IR LASER CHEMISTRY OF DIMETHYLNITRAMINE AND DIETHYLNITRAMINE

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The infrared multiphoton decomposition of dimethylnitramine and diethylnitramine in the gas phase under almost collisionless conditions has been studied with a tunable CO₂ laser. The steady state rate coefficient for their unimolecular decomposition were found to be \( k_{DMNA(St)} = 10^{5.5} \pm 0.1 \) (l/MW cm⁻²) s⁻¹, and \( k_{DENA(St)} = 10^{5.2} \pm 0.1 \) (l/MW cm⁻²) s⁻¹ for laser intensities in the range 3–15 MW cm⁻². The dependence of rate constants and product yields on laser fluence have indicated that the unimolecular dissociation of both nitramines occurs via scission of the N-NO₂ bond, and the main secondary reaction leading to the final photolysis products (nitrosamine and nitroxide) is the oxidation reaction of nascent dialkylamino radical with parent nitramine or NO₂ product.

KEY WORDS: IRMPD, nitramines

INTRODUCTION

The combustion of energetic molecules is accompanied with the release of substantial amounts of energy, and the formation of many small molecular species. However, the primary unimolecular decomposition of those molecules, as well as the following secondary reactions which are responsible for the formation of the final products, are not fully understood. Therefore, it is essential to determine the dynamics of initial fragmentation of energetic molecules under thermal excitation in the gas phase. Nitramines are among the most important energetic molecules, and the simplest are N,N-Dimethylnitramine (DMNA) and N,N-Diethylnitramine (DENA). The decomposition dynamics of both nitramines in the gas phase has been the subject of earlier and recent works using various forms of excitation, namely pyrolysis, laser-powered homogeneous pyrolysis (LPHP), shock tubes, laser-powered homogeneous pyrolysis (LPHP), and infrared multiphoton decomposition (IRMPD). It is generally suggested that the primary unimolecular dissociation pathway is the rupture of the weakest N-NO₂ bond, with a minor contribution from the isomerization to N-nitrite and subsequent NO elimination pathway observed in the laser pyrolysis experiments. The infrared multiphoton decomposition (IRMPD) technique present many advantages over the other techniques, the most important of which are: (a) the selective vibrational excitation of the parent molecules leaving the dissociation products intact, and (b) the controllable population of the desirable high vibrational levels by adjusting the laser intensity.
In the present work, we study the IRMPD of dimethylnitramine and diethyl-nitramine under almost collisionless conditions by using a tunable CO$_2$ laser. A qualitative analysis of the static cell measurements will be performed in order to evaluate the steady-state rate constant for the primary photodissociation channel of both nitramines. The threshold laser fluences for the lowest channel will also be determined for both nitramines. Finally, the primary photochemical reaction yield as a function of the well-defined fluence under constant irradiation conditions will be studied to provide additional evidence about the primary IR multiphoton dissociation dynamics of nitramines, and the consequent chemical mechanism that leads to the final products.

EXPERIMENTAL SECTION

The IR photolysis experiments were performed in the gas phase with a tunable TEA CO$_2$ laser (Lumonics Model 103-2) with a uniform energy density beam (with a beam cross-section of ca 7 cm$^2$). The laser fluence was in the range 0.2–1.0 J cm$^{-2}$ at different laser lines. The temporal profile of the laser pulse was recorded with a photon drag detector (Rofin 7441) and contained primarily a 80 ns spike followed by a 600 ns minor tail (10%). The laser beam was transmitted unfocused through a cylindrical pyrex cell of 4 cm diameter and 17 cm length with NaCl windows. The partial pressure of sample gases was measured with calibrated capacitance manometers (Validyne DP15).

The dimethylnitramine was synthesized by nitration of the corresponding dialkylformamide, while the diethylnitramine was synthesized by dehydrating the nitrate salt of diethylnitramine. Both nitramines were purified prior to use by distillation and subsequent degassing. The gaseous mixtures before and after photolysis were sampled by a capillary tubing leading to a high vacuum chamber and analysed by a quadrupole mass spectrometer (Balzers QMG511). All mass spectra were taken at an electron energy 70 eV. The mass spectrometer was interfaced to a DEC PDP-11/23 microcomputer, therefore all spectroscopic data were digitally stored and analyzed. The detailed assignment of both nitramines and their products mass spectra have been reported previously. The uncertainty in estimating the intensity of mass peaks and the various mass peak ratios was less than 10% and ca 15%, respectively.

RESULTS AND DISCUSSION

Dimethylnitramine samples (100 mTorr) were irradiated with constant laser fluence ($F = 0.3$ J cm$^{-2}$) at laser frequencies in the range 966–986 cm$^{-1}$ (R branch of 10.6 m band of CO$_2$ laser) that coincide with the CH$_3$ rocking absorption band at 987 cm$^{-1}$. Diethylnitramine samples (150 mTorr) were irradiated with laser frequencies in the range 1074–1085 cm$^{-1}$ (R branch of 9.6 m band of CO$_2$ laser) that lie within the CH$_3$ deformation absorption band at 1085 cm$^{-1}$. The IRMPD yield of both nitramines was red-shifted by 9–15 cm$^{-1}$ from the infrared absorption maximum, as
has been observed in large polyatomic molecules.\textsuperscript{11} Therefore, it is concluded that
the IRMPD of both nitramines is a purely photochemical process. No decomposition
was observed upon irradiation at laser frequencies far from the above spectral
ranges.

The total decomposition yield of both nitramines was studied as a function of
pressure at constant laser fluence (\(F = 0.8 \text{ J cm}^{-2}\)), and the data are shown in Figure 1.
The decomposition yields of dimethylnitramine were higher than those of diethylnitramine and showed a linear increase up to 200 mTorr. Therefore, a pressure of
150 mTorr was selected in most photolysis experiments to lie within the nearly-
collisionless regime. Furthermore, the total decomposition yield of both nitramines
was studied as a function of number of pulses, and showed a linear dependence up
to 50 pulses for DMNA and 200 pulses for DENA. Thus, dimethylnitramine samples
were irradiated up to 50 pulses while diethylnitramine samples were irradiated up
to 200 pulses in order to avoid complications from secondary product photolysis.

The laser fluence dependence of the remaining fraction \(F_r = \frac{[R_2\text{NNO}_2]}{[R_2\text{NNO}_2]_0}\)
(where \(R\) is CH\(_3\) or C\(_2\text{H}_5\)) was also studied using the 10R14 and 9R16 laser line for
DMNA and DENA, respectively. The data were analyzed according to the standard
procedure described in Ref. 18, and are presented in Figure 2. A linear regression
fit of the data provided the slope which gave the steady-state rate coefficients of the
unimolecular dissociation of DMNA and DENA

\[
\begin{align*}
\text{k}_{\text{DMNA}(st)} &= 10^{5.5 \pm 0.1} \text{ (I/MW cm}^{-2} \text{) s}^{-1} \\
\text{k}_{\text{DENA}(st)} &= 10^{5.2 \pm 0.1} \text{ (I/MW cm}^{-2} \text{) s}^{-1}
\end{align*}
\]

![Figure 1](image.png)

Figure 1. Total decomposition yield for both nitramines as a function of nitramine pressure. DMNA
and DENA samples were irradiated with 50 and 200 pulses at 971.9 cm\(^{-1}\) and 1075.9 cm\(^{-1}\) respectively,
with 0.8 J cm\(^{-2}\) laser fluence (• DMNA, + DENA).
Figure 2  The yield function $-\ln F_n$ versus the laser fluence, and the least-squares fit to the data for both nitramines. [DMNA] = 100 mTorr, yield after 50 pulses irradiation at 971.9 cm$^{-1}$; [DENA] = 150 mTorr, yield after 200 pulses irradiation at 1075.9 cm$^{-1}$ ($\bullet$ DMNA, $+$ DENA).

for laser intensities in the range 3–15 MW cm$^{-2}$. Thus, for a typical average laser intensity 10 MW cm$^{-2}$ the decay of both reactants into all primary chemical channels will reach a steady state and continue to decay with a unimolecular rate constant

$$k_{\text{uni}}(\text{st}) = 10^{6.5} \text{ s}^{-1} \text{ for DMNA},$$

$$k_{\text{uni}}(\text{st}) = 10^{6.2} \text{ s}^{-1} \text{ for DENA}.$$  

The fluence threshold for dissociation was 0.3 J cm$^{-2}$, equal for both nitramines within experimental error. The ratio of the two rate constants, $k_{\text{DMNA}}/k_{\text{DENA}}$, for the same laser intensity is equal to 2, which is in agreement with the theoretical value obtained by applying the approximate equation of Quack.$^{19}$ This equation predicts that the ratio $k_{\text{DMNA}}/k_{\text{DENA}} = (s_{\text{DMNA}}/s_{\text{DENA}})^{1.46} = 1.99$, where $s$ is the number of vibrational degrees of freedom. Furthermore, this equation provides the unimolecular rate constants for both decompositions within a factor of 2.

The IR laser photolysis of DMNA resulted in the formation of NO$_2$, dimethylnitrosamine (DMNO), CH$_2$NOH, NO, and (CH$_3$)$_2$NN(CH$_3$)$_2$ gaseous products. The ratio of mass peak intensities of all products versus initial DMNA signal intensity was plotted as a function of laser fluence, and the data are presented in Figures 3–6. The IR laser photolysis of DENA resulted in the formation of NO$_2$, diethylnitrosamine (DENO), (C$_2$H$_5$)$_2$NO, and NO gaseous products. The mass peak intensity
ratios of all products versus initial DENA signal intensity were plotted as a function of laser fluence, and are presented in Figures 7–10. The plots reveal that the formation of all photolysis products exhibits an almost linear dependence on fluence at low pulse energies. In the case of DMNA, the fluence threshold for the appearance of NO₂ is identical to that of DMNA decomposition (0.3 J cm⁻²), as shown in Figures 3 and 2 respectively. The fluence threshold for DMNO and (CH₃)₂NN(CH₃)₂ appearance is 0.4 J cm⁻² (Figures 3 and 4), and for CH₂NOH is 0.5 J cm⁻² (Figure 5). This is probably due to the fact that NO₂ is the sole primary photolysis product undergoing minor secondary reactions, while the other products are formed by secondary bimolecular reactions. In the case of DENA, the fluence threshold for the appearance of all final products is higher (= 0.6 J cm⁻²) than that of DMNA decomposition.

These results are in excellent agreement with previous scavenging experiments,⁹,¹⁰ suggesting that the primary unimolecular decomposition pathway is the scission of the weakest N-NO₂ bond

\[
\text{R}_2\text{NNO}_2 \rightarrow \text{R}_2\text{N} + \text{NO}_2
\]

followed by the oxidation reactions of nascent dialkylamino radical with parent molecule and NO₂ product

\[
\text{R}_2\text{N} + \text{R}_2\text{NNNO}_2 \rightarrow \text{R}_2\text{NO} + \text{R}_2\text{NNO}
\]

\[
\text{R}_2\text{N} + \text{NO}_2 \rightarrow \text{R}_2\text{NO} + \text{NO}
\]

and the recombination and disproportionation reactions

![Figure 3](image-url)  
Figure 3  The [NO₂]ₕ/[DMNA]₀ ratio as a function of laser fluence. [DMNA] = 100 mTorr; yield after 50 pulses at 971.9 cm⁻¹.
Figure 4 The $[\text{DENO}]_0/[\text{DMNA}]_0$ ratio as a function of laser fluence. $[\text{DMNA}] = 100$ mTorr; yield after 50 pulses at 971.9 cm$^{-1}$.

Figure 5 The $[\text{CH}_2\text{NOH}]_0/[\text{DMNA}]_0$ ratio as a function of laser fluence. $[\text{DMNA}] = 100$ mTorr; yield after 50 pulses at 971.9 cm$^{-1}$.
Figure 6  The $(\text{CH}_3)_2\text{NN(\text{CH}_3)}_2/\text{[DMNA]}_0$ ratio as a function of laser fluence. [DMNA] = 10 mTorr; yield after 50 pulses at 971.9 cm$^{-1}$.

Figure 7  The $[\text{NO}_2]/[\text{DENA}]_0$ ratio as a function of laser fluence. [DENA] = 150 mTorr; yield after 200 pulses at 1075.9 cm$^{-1}$. 
Figure 8  The $[\text{DENO}]_f/[\text{DENA}]_o$ ratio as a function of laser fluence. $[\text{DENA}] = 150 \text{ mTorr}$; yield after 200 pulses at 1075.9 cm$^{-1}$.

Figure 9  The $[(\text{C}_2\text{H}_5\text{NO})_2]/[\text{DENA}]_o$ ratio as a function of laser fluence. $[\text{DENA}] = 150 \text{ mTorr}$; yield after 200 pulses at 1075.9 cm$^{-1}$.
Figure 10  The [NO]/[DENA]₀ ratio as a function of laser fluence. [DENA] = 150 mTorr; yield after 200 pulses at 1075.9 cm⁻¹.

\[
\text{R}_2\text{N} + \text{R}_2\text{N} \rightarrow \text{R}_2\text{NNR}_2 \\
\rightarrow \text{R}_2\text{NH} + \text{Imine}
\]

producing the corresponding hydrazines, amines, and imines (where R is CH₃ or C₂H₅). At high laser fluences, the primary dialkylamino radicals undergo further IR multiphoton excitation resulting to their unimolecular decomposition via reactions:

\[
(\text{CH}_3)_2\text{N} \rightarrow \text{CH}_2=\text{N}-\text{CH}_3 + \text{H}
\]

(6)

\[
(\text{C}_2\text{H}_5)_2\text{N} \rightarrow \text{CH}_2=\text{N}-\text{C}_2\text{H}_5 + \text{CH}_3
\]

(7)

that yield H atoms and CH₃ radicals, which are mainly converted to H₂ and C₂H₆ observed in the photolysis products.

The oxidation reactions (2) and (3) are responsible for the formation of the main photolysis products nitrosamines, and NO. These reactions are currently under investigation by our group using the VLPR (very low pressure reactor) technique, in order to obtain their absolute rate constant values. The corresponding nitroxide radicals were observed only in the case of diethylnitramine photolysis. The diethyl nitroxide radical, (C₂H₅)₂NO, is a stable free radical due to the effective delocalization of the unpaired NO moiety orbitals, and to the rather high steric hindrance of the reactive site by the two ethyl groups.²⁰ On the contrary, the dimethylnitroxide radical, (CH₃)₂NO, is less stable and further reacts or decomposes producing nitrosomethane and formaldoxime. Finally, the recombination of dimethylamino radicals via reaction (4) produces tetramethylhydrazine that was observed in the final products, and there was no evidence of the recombination of diethylnitramine radicals. The disproportionation reaction (5) could not be verified since no amine or imine were observed in
our analyses. However, it is known that amines tend to adhere on glass walls and imines are trimerized and polymerized to non-volatile substances.\textsuperscript{21}

At last, the rates of NO\textsubscript{2}, R\textsubscript{2}NNO, and R\textsubscript{2}NNR\textsubscript{2} formation are,

\begin{equation}
\frac{d[NO_2]}{dt} = k_1 [R_2NNO_2] - k_3 [R_2N][NO_2] \tag{8}
\end{equation}

\begin{equation}
\frac{d[R_2NNO]}{dt} = k_2 [R_2N][R_2NNO_2] + k_3 [R_2N][NO_2] \tag{9}
\end{equation}

\begin{equation}
\frac{d[R_2NNR_2]}{dt} = k_4 [R_2N]^2 \tag{10}
\end{equation}

For the DMNA system, the contribution of oxidation reaction (3) is minor, thus $d[NO_2]/[DMNA]$ is proportional to $k_1$ (eq. 8) and linearly dependent on fluence as in Figure 3. Similarly, $d[DMNO]/[DMNA]$ is proportional to $k_2[(CH_3)_2N]^2$ (eq. 9) that is almost proportional to $k_1$ and thus to fluence, as shown in Figure 4. The yield of $[(CH_3)_2NN(CH_3)_2]$ is proportional to $[(CH_3)_2N]^2$ (eq. 10), and has a quadratic dependence on fluence (Figure 6). For the DENA system, the contribution of recombination reaction (4) is minor, therefore the steady-state concentration of $(C_2H_5)_2N$ is higher and the contribution of oxidation reaction (3) becomes important. Thus, the dependence of NO\textsubscript{2}, DENO, NO, and $(C_2H_5)_2NO$ yield on fluence must be of quadratic form, as shown in Figures 7–10.

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