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reactions involving polyatomic molecules. Work is now going ahead to extend the methods to the reactions between open-shell free radicals where interesting temperature effects on the rate constants are expected at low temperatures.[21]

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Infrared Multiphoton Decomposition of Diethylnitramine

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Irradiation of gaseous diethylnitramine with infrared radiation from a pulsed CO_2 laser under collision-free and collisional conditions resulted in the formation of diethylnitrosamine as the main product along with nitrogen dioxide, nitric oxide, formaldoxime, and diethyl nitroxide. Scavenging experiments with Cl_2, NO, and $(CD_3)_2NNO_2$ molecules have shown that the primary channel of unimolecular dissociation of diethylnitramine molecules is the scission of the N–NO_2 bond, with a steady-state rate constant of $10^{5.2\pm0.1}(I/\text{MW cm}^{-2})$ s^{-1} for laser intensities in the range 3–15 MW cm^{-2} at an irradiation frequency of 1075.9 cm^{-1}. A qualitative analysis of the chemical mechanism leading to the formation of final products as well as the importance of the diethylamino radical oxidation reactions is presented.

Introduction

Nitramines are among the most important compounds in the area of high explosives and propellants with well-known members such as 1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). These characteristics can be attributed to the energetics of the primary dissociation pathways as well as to the fast chemical reactions of the resultant primary product species.[1] The study of the industry-interesting nitramines of complex structure is often complicated by numerous side reactions, and their nonvolatile nature leads to mixed-phase chemistry.[2] Simpler nitramines offer the advantage of gas-phase studies and extending the results to the bulky members. The gas-phase decomposition mechanism of the simpler dimethylnitramine (DMNA) has been the subject of earlier and recent works using various excitation sources, namely, pyrolysis,[3,4] shock tubes,[5] laser-powered homogeneous pyrolysis,[6] and infrared multiphoton decomposition (IRMPD).[7] There is a general agreement on the scission of the N–NO_2 bond as the main unimolecular dissociation channel, with a minor contribution from the isomerization to N-nitrite and subsequent NO elimination channel observed in the laser pyrolysis experiments. However, the larger and still simple diethylnitramine (DENA) has not received equal attention; early pyrolysis experiments in the temperature range 180–240 °C revealed the N–NO_2 bond fission as the primary dissociation pathway with a thermal rate constant expressed by the equation $k = 10^{14.8}e^{-42.1/RT}$ s^{-1} (R in kcal mol^{-1} K^{-1}).[8] The proposed mechanism of the final products' formation incorporated the oxidation reaction of parent diethylnitramine molecules by nascent NO_2 and the reaction of the diethylamino radical generated in the initial step with the secondary product NO to form diethylnitrosamine.

In the present work, the IRMPD of diethylnitramine under collisionless conditions is studied in order to determine the primary channel of unimolecular decomposition and elucidate the chemical mechanism of the final products' formation. Scavenging experiments with Cl_2, NO_2, NO, and $(CD_3)_2NNO_2$ are carried out in order to reveal the complete chemical mechanism that follows the initial energy absorption. Finally, the IRMPD of the first two symmetrical dialkylnitramines are compared, and the relative importance of the HONO elimination channel in diethylnitramine is examined.

Experimental Section

Diethylnitramine ($(CH_3CH_2)_2NNO_2$) was prepared by the method of Wright,[9] dehydrating the nitrate salt of diethylamine ($(CH_3CH_2)_2NH_2^+NO_3^-$) in acetic anhydride with the use of $ZnCl_2$ as catalyst. The mixture of the desired compound along with side

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product diethylnitrosamine was subsequently quantitatively converted to diethylnitramine after prolonged treatment with 30% aqueous H_2O_2 under reflux with CF_3COOH as catalyst. After neutralization, diethylnitramine was distilled under reduced pressure, degassed, and stored in glass bulbs. The mass spectrum was found to be identical to that reported elsewhere.[10] Scavenger gases were commercially available (Linde) with the exception of dimethylnitramine-d_6, which was prepared according to published procedures.[11] Traces of nitrogen dioxide were removed from nitric oxide by distillation of the more volatile NO at −78 °C.

A tunable Lumonics TEA 103-2 CO_2 laser was used as the infrared radiation source with a relatively constant energy beam. The laser beam profile was Gaussian with a cross section of ca. 7 cm^2. The laser pulse energy was monitored with a calibrated thermopile (Lumonics Model 20D) and was found to have a maximum of 6 J at 1075.9 cm^{-1}. The laser pulse temporal profile was measured with a photon drag detector (Rofin 7441) and consisted of an 80-ns high-intensity spike followed by a 600-ns tail carrying a small part of the total pulse energy.

The experimental arrangement was similar to that used for the study of dimethylnitramine.[7] Essentially, it consisted of a photolysis cell with glass lines continuously evacuated by diffusion pumps with attached manifolds for gas supply and mixing. Gas pressures were measured with calibrated transducer gauges (Validyne DP15). Mixtures of diethylnitramine with scavenger gas were prepared immediately before use inside the photolysis cell (a cylindrical Pyrex tube of 17-cm length and 4-cm diameter with NaCl windows at both ends). The unfocused laser beam was transmitted through the entire cell with the exception of the experiments with scavenger gases where the beam was focused with a germanium lens of focal length $f = 10$ cm.

The gaseous mixtures before and after photolysis were analyzed by a quadrupole mass spectrometer (Balzers QMG511) located inside a high-vacuum chamber (working pressure $\sim 10^{-7}$ mbar). Gas analyses were performed by allowing a fraction of the mixture to flow through a needle valve and a 1-mm stainless steel capillary to a region close to the ionizer. All mass spectrometric data were taken at an electron energy of 70 eV. The mass spectrometer was interfaced to a DEC PDP-11/23 microcomputer. Acquisition and treatment of mass spectral data were carried out using software developed by us. Using mass spectra libraries, the contribution of every species was resolved after subtracting the background contribution and finally presented graphically as a function of the experimental parameters.

The experimental error in the mass spectral intensity measurements was <10%, and thus the asssociated error of the presented peak ratios was ca. 15%.

Results

CO_2 Laser Photolysis Experiments of Diethylnitramine. The infrared spectrum of diethylnitramine shows three absorption bands (958, 1033, and 1085 cm^{-1})[12] between 900 and 1100 cm^{-1}. Irradiation of gaseous diethylnitramine with photons slightly red-shifted relative to the absorption bands at 958 and 1033 cm^{-1} did not show any observable decomposition due to the low-energy output of the available laser lines combined with the expected low decomposition yield. Excitation of the medium-intensity absorption band at 1085 cm^{-1} with the 9R laser branch resulted in substantial decomposition with a sharp maximum at 1075.9 cm^{-1} (9R16 laser line), red-shifted by 9 cm^{-1} from the infrared absorption maximum. The magnitude of the shift is typical for polyatomic molecules and has also been observed in the IRMPD of dimethylnitramine.[7] However, the dissociation yields per pulse were too low to allow real-time observation of the primary photolysis products. Therefore, we performed static photolysis experiments with a large number of pulses in order to obtain sufficiently high yields of decomposition for mass spectrometric analysis. The decomposition yields showed a fairly linear behavior with the number of pulses; 200 pulses were used in most experiments. Both focused and unfocused laser beam experiments produced the same photolysis products, suggesting that the decomposition process and the chemical mechanism resulting in the final products are the same for both experimental conditions.

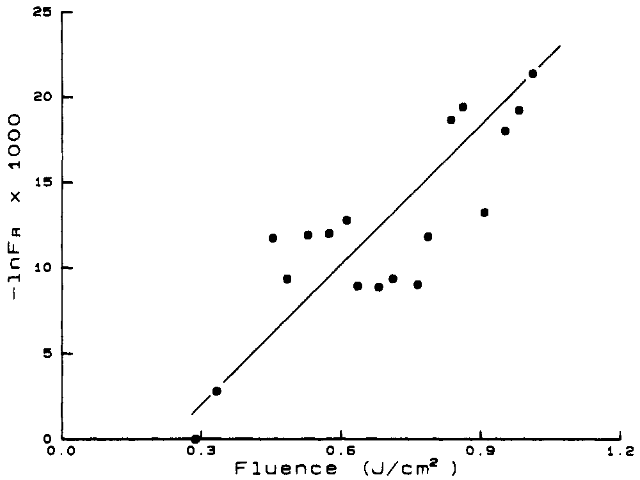


Figure 1. Yield function $-\ln F_R$ versus laser fluence and the least-squares fit to the data. Initial diethylnitramine pressure 150 mTorr; irradiation with 200 pulses at 1075.9 cm^{-1} (9R16 laser line).

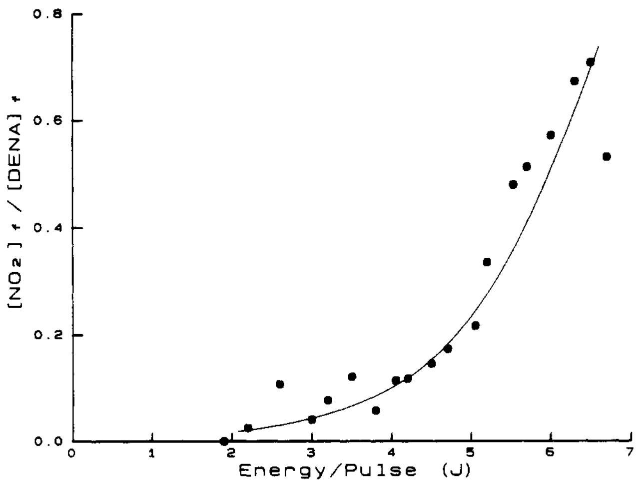


Figure 2. $[NO_2]_f/[DENA]_f$ ratio as a function of pulse energy. [DENA] = 150 mTorr; yields after 200 pulses at 1075.9 cm^{-1}.

The decomposition yield showed a linear dependence on the initial diethylnitramine pressure, up to its room-temperature vapor pressure (ca. 250 mTorr). However, a pressure of 150 mTorr was selected for the IRMPD to lie within the nearly-collisionless regime. The laser fluence dependence of the remaining fraction $F_R = [DENA]_f/[DENA]_0$ after 200 pulses with the 9R16 laser line was studied, and the results are presented in Figure 1. A linear regression fit of the data provided the slope[13] which gave the steady-state rate coefficient of the unimolecular dissociation of diethylnitramine, $k(st) = 10^{5.2\pm0.1}(I/MW\ cm^{-2})\ s^{-1}$ in the laser intensity range 3–15 MW cm^{-2}. The fluence threshold for dissociation was found to be 0.24 ± 0.03 J cm^{-2}. The errors associated with the determination of k(st) are due to experimental uncertainties.

The final concentrations of all products follow the same dependence on the laser energy as the decomposition yield of diethylnitramine, thus verifying their assignment as final photolysis products. A plot of the ratio of the NO_2 product peak intensity versus final diethylnitramine peak intensity as a function of laser fluence is presented in Figure 2. After peak contributions due to concurrent species fragmentation were subtracted, the following compounds were identified as gas-phase products of the IRMPD of diethylnitramine: diethylnitrosamine, $(CH_3CH_2)_2NNO$ (parent peak at m/e 102[10]), diethyl nitroxide, $(CH_3CH_2)_2NO$ (peaks at m/e 88, 74, and 60), formaldoxime, $CH_2{=}NOH$ (parent peak at m/e 45), NO_2 and NO (peaks at m/e 46 and 30, respectively). The peak at m/e 59 was tentatively assigned to acetaldoxime ($CH_3CH{=}NOH$)[14] or diethyl nitroxide, and the peak at m/e 31

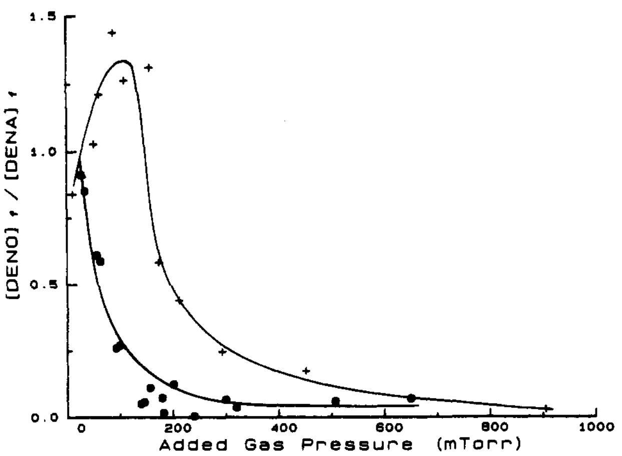


Figure 3. $[DENO]_f/[DENA]_f$ ratio as a function of added Cl_2 and NO pressures. DENA pressure 150 mTorr; irradiation with 200 pulses at 9R16 laser line (●, Cl_2; +, NO).

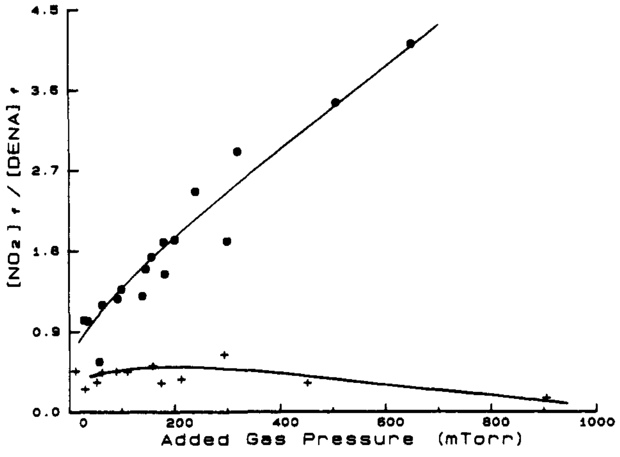


Figure 4. $[NO_2]_f/[DENA]_f$ ratio as a function of added Cl_2 and NO pressures. DENA pressure 150 mTorr; irradiation with 200 pulses at 9R16 laser line (●, Cl_2; +, NO).

was assigned to methyl nitrite (CH_3ONO). Ethane (CH_3CH_3) was not possible to identify among the photolysis products due to extensive fragmentation of the above compounds below *m/e* 30.

CO_2 Laser Photolysis Experiments of Diethylnitramine in the Presence of Scavenger Gases Cl_2, NO, and $(CD_3)_2NNO_2$. Mixtures of varying amounts of scavenger gases Cl_2 and NO with 150 mTorr of diethylnitramine were photolyzed with a focused laser beam geometry to enhance the decomposition yield. Considering the low IRMPD yield of diethylnitramine, the pressure range of added scavenger molecules was kept low in order to avoid collisional deactivation of diethylnitramine and retain the decomposition products to measurable concentrations. Cl_2 was a less efficient quencher than NO, while NO_2 was a very efficient quencher, causing the complete elimination of decomposition at even low (~150 mTorr) NO_2 pressures.

The dependence of the decomposition products yield (expressed as the ratio of the product intensity peak to the remaining nitramine parent peak) on the initial pressure of the added gases Cl_2 and NO is presented in Figures 3–6. The diethylnitrosamine yield shown in Figure 3 decreases sharply with increasing Cl_2 and NO pressures, although in the case of NO an initial increase is observed. The initial rise of the yield suggests a reaction leading to diethylnitrosamine while the later decay corresponds to increasing collisional deactivation of the hot nitramine molecules by NO molecules, reducing the unimolecular dissociation yield and the secondary reactions leading to nitrosamine. On the contrary, the NO_2 yield presents an almost linear increase with the Cl_2 pressure as shown in Figure 4. Also shown in Figure 4 is a small increase in NO_2 yield with NO pressure up to 150 mTorr, followed by a gradual decrease at large NO pressures.

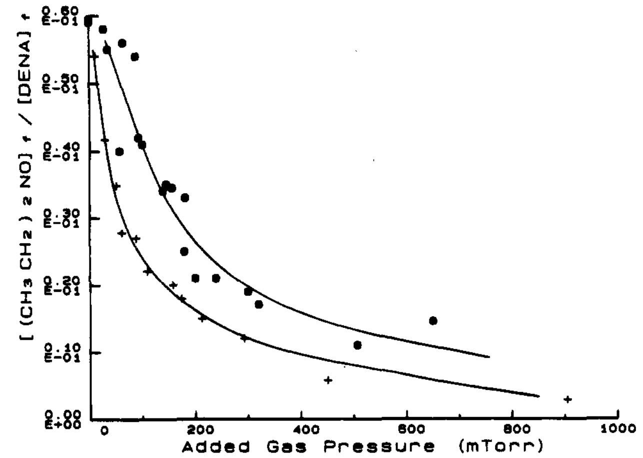


Figure 5. $[(CH_3CH_2)_2NO]_f/[DENA]_f$ ratio as a function of added Cl_2 and NO pressures. DENA pressure 150 mTorr; irradiation with 200 pulses at 9R16 laser line (●, Cl_2; +, NO).

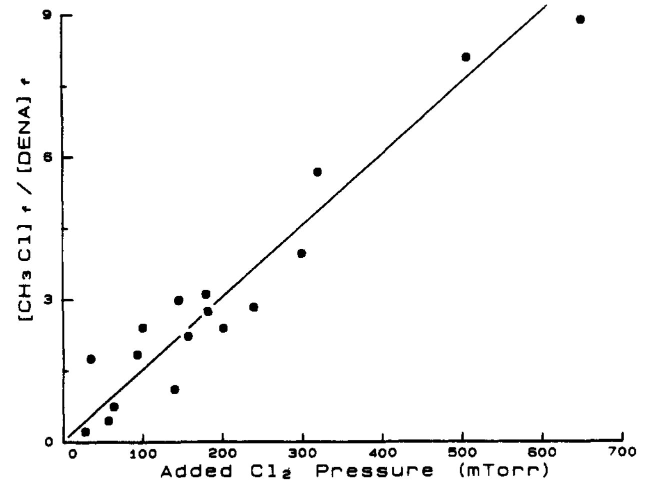


Figure 6. $[CH_3Cl]_f/[DENA]_f$ ratio as a function of added Cl_2 pressures. DENA pressure 150 mTorr; irradiation with 200 pulses at 9R16 laser line.

The diethyl nitroxide yield decreases sharply with Cl_2 or NO pressure as shown in Figure 5.

The formation of methyl chloride (CH_3Cl) was also observed with the addition of Cl_2 (detected at *m/e* 50 and 52 for both chlorine isotopes) and was found to increase almost linearly with added Cl_2 pressure (Figure 6).

The dependence of the NO yield on the Cl_2 pressure could not be estimated accurately due to the various contributions to the *m/e* 30 peak and the scattered data. However, a decrease of the NO yield with the Cl_2 pressure was evident, and complete suppression of NO was observed at high Cl_2 pressures.

Photolysis experiments of diethylnitramine with the addition of dimethylnitramine-d_6, $(CD_3)_2NNO_2$ (DMNA-d_6), were performed with an unfocused laser beam geometry. The DMNA-d_6 did not absorb the CO_2 laser radiation since the frequency used was out of resonance with any absorption band of DMNA-d_6. The addition of low (<50 mTorr) DMNA-d_6 pressures to avoid the excessive collisional deactivation resulted in the appearance of dimethylnitrosamine-d_6, $(CD_3)_2NNO$, at *m/e* 80 with no evidence of any other deuterated species.

Mass balance analysis of the overall diethylnitramine decomposition was not performed due to wall losses and varying flow conditions of the final gaseous photolysis products via the inlet capillary to the ionizer. However, the decomposition yield per pulse was very low, amounting to <2% at the maximum laser fluence.

Discussion

The advantage of the IRMPD process over other simple pyrolysis techniques is that the induced vibrational excitation is highly selective, producing excitation only to the parent molecules that absorb the infrared radiation and leaving intact the remaining molecular species.

The observed CO_2 laser decomposition of diethylnitramine is a photochemical process, since the overall decomposition yield depends on the laser frequency. The irradiation frequency at 1075.9 cm^{-1} (9R16 laser line) lies within the 1085-cm^{-1} infrared absorption band of diethylnitramine, which is probably correlated to ethyl group deformation modes.[15] Furthermore, the laser fluence dependence provides the range for the specific unimolecular dissociation rate constant $k_{uni} = (0.5–2.4) \times 10^6\ s^{-1}$ for laser intensities I = 3–15 MW cm^{-2}. The estimated overall diethylnitramine disappearance is mainly due to its unimolecular decomposition with only minor contribution from bimolecular reactions with diethylamino or methyl radicals ($k \leq 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ [16,17]) since their concentrations were low. The unimolecular infrared multiphoton decomposition of diethylnitramine may be considered as collisionless at low pressures (~150 mTorr), since the decomposition lifetime (0.4–1 μs) is shorter than the mean collision time (≃1 μs) and the laser pulse duration is 80 ns. For high CO_2 laser intensities ($I \simeq$ 40–120 MW cm^{-2}), the infrared multiphoton excitation of diethylnitramine (number of vibrational degrees of freedom s = 48) will lead to a vibrational overexcitation to levels well above the dissociation limit ($E \simeq 1.7D_0$).[18] The induced photodissociation will produce molecular fragments with a high degree of vibrational excitation and with a broad infrared spectrum shifted to lower frequencies.[19] Therefore, they may be further excited by the same laser pulse (the spike or the delayed tail) to even higher vibrational levels above the dissociation limit and undergo unimolecular decomposition.

Diethylnitramine is only a heavier analogue to dimethylnitramine, and their unimolecular decomposition dynamics are expected to be similar. Therefore, the primary unimolecular decomposition of diethylnitramine should be scission of the weak $N-NO_2$ bond (the weakest bond in the molecule) represented by the reaction

$$(CH_3CH_2)_2NNO_2 \rightarrow (CH_3CH_2)_2N + NO_2 \qquad \Delta H^\circ_{300} = +45.0\ \text{kcal/mol} \quad (1)$$

A second channel of unimolecular decomposition is likely to be the elimination of HONO that proceeds via the formation of a six-membered ring and is represented by the reaction

$$(CH_3CH_2)_2NNO_2 \rightarrow CH_3CH_2N{=}CHCH_3 + HONO \qquad \Delta H^\circ_{300} = -1.5\ \text{kcal/mol} \quad (2)$$

The approach of a terminal ethyl hydrogen atom toward an oxygen atom in order to form the six-membered ring is a more favorable process than the formation of the five-membered ring in the HONO elimination of nitroalkanes.[20,21] The elimination of HONO is accompanied by a 1,2-sigmatropic hydrogen-transfer process that produces the stable N-ethylethylidenimine, $CH_3CH_2N{=}CHCH_3$. A third channel of unimolecular dissociation would be the initial rearrangement of the nitro group and the formation of the corresponding N-nitrite, which is further decomposed by scission of the weak O–N bond,[6b] and is represented by the reaction

$$(CH_3CH_2)_2NNO_2 \rightarrow [(CH_3CH_2)_2NONO] \rightarrow (CH_3CH_2)_2NO + NO \qquad \Delta H^\circ_{300} = +41.3\ \text{kcal/mol} \quad (3)$$

Other single-bond fission pathways would not be competitive due to their high-energy requirements [C–H (~95), C–C (~90), C–N (92), N–O (90); values in parentheses are typical bond dissociation energies in kcal/mol[22,23]].

Our experimental results indicate that the main channel of unimolecular decomposition of diethylnitramine is the scission of the $N-NO_2$ bond, yielding vibrationally excited diethylamino radicals, $(CH_3CH_2)_2N$ ($E_v \leq$ 40 kcal/mol) and NO_2 molecules. This is clearly shown by the addition of NO that resulted in the scavenging of the diethylamino radicals through the recombination reaction

$$(CH_3CH_2)_2N + NO \rightarrow (CH_3CH_2)_2NNO \qquad \Delta H^\circ_{300} = -59.1\ \text{kcal/mol} \quad (4)$$

and hence an initial increase in the diethylnitrosamine yield (See Figure 3). Simultaneously, the yield of the other primary photofragment, NO_2, was increased (see Figure 4). Higher NO pressures resulted in a decrease in diethylnitrosamine and NO_2 (Figures 3 and 4) presumably due to the collisional deactivation of the diethylnitramine and hence reduced decomposition yield. Similarly, the addition of Cl_2 should lead to the formation of N-chlorodiethylamine via the reaction

$$(CH_3CH_2)_2N + Cl_2 \rightarrow (CH_3CH_2)_2NCl + Cl \qquad \Delta H^\circ_{300} = -14.1\ \text{kcal/mol} \quad (5)$$

and to an increase of NO_2 yield. Nevertheless, the chloramine could not be detected (expected parent peak at m/e 107/109), although the yield of NO_2 was found to increase with Cl_2 pressure (Figure 4). This indicates that either reaction 5 could not compete with the unimolecular decomposition of diethylamino radical (reaction 8 below) so there was no formation of N-chlorodiethylamine or a secondary IRMPD process led to N-chlorodiethylamine decomposition. There is also the chance the N-chlorodiethylamine does not possess the parent ion mass peak, which could not be verified. Reaction 5 also leads to the formation of chlorine atoms which may further react with parent molecules to produce HCl, NO_2, and N-ethylethylidenimine.[24]

Our results indicate that the HONO elimination and the nitro–nitrite isomerization channels do not contribute to more than 10%, since the yield of HONO and NO products was almost zero at high Cl_2 pressures. This suggests that the dissociation dynamics of nitramines is different from that of nitroalkanes.[20] This may be due to the weakness of the $N-NO_2$ bond (~45 kcal/mol) in comparison to the $C-NO_2$ bond (~60 kcal/mol) of nitroalkanes.

The nascent diethylamino radicals will primarily react with parent nitramine and NO_2 through the oxidation reactions

$$(CH_3CH_2)_2N + (CH_3CH_2)_2NNO_2 \rightarrow (CH_3CH_2)_2NO + (CH_3CH_2)_2NNO \qquad \Delta H^\circ_{300} = -17.8\ \text{kcal/mol} \quad (6)$$

$$(CH_3CH_2)_2N + NO_2 \rightarrow (CH_3CH_2)_2NO + NO \qquad \Delta H^\circ_{300} = -3.7\ \text{kcal/mol} \quad (7)$$

and will yield diethyl nitroxide, diethylnitrosamine, and NO. Reaction 6 is the main source of diethylnitrosamine and diethyl nitroxide. The addition of Cl_2 resulted in a sharp decrease in the yields of both these products (Figures 3 and 5), since the diethylamino radicals are reacting with Cl_2 through reaction 5.

The $(CH_3CH_2)_2NO$ radical has been identified by the characteristic mass peaks at m/e 88, 74, and 60; it has not been observed previously in the gas phase. This assignment was verified by performing IRMPD experiments on diethylnitrosamine in the presence of NO_2, where the main photolysis product was the stable diethyl nitroxide radical which gave the above mass spectrum peaks. Nitroxides are among the most stable free radicals due to the effective delocalization of the unpaired spin density in the N–O group. In addition, steric hindrance of their reactive center is another stabilization factor encountered in highly branched members. The electronically similar dimethyl nitroxide radical, $(CH_3)_2NO$, produced in the IRMPD of dimethylnitramine[7] is less stable due to its lower steric shielding from the smaller methyl groups and has not been observed. In solution, nitroxides are known to abstract labile hydroxylic or aminic hydrogen atoms and dimerize (in the absence of steric factors) in a quasi-reversible manner followed by hydrogen-transfer reactions between two nitroxide molecules.[25]

The nascent diethylamino radicals may also be excited within the same laser pulse to higher vibrational levels ($E \simeq$ 100 kcal/mol) and consequently undergo unimolecular decomposition

$$(CH_3CH_2)_2N \rightarrow CH_3CH_2N{=}CH_2 + CH_3 \qquad \Delta H^\circ_{300} = +22.6\ \text{kcal/mol} \quad (8)$$

yielding N-ethylmethylenimine and methyl radicals. The estimated Arrhenius parameters are $A \simeq 10^{15}\ s^{-1}$ and $E_\alpha \simeq$ 60 kcal/mol.[22]

This is confirmed by the addition of Cl_2, which results in the formation of methyl chloride via the reaction

$$CH_3 + Cl_2 \rightarrow CH_3Cl + Cl \qquad \Delta H^\circ_{300} = -26 \text{ kcal/mol} \quad (9)$$

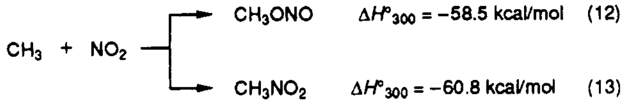
Indeed, the methyl chloride yield was found to increase sharply with the Cl_2 pressure (Figure 6). In a similar manner, the addition of NO promotes the formation of nitrosomethane via the recombination reaction

$$CH_3 + NO \rightarrow CH_3NO \qquad \Delta H^\circ_{300} = -40 \text{ kcal/mol} \quad (10)$$

and the nitrosomethane subsequently isomerizes to formaldoxime, $CH_2{=}NOH$. The latter was observed in the final products, and its yield was found to increase with NO pressure. In the absence of scavenger gases the methyl radicals will primarily react with parent molecules

$$CH_3 + (CH_3CH_2)_2NNO_2 \rightarrow CH_3O + (CH_3CH_2)_2NNO \qquad \Delta H^\circ_{300} = -31.9 \text{ kcal/mol} \quad (11)$$

and with NO_2



$$CH_3 + NO_2 \rightarrow CH_3ONO \qquad \Delta H^\circ_{300} = -58.5 \text{ kcal/mol} \quad (12)$$

$$CH_3 + NO_2 \rightarrow CH_3NO_2 \qquad \Delta H^\circ_{300} = -60.8 \text{ kcal/mol} \quad (13)$$

to produce diethylnitrosamine, methoxy radical, methyl nitrite, and nitromethane, which were observed in the final products. The methoxy radical would further react with diethylnitramine

$$CH_3O + (CH_3CH_2)_2NNO_2 \rightarrow CH_3OO + (CH_3CH_2)_2NNO \qquad \Delta H^\circ_{300} = +2.8 \text{ kcal/mol} \quad (14)$$

producing methyl peroxide radical that subsequently is converted to methyl hydroperoxide (CH_3OOH) by hydrogen abstraction reaction. Methyl hydroperoxide has been observed in the final products at *m*/*e* 48 and 47.

Finally, diethylamino radicals may also undergo disproportionation and recombination reactions

$$(CH_3CH_2)_2N + (CH_3CH_2)_2N \xrightarrow{k_d} (CH_3CH_2)_2NH + CH_3CH_2N{=}CHCH_3 \qquad \Delta H^\circ_{300} = -61.7 \text{ kcal/mol} \quad (15)$$

$$(CH_3CH_2)_2N + (CH_3CH_2)_2N \xrightarrow{k_r} (CH_3CH_2)_2NN(CH_3CH_2)_2 \qquad \Delta H^\circ_{300} = -61.7 \text{ kcal/mol} \quad (16)$$

leading to diethylamine, *N*-ethylethylidenimine, and tetraethylhydrazine. The recombination reaction (16) is expected to be less competitive than the disproportionation reaction (15) due to the steric repulsion between the attached ethyl groups during the N–N approach. The presence of both reactions could not be verified since none of the reaction products were observed in our analyses. However, this may be due to the fact that diethylamine and *N*-ethylethylidenimine have a high tendency to adhere on the glass walls and imines undergo efficient trimerization and polymerization to nonvolatile substances.[26]

A comparison of the IRMPD of diethylnitramine with that of dimethylnitramine shows that in both nitramines the main channel of unimolecular dissociation is the same, namely, the scission of the weak $N-NO_2$ bond. However, the ratio of their steady-state rate constants of unimolecular dissociation $k_{DMNA}/k_{DENA} = 2$, which is consistent with the RRKM theory. The number of vibrational degrees of freedom in diethylnitramine ($s = 48$) is almost a factor of 2 larger than that in dimethylnitramine ($s = 30$). Therefore, the laser-induced IR multiphoton excitation process raises the diethylnitramine molecules to very high vibrational levels (well above the dissociation limit). As a consequence, the nascent diethylamino radicals emerge with a high degree of vibrational excitation and may decompose by eliminating methyl radicals. On the contrary, the nascent dimethylamino radicals do not have the appropriate degree of excitation to undergo stabilization by elimination of hydrogen atoms.

Conclusions

The IRMPD of diethylnitramine in the gas phase under collisionless conditions proceeds through rupture of the weakest bond in the molecule, the $N-NO_2$ bond, and produces vibrationally excited diethylamino radicals and NO_2. The main reactions that follow diethylnitramine decomposition are the oxidation reactions of diethylamino radical with parent nitramine and NO_2 product that lead to the formation of diethylnitrosamine and diethyl nitroxide radical. The formation of methyl radicals by subsequent decomposition of nascent diethylamino radicals also induces parallel oxidation reactions of methyl radicals with parent nitramine and NO_2. The diethyl nitroxide radical was observed among the final products, demonstrating its stability in the gas phase at room temperature.

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Registry No. Cl_2, 7782-50-5; $(CD_3)_2NNO_2$, 72885-11-1; CH_3OOH, 3031-73-0; diethylnitramine, 7119-92-8; diethylnitrosamine, 55-18-5; nitrogen dioxide, 10102-44-0; nitric oxide, 10102-43-9; formaldoxime, 75-17-2; diethyl nitroxide, 10605-31-9; diethylamino radical, 29685-06-1; methyl chloride, 74-87-3.

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