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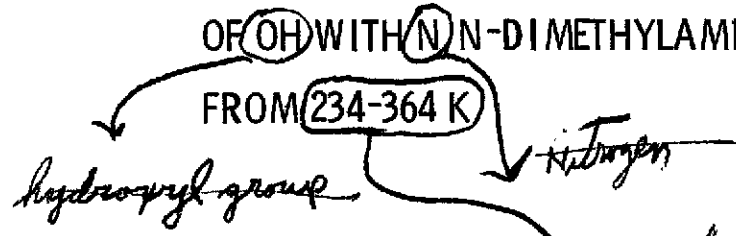
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RESEARCH REPORT

EV-113

ABSOLUTE RATE CONSTANTS FOR THE REACTION
OF OH WITH N,N-DIMETHYLAMINOETHANOL
FROM 234-364 K



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~~Two hundred — Thirty Four —~~
~~three hundred — sixty four — K~~

Environmental Science Department
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**RESEARCH
REPORT NO. ● EV-113**

Title ● Absolute Rate Constants for the Reaction of OH
with N,N-dimethylaminoethanol from 234-364 K

Date ● February 21, 1980

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Purpose

To investigate the kinetics of the hydroxyl radical (OH) reaction with N,N-dimethylaminoethanol, a water-based paint solvent component, and to estimate the potential for nitrosoamine and nitramine formation from this process.

Summary

The temperature-dependence of the rate of the reaction of OH with N,N-dimethylaminoethanol (DMAE) was investigated over the temperature range, 234 to 364 K. The reaction was studied using the flash photolysis-resonance fluorescence technique. The Arrhenius expression for this reaction is $(1.78 \pm 0.70) \times 10^{-10} e^{(-250 \pm 110)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is the first reported measurement of the kinetics of the OH radical reaction with DMAE.

A technique was developed for apportioning the overall reactivity of OH with amines to H-atom abstractions from individual C-H and/or N-H bonds within the amine. This technique was used to estimate the room-temperature rate constant for OH attack on DMAE. The technique predicts the overall rate constant within 10% of that measured in this work, and makes it possible to estimate the yields of initial products of the OH attack on amines.

A mechanism is proposed for the reactions occurring subsequent to the OH attack on DMAE. This makes it possible to estimate an upper limit for the dimethylnitrosoamine concentration, which is about 1.3 times the

amount formed from the same quantity of dimethylamine. However, other studies of amine photooxidation have reported significant quantities of substituted amides among the products. If this also happens in DMAE photooxidation, then dimethylnitrosoamine and dimethylnitramine concentrations will be reduced.

Since nitrosoamines photolyze readily under atmospheric conditions, it is possibly of greater importance to consider the potential for formation of more stable products of amine photooxidation, such as nitramines and substituted amides. Before one can evaluate the role of the atmospheric photooxidation of amines upon the formation of nitrosoamines, nitramines, etc., additional information is required on the ambient concentrations of amines and their sources.

Introduction

Nitrosoamines are suspected carcinogens and their possible formation in the atmosphere has been a subject of considerable interest [1]. The formation of nitrosoamines from the photooxidation of secondary and tertiary aliphatic amines has been investigated in several laboratories [2-6]. The early work [2,3] suggested that dimethylnitrosoamine (DMNA) could be formed from a few ppm of dimethylamine (DMA) in air containing comparable amounts of NO and NO₂. This reaction was found to occur in the dark. Nitrous acid (HONO) is formed in equilibrium with NO, NO₂, and water. It can presumably react with DMA in the dark, in a gas-phase reaction, or on the walls of a reaction vessel to form DMNA. DMNA was found to be photolyzed readily under atmospheric conditions [2-4].

Pitts et al. [4,5] have studied the photooxidation of secondary and tertiary amines in NO_x-air systems using solar irradiation. Both diethylamine (DEA) and triethylamine (TEA) were found to have very large dark losses, 20 to 50%, during the first hour. A 1% to 3% formation of diethylnitrosoamine (DENA) was observed during this dark reaction period. Upon irradiation, the 0.5 ppm of the amine initially present was totally removed. The principle carbon-containing products of this reaction were acetaldehyde (30 to 50%) and diethylnitramine (7 to 30%). Diethylformamide was present at about 9% conversion from TEA.

N,N-dimethylaminoethanol, (CH₃)₂NCH₂CH₂OH, is a tertiary amine used by General Motors as a solubilizing agent in water-based paint formulations.

Preliminary work has been performed to investigate the photooxidation of dimethylaminoethanol (DMAE) [6]. The principal products identified in this long-path infrared spectroscopic study were dimethylformamide and dimethylnitramine. The most important process in the initiation of the photooxidation of amines is their attack by hydroxyl radicals (OH). In the present study, absolute rate constants have been determined for the reaction of OH with DMAE over the temperature range 234 to 364 K, using flash photolysis-resonance fluorescence techniques.

Experimental

The apparatus and techniques used were similar to those described by others [7,8]. Hydroxyl radicals were produced by the vacuum ultraviolet photolysis of H_2O at wavelengths longer than the suprasil window cutoff (>160 nm). The flashlamp was typically operated at 68 J per flash and a repetition rate of one flash every three seconds. Flash energies as high as 127 J were used to check for effects of flashlamp intensity.

The OH concentration was monitored as a function of time after the flash by observing its resonance fluorescence. The OH resonance radiation was produced by flowing 1% H_2O in helium at about 5 torr (1 torr = 133.32 Pa) through a 2450 MHz microwave discharge. The resonance radiation was imaged into the reaction vessel at right angles to the flash. Resonance fluorescence from the OH radicals was observed at right angles to both the flash and resonance radiation with an EMI-9789QA photomultiplier and interference filter (peak λ = 310.7 nm, 16% T, fwhm = 4.3 nm). The intersection of the aperture of the detection system and

the resonance radiation defines the fluorescence viewing zone. This zone is well separated from the walls of the reaction vessel, thus minimizing the wall loss rate of OH radicals. The time-dependent signals from consecutive flashes were added in a Nuclear Data ND-100 multichannel analyzer operating in the multichannel scaling mode. Decay curves were generated by accumulating data from 100 to 300 flashes.

In order to avoid the accumulation of photolysis or reaction products, all experiments were performed with the gas mixture flowing through the reaction vessel. The flow rate of the gas mixture was such that the gas in the cell was typically exchanged more than four times between flashes. These high flow rates did not significantly affect the wall loss-rate for OH radicals. Gas mixtures were prepared by injecting liquid water and DMAE into a heated gas stream with a calibrated syringe pump. The diluent gas flow was maintained by a calibrated mass-flow controller. The partial pressure of water in the reaction vessel ranged from 0.02 to 0.49 torr, and the DMAE partial pressure ranged from 0.04 to 0.19 mtorr. The stated minimum purity levels for the substances used were He \geq 99.99% and DMAE > 98.0%. The amine was further purified by distillation, and gas chromatographic analysis showed that hydrocarbon impurities were less than 0.1%. The accuracy of mixture preparation was tested by collecting DMAE from the flowing gas stream and analyzing for the amine by an ion chromatographic technique.

The temperature of the reaction vessel was monitored by observing both gas temperature in the reaction vessel and the temperature of the bath fluid using copper-constantan thermocouples. The temperature in the

vessel was maintained constant by passing either a heated or cooled fluid through channels in the walls of the aluminum reaction vessel.

Results

The reaction of OH radicals with DMAE was studied over the temperature range 234 to 364 K, with typically 35 torr of helium as the diluent gas. The experiments were performed under pseudo-first-order conditions, i.e., the amine is in excess over the OH radical concentration, hence, OH radicals decayed according to the equation

$$\ln [\text{OH}] = k_{\text{obs}}t + \ln [\text{OH}]_0 \quad (1)$$

The observed pseudo-first-order rate constant, k_{obs} , is given by

$$k_{\text{obs}} = k_{\text{bi}}[\text{DMAE}] + k_{\text{d}} \quad (2)$$

where k_{bi} is the bimolecular rate constant for the OH + DMAE reaction, and k_{d} is the first-order rate constant for the loss of OH radicals, primarily by diffusion out of the reaction viewing zone.

Figure 1 shows a typical plot of the log of the fluorescence intensity versus the time after the flash. It should be noted that this decay is exponential over at least three half-lives. The observed pseudo-first-order rate constant for this particular set of conditions is given by the slope of the line. Figure 2 shows a plot of k_{obs} versus [DMAE] at 293 K. The slope of this line is the bimolecular rate constant for the reaction at this temperature. Table I presents a summary of the data collected for the reaction of OH with DMAE. Figure 3 shows an Arrhenius plot of the data for the reaction. The Arrhenius parameters are also listed in Table I.

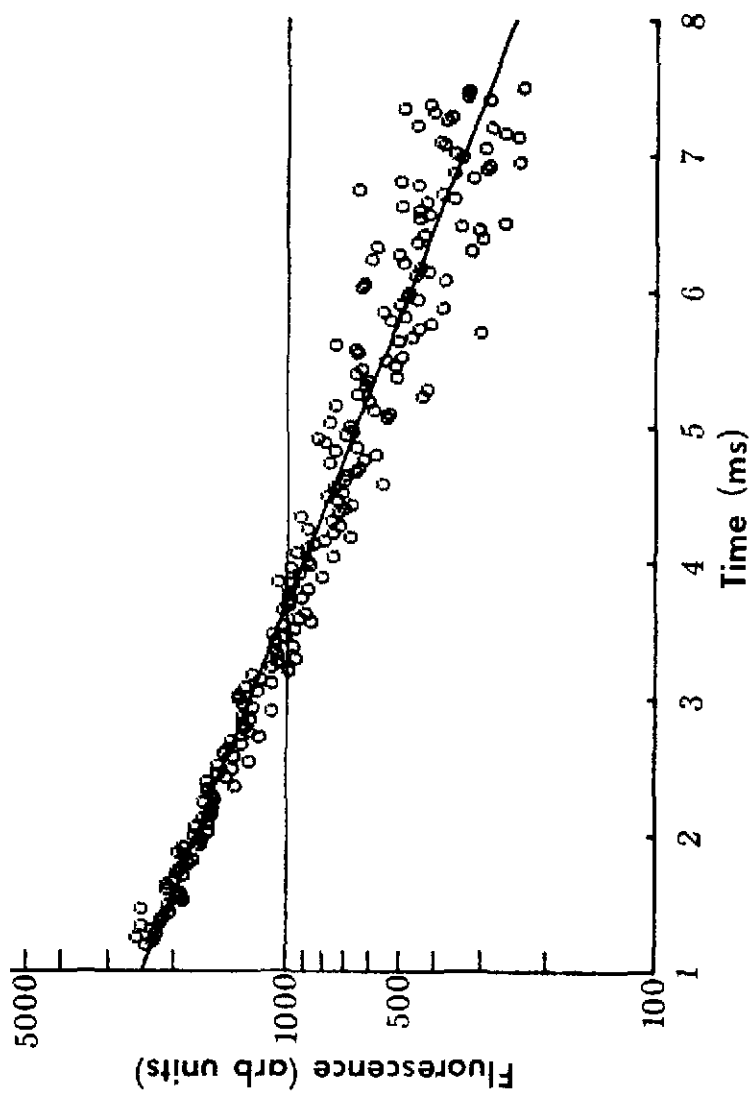


Figure 1. Semi-logarithmic plot of the OH fluorescence signal versus time after the flash. Experimental conditions: $[DMEA] = 2.00 \times 10^{12}$ molecule/cm³, $[H_2O] = 154$ mtorr, $P = 35$ torr, and $T = 298$ K.

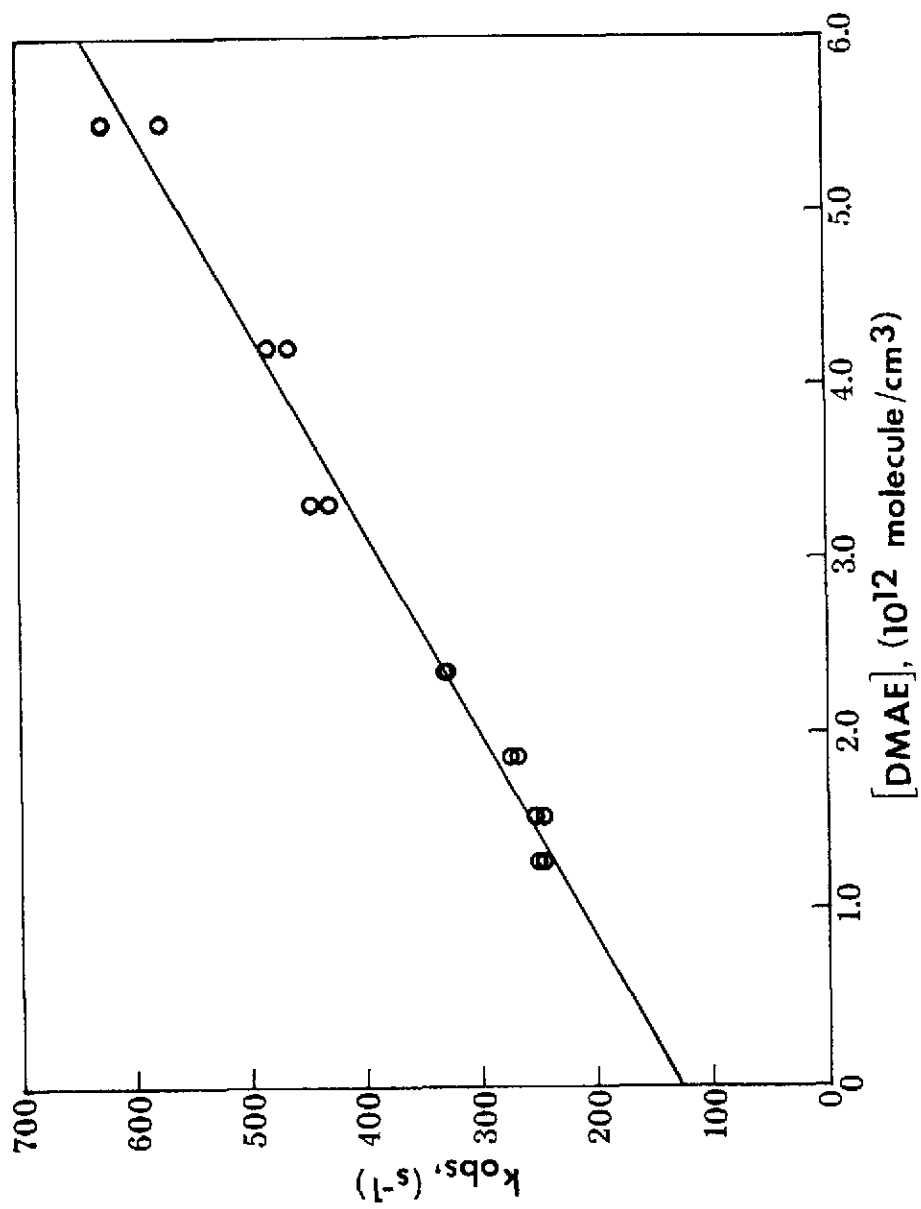


Figure 2. Plot of the observed pseudo-first-order decay constant for OH versus the DMAE concentration at 293 K.

Table I. Summary of experimental data and rate constants determined for the reaction OH + DMAE as a function of temperature.

T (K)	No. of Experiments	10^{12} DMAE molecule/cm ³	H ₂ O (mtorr)	Pressure (t)	Flash Energy (J)	Flash Energy (cm ³ molecule ⁻¹ s ⁻¹)	k _{bf} * (cm ³ molecule ⁻¹ s ⁻¹)
234	16	1.65-7.83	20-95	35	68	(5.86 ± 0.92)	$\times 10^{-11}$
269	18	1.58-6.18	112-435	35	68-100	(6.69 ± 1.50)	$\times 10^{-11}$
293	24	1.94-6.37	149-490	35	68-127	(7.89 ± 1.72)	$\times 10^{-11}$
333	14	1.27-5.52	110-488	35	68-127	(8.57 ± 0.78)	$\times 10^{-11}$
364	15	1.17-4.55	112-434	35	52-68	(7.94 ± 1.30)	$\times 10^{-11}$

Arrhenius Expression $(1.78 \pm 0.70) \times 10^{-10} \exp [-(250 \pm 110)/T]$

* Uncertainties are expressed as $\pm 2 \sigma$ values determined from the weighted least-squares fit of the data.

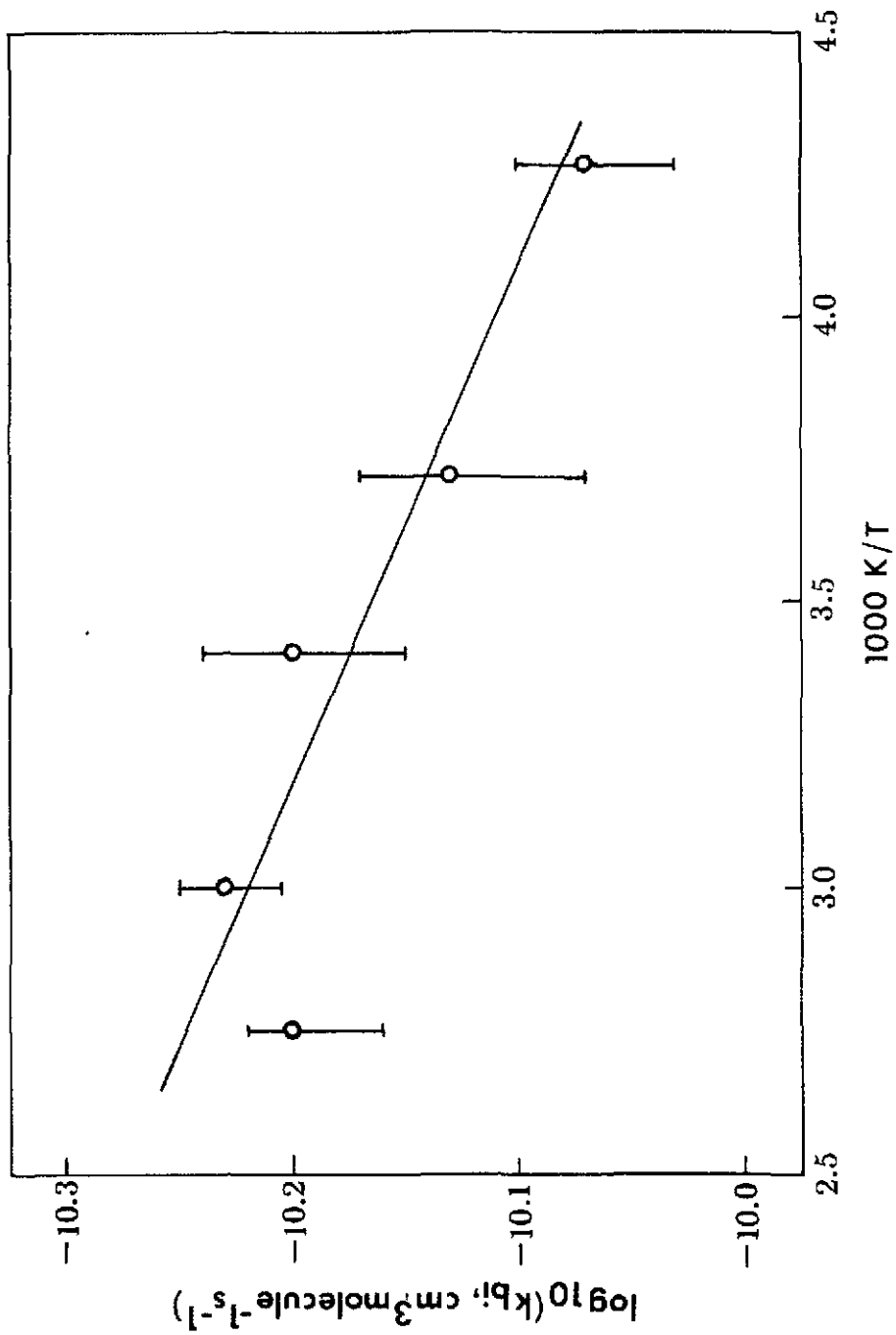


Figure 3. Arrhenius plot of the rate constant for the OH-DMAE reaction. Error bars shown are for $\pm \sigma$.

Discussion

The rates of OH radical reactions with other amines and ammonia have been reported previously [9-11]. Early studies of CH_3 and CF_3 radical reactions with amines concluded that the initial reaction involves hydrogen-atom abstraction [12]. It was suggested that OH would react analogously by H-atom abstraction from C-H and/or N-H bonds [11].

Table II summarizes the rate data for the OH reactions with the amines near 298 K. The reactivity is apportioned between individual C-H and N-H bonds by assuming that : (1) H-atom abstraction is the only reaction of significance, (2) the bond reactivity depends on the group and not on the molecule, and (3) that groups remote from the amine nitrogen do not show enhanced reactivity. The second and third assumptions are consistent with the previous work on CH_3 radical reactions with amines [12]. With these assumptions, sufficient information is available from studies of simple amines to estimate the rate constant for the OH-DMAE reaction, i.e., $6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This calculated rate constant is 85% of the OH-DMAE reaction rate observed in this work. Additional contributions could be made by the reactivity of the $-\text{CH}_2\text{OH}$ group. The reactivity of this group is expected to dominate in the reaction of OH with ethanol, $3.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [13]. If this reactivity is added to that estimated above, OH-DMAE reaction rate is predicted to within 10%. This agreement is well within the experimental uncertainties of the measurements.

Table II. Room temperature rate data for series of OH-amines reactions with overall rate apportioned to individual bonds.^a

Compound	k_{298} , $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Ref.	k/N-H - - - - $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	k/C-H(CH ₃) - - - - $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	k/C-H(CH ₂) - - - - $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
NH ₃	1.64×10^{-13}	9	$0.55 \times 10^{-13}{}^a$	-	-
CH ₃ NH ₂	2.20×10^{-11}	10	$0.08 \times 10^{-11}{}^a$	0.68×10^{-11}	-
(CH ₃) ₂ NH	6.54×10^{-11}	11	$2.48 \times 10^{-11}{}^a$	0.68×10^{-11}	-
(CH ₃) ₃ N	6.09×10^{-11}	11	-	$0.68 \times 10^{-11}{}^a$	-
CH ₃ CH ₂ NH ₂	2.77×10^{-11}	11	0.08×10^{-11}	-	$1.30 \times 10^{-11}{}^a$
(CH ₃) ₂ NCH ₂ CH ₂ OH	7.89×10^{-11}	This work	-	0.68×10^{-11}	1.30×10^{-11}

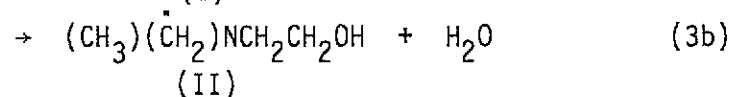
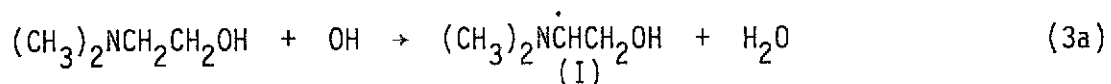
^a In NH₃ there are three equivalent hydrogens, so the rate per N-H bond is one-third of the room temperature value. For (CH₃)₃N there are nine equivalent hydrogens, which represent all CH₃ hydrogens on the carbon adjacent to the nitrogen. The primary amine N-H reactivity is determined from CH₃NH₂ and the secondary amine N-H reactivity is determined from (CH₃)₂N-H. The CH₂(C-H) is determined from CH₃CH₂NH₂.

The assumptions made in the estimation of bond reactivities in Table II can be tested by the comparison of the OH abstraction from the N-H bond in DMA relative to the total rate of reaction. Lindley et al. [14] have recently measured this ratio to be 0.37 ± 0.05 . From the data in Table II, this ratio is estimated to be 0.38. This is in excellent agreement with the recently measured value.

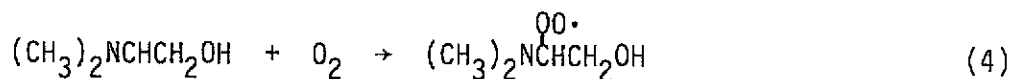
If one considered the observed temperature-dependencies of the other amines, one would find that they all exhibited a small negative activation energy [10,11]. Thus, one would predict a negative activation energy for the reaction of OH with DMAE. However, in this study, the OH reaction with DMAE has been observed to have a small positive activation energy. The reason for this difference is not currently understood. Hopefully, this issue will be clarified by additional studies of OH reactions with amines.

Atmospheric Significance

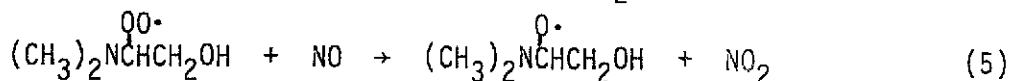
The OH radical attack on DMAE can result in two possible products



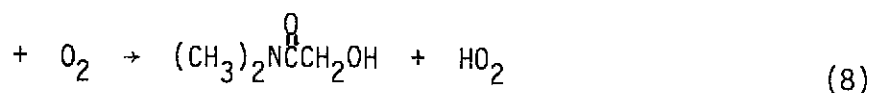
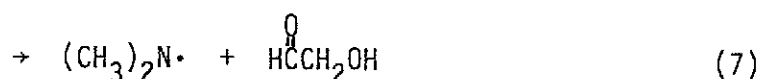
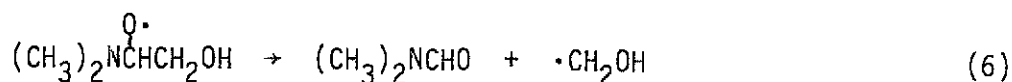
From Table II, reaction (3b) should account for about 60% of the reaction with OH, while (3a) should account for about 40%. The fate of these new radicals determine the ultimate products from the photooxidation. By analogy with alkyl radical reactions, the radical I is expected to react with molecular oxygen to form a peroxy radical:



This peroxy radical can react with NO to form NO₂ and an alkoxy radical



The alkoxy radical can either disproportionate or react with O₂ by a number of possible paths, i.e.,



Many of these products are consistent with those identified in previous amine photooxidation studies [4,6].

Lindley et al. [14] have evaluated the fate of the dimethylamino radical relative to DMNA formation. For comparative purposes, the maximum possible DMNA formation from DMAE can be estimated using the same assumptions. The DMNA photolysis rate is assumed to be 0.12 min⁻¹, based on a solar zenith angle of 40°, and the hydroxyl radical concentration is assumed to be 1 x 10⁻⁷ ppm. Using the mechanism above and assuming that reaction (7) dominates over (6) and (8), the relation for the steady-state DMNA concentration is

$$[(\text{CH}_3)_2\text{N-N=O}]_{ss} = \frac{0.0389 [(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}]}{4.6 [\text{NO}_2]/[\text{NO}] + 1.5 \times 10^{-6} [\text{O}_2]/[\text{NO}]} \quad (9)$$

which is 1.3 times the steady-state DMNA concentration found for DMA [14]. However, if reactions (6) and/or (8) were competitive with (7), the yield of DMNA would be reduced.

As has been suggested previously [4,14], nitramines are also expected to be products of amine photooxidation. Based on a similar analysis, the dimethylnitramine formation rate from DMAE could be as high as 1.3 times that estimated from DMA [14].

Radical II from reaction (3b) is expected to undergo a reaction chain similar to radical I. These reactions could lead to the formation of N,N-methylethanol substituted nitrosoamines and nitramines.

Additional studies of the photooxidation of DMAE are required to identify the products. Preliminary studies have identified N,N-dimethylformamide as one of the products of the photooxidation [reaction (6)] [6]. This suggests that reaction (7) is not the only reaction of importance in the set (6), (7), and (8). Hence, nitrosoamine and nitramine formation from DMAE should be less than 1.3 times that from DMA. This conclusion is also consistent with the observation that diethylformamide is a major product of the photooxidation of TEA.

Before one can evaluate the role of the atmospheric photooxidation of amines on the formation of nitrosoamines, nitramines, etc., one needs more information about mechanisms of the photooxidations, the ambient concentrations of amines, and their sources.

Acknowledgment

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