Photodissociation of Dimethylnitramine at 248 nm

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The production of OH $A^{2}\Sigma^{+}$, OH $X^{2}\Pi_{i}$, NO₂ $\tilde{A}^{2}B_{2}$, NO₂ $\tilde{X}^{2}A_{1}$, and NO $X^{2}\Pi$ following dimethylnitramine (DMNA) photolysis at 248 nm has been investigated by using laser-induced fluorescence and emission spectroscopies. NO₂ \tilde{A}^2B_2 , NO₂ \tilde{X}^2A_1 , and OH $X^2\Pi_i$ are formed via monophotonic, unimolecular pathways. The quantum yields for NO₂ \tilde{X}^2A_1 and OH $X^2\Pi_i$ production are estimated to be 0.15 and 0.004, respectively. The unimolecular production of NO $X^2 \Pi$ (v'' = 0) was not observed, implying its quantum yield is <0.001. OH $A^2 \hat{\Sigma}^+$ is formed via a two-photon, unimolecular process. These results are compared with previous studies investigating the thermal and photochemical decomposition of DMNA.

Introduction

Cyclic nitramines such as HMX and RDX are energetic materials used in propellants and explosives. One of the keys to understanding the ignition and combustion of these compounds is a characterization of the pathways involved in their unimolecular decomposition. This information is difficult to obtain since the utility of energetic materials is based on their propensity to undergo extremely rapid, exothermic reactions. Moreover, functionally useful nitramines may decompose via a number of possible pathways, and secondary bimolecular reactions involving product radicals may obscure the identity of the initial reaction products.

Because of these difficulties dimethylnitramine (DMNA), $(CH_3)_2NNO_2$, has been studied as a simple analogue expected to exhibit some of the processes important in cyclic nitramine decomposition. DMNA decomposition has been investigated in thermal pyrolysis,¹⁻⁴ "pulsed laser pyrolysis",⁵⁻⁷ photodissociation,^{8,9} and theoretical¹⁰⁻¹² studies. An early investigation of DMNA decomposition reported by Fluornoy¹ found that approximately 80% of the DMNA thermally pyrolyzed in a static bulb was converted to dimethylnitrosamine (DMNO), (CH₃)₂NNO. Since this product indicates that the C-N-C structure remains intact subsequent to the initial decomposition step, Fluornoy proposed that the rate-determining step for DMNA dissociation was a scission of the $(CH_3)_2N-NO_2$ bond;

$$(CH_3)_2 N - NO_2 \rightarrow (CH_3)_2 N + NO_2$$
(1)

Subsequent studies have corroborated the importance of this reaction step. Lin and co-workers came to this conclusion on the basis of the results of low-temperature static bulb and high-temperature single-pulse shock-tube experiments.⁴ Lazarou and Papagiannakopoulos⁹ have recently reported a study of the infrared multiphoton dissociation of DMNA that concludes that process 1 is the most important initial step for decomposition initiated in this manner. These researchers have also reported evidence that DMNO is formed via the reaction⁹

$$(CH_3)_2N + (CH_3)_2NNO_2 \rightarrow (CH_3)_2NO + (CH_3)_2NNO$$
 (2)

This reaction would account for the formation of DMNO in the static bulb experiments.

Golden and co-workers have studied DMNA decomposition following its infrared laser pyrolysis in a bath of argon. Using GC^{5,6} and mass spectrometric⁷ sampling techniques for product detection, these researchers conclude that a nitro-nitrite rearrangement

$$CH_3)_2NNO_2 \rightarrow (CH_3)_2NO-NO$$
 (3a)

followed by rapid scission of the (CH₃)₂NO-NO bond

$$(CH_3)_2NO-NO \rightarrow (CH_3)_2NO + NO$$
 (3b)

effectively competes with process 1 in their experiments.

An initial decomposition step that has been theoretically investigated is HONO elimination:

> $(CH_3)_2NNO_2 \rightarrow (CH_3)N(CH_2) + HONO$ (4)

To obtain Arrhenius parameters based on thermochemical data that are consistent with experimentally determined values. Shaw and Walker were required to postulate that HONO elimination contributed no more than 10% to the rate of DMNA decomposition.¹⁰ Similarly, Sumpter and Thompson have calculated that HONO elimination is not important for a random distribution of energy but proposed that the rate of this reaction would significantly increase by overtone excitation of one of the CH stretches.12

The decomposition of DMNA following its photolysis with UV radiation has also been studied. Mialocq and Stephenson demonstrated this approach in a picosecond laser study of the collisionless photodissociation of DMNA at 266 nm.8 These researchers found that the mechanisms forming NO₂ \tilde{X}^2A_1 and NO₂ \tilde{A}^2B_2

$$(CH_3)_2 NNO_2 \xrightarrow{h\nu} (CH_3)_2 N + NO_2(\tilde{X}^2 A_1)$$
 (1a)

$$\frac{h_{\nu}}{266 \text{ nm}} (CH_3)_2 N + NO_2(\tilde{A}^2 B_2)$$
(1b)

were monophotonic and collision-free and occurred in 6 ps or less.

In this paper, the results of photolyzing DMNA with 248-nm laser radiation are presented. Prompt emission features in the range 255-855 nm resulting directly from DMNA excitation have

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Figure 1. Schematic diagram of the experimental setup.

been recorded and assigned. Tunable laser-induced fluorescence (LIF) was used to probe the formation of ground state OH, NO, and NO₂ photoproducts. These results provide new insight into the physical and chemical processes that occur in the decomposition of DMNA.

Experimental Methods

A schematic diagram of the experimental apparatus used for this study is depicted in Figure 1. The experiments were conducted in a multipurpose, stainless steel vacuum chamber that was evacuated by a turbomolecular pump. An excimer laser (Lumonics, HyperEX 440) operated at 10 Hz with KrF (248 nm) was used to irradiate a flow of pure DMNA vapor. The pulse duration for this laser is approximately 15 ns fwhm. A gas processor cooled with liquid nitrogen was used to improve the stability of the photolysis beam fluence.

DMNA vapor was introduced into the vacuum chamber from an evacuated Pyrex flask containing a degassed sample of DMNA crystals. The purity of the sample was determined to be >95% from mass spectrometric and IR absorption analyses. Flow conditions were used to prevent reaction product builup. The flow conditions were established by fully opening the valve isolating the DMNA sample from the chamber and throttling the flow of effluent to the turbo pump with a gate valve to obtain the desired DMNA vapor pressure (1-8 mTorr). The pressure was monitored with a capacitance manometer (Datametrics, Type 600). A trap cooled with liquid nitrogen was installed between the turbo pump and the roughing pump to prevent pump oil from back-streaming into the photolysis region.

The photolysis beam entered and exited the vacuum chamber via MgF₂ windows. The unfocused beam was collimated with irises to a diameter of 0.7 cm. Photolysis beam energies were ≤ 5 mJ/pulse. These conditions were chosen on the basis of the tradeoff between (1) obtaining reasonable signal levels for onephoton excitation processes and (2) avoiding multiphoton excitation processes. The photon dependencies of the pathways leading to the various reaction products were measured by varying the fluence of the photolysis beam using calibrated dielectric filters (Acton Research). The absolute energy/pulse was measured with a disk calorimeter. Measurements of the energy/pulse were taken immediately before and after each data set to establish the stability of the photolysis beam intensity.

Fluorescence resulting directly from the photolysis event was collected at 90° to the photolysis beam by a fused silica lens and exited the vacuum chamber via a MgF₂ viewing port. The emission was focused on the entrance slit of a monochromator (Spex, 500M) equipped with an EMI 9558QB photomultiplier

tube (PMT). The spectral response and resolution of this arrangement were calibrated by using a standard lamp (Optronic Laboratories, UV-40) and a mercury lamp, respectively.

The output signal from the PMT was directed to a gated integrator (Stanford Research Systems, SR250) and displayed on a digital oscilloscope (Hewlett-Packard, 54111D, or LeCroy, 9400). The radiative lifetimes of the fluorescing products and the temporal delay between the photolysis pulse and boxcar gate were measured from the oscilloscope display. The start of the boxcar gate was typically set 50–100 ns following the arrival of the photolysis pulse to reduce noise. Spectra were recorded in digital form on a PC-AT computer via a commercial computer interface/software package (Stanford Research Systems).

For the LIF experiments, the probe beam was provided by an XeCl excimer-pumped dye laser (Lumonics HyperEX 400/HyperDYE 300) that was frequency doubled (HyperTRAK 1000) to obtain wavelengths less than 320 nm. The line width for the fundamental frequency of the dye laser is approximately 0.08 cm⁻¹ fwhm. The line width for wavelengths obtained by frequency doubling is approximately 0.16 cm⁻¹. The probe beam was directed collinear and counterpropagating with respect to the photolysis beam. The probe beam was collimated with irises to the same diameter (0.7 cm) as the pump beam. The delay between the arrival of pump and probe pulses was controlled by a digital delay generator (Stanford Research Systems, DG535). The boxcar gate was positioned to obtain the best signal-to-noise ratio. Fluorescence was collected as above, and the monochromator used as a bandpass filter to block laser scatter and extraneous fluorescence. Alternately, a PMT (Hamamatsu, R955) could be placed adjacent to the viewing port with a wavelength bandpass shaped by appropriate color filter glasses. The following detection schemes were used for probes of ground state OH, NO, and NO₂:

OH. The OH $A^2\Sigma^+ - X^2\Pi_i$ (1,0) and (0,0) electronic transitions are excited in the ranges 281–285 and 306–310 nm, respectively.¹³ When the (1,0) transition is excited, emission corresponding to the (1,1) transition was monitored by using a 10-nm fwhm bandpass filter centered at 313 nm (Corion). When exciting the (0,0) transition, emission corresponding to the (0,1) transition near 347 nm was monitored by using a WG-335, UG-11 (Schott), and 350-nm (Optics Technology) bandpass filter combination. Only the results obtained for excitation of the (0,0) band are presented below. The limited results obtained with (1,0) excitation are consistent with the results obtained with (0,0) excitation. However, DMNA is observed to photolyze at 281 nm, while photolysis at 308 nm is not observed, even when the beam is focused. Thus, excitation of the (0,0) band is considered a better choice for the OH probe.

Nascent OH rotational distributions were investigated, necessitating that the line intensities be corrected for probe energy fluctuations. This was accomplished by directing a portion of the probe beam to a photodiode and monitoring it as a function of wavelength. This beam was attenuated with a neutral density filter to avoid saturating the detector. To obtain probe laser fluxes such that the OH (0,0) transitions were not saturated, the probe beam was attenuated with calibrated dielectric filters (Acton Research) such that the signal was a linear function of the beam fluence. Beam energies used were $\leq 100 \mu J/pulse$.

 NO_2 . The NO₂ \tilde{A} - \tilde{X} transition was excited at 448 nm, and fluorescence at 464 nm was monitored by using the monochromator as a bandpass filter. A GG 450 (Schott) longpass filter was used to further reduce noise from laser scatter. These conditions were chosen based on preliminary experiments with pure NO₂ gas. Dispersed emission spectra obtained from the NO₂ photoproduct and room-temperature NO₂ were compared to establish that the same transition(s) was being excited in each case. Probe beam energies of ~3 mJ/pulse were used for exciting this molecule.

NO. The NO $A^2\Sigma^+-X^2\Pi$ (0,0) electronic transition is excited near 226 nm.¹⁴ In this case, emission associated with the (0,1)



Figure 2. Prompt emission spectrum following DMNA photolysis at 248 nm. (This is a composite of $\lambda < 400$ nm and $\lambda > 400$ nm scans.)

transition was monitored near 236 nm by using the monochromator as a bandpass filter. It should be noted that DMNA strongly absorbs 226-nm radiation ($\sigma = 1.3 \times 10^{-17} \text{ cm}^2$),¹⁵ and NO production due to the probe pulse was a potential problem. Nitrogen dioxide and other potential products of DMNA photolysis such as HONO may also dissociate at this wavelength to form NO. Attempts to circumvent these problems by using two-photon excitation LIF or 2 + 2 resonance-enhanced multiphoton ionization (REMPI) schemes were unsuccessful. For the results presented, the probe fluxes were reduced to levels such that the NO LIF signal observed without a prior photolysis pulse was negligibly small. This corresponded to probe beam energies <500 μ J/pulse.

Estimates of ground-state NO and NO₂ quantum yields were made by comparing LIF signal levels observed following DMNA photolysis with LIF signal levels observed for known pressures of room-temperature NO and NO₂. To obtain a calibration curve for the NO LIF signal, the capacitance manometer was used to establish the pressure of a 0.1% NO/Ar balance gas mixture (Matheson) for a given signal level. Calibration for the NO₂ signal was facilitated by using an ionization gauge (Varian, Model 563) to establish the pressure of neat NO₂ (Matheson, stated purity 98%). (Since the gauge is calibrated for N_2 , the gauge readout had to be corrected for the difference in the ionization potentials of NO₂ and N₂.)

An estimate of the OH quantum yield was made by comparing the OH LIF signal levels following DMNA photolysis with the OH LIF signal levels for the photolysis of nitric acid, HNO₃, obtained under identical conditions. HNO3 was obtained from the vapor above an 70 wt % HNO3 aqueous solution that had been subjected to several freeze-thaw cycles to eliminate dissolved gases. HNO₃ comprises 42% of the total vapor pressure above such a solution.¹⁶ In preliminary experiments, the photolysis of water at 248 nm was not observed for the photon fluxes used in these experiments. Also, within experimental error, the relative intensities of the OH rotational lines were the same over the pressure range (1-10 mTorr) studied. Thus, collisional quenching of OH by water is negligible at the pressures and time scales employed.

Results

Prompt Emission. The prompt emission spectrum observed following the photolysis of DMNA at 248 nm is shown in Figure 2. The feature centered at 310 nm is due to OH $A^2\Sigma^+ - X^2\Pi_i$ (0,0) emission. This assignment is based upon a computer simulation of the feature (see Figure 3). The simulation was generated from a computer program based on Einstein A coefficients reported by Dimpfl and Kinsey¹⁷ and spectroscopic data reported



Wavelength (A)

Figure 3. Comparison of (a) the experimentally observed emission feature at 309 nm following DMNA photolysis and (b) a computer-generated simulation of emission from the OH $A^2\Sigma^+$ (v' = 0) level. The simulation assumes a Boltzmann population distribution of the A-state rotational levels. The "temperature" corresponding to this distribution is 4200 K.



Figure 4. log-log plot of the OH $A^2\Sigma^+$ state and NO₂ \tilde{A}^2B_2 state emission intensity vs photolysis beam fluence.

by Dieke and Crosswhite.¹³ The simulation is based on a Boltzmann rotational population distribution in the A state. The "temperature" corresponding to this distribution is 4200 ± 500 Κ.

The simulation assumes that the OH $A^2\Sigma^+$ (v'=1) level is not populated. This assumption is based, in part, on the absence of emission attributable to the OH $A^2\Sigma^+-X^2\Pi$ (1,0) transition near 285 nm. However, the Franck-Condon factor for the (1,0) transition is relatively small compared to the (0,0) and (1,1)transitions near 310 nm, and interference from an unassigned feature at 289 nm may obscure such emission. Also, the (1,1)transition may be obscured due to overlap with the intense (0,0)band emission. On the basis of simulations of the feature centered at 310 nm, an upper limit on the ratio of v' = 1 to v' = 0 populations was determined to be 5%.

The features centered at 289 and 298 nm have not been assigned. The possibility that the feature at 289 nm was an OH (1,0) emission was addressed based on its observed radiative lifetime of ~ 100 ns at 5 mTorr of DMNA. The radiative lifetimes of both the v' = 0 and v' = 1 levels of the OH A state are approximately 700 ns.¹⁸ This value is approached for the feature attributed to the (0,0) band. Since the lifetime of the feature at 289 nm is significantly shorter, it is doubtful that it is associated with (1,0) emission. Also, it is not possible to generate the intensity distribution shown in Figure 2 with an upper limit of 5% on the ratio of v' = 1 to v' = 0 populations. Finally, the signal intensities of the features at 289 and 298 nm were observed to have quadratic dependencies with respect to variation in DMNA pressure and photolysis beam fluence. This implies that the features are the result of collision-induced processes following multiphoton ex-

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Figure 5. Comparison of the OH $A^{2}\Sigma^{+}$ (v' = 0)- $X^{2}\Pi_{i}$ (v'' = 0) LIF spectra obtained following 248-nm photolysis of (a) DMNA and (b) nitric acid.

citation of DMNA. Thus, further attempts to characterize the carrier of these features were not pursued.

log-log plots of the emission intensity vs photolysis beam fluence for the features ascribed to prompt emission from the OH $A^2\Sigma^+$ and NO₂ \tilde{A}^2B_2 states are presented in Figure 4. The slope of these plots yields a value of *n* for the equation

$$S = C(\Phi_{248})^n$$
(5)

where S is the emission (signal) intensity, Φ_{248} is the photolysis beam fluence, and C is a system-dependent constant. The value of n for OH A²Σ⁺ state emission is 1.97 ± 0.20, indicating that formation of this state requires two photons. A similar observation has been made for cyclic nitramine RDX.¹⁹ The value of n for NO₂ \tilde{A}^2B_2 state emission is 0.83 ± 0.20, indicating a one-photon excitation process. This result is similar to that obtained by Mialocq and Stephenson for DMNA photolysis at 266 nm.⁸ In addition, the intensity of OH A²Σ⁺ and NO₂ \tilde{A}^2B_2 emission as a function of DMNA pressure is linear, indicating these products are formed via unimolecular processes.

Laser-Induced Fluorescence. OH. A portion of the OH LIF spectrum obtained following DMNA photolysis is shown in FIgure 5. Within experimental error, the relative intensities of the OH rotational lines are the same over the pressure range studied (1-8 mTorr). This indicates that collisional quenching of the (nascent) OH rotational state distribution is negligible. The relative population distribution of the OH $A^2\Sigma^+$ state rotational levels was calculated from the measured line intensities via the Einstein Bcoefficients,17 after accounting for the fluorescence detection bias associated with the PMT/bandpass filter combination and integration of fluorescence signal over a gated time interval. Plots of the OH ${}^{2}\Pi_{i}$ rotational populations calculated from the measured line intensities are shown in Figure 6. The rotational population for the ground state is found to be similar to a Boltzmann distribution corresponding to a temperature of 2800 ± 500 K. A nonstatistical preference for populating ${}^{2}\Pi_{1/2}$ vs ${}^{2}\Pi_{3/2}$ states is not observed.20

To obtain intensity measurements for variations in pressure or photolysis beam fluence, the dye laser was scanned through the range 306.3-306.6 nm. This range contains the $R_1(6)-R_1(12)$ rotational lines of the OH $A^2\Sigma^+-X^2\Pi_{3/2}$ (0,0) transition. For a



Figure 6. Plot of the rotational population distributions for the OH $X^2 \Pi_i$ state formed following 248-nm photolysis of (\Box) DMNA and (\blacktriangle) nitric acid.

given photolysis beam fluence, the intensity vs DMNA pressure for each rotational line, $I_j(P_i)$, was determined. These distributions were then normalized, viz., $\sum_i I_j(P_i) = \text{constant}$, and the normalized distributions averaged. The same data reduction method was used for analyzing the intensity vs photolysis beam fluence data for a given DMNA pressure. A fit of the OH LIF signal intensity vs photolysis beam fluence data to eq 5 yields n = 0.9 ± 0.2 , indicating that OH X²II_i is formed following a one-photon excitation of DMNA. The OH signal was found to be a linear function of DMNA pressure, indicating the process is unimolecular.

The quantum yield for OH production was determined by establishing an LIF signal vs OH concentration calibration curve from the same experiments with HNO₃. A quantum yield near unity has been reported for the process²¹

$$HNO_3 \xrightarrow{h\nu} OH + NO_2$$
 (6)

A portion of the OH LIF spectrum obtained following the 248-nm photolysis of HNO₃ is shown in Figure 5. The OH ${}^{2}\Pi_{i}$ rotational populations formed via process 6 are shown in Figure 6. The rotational population distribution for this spectrum is similar to a 1400 ± 200 K Boltzmann distribution. Boltzmann-like rotational distributions have also been observed following HNO₃ photolysis at 266 and 193 nm. The 1400 K "temperature" obtained at 248 nm lies between the 1235 ± 50 K value reported by Zabarnick et al.²² for the photolysis of HNO₃ at 266 nm (lower energy) and the 2200 ± 500 K value reported by Jacobs et al.²³ for photolysis of HNO₃ at 193 nm (higher energy).

To compare OH densities that have different rotational population distributions, it is necessary to relate the population of individual levels to the entire population. Since the OH $X^2\Pi_i$ rotational distributions observed following both DMNA and HNO₃ photolysis at 248 nm are Boltzmann-like, the LIF signal levels for the two systems may be compared as follows. For a Boltzmann distribution where $kT \gg 2B(J + 1)$, the ratio of an individual line to the entire population, $N_J(T)/N(T)$, is given by¹⁴

$$N_{J}(T)/N(T) = (hcB/kT)(2J+1) \exp[-BJ(J+1)hc/kT]$$
(7)

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Figure 7. Comparison of the OH LIF signal intensity vs pressure for 248 nm photolysis of (O) DMNA and (A) nitric acid.



Figure 8. Comparison of the NO₂ LIF signal intensity vs pressure for (O) 248-nm photolysis of DMNA and (O) pure NO2 gas.

where h is Planck's constant, c is the speed of light, k is Boltzmann's constant, and B is the rotational constant. For two equal densities at different temperatures, T_1 and T_2 , the intensity for the Jth line in the distributions are related by

$$N_{J}(T_{1})/N_{J}(T_{2}) = (T_{2}/T_{1}) \exp[-(BJ(J+1)hc/k)((T_{2}-T_{1})/T_{2}T_{1})]$$
(8)

Figure 7 compares the OH $F_1(6)$ signal levels vs DMNA and HNO₃ pressures (obtained under the same experimental conditions) based on these considerations.

The quantum yield for a system may be calculated from

$$S_{\text{LIF}} = CN(\sigma_{248}\Phi_{248})(\sigma_{p}\Phi_{p})\varphi$$
(9)

where S_{LIF} is the signal intensity of the excitation transition, C is a constant depending on the experimental configuration, N is the number density of the parent, $\sigma_{248}(\sigma_p)$ is the absorption cross section of the parent (photoproduct), $\Phi_{248}(\Phi_p)$ is the photolysis (probe) beam fluence, and φ is the photoproduct quantum yield. For the case where $(\Phi_{248})' = (\Phi_{248})''$ and $(\sigma_p \Phi_p)' = (\sigma_p \Phi_p)''$, taking the ratio of $(S_{LIF})'/(S_{LIF})''$ and rearranging yields the relationship

$$\varphi' = S'_{\rm LIF}(N\sigma_{248}\varphi)''/S''_{\rm LIF}(N\sigma_{248})$$
(10)

where single and double primes denote DMNA and HNO₃ parameters, respectively. With substitution of (1) the absorption cross sections of DMNA ($\sigma'_{248} = 7.6 \times 10^{-18} \text{ cm}^2$)¹⁵ and HNO₃ ($\sigma''_{248} = 2 \times 10^{-20} \text{ cm}^2$),²⁴ (2) the OH quantum yield for HNO₃ photolysis at 248 nm ($\varphi'' \sim 1$),²¹ and (3) the ratio (N''/(N)' for $(S_{LIF})'/(S_{LIF})''$ (from, for example, Figure 7), the quantum yield for OH production following DMNA photolysis at 248 nm is estimated to be 0.004.

NO2. The NO2 LIF signal intensity vs DMNA pressure and NO₂ LIF signal intensity vs photolysis fluence indicate that ground-state NO₂ is formed via a monophotonic, unimolecular process(es). On the basis of a comparison of the LIF signal levels for photoproduct and room-temperature NO₂ (Figure 8), the quantum yield for NO_2 production is estimated to be 0.15. This

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result is similar to the result obtained by Mialocq and Stephenson (MS) for DMNA photolysis at 266 nm.⁸ With the DMNA absorption cross section at 266 nm obtained in our laboratory,15 a nominal quantum yield of 0.11 is obtained from the MS experimental results. It should be noted that both studies neglect the difference between the internal energy distributions in making the quantum yield estimate. Thus it is difficult to assess the accuracy of the estimates.

NO. No monophotonic, collision-free formation of NO $X^2\Pi$ (v''=0) was observed following DMNA photodissociation. This result is based on an extensive search for NO $A^2\Sigma$ (v' = 0) - $X^2\Pi$ (v''=0) LIF via excitation in the range 224-228 nm. The search was conducted at the highest pressure (8 mTorr) at which these experiments could be run. Partial pressures of room-temperature NO down to 1×10^{-7} Torr were readily observed. On the basis of the experimental data, we have calculated an upper limit of 0.001 on the quantum yield for unimolecular production of NO.

Discussion

The excitation of gas-phase DMNA with 248-nm radiation falls within an absorption continuum that onsets at approximately 300 nm and peaks near 230 nm.¹⁵ A semiempirical, molecular orbital interpretation of the UV absorption spectra of solution-phase DMNA²⁵ suggests excitation at 248 nm (5.0 eV) lies within three absorption bands: a predominantly $(\bar{\pi} \rightarrow \sigma^*_{\text{CNC},\text{NO}_2})$ transition at 4.25 eV; a $(\pi \rightarrow \pi^*) + (\bar{\pi}\sigma \rightarrow \sigma^*_{\text{CNC},\text{NO}_2})$ transition at 5.17 eV; and a $(\sigma_{\text{CNC}} \rightarrow \sigma^*_{\text{CNC}})$ transition at 5.21 eV. The relatively large quantum yield for NO₂ production versus other photoproducts is consistent with other studies on the decomposition of DMNA.

The observation of OH following a monophotonic, collision-free process suggests the possibility that DMNA may dissociate via an HONO elimination channel. Shaw and Walker¹⁰ have estimated this process to be 1-3 kcal/mol exothermic and to have an activation energy of 38 kcal/mol. Melius and Binkley²⁶ have calculated the activation energy for HONO elimination in (mono)methylnitramine to be 41 kcal/mol. Thus, the barrier for this channel is expected to be lower than the barrier to N-N bond scission (46.2 kcal/mol). The excitation of DMNA at 248 nm (115.3 kcal/mol) is sufficient to overcome the activation energy and dissociate the HO-NO bond (49.6 kcal/mol).²⁷ The large discrepancy between the OH and NO quantum yields indicate the observed OH is not the result of HONO dissociation. Ab initio calculations that may explain the production of OH are being considered. A more specific detection technique for HONO is desirable for determining the importance of the HONO elimination.

The importance of NO in the decomposition pathways of DMNA has been widely speculated. A conclusion of the recent low-pressure homogeneous pyrolysis study by Stewart et al.,⁷ which suggests that reaction 3b is important, is particularly intriguing. Our results indicate that unimolecular formation of NO is not important following DMNA photolysis at 248 nm.

Conclusion

The formation of OH $A^2\Sigma^+$, OH $X^2\Pi_i$, NO₂ \tilde{A}^2B , NO₂ \tilde{X}^2A_1 , and NO X²II following DMNA photolysis at 248 nm has been investigated in this study. The results were obtained in a predominantly collision-free experiment using LIF and emission spectroscopies for product detection. These techniques provide an alternative method for studying DMNA decomposition pathways, which have typically been inferred from end product or mass spectrometric analyses of DMNA decomposition initiated at higher pressures. NO₂ \tilde{A}^2B_1 , NO₂ \tilde{X}^2A_1 , and OH $X^2\Pi_i$ were formed via monophotonic, unimolecular pathways. The quantum yield for $NO_2 \bar{X}^2 A_1$ and OH $X^2 \Pi_i$ were estimated to be 0.15 and 0.004,

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respectively. An upper limit of 0.001 was established for the quantum yield of NO $X^2\Pi$ (v'' = 0). OH $A^2\Sigma^+$ was formed via a two-photon, unimolecular process.

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Spin-Orbit-Induced and Symmetry-Forbidden $\tilde{C}^2A_2 - \tilde{X}^2A_1$ Absorption of NO₂ Using Optical-Optical Double-Resonance Spectroscopy in the 588-591-nm Range

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The visible absorption bands of NO₂ in the 588-591-nm range have been proved to contain a vibronic transition to the dark \tilde{C}^2A_2 state by rotational analysis using the optical-optical double-resonance (OODR) techniques. The sequential two-photon excitation to the 2^2B_2 state via the visible excited state has allowed us to determine the rotational quantum numbers $(N'_{Ka,Kc})$ of six intermediate rovibronic levels. All the levels are assigned as $[N'(\nu_1) = \text{odd}, K_a = 0]$ and $[N'(\nu_2) = \text{even}, K_a = 0]$ from the first-step (v_1) and second-step (v_2) excitation, respectively. The intermediate state is verified to be a mixed state of dark \tilde{C}^2A_2 and light \tilde{A}^2B_2 coupled by spin-orbit interaction with the selection rules $\Delta N = \pm 1$ and $\Delta K_a = 0$. Although the \tilde{C}^2A_2 state is dark in the v_1 transition from \tilde{X}^2A_1 , it becomes a light state in the v_2 transition to 2^2B_2 . We have succeeded to detect a vibronic level of the \tilde{C}^2A_2 state lying at $T_v = 16970$ cm⁻¹ above $\tilde{X}^2A_1(0,0,0)$, possibly $\tilde{C}^2A_2(0,1,0)$.

Introduction

The visible absorption spectrum of NO₂ is well-known for its complexity due to state interactions.^{1,2} Many spectroscopic studies have been performed on this molecule, but details of the state interactions have not been well understood yet. The $\tilde{A}^2B_2-\tilde{X}^2A_1$ absorption dominates in the spectral region longer than 500 nm. The excited \bar{A}^2B_2 state is heavily perturbed by the vibronic coupling with the high-lying vibrational levels of the ground \tilde{X}^2A_1 state. As a result of this strong vibronic coupling, a number of admixture states with B_2 vibronic symmetry ($e^v B_2$) are detected as the upper state in the visible bands (the parallel B_2 -A₁ transition), which has been clearly demonstrated by the supersonic jet experiments of NO2.3-5 Recently, we have found another state interaction due to spin-orbit (and/or orbital rotation) coupling to mix "light" $e^{v}B_{2}$ (admixture of $e^{B_{2}} \otimes a_{1}$ and $e^{A_{1}} \otimes b_{2}$) and "dark" " A_1 (admixture of ${}^{\circ}B_2 \otimes {}^{\circ}b_2$ and ${}^{\circ}A_1 \otimes {}^{\circ}a_1$) vibronic levels.⁶

Although it is true that the major perturbations to \tilde{A}^2B_2 are caused by the high vibrational levels of X^2A_1 , it does not seem sufficient to explain the complexity of the NO₂ spectrum merely by the vibronic and spin-orbit coupling due to \tilde{X}^2A_1 . There exist another two excited states (\tilde{B}^2B_1 and \tilde{C}^2A_2) in the visible region, and they can also contribute to make the spectrum more complex. The $\tilde{B}^2B_1 - \bar{X}^2A_1$ absorption, which is known as Douglas-Huber bands,^{7,8} is observed in the spectral region of 370-460 nm. The

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 $\mathbf{\bar{B}}^2\mathbf{B}_1$ state can couple with the higher vibrational levels of $\mathbf{\bar{X}}^2\mathbf{A}_1$ by Renner-Teller interaction and, therefore, may have a chance to indirectly perturb \tilde{A}^2B_2 . Although the \tilde{C}^2A_2 state is symmetry forbidden from \tilde{X}^2A_1 , it can contribute to the perturbations in the $\tilde{A}^2B_2 - \tilde{X}^2A_1$ spectrum as a "dark" state by Renner-Teller or spin-orbit interaction. Recently, Weaver et al.⁹ have succeeded in the direct observation of the \tilde{C}^2A_2 state by the photoelectron spectroscopy of NO₂⁻. The origin of \tilde{C}^2A_2 is experimentally determined to lie at $T_0 = 2.028 \pm 0.009$ eV above \tilde{X}^2A_1 , in accordance with the ab initio calculation (1.84 ± 0.03 eV).¹⁰ Therefore, in the spectral region shorter than 612 nm, the dark \tilde{C}^2A_2 state may affect the visible spectrum of NO₂. However, due to the lack of conclusive experimental evidence and the difficulty in analyzing the disordered rotational structure, the contribution of \tilde{C}^2A_2 to the visible spectrum has not been experimentally confirmed to date.

The optical-optical double-resonance (OODR) spectroscopy of NO₂, which has been developed in our laboratory, has made great advances in understanding the spectrum.^{6,11-13} The stepwise excitation of NO₂ (through $2^2B_2 \leftarrow$ intermediate state $\leftarrow \bar{X}^2A_1$) followed by the observation of the UV emission corresponding to the $2^2B_2 \rightarrow \tilde{X}^2A_1$ transition provides simple OODR excitation spectra that can be easily assigned by using the well-established molecular parameters of the initial $\tilde{X}^2 A_1$ (0,0,0)¹⁴ and final $2^2 B_2$

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