Gas-Phase Reactions of (CH₃)₂N Radicals with NO and NO₂

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The absolute rate constants for the reactions of $(CH_3)_2N$ radicals with NO and NO₂ were determined in the gas phase and at room temperature by using the very low pressure reactor (VLPR) technique. The rates were $k_{(CH_3)_2N+NO} = (8.53 \pm 1.42) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ and $k_{(CH_3)_2N+NO_2} = (9.08 \pm 1.36) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. The reaction with NO₂ proceeds via two competitive pathways: the recombination pathway $(CH_3)_2N + NO_2 \rightarrow (CH_3)_2NNO_2$, with a rate constant $k_{2a} = (3.18 \pm 0.48) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, and the oxidation pathway $(CH_3)_2N + NO_2 \rightarrow (CH_3)_2NONO^* \rightarrow (CH_3)_2NO + NO$, with a rate constant $k_{2b} = (6.36 \pm 0.74) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. The oxidation pathway is ca. 2.2 times faster than the recombination one, and the ratio $k_{2a}/k_{2b} = 0.45 \pm 0.15$. Conventional transition state theory analysis indicates that the involved transition states are loose, with the N···N or N···O bond lengths equal to ca. 2.5 Å.

Introduction

The reactions of NH₂ radical with various compounds have been studied extensively,¹ due to their importance in combustion and atmospheric chemistry. In particular, the reactions of NH₂ with NO and NO₂ are very fast,^{2,3} while the reaction of NH₂ with O₂ is slow.⁴ However, the reactions of (CH₃)₂N radical with NO and NO₂ have not been studied in the past, although they may play a significant role in the chemistry of the atmosphere. Only the relative reaction rates of (CH₃)₂N radicals with NO, NO₂, and O₂ have been measured with the FTIR technique.⁵

(CH₃)₂N radicals appear as primary reaction products in the gas-phase photochemistry of dimethylnitrosamine⁶ and are probable intermediate species in the reaction of dimethylamine with nitrogen oxides,⁷ leading to the formation of dimethylnitrosamine. Dimethylamine and nitrogen oxides are among the major pollutants in urban and industrial atmospheres.⁸ Hence, the reactions of $(CH_3)_2N$ radicals with NO and NO₂ should be determined in order to evaluate the potential hazard of nitrosamine formation. These reactions also occur as secondary reactions in the thermal and photochemical decomposition of dimethylnitrosamine and dimethylnitramine.⁶ The absolute rate constants for the recombination and disproportionation reactions of $(CH_3)_2N$ radicals at room temperature were determined recently by our group,⁹ and the rates were found to be $k_r = (1.70 \pm 0.19)$ × 10⁻¹² cm³ molecule⁻¹ s⁻¹ and $k_d = (4.19 \pm 0.52) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, respectively.

In this work we measure the absolute rate constants for the reactions of $(CH_3)_2N$ radicals with NO and NO₂

$$(CH_3)_2 N + NO \rightarrow (CH_3)_2 NNO$$
(1)

$$(CH_3)_2 N + NO_2 \rightarrow (CH_3)_2 NNO_2$$
(2a)

$$\rightarrow (CH_3)_2 NONO^* \rightarrow (CH_3)_2 NO + NO (2b)$$

$$\rightarrow \text{HONO} + \text{CH}_3\text{N} = \text{CH}_2 \qquad (2c)$$

at room temperature by using the very low pressure reactor (VLPR) technique. The partial reaction rates of reaction 2, according to scheme 2, are also determined, and the relative contribution of the three reaction pathways is estimated. Finally,

TABLE 1: Typical Signal Intensities and Steady-State Concentrations of Tetramethylhydrazine and Dimethylaminyl Radical and the Corresponding Flow Rates and Concentrations of Nitric Oxide⁴

I _{™H,0}	[TMH] ₀ (×10 ¹¹)	I _{TMH}	[TMH] (×10 ¹¹)	[R], (×10 ¹¹)	[R] (×10 ¹¹)	F _{NO} (×10 ¹⁵)	[NO] (×10 ¹¹)
0.31	3.72	0.30	3.66	5.68	5.64	3.19	42.01
0.32	3.86	0.27	3.25	5.79	5.32	8.42	110.98
0.34	4.10	0.25	3.03	5.97	5.13	12.07	159.07
0.32	3.89	0.23	2.83	5.81	4.96	17.96	236.63
0.32	3.80	0.21	2.56	5.75	4.71	23.97	315.85
0.30	3.65	0.14	1.74	5.63	3.89	38.69	509.78
0.29	3.51	0.15	1.80	5.52	3.95	43.03	566.96
0.27	3.29	0.12	1.49	5.35	3.60	61.45	809.69
0.27	3.22	0.09	1.06	5.29	3.03	83.30	1097.65
0.27	3.21	0.07	0.90	5.28	2.79	96.50	1271.53

^{*a*} Nitric oxide gas flow is in molecule s^{-1} ; steady-state concentrations are in molecule cm⁻³. Signal intensities are in arbitrary units normalized relative to the mass spectrometer and lock-in amplifier sensitivities used.

an approximate description of the involved transition states is presented by using the conventional transition state theory.

Experimental Section

The experiments were performed with the VLPR technique, which has been described in great detail previously.¹⁰ In this technique the bimolecular reaction occurs in a Knudsen cell at steady-state concentrations of less than 1×10^{14} molecule/cm³. The uniform viscous flows of two reacting species are introduced into the reaction cell through two separate inlets, and they are allowed to react for a short period of time. Then, both reactants and products escape from the reaction cell through an exit orifice into the first stage of a differentially pumped system. In this way, a continuous molecular beam is formed that is sampled with a quadrupole mass spectrometer at the second vacuum chamber. The molecular beam is modulated with a tuning fork chopper at the entrance of the second vacuum chamber; thus, the mass spectrometric signal is amplified with a lock-in amplifier up to 3 orders of magnitude.

The interior surfaces of the reaction cell ($V = 300 \text{ cm}^3$) were coated with halocarbon wax to inhibit wall recombinations. The escape rates for the various species were estimated by using the expression $\gamma(T/M)^{1/2}$ s⁻¹, where T is the absolute temperature and M is the molecular weight. The parameter γ was determined experimentally by following the first-order decay rate (of the mass spectrometric signal) after a fast halt of the flow for molecules with different weight. For the exit orifice used, 5 mm, the parameter γ was 0.796.

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TABLE 2: Typical Signal Intensities and Steady-State Concentrations of Tetramethylhydrazine, Dimethylaminyl Radical, Nitrogen Dioxide, Dimethylnitramine, and Dimethylnitroxyl Radical⁴

[TMH]。 (×10 ¹¹)	[TMH] (×10 ¹¹)	[R]。 (×10 ¹¹)	[R] (×10 ¹¹)	I _{NO2}	[NO ₂] (×10 ¹¹)	I _{DMNA}	[DMNA] (×10 ¹¹)	I _{DMNX}	[DMNX] (×10 ¹¹)
12.79	5.27	10.54	6.77	5.85	106.91	0.24	13.89	1.58	29.38
11.90	4.15	10.17	6.01	9.52	174.03	0.38	21.67	1.90	35.32
12.48	3.25	10.41	5.31	10.58	193.42	0.45	25.84	2.07	38.51
12.89	3.60	10.58	5.59	11.12	203.29	0.53	29.96	2.23	41.64
6.57	4.91	7.56	6.53	1.61	29.51	0.04	2.39	0.31	5.86
6.88	4.08	7.73	5.95	2.80	51.27	0.08	4.43	0.56	10.37
6.72	3.45	7.64	5.47	4.17	76.31	0.14	8.05	0.72	13.33
6.85	2.44	7.72	4.61	4.49	82.18	0.14	7.74	0.81	15.10
5.70	1.48	7.03	3.59	8.85	161.75	0.19	10.98	0.97	17.98
5.69	1.12	7.03	3.12	11.70	213.88	0.27	15.37	1.27	23.67

^a Steady-state concentrations are in molecule cm⁻³. Signal intensities are in arbitrary units normalized relative to the mass spectrometer and lock-in amplifier sensitivities used.



Figure 1. Plot of $T_1 = (\rho - 1)\{k_{escR} + 2(k_r + k_d)([R]_o + [R])\}$ versus [NO] at 303 K, where ρ [R]_o/[R]. Symbol size reflects the propagated errors (2σ) .

 $(CH_3)_2N$ radicals (R) were produced by thermal decomposition of $(CH_3)_2NN$ =NN $(CH_3)_2$ (TMT) diluted in He (5% mixture). The TMT/He mixture was introduced in the reaction cell through a capillary of 3-mm diameter, whose last portion (1.5 cm long) close to the reaction cell was widened (5-mm diameter) and heated externally by a resistance wire. The wall temperature was kept constant at ca. 480 K, and this resulted in ca. 40% decomposition of TMT. The total pressure in the heated volume was less than 4 mTorr, and the $(CH_3)_2N$ radical concentration was ca. 4×10^{12} molecule/cm³. Hence, the radical residence time in the heated volume is less than 1 ms, so its self-reactions occur mainly in the Knudsen cell.

The steady-state concentrations of NO and NO2 were estimated from measurements of the relative flow rates. The steady-state concentrations of (CH₃)₂NN(CH₃)₂ (TMH), (CH₃)₂NH (DMNA), and (CH₃)₂NO (DMNX) were also determined by measuring the mass peak intensities, I_{TMH} (m/e = 88), I_{DMNA} (m/e = 90), and I_{DMNX} (m/e = 60), respectively. The peak intensities $I_{\rm M} = \alpha_{\rm M} F_{\rm M} = \alpha_{\rm M} k_{\rm escM} V[{\rm M}]$, where $\alpha_{\rm M}$ is a calibration factor characteristic of each molecule, $F_{\rm M}$ is the flow rate, V is the cell volume, and k_{escM} is the escape rate. The α_{M} factors for TMH, DMNA, and DMNX were determined from accurate calibration curves, I_M versus F_M . The calibration curve for DMNX was obtained by flowing pure (CH₃)₂NOH, which should have a similar calibration curve at m/e = 60. All flow rates were determined by monitoring the pressure drop in a known volume, with an accuracy of ca. $\pm 5\%$. In each experimental run the intensities of all mass spectrum peaks of interest were recorded simultaneously and stored digitally in a microcomputer (PDP-11/23), where the analysis was performed later. Finally, the system was tested by measuring the rate constant of the wellknown reaction of Clatoms with CH_4 , and this rate was in excellent agreement with the accepted value.¹

Tetramethyl-2-tetrazene was prepared by following the procedure of Madgzinski et al.¹¹ NO and NO₂ gases were commercially available (Aldrich) and were degassed several times prior to use. Also, dimethylnitramine was synthesized by nitration of the corresponding dialkylformamide¹² and was further purified by subsequent degassing.

Results

For the reaction of $(CH_3)_2N$ radicals with NO, the mass spectrometric analysis showed that the final products were $(CH_3)_2$ -NNO (m/e = 74), $(CH_3)_2NH$ (m/e = 45), and $(CH_3)_2NN (CH_3)_2(m/e = 88)$. The last two products are due to self-reactions of $(CH_3)_2N$ radicals. Thus, the reaction scheme under study is

$$(CH_3)_2 NN = NN(CH_3)_2 \xrightarrow{k_{dec}} 2(CH_3)_2 N + N_2$$
$$(CH_3)_2 N + NO \xrightarrow{k_1} (CH_3)_2 NNO \qquad (1)$$

$$(CH_3)_2N + (CH_3)_2N \xrightarrow{k_r} (CH_3)_2NN(CH_3)_2$$
$$\xrightarrow{k_4} (CH_3)_2NH + CH_3N = CH_2$$

By considering the steady-state approximation for TMT, R, and TMH species, we obtain the equations

$$k_{1}[\text{TMT}] = \Delta[\text{TMT}]k_{\text{escTMT}} \qquad (I)$$

$$2\Delta[\text{TMT}]k_{\text{escTMT}} = 2(k_{\text{r}} + k_{\text{d}})[\text{R}]_{\text{o}}^{2} + k_{\text{escR}}[\text{R}]_{\text{o}} \quad (\text{II})$$

$$2\Delta[\text{TMT}]k_{\text{escTMT}} = 2(k_{\text{r}} + k_{\text{d}})[\text{R}]^2 + k_{\text{escR}}[\text{R}] + k_1[\text{R}][\text{NO}] \text{ (III)}$$

$$k_{\rm r}[{\rm R}]^2 = k_{\rm escTMH}[{\rm TMH}]$$
 (IV)

where Δ [TMT] is the difference in the steady-state concentration of TMT due to the thermal decomposition, [TMH] is the steadystate concentration of TMH, and k_{escM} values are the escape rate constants of species M through the orifice used. [R]_o and [R] are the steady-state concentrations of (CH₃)₂N radicals in the absence and presence of NO, respectively, and are given by the expressions (derived from eq IV)

$$[R]_{o} = \{k_{escTMH}[TMH]_{o}/k_{r}\}^{1/2}$$
(V)

$$[R] = \{k_{escTMH}[TMH]/k_r\}^{1/2}$$
(VI)



Figure 2. Plot of $T_2 = (\rho - 1)\{k_{escR} + 2(k_r + k_d)([R]_o + [R])\}$ versus [NO₂] at 303 K, where ρ [R]_o/[R]. Symbol size reflects the propagated errors (2 σ).



Figure 3. Plot of $S_1 = k_{\text{sscDMNA}}[DMNA]/\{k_{\text{sscTMH}}[TMH]/k_t\}^{1/2}$ versus [NO₂] at 303 K. Symbol size reflects the propagated errors (2σ) .

where $[TMH]_o$ and [TMH] are the steady-state concentrations of TMH in the absence and presence of NO, respectively. By combining eqs I–IV, we obtain the expression

$$T_{1} = (\rho - 1)\{k_{escR} + 2(k_{r} + k_{d})([R]_{o} + [R])\} = k_{1}[NO] (VII)$$

where $\rho = [R]_0/[R]$ and k_r and k_d are the recombination and disproportionation rates that were determined previously.⁹ Their values are $k_r = (1.70 \pm 0.19) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and k_d = (4.19 ± 0.52) × 10⁻¹² cm³ molecule⁻¹ s⁻¹, respectively. Therefore, the plot of T_1 versus [NO] should yield a straight line with a slope equal to k_1 and zero intercept.

Experiments were performed at a constant degree of TMT decomposition (ca. 40%) and at different NO concentrations. Typical flow rates of NO, signal intensities, and steady-state concentrations of TMH, R, and NO are presented in Table 1. The linear least-squares fits of the data at 303 K yield a straight line with zero intercept, as shown in Figure 1. The rate constant k_1 derived from this plot was $k_1 = (8.53 \pm 1.42) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, and the experimental error was 17% (2 σ).

For the reaction of $(CH_3)_2N$ radicals with NO₂, the mass spectrometric analysis showed that the final products were $(CH_3)_2$ -NNO₂ (m/e = 90), $(CH_3)_2NO$ (m/e = 60), $(CH_3)_2NH$ (m/e = 45), and $(CH_3)_2NN(CH_3)_2$ (m/e = 88). Thus, in addition to the radical self-reactions, the following two reaction are present:



Figure 4. Plot of $S_2 = k_{escDMNX}[DMNX]/{k_{escTMH}[TMH]/k_r}^{1/2}$ versus [NO₂] at 303 K. Symbol size reflects the propagated errors (2 σ).



Figure 5. Plot of $k_{escDMNA}$ [DMNA]/{ $k_{escDMNX}$ [DMNX] versus [NO₂] at 303 K. Symbol size reflects the propagated errors (2σ).

$$(CH_3)_2 N + NO_2 \rightarrow (CH_3)_2 NNO_2$$
(2a)

$$\rightarrow (CH_3)_2 NONO^* \rightarrow (CH_3)_2 NO + NO (2b)$$

The third possible reaction pathway (2c) yielding HONO and $CH_3N=CH_2$ could not be verified in our system, since both products have primary mass peaks which coincide with prominent mass peaks of the main products. In a similar manner, by assuming the steady-state approximation for all species we obtain the expression

$$T_2 = (\rho - 1)\{k_{escR} + 2(k_r + k_d)([R]_o + [R])\} = k_2[NO_2] \text{ (VIII)}$$

Therefore, a plot of T_2 versus [NO₂] should yield a straight line with a slope equal to k_2 and zero intercept. Typical steady-state concentrations of TMH and R at various NO₂ concentrations are presented in Table 2. The linear least-squares fits of the data at 303 K yield a straight line with zero intercept, as illustrated in Figure 2. The total rate constant k_2 derived from this plot was $k_2 = (9.08 \pm 1.36) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and the experimental error was 15% (2σ).

Furthermore, the partial rate constant for reaction (2a) can be estimated by considering the steady-state approximation for DMNA, which is given by equation

$$k_{2a}[R][NO_2] = k_{escDMNA}[DMNA]$$
(IX)

TABLE 3: Rate Constants (cm³ molecule⁻¹ s⁻¹) for Reactions of $(CH_3)_2N$, NH_2 , CH_3 , CH_3O , and CH_3O_2 Radicals with NO and NO₂ at 300 K

radical	$k_1 \times 10^{14}$	$k_{2a} \times 10^{13}$	$k_{2b} \times {}^{13}$	k_{2a}/k_1	ref
(CH ₃) ₂ N	8.53 ± 1.42	3.18 ± 0.48	6.36 ± 0.74	3.73 3.79	this work 5
NH2 CH3 CH3O CH3O2	1810 ± 120 2 320–580 760	10–17 10 650 ± 320	230	50-85 0.31-0.17	1, 13 14 14 1

Substituting [R] from eq VII, we obtain the expression

$$S_1 = k_{\text{escDMNA}} [\text{DMNA}] / \{k_{\text{escTMH}} [\text{TMH}] / k_r\}^{1/2} = k_{2a} [\text{NO}_2]$$
(X)

Hence, a plot of S_1 versus [NO₂] should yield a straight line with a slope equal to k_{2a} and zero intercept. Typical steady-state concentrations of TMH, R, and DMNA at different NO₂ concentrations are presented in Table 2. The linear least-squares fits of the data at 303 K yield a straight line with zero intercept, and this plot is presented in Figure 3. The rate constant k_{2a} derived from this plot was $k_{2a} = (3.18 \pm 0.48) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, and the experimental error was 15% (2 σ).

Similarly, the partial rate constant for reaction 2b can be determined by considering the steady-state approximation for DMNX, which is given by equation

$$k_{2b}[R][NO_2] = k_{escDMNX}[DMNX]$$
(XI)

Substituting [R] from eq VII, we obtain the expression

$$S_2 = k_{\text{escDMNX}} [\text{DMNX}] / \{k_{\text{escTMH}} [\text{TMH}] / k_{\text{r}} \}^{1/2} = k_{2b} [\text{NO}_2] \quad (\text{XII})$$

Thus, a plot of S_2 versus [NO₂] should yield a straight line with a slope equal to k_{2a} and zero intercept. Typical steady-state concentrations of TMH, R, and DMNX at different NO₂ concentrations are presented in Table 2. The linear least-squares fits of the data at 303 K yield a straight line with zero intercept, and this plot is presented in Figure 4. The rate constant k_{2b} derived from this plot was $k_{2b} = (6.36 \pm 0.74) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, and the experimental error was 12% (2 σ).



Figure 6. Transition state geometry for the recombination reaction $(CH_3)_2N + NO$.

By dividing eqs IX and XI, we obtain the expression

$$\frac{k_{2a}}{k_{2b}} = \frac{k_{escDMNA}[DMNA]}{k_{escDMNX}[DMNX]}$$
(XIII)

A plot of $k_{escDMNA}$ [DMNA]/ $k_{escDMNX}$ [DMNX] versus [NO₂] should give a straight line. This plot shows a minor dependence on NO₂ concentration, as shown in Figure 5, and the ratio $k_{2a}/k_{2b} = 0.45 \pm 0.15$.

Discussion

The reaction rates obtained in the present experiments may be compared with those of NH_2 , CH_3 , and CH_3O radicals with NO and NO_2 .^{13,14} These reaction rates are summarized in Table 3. Inspection of Table 3 reveals the following: (i) NO reacts much

TABLE 4: Estimation of S^{*}(298) for [(CH₃)₂N···NO] Transition State

degrees of freedom		frequency (cm ⁻¹)	S° , cal mol ⁻¹ K ⁻¹
translational $S_{tr} = 37.0 + (2000)$ rotational $S_{ext,rot} = 11.595 + (1000)$ $(I_A I_B I_C = 3.453 \times 10^{6})$	$\frac{3}{2}R \ln(M^{4}/40) (M = 74 \text{ amu}) + (R/2) \ln (I_{A}I_{B}I_{C}) - \ln \sigma$ amu ³ Å ⁶ , $\sigma = 1$)		38.84 26.60
vibrational assignment			
VC-N	$(DMNO \nu_{sym,C-N} = 844 \text{ cm}^{-1})$ $((CH_3)_2N 950 \text{ cm}^{-1})$	900	0.15
$\nu_{C-N} + \delta_{HCN}$	$(DMNO \nu_{asym,C-N} = 1287 \text{ cm}^{-1})$ ((CH ₃) ₂ N 1290 cm ⁻¹)	1290	0.03
δCNC	(DMNO skeletal deformation = 400 cm^{-1}) ((CH ₃) ₂ N 1170 cm ⁻¹)	600	0.47
(2) t_{CH_3}	$((CH_3)_2N 230 \text{ cm}^{-1})$ V = 2.9 kcal/mol $I_* = 2.9 \text{ amu } Å^2$	219. $V^* = 2.9 \text{ kcal/mol}$ $I^* = 3.2 \text{ amu } \text{\AA}^2$	4.00
remaining dimethylaminyl i	adical vibrations $(n = 16)$		2.48
ν Ν =0	(DMNO 1439 cm ⁻¹) (NO 1875 cm ⁻¹)	1600	0.008
ν_{N-N}	(DMNO 1058 cm ⁻¹)	r.c.	
δςνν	(DMNO skeletal rock 354 cm ⁻¹)	420	0.90
δ _{CNN}	(DMNO skeletal wag 229 cm ⁻¹)	300	1.40
δονν	$(DMNO 682 \text{ cm}^{-1})$	890	0.20
t _{NNO}	(free internal rotation about N···N $I_r = 12.01 \text{ amu } \text{\AA}^2$, N···N = 2.5 Å)		7.08
electronic $S_{el} = R \ln(2S + 1)$	(S = 0)		0 82.16

 $\Delta S^{\bullet}(298) = 82.16 - 116.1 = -33.94 \text{ cal mol}^{-1} \text{ K}^{-1} \left(S^{\circ}_{(CH_3)_2N} = 65.8, S^{\circ}_{NO} - 50.3 \right)$ $A_{300} (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 10^{-5.72} (T/298)^2 \exp(\Delta S^*/R) = 10^{-13.09}$

IABLE 5: Estimation of $S'_{(298)}$ for $ (CFi_3)_2 N\cdots NO_2 $ i fansition	n State
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degrees of freedom		frequency (cm ⁻¹)	S°, cal mol ⁻¹ K ⁻¹
translational $S_{tr} = 37.0 + (2)$ rotational $S_{ext,rot} = 11.595 - (I_A I_B I_C = 8.778 \times 10^6)$	$\frac{3}{2}R \ln(M^*/40) \ (M = 90 \text{ amu})$ + $(R/2) \ln(I_A I_B I_C) - \ln \sigma$ $i \text{ amu}^3 Å^6, \sigma = 1)$		39.42 26.16
vibrational assignment			
ν _{C-N}	(DMNA $\nu_{sym,CNC} - 838 \text{ cm}^{-1}$) ((CH ₃) ₂ N 950 cm ⁻¹)	900	0.15
$\nu_{\rm C-N} + \delta_{\rm HCN}$	$(DMNA \nu_{asym,CNC} = 1292 \text{ cm}^{-1})$ $((CH_3)_2N 1290 \text{ cm}^{-1})$	1 290	0.03
δene	(DMNA skeletal deformation -427 cm^{-1})	500	0.70
(2) t_{CH}	$(DMNA t_{CH_3} = 107 \text{ cm}^{-1})$	100	6.80
(2) t_{NO_2}	(free internal rotation about N-N		
• • •	$I_{\rm f} = 21.62 \text{ amu } Å^2, \text{ N} \cdots \text{N} = 2.5 \text{ Å})$		7.67
remaining dimethylaminyl	radical vibrations $(n = 16)$		2.48
νnn	$(DMNA 1248 \text{ cm}^{-1})$	r.c	
(2) δ _{CNN}	$(DMNA (\gamma_{NN}) 225, (\delta_{NN}) 350 \text{ cm}^{-1})$	(2) 225	4.00
(2) δ _{ONN}	$(DMNA (r_{NO_1}) 619, (w_{NO_2}) 762 \text{ cm}^{-1})$	(2) 225	4.00
$\nu_{a}(NO_{2})$	$(DMNA 1528, NO_2 1621 \text{ cm}^{-1})$	1570	0.01
$\nu_{\rm s}({\rm NO}_2)$	$(DMNA 1304, NO_2 1320 \text{ cm}^{-1})$	1310	0.03
δ _{NO2}	$(DMNA 626, NO_2 648 \text{ cm}^{-1})$	635	0.41
electronic $S_{el} = R \ln (2S +$	1) $(S = 0)$		0
			91.86

 $\Delta S^{*}(298) = 91.86 - 123.1 = -31.24 \text{ cal mol}^{-1} \text{ K}^{-1} (S^{\circ}_{(CH_{3})_{2}N} = 65.8, S^{\circ}_{NO_{2}} = 57.3)$ $A_{300} (\text{cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}) = 10^{-5.72} (T/298)^{2} \exp(\Delta S^{*}/R) = 10^{-12.50}$

TAI	BLE	6:	Estimation	of 3	S [*] (298)	for	[(C	(H3)2N	ON⊧	=0]	Transition	State
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degrees of freedom		frequency (cm ⁻¹)	S°, cal mol ⁻¹ K ⁻¹
translational $S_{tr} = 37.0 +$ rotational $S_{ext,rot} = 11.595$ $(I_A I_B I_C = 1.026 \times 10^{-10})$	$(3/2)R \ln(M^*/40) (M = 90 \text{ amu})$ + $(R/2) \ln(I_A I_B I_C) - \ln \sigma$ $V^7 \text{ amu}^3 Å^6, \sigma = 1)$		39.42 27.68
vibrational assignment ν_{C-N} $\nu_{C0N} + \delta_{HCN}$ δ_{CNC} (2) t _(CH₃) $\nu_{a}(NO_{2})$ $\nu_{b}(NO_{2})$ $\delta(NO_{2})$	$\begin{array}{l} ((CH_3)_2N \ 950 \ cm^{-1}) \\ ((CH_3)_2N \ 1290 \ cm^{-1}) \\ ((CH_3)_2N \ 1170 \ cm^{-1}) \\ (DMNA \ t_{CH_3} = \ 107 \ cm^{-1}) \\ (NO_2 \ 1621 \ cm^{-1}) \\ (NO_2 \ 1320 \ cm^{-1}) \\ (NO_2 \ 648 \ cm^{-1}) \end{array}$	900 1290 800 100 1500 1300 630	0.15 0.03 0.22 6.80 0.01 0.03 0.40
remaining dimethylaminyl	radical vibrations $(n = 16)$		2.48
^ν n-0 (2) δ _{CN-0} δn0-n ^t n-0n0 ^t n0-n0	$(I_r = 22.918 \text{ amu Å}^2, \text{N} \cdots \text{ONO} = 2.5 \text{ Å})$ $(I_r = 11.410 \text{ amu Å}^2, \text{NO} \cdots \text{NO} = 1.19 \text{ Å})$	r.c (2) 600 700	1.20 0.30 7.73 7.03
electronic $S_{\rm el} = R \ln(2S +$	1) $(S = 0)$		0 93.28

 $\Delta S^{*}(298) = 93.28 - 123.1 = -29.82 \text{ cal mol}^{-1} \text{ K}^{-1} (S^{\circ}_{(CH_{3})_{2}N} = 65.8, S^{\circ}_{NO_{2}} = 57.3)$ $A_{300} (\text{cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}) = 10^{-5.72} (T/298)^{2} \exp(\Delta S^{*}/R) = 10^{-12.20}$

slower with $(CH_3)_2N$ radical than with NH_2 and CH_3O radicals, and equally fast with CH₃ radicals. (ii) The recombination reaction of $(CH_3)_2N$ radicals with NO₂ is 3.73 times faster than the recombination reaction of (CH₃)₂N radical with NO, and this is in excellent agreement with a previous value of 3.79.5 (iii) For the reaction of $(CH_3)_2N$ radicals with NO_2 the disproportionation pathway is 2.2 times faster than the recombination pathway, and almost the same holds for the reaction of C_2H_5 radicals with NO₂.¹⁵ However, for the reaction of CH₃ radicals with NO₂, the recombination pathway is much slower than the oxidation pathway, with a ratio of ca. 0.04-0.08.14 It appears that in most reactions of alkyl, alkoxy, and aminyl radicals with NO₂, the oxidation pathway is faster than the recombination pathway. (iv) The slight dependence of the ratio k_{2a}/k_{2b} on NO₂ concentration suggests that a secondary reaction between (CH₃)₂-NO and NO₂ starts to compete at higher NO₂ concentrations. (v) Finally, the sum and the ratio of the individual obtained reaction rates, k_{2a} and k_{2b} , are in excellent agreement with the experimental values of the total reaction rate, k_2 , and the ratio k_{2a}/k_{2b} , and this constitutes an additional argument that reaction 2 proceeds mainly through two reaction pathways.

The thermochemical kinetics version of conventional transition state theory¹⁶ was employed to provide insight into the transition state (TS) geometry. The reactions under study are highly exothermic recombination reactions with almost zero activation barrier.¹⁷ Hence, their preexponential A factor, given by the expression $A = 10^{-5.72}(T/298)^2 \exp(\Delta S^*/R)$, will be equal to the experimental rate constant. Here, ΔS^* is the entropy change to form 1 mol of transition state complex from reactants.¹⁶ Estimation of the absolute entropies for both reactants and transition state requires knowledge of their geometry and vibrational frequencies. The absolute entropy of (CH₃)₂N radicals has been previously estimated as S°_{300} {(CH₃)₂N} = 65.8 cal/ (mol K).⁹ Thus, the absolute entropy of the TS is obtained from the experimental rate, and is computed by fitting the geometry and the vibrational frequencies.

For reaction 1, the experimental rate k_1 correlates to an entropy change $\Delta S^* = -(33.84 \pm 0.34)$ cal/(mol K), which corresponds to an absolute entropy $S^{\circ}(TS_1) = 82.26 \pm 0.34$ cal/(mol K). The transition state is formed by coupling the unpaired electrons of the N atoms in (CH₃)₂N and NO reactants; thus, the C--N···N angle will be ca. 110°, and the NO molecule will lie on a plane

perpendicular to the radical plane (C--N--C). This TS is expected to be loose, in agreement with the inverse process of unimolecular decomposition of dimethylnitrosamine which appears to occur through a similar loose TS.⁶ The critical distance of approach of the N atoms will be equal to the sum of their van der Waals radii, ca. 3.4 Å.^{17,18} However, at N...N distances shorter than 1.7 Å, steric hindrances begin to appear for the rotation around the N...N bond (between O atom and CH₃ groups). The rotational entropy shows very little dependence (ca. 1%) on the N...N distance in the range from 1.7 to 3.4 Å. Thus, the N-N distance takes an average value of ca. 2.5 Å. The vibrational frequencies are considered similar to those of DMNO,19 with the exception of all frequencies associated with the newly formed N---N bond which are increased by ca. 20%. The internal rotation around the N---N bond is treated as one-dimensional free rotation.¹⁶ All vibrational frequency assignments and the entropy calculations are included in Table 4, and the transition state geometry is shown in Figure 6.

For reaction 2 there are two reaction pathways. The absolute transition state entropies for both recombination (2a) and oxidation (2b) pathways are estimated as $S^{\circ}(TS_{2a}) = 91.89 \pm$ 0.30 cal/(mol K) and $S^{\circ}(TS_{2b}) = 93.27 \pm 0.23$ cal/(mol K), respectively. A similar thermochemical analysis for both pathways indicates that the involved transition states are loose and that N...N or N...O bond lengths are ca. 2.5 Å. All vibrational frequency assignments²⁰ and the entropy calculations are presented in Tables 5 and 6. Indeed, the inverse processes of unimolecular decomposition of $(CH_3)_2NNO_2$ and $(CH_3)_2NONO$ occur through similar loose transition states as well.6

The exothermicity of reactions 1 and 2a is ca. 46 kcal/mol, since the strength of the N--N bond in both $(CH_3)_2$ NNO and $(CH_3)_2NNO_2$ molecules is ca. 46.5 ± 0.5 kcal/mol.²¹ Reaction 2b is also exothermic by ca. 17 kcal/mol, since $\Delta H^{\circ}_{f}((CH_{3})_{2}N)$ = 38.5 kcal/mol²² and $\Delta H^{\circ}_{f}((CH_{3})_{2}NO) = 8.2$ kcal/mol at 300 K.²³ However, radical-radical recombination reactions have approximately zero activation energies,¹⁸ and the A_r factors are given by the expression $\ln A_r = \ln A_{dec} - \Delta S^{\circ}/R$, where ΔS° is entropy change for the reverse reaction of unimolecular decomposition.¹⁶ The A^{∞}_{dec} factor for $(CH_3)_2$ NNO decomposition was determined from pyrolysis experiments as $10^{15.5}$ s⁻¹;^{6b} thus $A^{\infty}_{1(300)}$ $\approx 6.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, since $S^{\circ}_{300}((CH_3)_2 \text{NNO}) =$ 71.4 cal/(mol K)²⁴ and $S^{\circ}_{300}((CH_3)_2N) = 65.8 \text{ cal/(mol K)}.^9$ Similarly, the A^{∞}_{dec} factor for $(CH_3)_2NNO_2$ decomposition was determined from pyrolysis experiments as $10^{15.9}$ s⁻¹;^{6b} thus $A^{\infty}_{2a(300)}$ $\approx 1.64 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, since $S^{\circ}_{300}((CH_3)_2 NNO_2) =$ 78.3 cal/(mol K).²⁴ Therefore, both reaction rates, k_1 and k_{2a} , are approximately at the high-pressure limit at 300 K, and the measured A values are in reasonable agreement with the estimated values.

Conclusions

The absolute rate constants for the reactions of $(CH_3)_2N$ radicals with NO and NO₂ were determined at 303 K. The reaction of $(CH_3)_2N$ radicals with NO₂ is 8 times faster than that with NO. Furthermore, the reaction of $(CH_3)_2N$ with NO₂ proceeds via two competitive pathways, the recombination and oxidation pathways. The latter is ca. 2.2 times faster than the former. Our results suggest that (CH₃)₂N radicals formed in the atmosphere may react with NO and NO₂ and form (CH₃)₂NNO and $(CH_3)_2NO$ or $(CH_3)_2NNO_2$ at significant rates even when the NO and NO₂ concentrations are in the range of 10 ppm. In

addition, the oxidation reaction of $(CH_3)_2N$ radicals by NO₂ plays an important role in the decomposition mechanism of (CH₃)₂NNO₂. Finally, all reactions proceed through a loose transition state, with N...N or N...O bond lengths of ca. 2.5 Å.

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