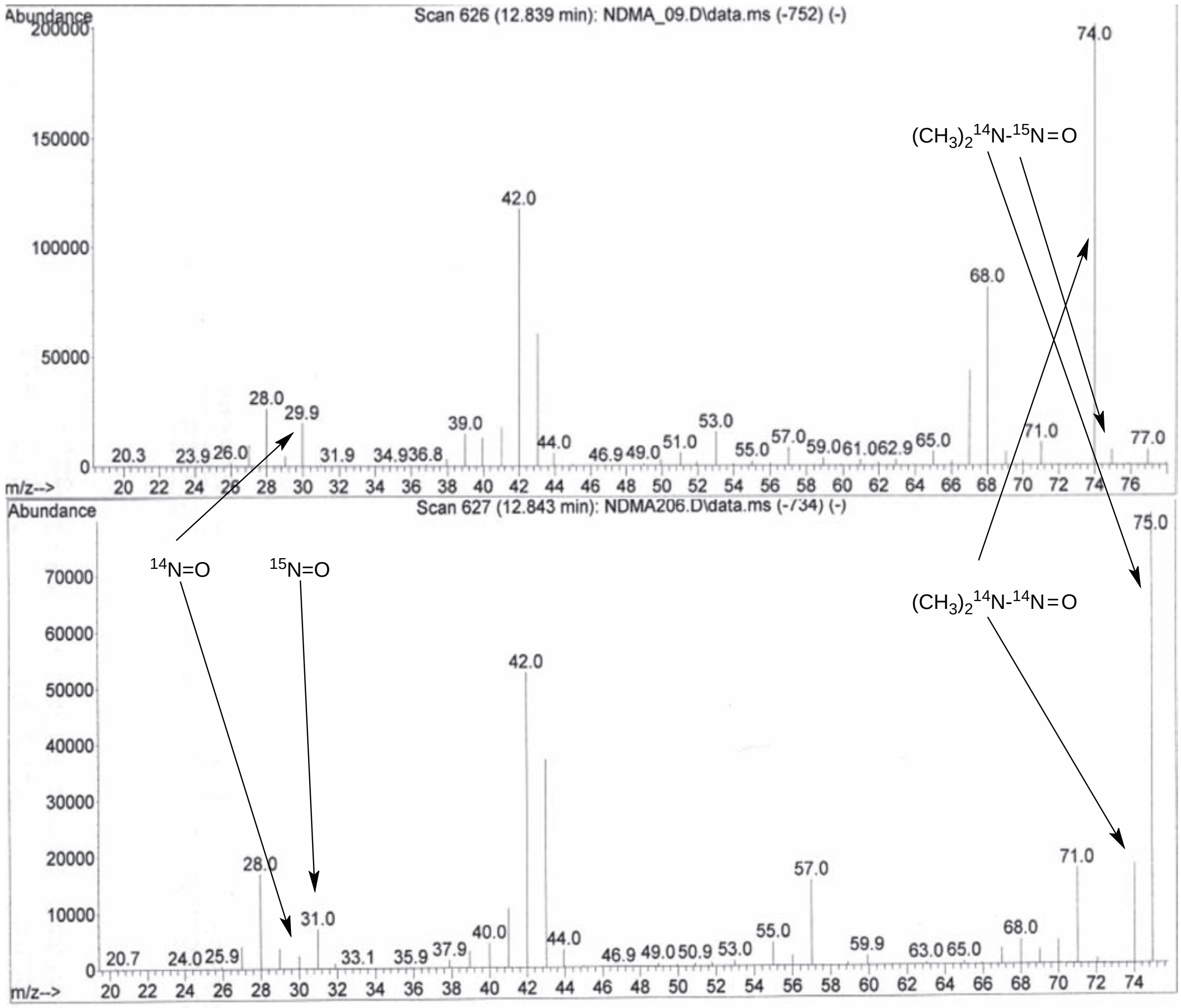

Fig. 1. Upper scan: Full scan spectra of NDMA identified in post-reaction mixtures of ferrate and DMA (without nitrite addition: pH 8.25, K_2FeO_4 concentration of 1.27 mM K_2FeO_4/DMA molar ratio of 1.93:1) and in post-reaction mixtures of permanganate and DMA with nitrite addition (see lower scan). pH = 8.25, $KMnO_4$ concentration of 1.27 mM, $KMnO_4$/DMA molar ratio of 0.29:1 [M/M]. $(CH_3)_2{}^{14}N{-}{}^{14}N = O$ and $(CH_3)_2{}^{14}N{-}{}^{15}N = O$: molecular ions of NDMA m/z = 74 and m/z = 75, which contain nuclides ^{14}N and ^{15}N respectively. $^{14}N = O$ and $^{15}N = O$: ions of m/z = 30 and m/z = 31 which contain nuclides ^{14}N and ^{15}N, respectively.

and the amount of nitrite of 0%, 25%, 50%, 75% and 100% of moles of nitrite (required to reduce permanganate to MnO_2 in the reaction mixture), according to the following reaction:

$$2KMnO_4 + 3NaNO_2 + H_2O \rightarrow 3NaNO_3 + 2MnO_2 + 2KOH \quad (1)$$

The results obtained for permanganate concentration of 1.27 mM $KMnO_4$ are shown in Fig. 2.

The results as presented in Fig. 2 show that the addition of nitrite to the reaction mixture significantly increases the amount of NDMA formed. On the other hand, no correlation between the nitrite concentration and the amount of NDMA formed was observed.

3.2.2. Ferrate

The same experiment was also carried out for ferrate application in the following conditions: pH 8.25, ferrate concentration of 1.01 or 1.27 mM K_2FeO_4, K_2FeO_4/DMA molar ratio of 1.15:1 and the amount of nitrite of 0%, 25%, 50%, 75% and 100% of moles of nitrite (required to reduce ferrate to Fe_2O_3 in the reaction mixture), according to the following reaction:

$$2K_2FeO_4 + 3NaNO_2 + 2H_2O \rightarrow Fe_2O_3 + 3NaNO_3 + 4KOH \quad (2)$$

The results obtained for ferrate concentration of 1.01 mM K_2FeO_4 are shown in Fig. 3.

The results as presented in Fig. 3 indicate that the addition of nitrite to the reaction mixture significantly decreases the amount of NDMA only for the highest dose of nitrite (100%). The addition of lower doses of nitrite (25%–75%) resulted in an insignificant decrease of the NDMA formation yield. On the other hand, for these doses of nitrite, no correlation between the nitrite concentration and the amount of NDMA formed was observed. However, similarly to the phenomenon observed in permanganate application, the addition of nitrite to the reaction mixture is not necessary for NDMA formation.

The results obtained for the application of both oxidants, show significant differences between times of vanishing of the two oxidants during their reactions with DMA. While the presence of permanganate in the reaction mixture was observed up to the 20th hour of reaction, the presence of ferrate in the reaction mixture was observed only up to the 6th hour of reaction. Furthermore, for both oxidants, the presence of nitrite has an impact on NDMA formation. Adding nitrite to the reaction mixture, however, is not necessary for NDMA formation, since NDMA is also formed without the addition of nitrite. Nitrite was also found in the reaction mixtures as a result of DMA oxidation even when nitrite was not added to the reaction mixtures neither for permanganate application [11] nor for ferrate application. The presence of formic acid in the post-reaction mixtures of both oxidants confirms DMA destruction when both oxidants are applied.

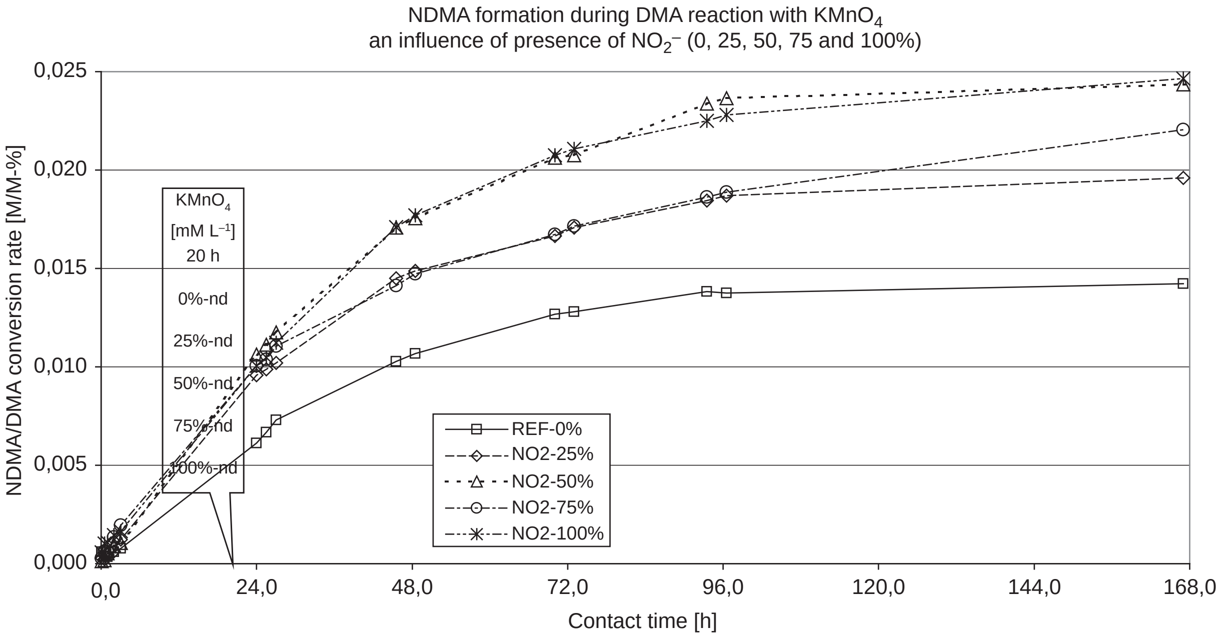

Fig. 2. NDMA formation during DMA reaction with $KMnO_4$. The influence of the presence of NO_2^- (0%, 25%, 50%, 75% and 100% of nitrite dose which is necessary for nitrite oxidation to nitrate by permanganate according to the reaction (Eq. 1)). pH = 8.25, $KMnO_4$ concentration of 1.27 mM, $KMnO_4$/DMA molar ratio of 0.29:1 [M/M], nd- not detected.

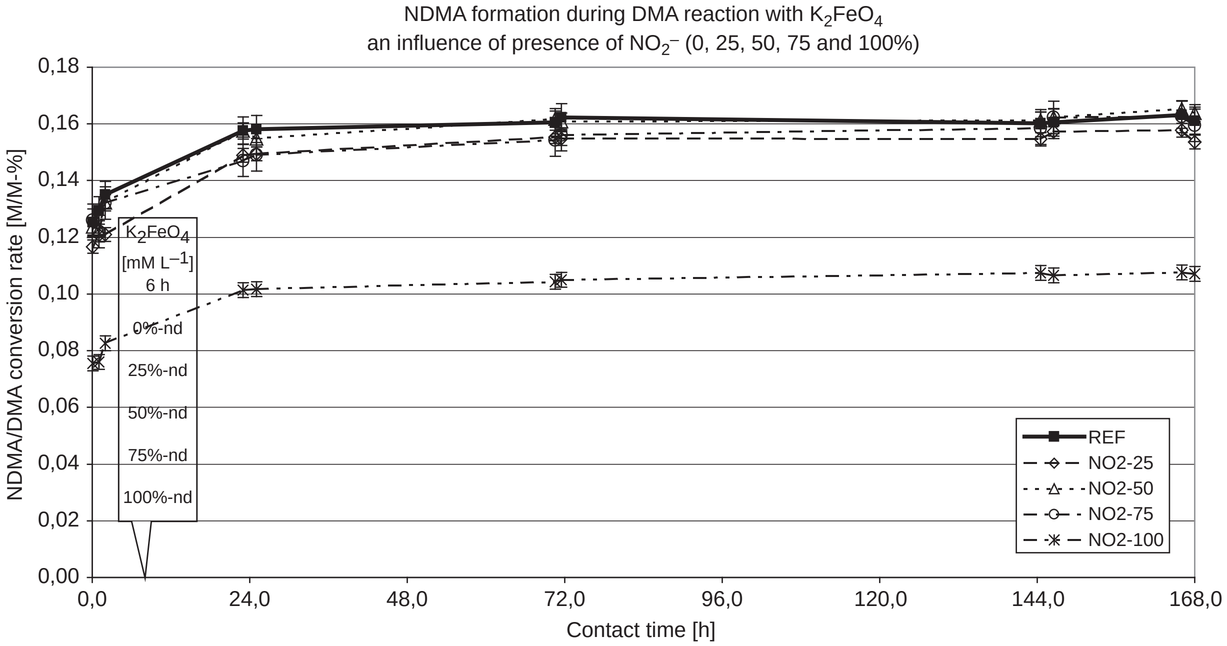

Fig. 3. NDMA formation during DMA reaction with K_2FeO_4. The influence of the presence of NO_2^- (for 0%, 25%, 50%, 75% and 100% of nitrite dose, which is necessary for oxidation of nitrite to nitrate by ferrate according to the reaction (Eq. 2)). pH = 8.25, K_2FeO_4 concentration of 1.01 mM, K_2FeO_4/DMA molar ratio of 1.15:1 [M/M], nd- not detected.

Differences in the amount of NDMA formed in the presence and in the absence of nitrite suggest a double role of nitrate in this process. The nitrosating molecule is likely to be formed as a result of DMA oxidation. The nitrite added to the reaction mixture may act as both the source of the nitrosating molecule and the nitrosating molecule's carrier ($^*NO + NO_2^- \rightarrow N_2O_3$) [14].

3.3. *Influence of relative dose of* $^{15}NO_2^-$ *on isotopic composition of NDMA*

The aim of these experiments was to verify the thesis that nitrosation process is responsible for NDMA formation, as a result of permanganate/ferrate reactions with aqueous solution of DMA. To this end, the post reaction mixtures for experiments mentioned above, during which labeled nitrite was applied, were selected. All these mixtures were extracted with dichloromethane (according to the procedure described in section 2.3.2.) and analyzed withGC-MS technique, both with full scan and SIM mode. Abundances of the following ions were analyzed: m/z = 30 ($^{14}N = O$), m/z = 31 ($^{15}N = O$), m/z = 74 (NDMA $(CH_3)_2N^{14}–N^{14} = O$)and m/z = 75 (NDMA $(CH_3)_2N^{14} – N^{15} = O$). If nitrosation mechanism is responsible for NDMA formation, nitrite (either added to reaction mixture or formed during DMA oxidation) should be the source of the nitrosating agent. The nitrosating agent (or its part) should be detected as a part of the NDMA molecule (N = O group).

The results obtained for permanganate and ferrate applications are presented in Figs. 4 and 5 respectively.

Ions responsible for the presence of ^{15}N nitrogen in the NDMA molecule (i.e. m/z = 31 and m/z = 75) were found in all extracts of post-reaction mixtures (see Fig. 1.). The ^{15}N nitrogen isotope naturally exists in the environment as a minor additive to ^{14}N isotope (in the ratio of 0,33% of ^{14}N isotope). Therefore, both mentioned ions were detected even in the extracts into which labeled nitrite was not added. However, the abundance of ions responsible for the presence of ^{15}N nitrogen in the NDMA molecule (i.e., m/z = 31 and m/z = 75) was significantly higher in extracts into which labeled nitrite was added: about ten times in the case of permanganate application and a few times in the case of ferrate. This phenomenon was observed despite the different influence that nitrite presence has on yield of NDMA formation observed for permanganate and ferrate application. Furthermore, the increase in the nitrite dose resulted in the increases of relative abundances of the two observed ions. This phenomenon was observed for the two oxidants. On the other hand, application of the same molar doses of nitrite (added to reaction mixtures of both oxidants) shows different results in relative abundances of m/z = 31 and m/z = 75 ions, depending on whether permanganate or ferrate was applied.This phenomenon can be explained twofold: (a) by different oxidant/DMA molar ratios (b) by significant differences in reaction rate constants of permanganate and ferrate

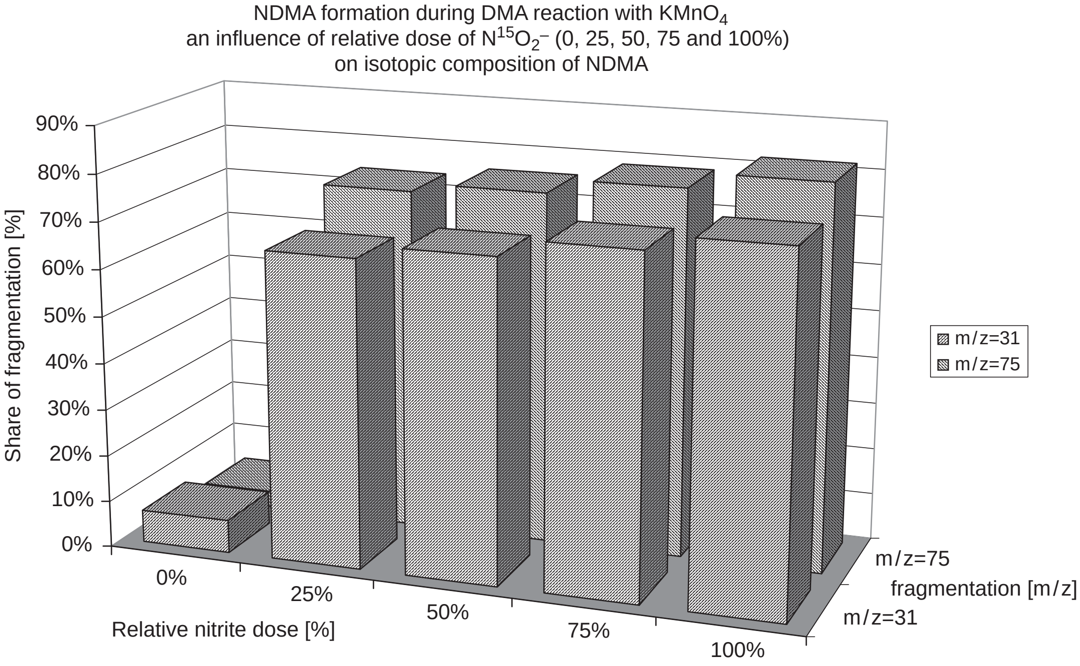

Fig. 4. NDMA formation during DMAma reaction with $KMnO_4$. The influence of the relative dose of $N^{15}O_2^-$ (0%, 25%, 50%, 75% and 100%) on isotopic composition of NDMA. pH = 8.25, $KMnO_4$ concentration of 1.27 mM, $KMnO_4$/DMA molar ratio of 0.29:1 [M/M].

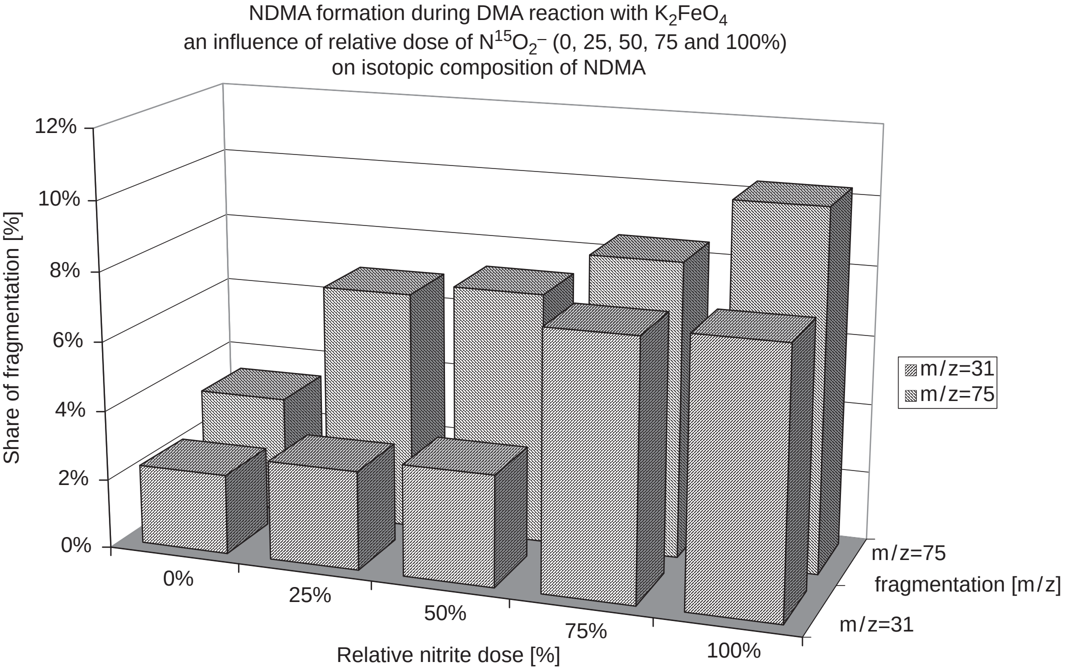

Fig. 5. NDMA formation during DMA reaction with K_2FeO_4. The influence of the relative dose of $^{15}NO_2^-$ (0%, 25%, 50%, 75% and 100%) on isotopic composition of NDMA pH = 8.25, K_2FeO_4 concentration of 1 mM, K_2FeO_4/DMA molar ratio of 1.15:1 [M/M].

with other components of their reaction mixtures (see the increase of NDMA concentration vs. contact time in Figs. 2 and 3). Another phenomenon was observed as well: the presence of NDMA without labeled nitrogen was still noticed in the post-reaction mixture, also when the amount of labeled nitrite added to the reaction mixture equaled 100% of moles of nitrite required to reduce both oxidants in the reaction mixtures. This means that there are two independent sources of the nitrosation agent in these reactions: one originating from labeled nitrite and the other one originating from nitrite formed as a result of DMA oxidation.

4. Proposed pathway of NDMA formation

Phenomena observed during reactions of both oxidants with aquatic solution of DMA and labeled nitrite (presence of labeled and non-labeled NDMA in post reaction mixture) can be explained as a result of a chain of reactions of NDMA formation shown in Fig. 6. An oxidant (permanganate of ferrate) added to the aqueous solution of DMA and labeled nitrite (^{15}N) reacts both with DMA and labeled nitrite. The nitrosating agent ($^{15}N^*=O$) is formed as a result of the multi-steps reaction of oxidant with labeled nitrite. Simultaneously, part of DMA is oxidized: both, the methyl groups, as well as nitrogen are oxidized during this reaction. The methyl groups of DMA are oxidized to methanol, formaldehyde and formic acid depending on the oxidant/DMA rate (both HCHO and HCOOH were discovered in post-reaction mixture and the amount of HCOOH formed reached a few percent of initial amount of DMA) and finally to carbon dioxide. On the other hand, nitrogen in DMA molecule is oxidized to nitrite and nitrate (both of these compounds were also discovered in the post-reaction mixture). Subsequently, the rest of the oxidant reacts with nitrite (originating from DMA oxidation) to form the non-labeled nitrosating agent ($^{14}N^* = O$). These two nitrosating agents (i.e., $^{15}N^* = O$ and $^{14}N^* = O$) react with the remaining part of DMA to form both labeled NDMA ($(CH_3)_2N^{14}–N^{15} = O$) and non-labeled NDMA ($(CH_3)_2N^{14}$ $N^{14} = O$). The mechanism of nitrosation agent formation ($N^* = O$) is still unsolved. However, the results of investigations presented by Schreiber and Mitch [6] and Uppu and Pryor [7], suggest that *N = O could be formed as a result of a multi-step reaction of oxidant with nitrite via formation of peroxynitrous acid or peroxynitrite ion. Based on the above presented results and discussion, nitrosation as a mechanism of NDMA formation during oxidation of DMA with permanganate or ferrate, should be responsible for these reactions.

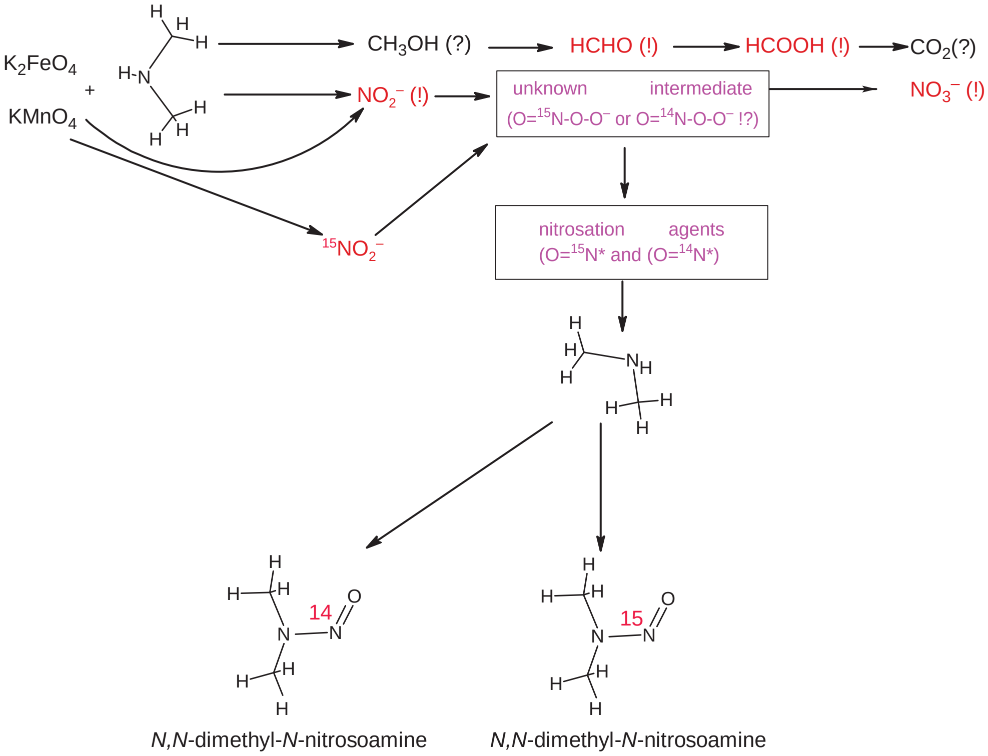

Fig. 6. The proposed mechanism of NDMA formation during ferrate or permanganate reactions with aqueous solutions of dimethylamine (DMA) in the presence of labeled ^{15}N nitrite. (?)—Compounds which are probably formed, (!)—Compounds identified in post-reaction mixtures.

5. Conclusions

1. Oxidation of DMA aqueous solutions with ferrate leads to the formation of NDMA. The efficiency of the reaction is considerable only if ferrate concentration significantly higher than typically applied in water treatment.
2. Presence of nitrite has impact on the yield of NDMA formation during permanganate or ferrate reaction with aqueous solution of DMA.
3. The presence of ^{15}N nuclide (added as $^{15}NO_2^-$ ion to reaction mixture) in the NDMA molecule, in the higher than normal abundance, clearly shows, that nitrite is the source of nitroso group in the NDMA molecule. Thus the mechanism of nitrosation of DMA is responsible for NDMA formation during permanganate/ferrate reactions with aqueous solution of DMA.

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