# Kinetic and Theoretical Study of the Nitrate (NO<sub>3</sub>) Radical Gas Phase Reactions with *N*-Nitrosodimethylamine and *N*-Nitrosodiethylamine

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**Supporting Information** 

**ABSTRACT:** The reaction rates of  $(CH_3)_2NNO$  and  $(CH_3CH_2)_2NNO$  with NO<sub>3</sub> radicals were determined relative to formaldehyde  $(CH_2O)$  and ethene  $(CH_2CH_2)$  at 298 ± 2 K and 1013 ± 10 hPa in purified air by long path FTIR spectroscopy. The reactions are too slow to be of importance at atmospheric conditions:  $k_{NO_3+(CH_3)_2NNO} = (1.47 \pm 0.23) \times 10^{-16}$  and  $k_{NO_3+(CH_3CH_2)_2NNO} = (5.1 \pm 0.4) \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (1 $\sigma$  error limits). Theoretical calculations, based on CCSD-(T\*)-F12a/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ results, predict the corresponding imines as the sole primary products in nitrosamine reactions with NO<sub>3</sub> and OH radicals.

# **1. INTRODUCTION**

The first report of nitrosamines in ambient air appeared 40 years ago.<sup>1</sup> Nitrosamines are known to be formed in the atmospheric photo-oxidation of secondary and tertiary amines<sup>2-6</sup> originating in a wide range of sources.<sup>7</sup> Gas phase photo-oxidation of *N*,*N*-disubstituted amides was recently identified as an additional source to nitrosamines.<sup>8</sup> Planned large scale implementation of amine-based technology for carbon capture and storage (CCS) may reduce  $CO_2$  emissions from new and existing fossil fuel point sources, but the operation will likely result into small but still important discharges of solvent amines and other process degradation products, including nitrosamines and simple aliphatic amines, to the atmosphere.<sup>9</sup> Such installations may therefore present significant perturbations to the natural amine and nitrosamine budgets.

For dimethylamine the atmospheric reaction sequence leading to N-nitrosodimethylamine is<sup>3</sup>

$$(CH_3)_2NH + \dot{X} \rightarrow \dot{C}H_2NHCH_3 + HX; \dot{X}$$
  
= OH, NO<sub>3</sub>, Cl (1a)

$$\rightarrow (CH_3)_2 \dot{N} + HX \tag{1b}$$

$$(CH_3)_2\dot{N} + NO \rightarrow (CH_3)_2NNO$$
 (2)

Although  $O_2$  reaction with amino radicals,  $R_1R_2\dot{N}$ , is 6 orders of magnitude slower than the corresponding NO and  $NO_2$  reactions,<sup>3</sup> it is still dominating at atmospheric conditions,



and *N*-nitrosodimethylamine and *N*-nitrosodiethylamine are only minor products in the atmospheric photo-oxidation of respectively dimethylamine<sup>3,4</sup> and diethylamine.<sup>2,5</sup>

The nitrosamine chromophore has a characteristic  $n \rightarrow \pi^*$  transition in the UV-A region and nitrosamine compounds are rapidly photolyzed in sunlight with a characteristic average lifetime of less than an hour:<sup>10</sup>

$$(CH_3)_2 NNO \rightarrow (CH_3)_2 \dot{N} + NO$$
 (2-)

Other atmospheric nitrosamine removal processes include reaction with OH, Cl atoms, NO<sub>3</sub> radicals, and O<sub>3</sub>. The reaction of OH radicals with *N*-nitrosodimethylamine was studied by Tuazon et al.<sup>11</sup> employing long-path FTIR, and by Zabarnick et al. using the two-laser photolysis/LIF probe technique,<sup>12</sup> reporting rate coefficients of  $(2.4 \pm 0.4)$  and  $(3.6 \pm 0.1) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K, respectively. With  $[OH]_{24h} = 10^6$  cm<sup>-3</sup>,<sup>13</sup> the average atmospheric lifetime of nitrosamines with respect to reaction with OH will therefore be around 3 days or around 100 times longer than the average photolysis lifetime; nitrosamine loss by reaction with OH radicals is therefore of no importance in the natural atmosphere.

The gas phase reactions of  $\rm NO_3$  radicals with amines are extremely fast,  $^{10}$  and a considerable nitrosamines build-up may

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potentially take place during the nighttime. It is, consequently, important to characterize all possible nighttime nitrosamine loss processes including reaction with NO<sub>3</sub> radicals.

## 2. EXPERIMENTAL SECTION

*Caution! N*-Nitrosodimethylamine (NDMA) and *N*-nitrosodiethylamine (NDEA) are potent mutagens and carcinogens<sup>14</sup> and should be handled with the utmost care.

**Chemicals.** For both dimethylnitrosamine<sup>15</sup> and diethylnitrosamine,<sup>16</sup> modifications of previously published methods are utilized. Because of the above-mentioned risks, the syntheses are thoroughly described below.

Safety Precautions. Standard precautions have been implemented when working with these compounds, i.e. use of gloves, laboratory coat and safety goggles. All reactions have been done in an inert atmosphere  $(N_2)$  in a well-ventilated fume hood. Work has been performed behind safety shields. All chemical waste is sealed in special flasks and sent to authorized companies for destruction of such materials.

Dimethylnitrosamine. Dimethylamine hydrochloride (25.3 g, 0.312 mol, 1 equiv) was dissolved in water (15 mL) and the reaction mixture was acidified with 2 M HCl (1 mL). The mixture was stirred vigorously and heated to around 75 °C. Next, sodium nitrite (24.3 g, 0.352 mol, 1.08 equiv) was dissolved in water (30 mL) and slowly added to the reaction mixture by means of a dropping funnel over a period of 1 h. The reaction mixture was tested regularly with litmus paper and small volumes of 2 M HCl were added from time to time to ensure an acidic reaction environment. Following the complete addition of sodium nitrite, the reaction mixture was then stirred for 2 h. Next, the reaction mixture was distilled until essentially dry, after which 15 mL of water was added to the flask and the process repeated. The distillates were combined and potassium carbonate was added in order to "salt out" the dimethylnitrosoamine. The upper organic layer was separated and the water phase was extracted three times with ether. The combined organic phases were dried (K<sub>2</sub>CO<sub>3</sub>) and distilled using a Claisen-Vigreux apparatus. Yield: 21.7 g (94%) of a pale yellow oil. Bp: 145-146 °C/760 mmHg (lit. 15 149-150 °C/755 mmHg). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.04 (s, 3H), 3.76 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  32.84, 40.61 ppm.

Diethvlnitrosamine. Diethvlamine hydrochloride (50.0 g. 0.456 mol, 1 equiv) was dissolved in water (40 mL) and the reaction mixture was acidified with 2 M HCl (4 mL). The mixture was stirred vigorously under an nitrogen atmosphere for 5 min and then heated to 70-75 °C. Sodium nitrite (34.0 g, 0.493 mol, 1.1 equiv) was dissolved in water (50 mL) and slowly added to the reaction mixture by means of a dropping funnel over a period of 1 h. The reaction mixture was tested regularly with litmus paper, and small volumes of 2 M HCl were added from time to time to ensure an acidic reaction environment. The reaction mixture was then stirred for an additional 2 h, and then allowed to be cooled to ambient temperature. Two distinct phases were then observed, with a faint yellow organic layer being on top. The reaction mixture was saturated with NaCl, and the contents were poured into a separatory funnel. The organic layer was separated, and the aqueous phase extracted with diethyl ether  $(3 \times 50 \text{ mL})$ . The combined organic phase was dried  $(K_2CO_3 + MgSO_4)$ . Concentration in vacuo and distillation of the yellow residue using an ordinary Claisen–Vigreux set up gave 30.9 g (68%) of the product as a pale yellow oil. Bp: 55-58 °C/10-13 mmHg. (lit.<sup>17</sup> 177 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.06 (t, 3H, J

7.5 Hz), 1.36 (t, 3H, J 6.9 Hz), 3.56 (q, 2H, J 7.5 Hz), 4.09 (q, 2H, J 7.5 Hz).  $^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  11.11, 13.95, 38.60, 47.15 ppm.

Formaldehyde was prepared by heating paraformaldehyde (Sigma-Aldrich 95%) and trapping the vapors at liquid nitrogen temperature. The trapped mixture was slowly warmed and pure CH<sub>2</sub>O was collected in a bulb on a vacuum line and subsequently flushed into the reaction chamber in a stream of N<sub>2</sub>. Ethene (Sigma-Aldrich, > 99.9%) was transferred to a bulb on a vacuum line and flushed into the reaction chamber in a stream of N<sub>2</sub>. NO<sub>3</sub> was generated in the reactor by thermal dissociation of N<sub>2</sub>O<sub>5</sub> that was synthesized by mixing O<sub>3</sub> with excess NO<sub>2</sub> in purified air and trapping the mixture at -80 °C. HNO<sub>3</sub> and NO<sub>2</sub> was removed at low pressures on a vacuum line.

**Relative Rate Experiments and Reference Spectra.** The experiments were carried out in a 240 L electropolished stainless steel smog chamber (herein referred to as the Oslo chamber) equipped with a White type multiple reflection mirror system adjusted to 120 m optical path length for rovibrationally resolved infrared spectroscopy. IR spectra were recorded with a Bruker IFS 66v FTIR instrument employing an LN<sub>2</sub>-cooled MCT detector. All experiments were carried out in synthetic air (AGA 99.99%; CH<sub>4</sub>, CO and NO<sub>x</sub> < 100 ppbV) at 298 ± 2 K. Initial partial pressures of the nitrosamines and reference compounds (ethene and formaldehyde) were in the range of 0.1–1.5 Pa and the cell was filled to 1013 ± 10 hPa with synthetic air. As a standard, 128 scans were coadded at a nominal resolution of 0.5 cm<sup>-1</sup> and Fourier transformed using boxcar apodization.

The kinetics of the reactions between nitrosamine and NO<sub>3</sub> were studied by the relative rate method in which the compound under study is competing with a reference compound for reaction with in situ generated radicals. Assuming that the reactants react solely with the same radical and that none of the reactants are reformed in any side reactions, the relative rate coefficient,  $k_{\rm rel}$ , is given according to the following expression:

$$\ln\left\{\frac{[\text{sample}]_{0}}{[\text{sample}]_{t}}\right\} = k_{rel} \cdot \ln\left\{\frac{[\text{reference}]_{0}}{[\text{reference}]_{t}}\right\}, \ k_{rel} = \frac{k_{\text{sample}}}{k_{\text{reference}}}$$
(I)

where [reference]<sub>0</sub>, [sample]<sub>0</sub>, [reference]<sub>t</sub>, and [sample]<sub>t</sub> are concentrations of the reference and the sample (nitrosamine) at the start and at time t, respectively, and  $k_{sample}$  and  $k_{reference}$  are rate coefficients. A plot of  $ln{[sample]_0/[sample]_t}$  vs  $ln{[reference]_0/[reference]_t}$  will thus give the relative reaction rate coefficient  $k_{rel} = k_{sample}/k_{reference}$  as the slope from which  $k_{sample}$  is then derived. Data from independent experiments have been analyzed jointly according to eq I using a weighted least-squares procedure that includes uncertainties in both reactant concentrations.<sup>18</sup> The estimated uncertainty in the concentration determination by FTIR was taken as either 1% of the initial concentration or  $3\sigma$  from the least-squares spectral analysis, whichever the largest.

Control experiments were performed to check for loss of nitrosamines and reference compounds via "dark chemistry" and heterogeneous reactions in the reactor with purified air as diluent in experiments lasting for 2 h. The lifetimes were found to be in the order of days, hence "dark chemistry" and surfaceloss were consequently neglected in the analyses.

The experimental FTIR spectra were analyzed using a global nonlinear least-squares spectral fitting procedure.<sup>19</sup> In this method, the spectrum of the mixture of absorbing species is first simulated by calculation from initial estimates of the absorber concentrations. The calculation is then iterated to minimize the residual between the measured and simulated spectrum to adjust the absorber concentrations, continuum level and instrument line shape parameters. When possible, absorption coefficients are calculated from the HITRAN database;<sup>20</sup> if HITRAN line parameter data are not available, high-resolution FTIR spectra are used to approximate the absorption coefficients. In the present study, we recorded reference spectra of CH2=CH2, CH2O, N2O5, (CH3)2NNO and  $(CH_{3}CH_{2})_{2}NNO$ ; the latter two are shown in Figures S1 and S2, respectively, while Table S1 (Supporting Information) sums up the wavenumber regions employed and the chemical components included in the spectral analyses.

# 3. THEORETICAL CALCULATIONS

**Electronic Structure Calculations.** Reaction enthalpies were calculated from the G4 model chemistry,<sup>21</sup> which is reported to reproduce the G3/05 test set<sup>22</sup> with average absolute deviation of around 3.5 kJ mol<sup>-1</sup>. The G4 results are collected in Table S2 in the Supporting Information. Potential energy surfaces (PES) of reactions were explored in M06-2X<sup>23</sup> calculations with the aug-cc-pVTZ basis set,<sup>24,25</sup> and intrinsic reaction coordinate paths were followed to verify that the saddle points connect to the correct reactants and products. To obtain more reliable energies for the stationary points of the PES, single point energies were obtained in CCSD(T\*)-F12a/aug-cc-pVTZ/M06-2X/aug-cc-pVTZ computations. Gaussian 09<sup>26</sup> was used in M06-2X and G4 calculations whereas MOLPRO<sup>27</sup> was used for the CCSD(T\*)-F12a calculations.

**Master Equation Modeling.** Master equation calculations were carried out employing the program MESMER (master equation solver for multi-energy-well reactions).<sup>28</sup> Energies and molecular data were taken from the CCSD(T\*)-F12/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculations. The energy transfer in collisions with N<sub>2</sub> and O<sub>2</sub>,  $\langle \Delta E_{down} \rangle$ , was set to 250 cm<sup>-1</sup>.

# 4. RESULTS AND DISCUSSION

**Kinetic Study.** Initial studies of the NO<sub>3</sub> radicals reaction with the nitrosamines indicated the reactions to be very slow and only two reference compounds were found to be suitable: formaldehyde and ethene. On the basis of a critical review of all experimental data, the currently recommended rate coefficients for the reactions of NO<sub>3</sub> radicals with ethene and formaldehyde are respectively  $2.1 \times 10^{-16}$  and  $5.5 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K; the uncertainty factors are ~1.6 ( $\Delta \log_{10} k = \pm 0.20$ ).<sup>29</sup>

The quality of the spectral subtraction procedure behind the relative rate data is illustrated for the more crowded infrared spectra of the  $(CH_3CH_2)_2NNO/CH_2=CH_2/NO_3$  system obtained after 226 min of reaction in Figure 1; the infrared spectra of the  $(CH_3CH_2)_2NNO/CH_2O/NO_3$  system are simpler to analyze in the sense that the bands of  $(CH_3CH_2)_2NNO$  and  $CH_2O$  do not overlap in this region. It can be seen from Figure 1 that essentially all spectral features are accounted for; the residual absorptions around 1060 and 1020 cm<sup>-1</sup> grow larger with time of reaction and eventually affect the reliability of the analysis method. The later spectra of the experiments were therefore not included in the final data analyses. There are no other clear spectral indications of

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**Figure 1.** FTIR spectrum  $(1120-875 \text{ cm}^{-1})$  of the  $(CH_3CH_2)_2NNO/CH_2=CH_2/NO_3$  system after 226 min of reaction, and of the individual compounds included in the spectral analysis. The spectra have been shifted in absorbance for the sake of distinguishability.

organic products formed in the reaction. No additional product information was obtained from oxidation experiments without the reference compounds being present.

Figure 2 summarizes the experimental data for  $(CH_3CH_2)_2NNO$  where the following relative rates  $(1\sigma$ -errors) were determined:  $k_{(CH_3CH_2)_2NNO+NO_3}/k_{CH_2O+NO_3} = 0.882 \pm 0.006$  (intercept:  $-0.0015 \pm 0.0015$ ),  $k_{(CH_3CH_2)_2NNO+NO_3}/k_{CH_2CH_2+NO_3} = 2.594 \pm 0.024$  (intercept:  $0.0017 \pm 0.0015$ ). Constraining the intercepts to zero results in  $k_{(CH_3CH_2)_2NNO+NO_3}/k_{CH_2O+NO_3} = 0.8760 \pm 0.0026$  and  $k_{(CH_3CH_2)_2NNO+NO_3}/k_{CH_2CH_2+NO_3} = 2.618 \pm 0.011$ . Taking todays recommended values for  $k_{CH_2CH_2+NO_3}$  and  $k_{CH_2O+NO_3}$ , places  $k_{(CH_3CH_2)_2NNO+NO_3}$  at respectively 4.8 and 5.5 ×  $10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> on an absolute scale at 298 K.

The  $(CH_3)_2NNO + NO_3$  reaction is very slow-near the lower limit for reactions that can be studied in the Oslochamber-and the results are consequently sensitive to systematic errors. Figure 3 summarizes the results from two independent experiments with CH2O as reference compound from which  $k_{(CH_3)_2NNO+NO_3}/k_{CH_2O+NO_3} = 0.239 \pm 0.010$ (intercept:  $-0.0025 \pm 0.0014$ ,  $1\sigma$  errors) was derived, and results from three independent experiments with CH<sub>2</sub>CH<sub>2</sub> as reference compound from which  $k_{(CH_3)_2NNO+NO_3}/k_{CH_2CH_2+NO_3} =$  $0.778 \pm 0.020$  (intercept:  $-0.0015 \pm 0.0015$ ) was derived. Constraining the intercepts to zero results in  $k_{(CH_3),NNO+NO_3}$  $k_{\rm CH_2O+NO_3} = 0.223 \pm 0.0049$  and  $k_{\rm (CH_3)_2NNO+NO_3}/k_{\rm CH_2CH_2+NO_3} =$  $0.760 \pm 0.009$ . On an absolute scale these results place  $k_{(CH_3),NNO+NO_3}$  at 1.60 and  $1.22 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. The quality of the spectral subtraction procedure behind the relative rate data is illustrated for the  $(CH_3)_2NNO/CH_2 =$  $CH_2/NO_3$  system in Figure 4. It can be seen that essentially all spectral features are accounted for; the small residual around  $1050 \text{ cm}^{-1}$  does not originate from the infrared bands of the





**Figure 2.** (A) Decays of  $(CH_3CH_2)_2$ NNO and  $CH_2O$  in the presence of NO<sub>3</sub> radicals plotted as  $ln\{[(CH_3CH_2)_2NNO]_0/[(CH_3CH_2)_2NNO]_t\}$  vs.  $ln\{[CH_2O]_0/[CH_2O]_t\}$ . Analysis of 22 data points from two experiments (different symbols for each of the two experiments) give a relative rate coefficient  $k_{(CH_3CH_2)_2NNO+NO_3}/k_{CH_2O+NO_3} = 0.882 \pm 0.006 (1\sigma)$ . (B) Decays of  $(CH_3CH_2)_2NNO$ and  $CH_2CH_2$  in the presence of NO<sub>3</sub> radicals plotted as ln- $\{[(CH_3CH_2)_2NNO]_0/[(CH_3CH_2)_2NNO]_t\}$  vs.  $ln\{[CH_2CH_2]_0/[CH_2CH_2]_t\}$ . Analysis of 28 data points from 2 experiments (different symbols for each of the two experiments) give a relative rate coefficient  $k_{(CH_3CH_2)_2NNO+NO_3}/k_{CH_2CH_2+NO_3} = 2.594 \pm 0.024 (1\sigma)$ .

potential primary product,  $CH_3N=CH_2$  (see later). No additional product information was obtained from experiments without the reference compounds being present.

Table 1 summarizes the kinetic results from which it can be seen that absolute values obtained in the experiments with ethane as reference compound in both cases are larger than the corresponding values obtained using formaldehyde as reference compound. Considering an uncertainty factor of ~1.6 in the absolute rate coefficients for NO<sub>3</sub> reaction with the two reference compounds, the present relative rate results are in internal agreement and we recommend using the average values  $(1.47 \pm 0.23) \times 10^{-16}$  and  $(5.1 \pm 0.4) \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup>



**Figure 3.** (A) Decays of  $(CH_3)_2$ NNO and  $CH_2O$  in the presence of NO<sub>3</sub> radicals plotted as  $ln\{[(CH_3)_2NNO]_0/[(CH_3)_2NNO]_t\}$  vs.  $ln\{[CH_2O]_0/[CH_2O]_t\}$ . Analysis of 18 data points from two experiments (different symbols for each of the two experiments) give a relative rate coefficient  $k_{(CH_3)_2NNO_2+NO_3}/k_{CH_2O+NO_3} = 0.239 \pm 0.010$ . (B) Decays of  $(CH_3)_2$ NNO and  $CH_2CH_2$  in the presence of NO<sub>3</sub> radicals plotted as  $ln\{[(CH_3)_2NNO]_0/[(CH_3)_2NNO]_t\}$  vs.  $ln\{[CH_2CH_2]_0/[CH_2CH_2]_t\}$ . Analysis of 55 data points from three experiments (different symbols for each of the three experiments) give a relative rate coefficient  $k_{(CH_3)_2NNO+NO_3}/k_{CH_2CH_2+NO_3} = 0.778 \pm 0.020$ .

 $s^{-1}$  at 298 K as rate coefficients for the NO<sub>3</sub> radical reactions with (CH<sub>3</sub>)<sub>2</sub>NNO and (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NNO.

**Theoretical Study.** The NO<sub>3</sub> radical reactions with NDMA and NDEA are slow and the experimental study revealed no clear spectral features that could be used to identify primary products formed in the reactions. A simple model of a reaction sequence  $A \rightarrow B \rightarrow C$  in which the rate coefficient of the second step is 10 times that of the first step shows that the maximum concentration of B is <8% of  $A_{t=0}$  and that the maximum is obtained when 20% of A has reacted. The rate coefficient for NO<sub>3</sub> reaction with CH<sub>3</sub>N=CH<sub>2</sub> is unknown, but it is likely somewhat smaller than that for NO<sub>3</sub> reaction with CH<sub>3</sub>CH=CH<sub>2</sub> (9.5 × 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298



**Figure 4.** FTIR spectrum  $(1120-875 \text{ cm}^{-1})$  of the  $(CH_3)_2NNO/CH_2=CH_2/NO_3$  system after 102 min of reaction and of the individual compounds included in the spectral analysis. The spectra have been shifted in absorbance for the sake of distinguishability.

K),<sup>30</sup> which is around 60 times that for NO<sub>3</sub> reaction with NDMA. It is therefore likely that the primary product in NO<sub>3</sub> + NDMA/NDEA reactions may well evade detection by FTIR in our experiments.

The NO<sub>3</sub> radical presents a computational challenge; it is currently not possible to calculate the electronic structure of the NO<sub>3</sub> radical correctly using any standard size extensive method that is also applicable to larger systems.<sup>31</sup> The energetics of NO<sub>3</sub> radical reactions were therefore placed on an absolute scale using the theoretical results for the corresponding OH radical reactions and standard enthalpies of formation (in kJ mol<sup>-1</sup>) from the NIST-JANAF Themochemical Tables<sup>32</sup> for OH (38.99), H<sub>2</sub>O (-241.83), NO<sub>3</sub> (71.13), and HNO<sub>3</sub> (-134.31). With the exception of NO<sub>3</sub> radical reactions, the enthalpies included with the individual reactions stem from G4calculations.

It is well-known that NO<sub>3</sub> radical reactions with alkanes and many substituted alkanes proceed by H-abstraction from the various  $-CH_3$ ,  $>CH_2$  and >CH- groups.<sup>33</sup> The initial steps in the OH and NO<sub>3</sub> radical reactions with NDMA are

$$(CH_3)_2 NNO + OH \rightarrow CH_3 N(NO)\dot{CH}_2 + H_2O,$$
  
 $\Delta H_{298K}^{\circ} = -121 \text{ kJ mol}^{-1}$ 
(3)

$$(CH_3)_2NNO + NO_3 \rightarrow CH_3N(NO)\dot{C}H_2 + HNO_3,$$
  
 $\Delta H_{298K}^{\circ} = -46 \text{ kJ mol}^{-1}$ 
(4)

The  $CH_3N(NO)\dot{C}H_2$  radical may either dissociate (eject NO) or add  $O_2$ , forming a vibrationally hot peroxy radical:

$$CH_{3}N(NO)\dot{C}H_{2} \rightarrow CH_{3}N = CH_{2} + NO,$$
$$\Delta H_{208K}^{\circ} = -45 \text{ kJ mol}^{-1}$$
(5)

$$CH_{3}N(NO)\dot{C}H_{2} + O_{2} \rightarrow CH_{3}N(NO)CH_{2}O\dot{O}^{\dagger},$$
  
$$\Delta H_{298K}^{\circ} = -99 \text{ kJ mol}^{-1}$$
(6)

The barrier to NO ejection was calculated to be around 14 kJ mol<sup>-1</sup> placing it well below the entrance energy of the reactants (structures and energies of the relevant stationary points on the potential energy surface are collected in Tables S3 and S4 in the Supporting Information). In addition, the CH<sub>3</sub>N(NO)ĊH<sub>2</sub> radical is formed with some excess internal energy,  $\sim 70$  kJ  $mol^{-1}$  in the OH reaction and ~25 kJ  $mol^{-1}$  in the NO<sub>3</sub> reaction assuming equipartitioning of the reaction enthalpy and disregarding any barriers to reaction. The branching between the dissociation reaction 5 and the addition reaction 6 was examined using a master equation model in which reaction 6 was treated as an energy independent, irreversible sink of  $CH_3N(NO)\dot{C}H_2$  with a rate coefficient of  $8 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (approximate value for the  $CH_3CH_2\dot{C}H_2 + O_2$ reaction  $^{29}$ ). The calculations show that reaction 5 is so fast (~7  $\times$  10^{11} s^{-1}) that, even disregarding excess internal energy in the CH<sub>3</sub>N(NO)CH<sub>2</sub> radical, peroxy-radical formation can be completely neglected at atmospheric conditions. For comparison, our previous experimental and theoretical study of OH and Cl atom reactions with the corresponding nitramine, CH<sub>3</sub>N(NO<sub>2</sub>)CH<sub>3</sub>,<sup>34</sup> reveal a higher barrier to N-N scission in CH<sub>3</sub>N(NO<sub>2</sub>)ĊH<sub>2</sub> than in CH<sub>3</sub>N(NO)ĊH<sub>2</sub>, and that CH<sub>3</sub>N-(NO<sub>2</sub>)CHO is a major product in the Cl atom initiated oxidation of CH<sub>3</sub>N(NO<sub>2</sub>)CH<sub>3</sub>. Because of the higher exothermicity of OH than Cl abstraction reactions, the imine will, however, also be the dominant product in the atmospheric  $CH_3N(NO_2)CH_3$  photo-oxidation.

For diethylnitrosamine, the dominant route in reactions with OH and NO<sub>3</sub> is H-abstraction from one of the - CH<sub>2</sub>- groups (the Atkinson SAR<sup>35</sup> for OH reactions with organics predicts 2% CH<sub>3</sub> abstraction and 98% CH<sub>2</sub> abstraction):

Table 1. Experimental Relative Rate Coefficients and Derived Absolute Rate Coefficients  $(/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$  for the Reactions of Nitrosamines with NO<sub>3</sub> Radicals  $(1\sigma$ -errors)

nitramine	reference compound	$k_{ m rel}$	$k_{ m ref}^{\ a}$	$k_{ m Nitrosamine+NO_3}$
(CH <sub>3</sub> ) <sub>2</sub> NNO	CH <sub>2</sub> O	$0.239 \pm 0.010$	$5.5 \times 10^{-16}$	$1.31 \times 10^{-16}$
	CH <sub>2</sub> CH <sub>2</sub>	$0.778 \pm 0.020$	$2.1 \times 10^{-16}$	$1.63 \times 10^{-16}$
				$(1.47 \pm 0.23) \times 10^{-16}$
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NNO	CH <sub>2</sub> O	$0.882 \pm 0.006$	$5.5 \times 10^{-16}$	$4.85 \times 10^{-16}$
	$CH_2CH_2$	$2.593 \pm 0.024$	$2.1 \times 10^{-16}$	$5.45 \times 10^{-16}$
				$(5.1 \pm 0.4) \times 10^{-16}$

<sup>a</sup>Reference rate coefficients from ref 29.

$$(CH_3CH_2)_2NNO + NO_3 \rightarrow CH_3CH_2N(NO)\dot{C}HCH_3 + HNO_3,$$
$$\Delta H_{298K}^{\circ} = -49 \text{ kJ mol}^{-1}$$
(8)

The barrier to NO ejection in the  $CH_3CH_3N(NO)\dot{C}HCH_3$ radical is calculated to be very low, ~ 4 kJ mol<sup>-1</sup> (structures and energies of the relevant stationary points on the potential energy surface are collected in Tables S5 and S6 in the Supporting Information). It can therefore be concluded that  $CH_3CH_3N=CHCH_3$  will be the only product resulting from the NDEA + OH/NO<sub>3</sub> reactions.

# 5. CONCLUSIONS AND IMPLICATIONS

From extensive reviews, it is established that NO<sub>3</sub> radicals in general reacts with saturated compounds through Habstraction, forming nitric acid, and with unsaturated compounds through addition.<sup>33,36</sup> The gas phase reactions of NO3 radicals with amines are as already mentioned extremely fast; Cabañas Galán<sup>37</sup> and Nielsen et al.<sup>5</sup> report NO<sub>3</sub> rate coefficients in the range  $10^{-13}$ - $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> contrasting the 2-3 orders of magnitude lower reactivity of nitrosamines toward NO<sub>3</sub>. Obviously, the electron withdrawing nitroso-group changes the electronic structure of dimethylamine (DMA) significantly. According to the theoretical calculations the average C-H and C-N bond distances in NDMA are shortened by respectively 0.004 and 0.005 Å relative to their values in DMA. The average atomic charge on the methyl group hydrogen, calculated according to the Merz-Singh-Kollman scheme,<sup>38</sup> change from +0.059 to +0.124, whereas the atomic charge on the amino nitrogen change from -0.617 in DMA to +0.442 in NDMA. Availability of the lone pair electrons on the amino nitrogen to the electrophilic NO<sub>3</sub> radical is consequently lower in NDMA than in DMA, and the simultaneous decrease in electron density around the methyl hydrogen will lower the reactivity toward NO<sub>3</sub>.

Atkinson<sup>33</sup> reported a correlation of the H atom abstraction rate coefficients per equivalent C-H bond for the room temperature reactions of NO3 and OH radicals with a series of alkanes and aldehydes, and used this relationship to extrapolate a first Structure-Activity Relationship (SAR) for NO3 radical reactions from the existing general SAR for OH radical reaction with organics.<sup>39,40</sup> The NO<sub>3</sub>-SAR has group rate constants  $k_{\text{NO}_3}^{\text{prim}} = 7.0 \times 10^{-19} \text{ and } k_{\text{NO}_3}^{\text{sec}} = 1.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for  $-CH_3$  and  $-CH_2-$ , and a general relation between substituent factors  $F_{NO_3}(X) = [F_{OH}(X)]^{1.611}$ . More recently Kerdouci et al.<sup>41</sup> presented a new NO<sub>3</sub>–SAR based on data for alkanes, alkenes, dienes, terpenes, and saturated and unsaturated oxygenated compounds including alcohols, ketones, ethers, and esters in which  $k_{\rm NO_3}^{prim} = 1.00 \times 10^{-18}$  and  $k_{\rm NO_3}^{\rm sec} =$  $2.56 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, F_{\text{NO}_3}(-\text{CH}_3) = 1 \text{ and}$  $F_{\rm NO_3}(>CH_2) = 1.02$ . Taking  $F_{\rm OH}(>NNO) = 9.3$  from the Atkinson OH-SAR<sup>40</sup> implies  $F_{NO_3}(>NNO) = 36$  that results in the following predictions:  $k_{(CH_3)_2NNO+NO_3} = 7.2 \times 10^{-17}$  and  $k_{(CH_3CH_2)_2NNO+NO_3} = 1.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The experimental values are around a factor of 2 larger than the predicted values that essentially are proportional to

 $F_{\text{NO}_3}(>\text{NNO})$ ; a value of  $F_{\text{NO}_3}(>\text{NNO}) = 88$  will reproduce the two experimental values within ±15%.

Measured ground-level NO<sub>3</sub> radical concentrations range up to  $10^{10}$  cm<sup>3</sup>, and a 12-h nighttime average concentration of  $5 \times 10^8$  cm<sup>3</sup> have been proposed.<sup>33,36</sup> With  $[NO_3]_{12h} = 5 \times 10^8$  cm<sup>-3</sup>, the atmospheric lifetime of nitrosamines with respect to reaction with NO<sub>3</sub> radicals will be in the order of months, whereas the characteristic time for atmospheric removal of nitrosamine by photolysis is only 30 min.<sup>5,42</sup> As mentioned in the introduction, the average atmospheric lifetime of nitrosamines with respect to reaction with OH is around 3 days. Nitrosamine loss by gas phase reactions with OH and NO<sub>3</sub> radicals is therefore of no importance in the natural atmosphere.

Other gas phase nitrosamine removal processes include transfer to the atmospheric aqueous phase consisting of cloud droplets, fog, rain, and of water-containing aerosol particles, and possible reactions with various radicals and  $O_3$  in the aqueous phase. Nitrosamines have been reported in high concentrations (NDMA > 1 nM) in Californian fogwater samples,<sup>43,44</sup> and recently also in much lower concentrations (NDMA ~ 0.07 nM) in fog samples collected at the west coast of Norway.<sup>45</sup> We note that all reported data are based on solid phase extraction involving coconut charcoal, which is known to catalyze transformation of secondary amines to produce trace levels of *N*-nitrosamines under ambient aerobic conditions.<sup>46</sup> The results should therefore be considered with some skepticism.

Considering that the Henrýs Law constants are  $1.8 \times 10^{-6}$  of  $6.6 \times 10^{-6}$  atm m<sup>3</sup> mol<sup>-1</sup> at 37 °C for NDMA and NDEA, respectively,<sup>47</sup> and that fog and clouds have liquid water content in the ranges 0.02-0.2 and 0.1-3 cm<sup>3</sup> m<sup>-3</sup>, respectively,<sup>48</sup> the equilibrium fractions of NDMA dissolved in the fog and cloud droplets will amount to less than 0.3%, respectively 4% of the total atmospheric NDMA content. Any liquid phase nitrosamine removal process must therefore be very fast to compete with the gas phase photolysis. Recent results by Weller and Herrmann<sup>49</sup> confirm that the liquid phase reactions of nitrosamines with O<sub>3</sub> and NO<sub>3</sub> radicals are too slow to be of general importance. This narrows the relevant atmospheric liquid phase sinks to OH radical reactions in maritime clouds ([OH]<sub>average</sub>  $\approx 2.0 \times 10^{-12}$  M) and remote deliquescent particles ([OH]<sub>average</sub>  $\approx 3.0 \times 10^{-12}$  M), <sup>50</sup> for which the lifetimes of NDMA ( $k_{OH} \approx 4 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>)<sup>51-53</sup> and NDEA ( $k_{OH} \approx 7 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>)<sup>54</sup> are estimated to be in the order of 10–20 min.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b05440.

Infrared spectral regions employed and chemical species included in the quantification of reactants (Table S1), energies, enthalpies, and Gibbs free energies (hartree) from G4 calculations (Table S2), energies of CH<sub>3</sub>N-(NO) $\dot{C}H_2$  and the saddle point to NO ejection and the energy difference between the two stationary points (Table S3), Cartesian coordinates of CH<sub>3</sub>N(NO) $\dot{C}H_2$ , the saddle point to NO ejection (Table S4), energies (hartree) of CH<sub>3</sub>CH<sub>2</sub>N(NO) $\dot{C}HCH_3$  and the saddle point to NO ejection and the energy difference (/kJ mol<sup>-1</sup>) between the two stationary points (Table S5),

Cartesian coordinates of CH<sub>3</sub>CH<sub>2</sub>N(NO)ĊHCH<sub>3</sub> and the saddle point to NO ejection (Table S6), infrared absorbance spectrum of ~200 ppm·m *N*-nitrosodimethylamine at 298 K (Figure S1), and infrared absorbance spectrum of ~200 ppm·m *N*-nitrosodiethylamine at 298 K (Figure S2) (PDF)

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#### Notes

The authors declare no competing financial interest.

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