of the ferriin concentration in the vicinity of the tip and by the fact that the inner mould is passed by the front side of the tip during the formation of a new center. Therefore a region of low ferriin becomes a part of the trough in front of the next wave just emananting from the tip. A preliminary analysis showed a significant modulation of the ferriin concentration along the spiral trough as well as on the crest. The concentration inhomogeneity moved with the wave and was smoothed out when it spread. This phenomenon was reported earlier for ferroin^{3,22,23} as well as for cerium- and manganese-catalyzed spirals in BZ solution²⁴ under the title "speckle formation". At that time speckle formation was discussed in connection with hydrodynamic flow generated by natural convection. The inhomogeneities have to be clearly distinguished from the so-called "mosaic" pattern.^{7,25,26} The latter are stationary and do not move with the waves.

Our results suggest that the dynamics of the emanation of a spiral wave from its center is a delicate interplay of an excited spot, the tip, with the excitable domain opened up by the relaxing back of the precursor wave. The main factors that regulate the dynamics are the relaxation kinetics after full excitation and the dispersion relation describing the critical concentration levels for

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excitability as well as the spreading speed when the regime of excitability has infected a particular site.

In addition, systematic functional dependencies of the sulfuric acid concentration, i.e., [H⁺], have been presented for the maxima and minima of the ferriin concentration in wave profiles as well as for the maximum gradients. The measured wave parameters are smooth and show no evidence for a qualitative transition when the excitability of the BZ medium is varied due to a variation of $[H_2SO_4]$ between 0.15 and 0.70 M. The data may serve as a sound basis for appropriate extensions of the BZ reaction mechanism and its reduction to numerical models describing the wave formation in an excitable BZ medium since our results are not in accordance with the [H⁺] dependency of the Oregonator model²⁷⁻²⁹ for wave profiles.

The previous considerations will be elaborated on in a second paper focusing on a quantification of the interaction between the tip and the relaxing back of the outward moving precursor wave. It would be interesting to discuss these data in light of new results on spiral waves moving on the surface of a sphere supported by a gel.30

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Production of NCI(a) by Thermal Decomposition of CIN_3

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Thermal decomposition of ClN₃ by pulsed CO₂ laser pyrolysis has been investigated by using SF₆ as a sensitizer. The electronically excited decomposition products, NCl(a) and NCl(b), were monitored by absolute time-resolved emission spectroscopy while CIN₃ was followed by ultraviolet absorption. The results indicate a higher barrier to dissociation of CIN₃ than FN₃, consistent with ab initio calculations, and an NCl(a) yield of order unity, based on a nominal 0.7/s radiative rate for the NCl(a-X) transition. Studies of simultaneous dissociation of FN₃ and ClN₃ have also revealed that NCl(a), when coproduced with NF(a), upconverts the latter species to NF(b) efficiently (in the presence of trace I_2) and cooperatively pumps the IF(B)state (upon addition of CF₁I) by an energy pooling mechanism that does not involve NF(b) as an intermediate. These results indicate a potential for development of chemical lasers that operate on either the NF($b \rightarrow X$) or IF($B \rightarrow X$) transitions at visible wavelength.

Introduction

Production of electronically excited metastable species via direct chemical reaction is central to the development of short-wavelength chemical lasers such as the near-infrared O₂-I system. Here the reaction of Cl₂ gas with base-saturated H₂O₂ generates the 1.0-eV metastable species $O_2(a^1\Delta)$ which subsequently pumps the I* lasing species by resonant energy transfer.^{1,2} In the continued pursuit of this type of laser, which is operable at visible wavelengths, generation of large concentrations of metastable NF($a^{1}\Delta$) has recently been demonstrated³ by fast thermal dissociation of gaseous FN₃. Also reaction with and energy transfer from NF(a) to Bi has been shown to result in intense visible $BiF(A \rightarrow X)$ radiation^{1,4} between 430 and 470 nm. Since NF(a) stores 1.4 eV of electronic energy,¹ the excitation of the BiF(A) state at 2.8 eV requires at least two collisions with this metastable species and

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a mechanism for energy pooling. Production of 528-nm NF(b-X) emission has also been demonstrated⁵ by resonant energy pooling between chemically generated NF(a) and I* obtained by pulsed laser excitation of ground-state I atoms. Another potential chemical laser is based on excitation of the IF(B-X) transitions from 520 to 720 nm by multiple collisions⁶ with $O_2(a)$.

Metastable NCl($a^{1}\Delta$) carries approximately 1500 cm⁻¹ more electronic energy $^{1, \tilde{7}}$ than $O_2(a)$ and is of the same electronic symmetry. Consequently, NCl(a) may be used as a potential in situ pump for I* by energy transfer to ground-state I atoms (in place of an external laser) to generate NF(b) or as a replacement for $O_2(a)$ in the O_2 -I or potential IF(B-X) chemical laser systems. Use of NCl(a) to generate NF(b) or IF(B) is interesting, if it can be obtained by thermal dissociation of ClN₃, because the production and dissociation of ClN₃ and FN₃ can then be easily integrated with each other in a common reactor scheme to generate mixtures of the corresponding metastable species. Since the processes of $X + N_3$ reaction and thermal dissociation of XN_3 are physically similar in the exit channel and Coombe⁸ has found that metastable singlet NX molecules are produced by the reactive mechanism with $\bar{X} = F$ and Cl, our previous results on FN₃ dissociation² suggested that thermal dissociation of ClN₃ might also be expected to yield metastable singlet NCl products. Therefore, we have investigated CO₂ laser pyrolysis of ClN₃ as a potential source of NCl(a) and have studied production of the NF(b) and IF(B) states in the simultaneous presence of NF(a)and NCl(a).

Theory

Covalent azides, such as FN₃ and ClN₃, have relatively weak central bonds.^{9,10} Consequently, these species may be thought of as complexes formed from more tightly bound NX and N₂ molecules, as described in our prior work,³ which discusses the potential energy surfaces in greater detail. Since the electronic ground states of FN₃ and ClN₃ are both of singlet character,^{11,12} the spin-allowed dissociation products are either singlet (metastable) NX and singlet (ground state) N2 or triplet (ground state) NX and triplet (metastable) N_2 . The singlet products are favored, however, because the triplet states of N_2 are several electronvolts higher in energy¹ than the singlet states of NF or NCl. The heats of formation^{11,12} of these halogen azides are, however, large enough to allow dissociation into the singlet products by an exothermic reaction. Therefore, dissociation of FN₃ and ClN₃ only requires sufficient excitation to overcome the potential barrier which lies between the bound XN_3 ground state and the separated NX(a,b)and N₂ products. Since the central bond is weak, it is anticipated that thermal excitation may be adequate to induce rapid dissociation of the halogen azides at modest temperatures. Once initiated, the dissociation of FN3 and CIN3 is expected to proceed to completion, since the associated enthalpy change will increase the gas temperature. Consequently, the primary role of temperature is to control the rate of dissociation, rather than to compensate a thermodynamic deficit.

Ab initio self-consistent field (SCF) calculations of the equilibrium structure and potential energy surfaces of the ¹A' ground states of FN_3 and ClN_3 were performed in optimized C_s geometry with the GAUSSIAN 88 electronic structure code¹³ using Pople's split-valence (6-31G*) basis sets.¹⁴ Gradient optimizations were performed to locate the geometries of both the equilibrium structure and the transition state. In the case of FN₃, similar

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Figure 1. Results of ab initio calculations of the barriers to thermal dissociation of the halogen azides.

calculations have shown a significantly higher barrier to dissociation by stretching of the F-N₃ bond than by central bond fission.³ To ensure that stationary points of the correct curvature have been found, harmonic vibrational frequencies were computed for the equilibrium structure (all real frequencies) and for the transition structure (one imaginary frequency). The SCF calculations yielded equilibrium structures that were in close agreement with the experimental results of Christen et al.¹⁵ for FN_3 and of Cook and Gerry¹⁶ for ClN₃. The average error in the bond lengths and bond angles were 0.03 Å and 1.5°, respectively. It is well-known that SCF frequencies are uniformly too large and that a scaling of the SCF force field is required for comparison with experimental results. A uniform scaling factor of 0.86 was found to bring the calculated vibrational frequencies of FN₃ into good agreement with the data of Gholivand, Schatte, and Willner.¹⁷ This same factor was successfully applied in the ClN₃ calculations, which yielded vibrational frequencies in reasonable agreement with the matrix isolation results of Milligan and Jacox.¹⁸ Comparing the equilibrium and transition states, the classical barrier height of ClN₃ was calculated as 0.67 eV or 5444 cm⁻¹, approximately 1600 cm⁻¹ larger than in FN₃. These barrier heights are reduced slightly by corrections for zero point vibrational energy; however, correlated calculations¹⁹ of FN₃ at the CCD/6-31G* level of theory demonstrate a somewhat greater correction in the opposite direction, indicating that the actual barrier in ClN₃ may be slightly larger than the classical estimate.

The paths of steepest descent from the optimized transition-state geometry were calculated backward toward the equilibrium state and forward to dissociation into $NX(a) + N_2$ products, using the intrinsic reaction coordinate pathfinder of Schmidt et al.²⁰ as shown in Figure 1. At large $XN-N_2$ separations, these pathways are not reliable since the dissociating molecule must take on the diradical character of the NX($a^{1}\Delta$) product which cannot be correctly represented at the restricted Hartree-Fock level of theory. A multiconfiguration analysis of this dissociation region will progressively lower these potential surfaces as the molecule breaks apart into separated products. In our previous work³ on FN₃, we obtained an experimental barrier height of approximately 0.63 eV, or 1240 cm⁻¹ greater than the classical barrier shown in Figure The relative heights of the calculated barriers for FN₃ and ClN₃, however, should be accurately predicted at the SCF level of theory since the electronic structure and geometry of these two halogen azides are quite similar.

In the case of FN_3 , similar calculations^{3,19} have also shown that the repulsive triplet state which correlates to $N_2 + NF(X^3\Sigma)$

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Figure 2. Schematic diagram of the apparatus used to study thermal decomposition of ClN_3 and energy-transfer reactions of NCl(a).

crosses the potential surface leading to excited NF(a,b) fragments on the products side of the barrier to dissociation. This condition guarantees a high yield of NF(a) upon thermal dissociation of FN_3 , as observed,³ since the $FN-N_2$ molecule will pass through the spin-forbidden crossing region only once after surmounting the barrier to dissociation. In contrast, thermal dissociation of HN₃ yields primarily NH($X^{3}\Sigma$) products because the singlettriplet crossing occurs inside the barrier to dissociation.²⁰ Although the probability of changing from the singlet to the triplet surface is typically less than 10⁻² each time the crossing region is encountered,²¹ the azide is allowed to leak away into ground-state products because the crossing region is encountered many times before the molecule acquires enough energy to surmount the barrier to dissociation. If the triplet potential curves of ClN₃ are similar to FN_3 rather than HN_3 in this respect, then a high yield of NCl(a) can also be expected upon thermal dissociation of the parent molecule.

Experimental Section

Generation of ClN_3 . The apparatus used for generation of NCl(a) radicals and for studying their energy-transfer reactions is shown schematically in Figure 2. Dilute flows of ClN_3 in inert carrier gas were produced by a method following Coombe¹² in which a 10% mixture of Cl₂ in Ar was slowly passed over moist NaN₃ contained in an ice-chilled glass U-tube. An electronic mass flow meter that was calibrated with He to a wet test meter was used to measure the Cl₂ flow. The reactor was operated at approximately 350 Torr total pressure and at a net flow of 3.5 sccs. Approximately 1 g of NaN₃ powder was suspended on glass wool that was loosely packed into a 10-15 cm long section at the bottom of the 2.5 cm diameter U-tube. Moisture was added to the reactor by soaking the glass wool in water and then pressing out the excess before treating it with NaN₃. The gaseous product of the Cl_2 + NaN₃ reaction was dried by passage through a 5 cm diameter \times 15 cm long column of anhydrous CaSO₄. In the absence of moisture, the yield of ClN₃ from the reactor was diminished significantly. Infrared absorption of the effluent gas from this generator was studied by using a low-pressure gas cell with IR

transmitting windows and a Fourier transform spectrometer (FTS). The IR spectra showed strong absorption bands¹⁸ at 720, 1140, and 2060 cm⁻¹, confirming the presence of ClN₃. Mass spectra of the generator effluent also showed no significant peak at m/e = 43 and strong peaks at m/e = 49, 51, 70, 72, and 74, which suggests a low yield of HN₃ and indicates a significantly higher yield of ClN₃ (measured as N³⁵Cl and N³⁷Cl) as well as unreacted Cl₂. The line strengths of the chlorinated species were found to be in proportion to the natural abundance of the Cl isotopes.²³

The absolute concentration of ClN₃ in the effluent of the generator was measured by UV absorption spectroscopy using a gas cell with sapphire windows, a spectrometer-filtered deuterium lamp as the source, and a 1P28 photomultiplier tube (PMT) that was coupled to a picoammeter as the detector. The wavelength band most suitable for the CIN₃ absorption diagnostic was also significantly absorbed by HN₃ which is a potential impurity due to the use of H_2O as a catalyst for the $Cl_2 + NaN_3$ reaction. Therefore, absorption measurements at three UV wavelengths (224, 241, and 254 nm) were performed. In this wavelength range, the absorption cross section of HN₃ varies significantly, whereas the absorption by ClN₃ is nearly constant. The relative optical densities of the effluent gas at these three wavelengths indicated that ClN₃ was the only significant absorber and that no detectable amounts of HN₃ were present. Thus, with knowledge^{12,24} of the extinction coefficient, the concentrations of CIN₃ could be measured routinely by UV absorption at 241 nm. The typical ClN₃ concentration corresponded to approximately 50% of the Cl₂ flow that was admitted to the generator.

Attempts were also made to generate ClN₃ free from Cl₂ and HN₃ by mixing the Cl₂ with dry NaN₃ in a batch reactor and allowing sufficient time for completion of the reaction. In this method, approximately 700 Torr of 10% Cl₂ in Ar was mixed with 100 g of freshly ground NaN₃ in a 2-L Teflon-lined steel reactor. Stirring of the azide charge with a Teflon-coated magnetic rod was necessary since the azide surface was rapidly passivated. The FTS diagnostic demonstrated that the reaction was slow but complete after 5-10 h with essentially total utilization of the Cl₂ and efficient conversion to ClN₃ which could then be withdrawn as needed. The ClN_3 decayed to one-half its initial value (70 Torr) in approximately 24 h. The rate of FN₃ decay at 300 K is significantly faster³ than the corresponding rate of ClN₃ decay, as expected, since the latter species is stabilized by a higher barrier to dissociation, as shown in Figure 1. Equivalent results were obtained with the ClN₃ obtained from either generator; however, the flowing reactor was found to offer the convenience of longer run time.

Pyrolysis Reactor. Additional Ar buffer gas and a controlled flow of SF_6 (that acts as a sensitizer) were added to the effluent of the ClN₃ generator and the mixture was admitted to a cross-shaped stainless steel reaction cell in which the reactive gas flow, the CO₂ laser beam, and the viewing axis for the emitted radiation were all mutually orthogonal. The CO₂ laser beam entered and exited the reactor through NaCl windows that were purged with Ar flows and isolated from the center of the reactor by apertures (Figure 2) so that absorption of the infrared photons only occurred within the central chamber of the reactor. The emitted radiation was detected through a quartz window that was not purged. All of the reactor gases were pumped off to vacuum via an adjustable throttling valve, and the corresponding increase in total reactor pressure with the addition of each gas was monitored via a precision capacitance manometer. Since addition of the reactive gases had little effect on the mean molecular weight of the gas mixture in the reactor, the discharge coefficient was not altered significantly. Consequently the partial pressures were taken as additive. The gas pressure in the UV absorption cell of the ClN₃ diagnostic was measured with an inductance transducer from which the mole fraction of the ClN_3 in the generator effluent was determined by using the ClN₃ concentration measurement

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described above. Typically the total pressure in the reactor was 35-150 Torr which consisted of 5-15 Torr of SF₆, 30-300 mTorr of ClN₃, and balance Ar buffer gas and window purge.

In some experiments, a dilute mixture of FN₃ in He was added to the reactor in near equimolar concentration to the ClN₃ along with variable concentrations of HI or CF₃I and a dilute I₂/He gas mixture that was obtained by passing the carrier gas through a 4 cm diameter \times 10 cm deep bed of I₂ crystals at ambient temperature and reduced pressure. The fraction of I₂ in this flow was calculated from its vapor pressure²³ and a measurement of the total gas pressure in the saturator. Typically, this procedure overestimates the I₂ mole fraction in the flow; however, prior experience²⁵ has shown by absorption measurements (similar to those used for ClN₃) that the error is less than a factor of 2. The FN₃ generator and diagnostics have been described in detail in prior publications.^{3,26}

A nominal 10-J pulsed CO₂ laser was softly focused to a 1 cm diameter spot at the center of the reactor by a 100 cm focal length concave mirror. A variable pressure SF₆ cell with NaCl windows was also interposed between the laser and the reactor to partially absorb the 10.6- μ m radiation and thereby control the fluence at the reactor, since the laser itself was not easily adjusted. The cell was composed of two NaCl windows spaced 2.5 cm apart and was filled with 0-50 Torr of SF₆. The function of the CO_2 laser was to rapidly heat the gas in the reactor by excitation of the vibrational modes of SF₆, which are promptly thermalized upon collisions with the buffer gas. The suddenly increased gas temperature then triggers dissociation of the halogen azides. After passage through the reactor the laser beam was monitored for pulse energy by an electrically calibrated power (joule) meter. Only a small fraction (<33%) of the incident laser energy was actually absorbed by the SF₆ in the reactor.

Optical Diagnostics. The emission detectors included a gated optical multichannel analyzer (OMA) for collection of visible spectra and a filtered Si photodiode that was interfaced to a step-adjustable-gain preamplifier and a digital signal averager for monitoring the time profiles of the metastable products. The temporal resolution of the recording system was limited by the bandwidth of the preamplifier, which was inversely proportional to the selected gain setting. The sensitivity and temporal response of the entire recording system was determined by using a freshly calibrated Tektronix Model 2235 oscilloscope and pulse generator with a known $(\pm 1\%)$ resistance to obtain a standard current pulse that was measured in place of the photodiode. The time profile of the ClN, concentration subsequent to the CO₂ laser pulse was also monitored by UV absorption (over a 2.5 cm active path length) using a D_2 lamp as the source and a filtered PMT detector that was coupled to the signal averager. The time-resolved absorption diagnostic is not shown in Figure 2 for the sake of clarity. The synchronizing electrical trigger pulses for the signal averager were obtained directly from the CO₂ laser discharge circuit.

The Si photodiode (EG&G Model SGD-444) was calibrated with a number of selected interference filters using a standard lamp that is traceable to the National Bureau of Standards (now known as the National Institute of Standards and Technology) so that the absolute NF(b) and NCl(a,b) concentrations could be calculated from the signals obtained. Our results confirmed the manufacturer's specifications in regard to the sensitivity of the detector. The recorded signals (in volts) were taken as the product of the active volume in the reactor, the concentration of the species detected, the corresponding A coefficient, the solid angle of the 1-cm² detector area (as measured from the center of the reactor) divided by 4π , the transmission factor of the filter for the radiation detected, the quantum efficiency of the detector (in ampere-seconds/photon), and the transconductance gain of our recording system (in volts/ampere). The filter factors were obtained by measuring their transmission as a function of wavelength on a commercial spectrophotometer and then comparing this data



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CZ N₃ CONCENTRATION (ARB. UNITS)

Figure 3. Time profile of ClN_3 concentration following excitation by a pulsed CO_2 laser in the presence of SF_6 as a sensitizer.

8

TIME (MICROSECONDS)

10

12

14

16

with the known emission spectra^{27,28} in the case of NCl(a,b) and by measurement of the NF(b-X) emission via the OMA with and without the corresponding filter in front of the source. Filters were selected with bandwidths that were matched to the width of the emission spectrum in each case. The active volume was taken as the product of the cross-sectional area of the exciting laser beam (as measured by thermal image paper at the center of the reactor) and the length along the beam that was within the detector's field of view, as controlled by a slit (Figure 2) that was located close to the emitting region and suitably far from the photodiode to approximately collimate the light that was detected. As will be shown, the major uncertainty in the determination of the NCl(a) yield was the lack of a reliable value for the corresponding A coefficient.

Results and Discussion

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Dissociation Rate. Figure 3 shows the decay of a nominal initial 300 mTorr concentration of ClN₃ at a total pressure of 150 Torr in the reactor following pulsed excitation by the CO₂ laser at a fluence of approximately 1 J/cm². From parallel studies of FN_3 decomposition³ the gas temperature in the active region of the reactor is known to approach 1200 ± 100 K with similar laser pulse energies and is relatively constant during the process of dissociation since the absorbed photon energy is large compared to the chemical heat release due to the use of a high diluent ratio. Under these conditions, FN_3 dissociates roughly twice as fast³ as ClN₃. The 4-µs decay of ClN₃ at 1200 K and 150 Torr pressure (Figure 3) and the 24-h decay at 300 K and 700 Torr pressure that was observed in the dry reactor are both well fit to a dissociation rate of $(7 \times 10^{-11} \text{ cm}^3/\text{s})(T/300 \text{ K})^{0.5} \exp(-9600 \text{ K}/T)$ which corresponds to a barrier height of 0.79 ± 0.07 eV. This result, which exceeds the classical estimate for dissociation of ClN₃ by 930 cm⁻¹, is in line with our theoretical expectations as described earlier. The uncertainty quoted for the barrier height reflects the accuracy of the high-temperature measurement.³ As in our previous work on FN₃, another potential source of error is the possibility of catalyzed decomposition of the ClN₃ on the walls of the dry reactor at 300 K. Corrections for this source of error, however, tend to increase both the activation energy and the prefactor of the exponential in the rate law. Since the prefactor is already at the gas kinetic limit, it follows that the decomposition at room temperature is essentially thermal. The errors in the measured decomposition rates were not deemed to be significant since these only have a weak logarithmic effect on the determination of the activation energy. The prefactor of the exponential term in the ClN₃ dissociation rate, however, is approximately 20 times larger than the corresponding quantity³ for dissociation of FN₃. This factor, which represents the rate of thermal excitation of the azide in collisions with the buffer gas, may be larger in the



Figure 4. Visible spectrum of NCl($b \rightarrow X$) emission generated from thermal decomposition of CIN₃.

present ClN₃ experiments (which used Ar buffer gas) due to a mass effect, since our prior work on FN3 dissociation was conducted using He as the diluent.

NCl(a,b) Production. When the ClN₃ was dissociated a red flash was observed in the reactor which was confirmed by the OMA as NCl($b \rightarrow X$) emission.^{1,27} The emission spectrum is shown in Figure 4. Production of NCl(b) essentially guarantees that a much larger yield of NCl(a) will be obtained since the latter state is of the same spin as the former but is less highly excited. The visible emission was also extinguished upon elimination of the SF_6 from the reaction cell, confirming its role as a sensitizer. Direct interaction of the ClN₃ with the CO₂ laser is not expected because the halogen azide has no significant absorption¹⁸ at the 10.6- μ m wavelength.

The near-infrared NCl($a \rightarrow X$) emission was detected by using the Si photodiode and a $1.06 \mu m$ interference filter. Since the $NCl(a \rightarrow X)$ emission^{27,28} has a very narrow wavelength distribution, similar in appearance to Figure 4, it was possible to test for overlapping emissions due to other species by first using a narrow-band interference filter that was closely matched to the spectrum of the NCl($a \rightarrow X$) emission and then using a second filter that is centered at the same wavelength with approximately 5 times the bandwidth. Upon comparing the results, good agreement was obtained after correcting the data for the difference in filter transmissions at the $NCl(a \rightarrow X)$ emission wavelength. This procedure demonstrates that NCl(a) was indeed produced and that no other species were emitting significantly at the detection wavelength.

The time profiles of the NCl(a) and NCl(b) concentrations are shown in Figure 5. Since the intensity of NCl(a-X) emission was small compared to the NCl(b-X) signal, it was necessary to record the NCl(a) time profile using higher gain in the preamplifier for accurate digitization. This procedure limited the temporal resolution of the NCl(a) signal to 5 μ s, which in turn limited the apparent rate of rise of the NCl(a) concentration. The NCl(b) signal was recorded at reduced gain, but with 10× higher bandwidth, which accounts for the lower signal to noise ratio of the data. The rise of the NCl(b) time profile, however, is in good agreement with the corresponding decay of the ClN₃ concentration as shown in Figure 3. This result demonstrates that excited NCl(b) and presumably NCl(a) are nascent products of the dissociation process rather than the result of secondary reactions.

The NCl(a) and NCl(b) yields were determined from their emission intensities by using the calibration procedure described in the Experimental Section. The decay of the metastable NCl radicals is thought to be due to self-annihilation which is known to be the principal loss channel³ for NF(a) obtained from thermal decomposition of FN₃. Since the rate of NCl(a) decay is relatively fast, the processes of CIN₃ dissociation and the NCl(a) self-annihilation significantly overlap in time. Therefore, the correct initial concentration of NCl(a) was obtained by extrapolating the decay curves back to t = 0. Care was taken to perform the NCl(a) yield experiments at the lowest practical ClN₃ concentrations to slow the self-annihilation rate and thereby minimize the error due



Figure 5. Temporal profiles of NCl(a) and NCl(b) on two different time scales. The early portion of the NCl(a) signal (dashed line) was obscured by electrical noise from the CO₂ laser (fired at t = 0) and the corresponding rise time was limited by the bandwidth of the preamplifier.

to extrapolation. This procedure also tends to minimize errors that result from the limited bandwidth of the preamplifier.

The yield of NCl(b) per ClN₃ molecule was found to be approximately 0.5%, based on the 1600/s value of the A coefficient reported by Coombe et al.¹² The A coefficients for the NCl($a\rightarrow X$) transition that are reported²⁸⁻³⁰ in the literature, however, vary widely from about 487/s to 0.27/s. Since this rate constant directly influences the yield calculation we found it necessary to evaluate the corresponding references. Normally the longest radiative lifetime (\sim 4 s) is presumed to be correct since systematic errors due to quenching and diffusion tend to shorten the measured decay time. This result, however, was obtained in an argon matrix²⁹ which requires a significant correction based on the index of refraction for use in the gas phase and is therefore subject to error in either direction. Theoretical calculations by Yarkony³⁰ tend to support a 1.4-s lifetime, as do the reported trends in the NX(a) state lifetimes and the b/a lifetime ratios^{12,28-32} in the series defined by X = F, Cl, and Br. Therefore, we calculated our NCl(a) yield using the corresponding A coefficient of 0.7/s.

The yield of NCl(a) was also found to be a complex function of the CO₂ laser energy. Initially the yield increased with pulse energy because at low laser fluences the gas temperature is too small to dissociate the ClN₃ on a time scale that is shorter than the decay time due to self-annihilation. Once dissociation becomes rapid compared to the subsequent decay, further increases in gas temperature do not increase the yield of NCl(a) substantially and may potentially act to reduce the NCl(a) yield by opening other dissociation channels that do not lead to metastable products. At still higher laser fluences, the yield of NCl(a) apparently increases again, possibly due to a multiphoton phenomena. Therefore, relative NCl(a) yields were first determined as a function of CO₂ laser energy and then absolute measurements were performed at

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TABLE I: Production of NF(b) by Halogen Azide Dissociation

partial pressure, Torr				rel intensity of $NF(b \rightarrow X)$
SF ₆	FN ₃	CIN3	I ₂	emission
10.7	0.10			1.0
10.7	0.10	0.14		3.7
10.7	0.10	0.14	≤0.02	27.5
7.5	0.08		≤0.02	2.5
	SF ₆ 10.7 10.7 10.7 7.5	partial pr SF ₆ FN ₃ 10.7 0.10 10.7 0.10 10.7 0.10 10.7 0.10 7.5 0.08	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c } \hline partial pressure, Torr \\ \hline \hline SF_6 & FN_3 & ClN_3 & I_2 \\ \hline 10.7 & 0.10 & \\ 10.7 & 0.10 & 0.14 & \\ 10.7 & 0.10 & 0.14 & \leq 0.02 \\ \hline 7.5 & 0.08 & \leq 0.02 \\ \hline \end{tabular}$

the optimum fluence of approximately 1 J/cm², where a numerical NCl(a) state yield of 110% was obtained, using the 0.7/s value of the A coefficient.

If the NCl(a) yield is recalculated by using the largest value of the A coefficient²⁸ reported in the literature (498/s) then a 10-fold smaller yield of NCl(a) is obtained than of NCl(b). This result is physically unrealistic since reactions tend to populate the lowest energy product state that is allowed by spin selection rules. Since both NCl(a) and NCl(b) are singlets, the ClN₃ dissociation will strongly prefer the lower energy (a) state as in the case of FN₃ dissociation where typically 100 NF(a) radicals are generated for every NF(b) radical.³ Also, if the NCl(a) yield is smaller than the NCl(b) yield, the reaction would have to proceed efficiently to products that are either spin forbidden, such as $NCl(X^{3}\Sigma)$ or energetically unfavorable, such as $Cl + N_3$, since all of the ClN_3 dissociates (as shown in Figure 4) and the combined NCl(a,b) yield would be small compared to unity. Consequently, our yield data suggest that the largest value of the A coefficient reported in the literature is overestimated by 2-3 orders of magnitude.

The window purges on the reactor, which act along the path of the laser beam, have a mean velocity of approximately 100 cm/s through the apertures that are shown in Figure 2. Therefore, some of the azide molecules were swept out of the active volume of the reactor. Since we calculated our NCl(a,b) yields assuming a uniform spatial distribution of the parent molecules, the resultant yield that was measured should have been less than 100%. Prior experience with this reactor has shown that the correction factor for this effect is approximately 2. Consequently our data also suggests that the smallest values of the A coefficient reported in the literature^{29,30} are underestimated by less than 1 order of magnitude.

Since excited-state yields tend to either approach unity, in the case of an effective spin constraint (as expected here) or a very small statistical yield (typically less than 1%) in the absence of such constraints, it follows that dissociation of ClN₃ is at least a moderately efficient source of NCI(a). Therefore, apart from a somewhat larger activation barrier, the thermal dissociation of ClN₃ parallels the case of FN₃. Precise determination of the NCl(a) yield, however, will have to await a better measurement of the A coefficient for the NCl(a-X) transition.

Self-Quenching. The peak NCl(a) concentration in the experiments reported above was approximately 3×10^{15} /cm³ (assuming a 100% yield from ClN₃) and a 40- μ s half-life was observed, as shown in Figure 5. As in the case of FN_3 , it is unlikely that this decay can be accounted for by reaction with or quenching by the buffer gas, SF_6 , or N_2 by-product that is generated³ and the decay occurs well after the ClN₃ is dissociated. If the quenching of the NCl(a) is therefore attributed entirely to selfannihilation, the corresponding rate constant is about 8×10^{-12} cm^3/s , somewhat faster than for NF(a) which self-annihilates^{3,33,34} at a rate of $(3-5) \times 10^{-12} \text{ cm}^3/\text{s}$. Since other factors may still contribute to the observed decay rate and the yield of NCl(a) from ClN₃ may be less than 100%, this result should only be interpreted as an approximation. Further research is required to determine the decay kinetics of NCl(a) in detail.

NF(b) Production. Upconversion of NF(a) to NF(b) was investigated by the simultaneous dissociation of near equimolar concentrations of FN₃ and ClN₃. The NF($b \rightarrow X$) emission was detected with an appropriately filtered Si photodiode coupled to the data acquisition system described previously. Table I shows that emission from NF(b) was weakly enhanced by addition of either ClN_3 or trace I_2 to the FN₃ in the reactor. Production of NF(b) from NF(a) in the presence of trace I_2 (but not ClN₃) has also recently been studied in a flow tube by Setser,34 who obtained results that are comparable to the last entry in Table using the $F + N_3$ reaction (which also passes through FN₃ as an intermediate collision complex) to generate NF(a). In our experiment, however, simultaneous addition of both ClN₃ and trace I₂ yielded the most dramatic increase of the NF(b) concentration, by a large margin. Since the ratio of NF(b) to NF(a) obtained from thermal dissociation³ of FN₃ is approximately 1/100, Table I demonstrates that roughly one-fourth of the NF(a) radicals were upconverted to the NF(b) state.

These data also prove that the yield of NCl(a) from ClN_3 is at least 12.5%, independent of the value of the related A coefficient, since at most one NF(a) radical can be upconverted to the b state per NCl(a) molecule that is generated, assuming a 70% yield of NF(a) from FN₃ as measured previously.³ With this result in hand, it is now possible to place upper limits of 5.6/s on the A coefficient and 6.4×10^{-11} cm³/s for the self-annihilation rate of NCl(a). The actual values, however, may be up to an order of magnitude smaller in each case if the NCl(a) yield approaches unity as suggested earlier by the relative intensities of the NCl(a,b \rightarrow X) emission signals.

In this system, NCl(a) may potentially contribute to the production of NF(b) via the mechanism in reactions 1–9. Reaction 1

$$SF_6 + h\nu (10.6 \ \mu m) \rightarrow SF_6(\nu) \tag{1}$$

$$SF_6(v) + M \rightarrow SF_6 + M + \Delta$$
 (2)

$$FN_3 + \Delta \rightarrow NF(a) + N_2$$
 (3)

$$ClN_3 + \Delta \rightarrow NCl(a) + N_2$$
 (4)

 $NF(a) + NCl(a) \rightarrow NF(b) + NCl(X)$ (5)

$$2NCl(a) + I_2 \rightarrow 2NCl(X) + 2I \tag{6}$$

$$NCl(a) + I \rightarrow NCl(X) + I^*$$
(7)

$$I^* + NF(a) \rightarrow NF(b) + I$$
 (8)

$$NF(b) \rightarrow NF(X) + h\nu (528 \text{ nm})$$
 (9)

is well-known and is based upon an optical resonance between the CO_2 laser radiation and the vibrational modes of SF₆. Since the laser fluence in our experiments was well below the threshold³⁵ for significant multiphoton dissociation of the SF_6 and the pressure was relatively high, the yield of F atoms is expected to be small in comparison to the added reactants and therefore easily scavenged by reactions with FN₃ or ClN₃ to yield N₂ and either NF₂ or NFCl as benign byproducts. Hence absorption of the CO₂ laser radiation only served to heat the bath gas upon thermalizing collisions with vibrationally excited SF₆ molecules.³⁶ The sudden addition of heat and the associated jump in gas temperature due to reactions 1 and 2 enables the dissociation of FN₃ to produce NF(a) by reaction 3 which has been demonstrated in our previous investigation.³ Reaction 4 is the analogous dissociation of CIN₃ which has been demonstrated in the present investigation to generate NCl(a) efficiently. The reaction of NF(a) and NCl(a) is sufficiently energetic to produce NF(b) but appears to occur slowly, as expected, since reaction 5 violates conservation of spin. The primary role of NCl(a) in this system, however, appears to be excitation of I atoms to the $I^*(5p^2P_{1/2})$ state by reaction 7 in a manner analogous to the pumping of I* by $O_2(a)$ molecules in the O_2 -I laser system.¹ In parallel experiments, Bower and Yang³⁷ have used the $Cl + N_3$ reaction to generate NCl(a) in a flow tube and have independently shown that I* is rapidly produced by resonant energy transfer from this metastable species. In our experiment, the I atoms are obtained by dissociation of I_2 which

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may be either thermal in nature or the result of energy transfer from NCl(a) as indicated by reaction 6, since analogous multiple collisions with $O_2(a)$ are known³⁸ to dissociate I₂. Production of NF(b) by reaction 8 between I* and NF(a) is also highly resonant and spin-allowed and has been demonstrated to occur rapidly.⁵ Since the I/I* atoms can cycle back and forth between the NCl(a) and NF(a) molecules, their role is catalytic (one I atom can upconvert several NF molecules). Consequently, only trace concentrations of I_2 are required to significantly enhance the production of NF(b).

Addition of HI in place of I_2 was also expected to enhance the yield of NF(b), provided the concentration of F atoms present was adequate to yield a significant quantity of ground-state I atoms via the fast reaction³⁹

$$F + HI \rightarrow HF + I$$
 (10)

The effect of HI addition was found to be much less dramatic than expected, however, as the yield of NF(b) saturated with the addition of up to 250 mTorr of HI, showing only a 60% enhancement over the yield that was obtained in the absence of HI. The yield of NF(b) was also a highly nonlinear function of the iodide addition as a 30% enhancement was obtained upon adding only 50 mTorr of HI. These data reinforce the notion that the concentration of F atoms in our experiment was relatively small, since enhancement of the NF(b) production by addition of HI is limited in comparison to the results obtained upon addition of much smaller concentrations of I₂. Also the saturation characteristic that is observed suggests that F atoms, rather than HI, are the limiting reagent. It is therefore unlikely that I atoms or IF molecules were formed in significant quantities due to the fast reaction40

$$\mathbf{F} + \mathbf{I}_2 \to \mathbf{I}\mathbf{F} + \mathbf{I} \tag{11}$$

Consequently, the dissociation of I_2 into I atoms must have occurred either thermally or by the action of NCl(a) as indicated by reaction 6. This result is also significant because IF is a known fast quencher^{41,42} of NF(b).

IF(B) Production. Several researchers^{6,43-45} have found that the $B^3\Pi_0$ states of CIF, BrF, and IF can be obtained upon addition of $O_2(a)$ to processes that are likely to populate the lower ${}^3\Pi_1$ and ${}^{3}\Pi_{2}$ states of the interhalogens, such as three-body recombination and $F + I_2$ or $X + O_2F$ reaction, where X = Cl, Br or I. In each case, these investigators have theorized that $O_2(a)$ acts to promote the ${}^{3}\Pi_{1}$ or ${}^{3}\Pi_{2}$ intermediates to the higher energy B state via the process of energy pooling. If these same states can be accessed by energy transfer from NF(a) to ground-state interhalogens and if NCl(a) can act in the place of $O_2(a)$, then it should be possible to excite the B-X transitions of a number of interhalogen species following thermal dissociation of mixtures of FN₃ and ClN₃. Our initial investigation focused on IF, since it is a well-known lasing species,⁴⁶ although other possibilities certainly exist and deserve attention.

The potential for pumping of IF(B) by NF(a) and NCl(a) and for subsequent laser action is shown in Figure 6. The ${}^{3}\Pi_{1}$ state is not shown as it lies too high^{6,45,47} to be excited by NF(a). The energy levels of the ${}^{3}\Pi_{2}$ states in the interhalogens are largely unknown;⁴⁸ however, the ${}^{3}\Pi_{2}$ state in IF has been located as the

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Figure 6. Energy level diagram of IF showing resonances with NF(a) and NCl(a).

terminal energy level of a pulsed electric discharge laser transition⁴⁹ and has recently been studied in matrix by Heaven and Nicolai.50 These authors estimate a gas-phase energy of approximately 13 500 cm⁻¹ between the potential minima of the ${}^{3}\Pi_{2}$ and X¹ Σ states of IF. Excitation of IF(${}^{3}\Pi_{2}$) by NF(a) therefore requires approximately 2000 cm⁻¹ of vibrational energy in the IF(X) ground state, since prior studies⁵¹ have shown that E-E transfer from highly vertical molecules⁵² such as NF is not sensitive to the vibrational distribution of the donor species. The necessary vibrational excitation of the IF(X) ground state is obtained thermally, however, in about 1 out of 10 collisions at a temperature of 1200 K. Pumping of IF(B) from the ${}^{3}\Pi_{2}$ state by NCl(a), on the other hand, is sufficiently exothermic that some of the product molecules may be generated above the 22 300 cm⁻¹ predissociation limit,⁶ depending on the amount of electronic energy that is converted into translational and rotational forms of excitation. Due to a lack of resonance, NF(a) is not expected to be effective at either pumping or dissociating the IF(B) state when starting from the ${}^{3}\Pi_{2}$ energy level.

At the high pressure of our experiment, vibrational relaxation occurs at a much faster rate than radiation from the excited B state.⁵³ Therefore, the IF(B) will preferentially decay from its lowest vibrational energy levels to vibrationally excited energy levels of the IF(X) ground state that are not thermally populated, since the Franck-Condon factors⁵⁴ strongly favor the transitions from v' = 0 to $v'' \sim 5-6$. This phenomenon, which helps to maintain a population inversion, results from the displacement of the potential minimum of the IF(B) state to larger internuclear separation than occurs in the ground state. Consequently, we added CF₃I to our reactor as a potential source of ground-state IF(X) molecules, to investigate the pumping of this highly desirable laser transition by NF(a) and NCl(a).

Mixtures of SF₆, approximately 100 mTorr each of FN₃ and ClN₃, and trace CF₃I were subjected to pulsed CO₂ laser radiation

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to yield significant amounts of IF(B-X) emission. In addition to the cooperative mechanism outlined above, this emission could also result from pumping by NCl(a) without participation of NF(a), in a manner analogous to the known pumping of IF(B)by $O_2(a)$, or by the action of NF(b) independent of NCl(a), as previously recorded in this laboratory.^{51,55} These prior (NF/IF transfer) experiments also demonstrated that NF(a) was not effective at producing the IF(B) state in the absence of other energetic species. In the present experiments, the IF(B-X)emission was reduced approximately 4-fold upon elimination of the FN₃. This result demonstrates that the majority of the observed IF(B-X) emission requires either NF(a) or NF(b). By adding trace I_2 , to greatly enhance the NF(b) yield, at the expense of NF(a) and NCl(a), it was possible to show that only a very small fraction of the observed emission was due to transfer from the b state, since the yield of IF(B) was found to decline. Consequently, our data tends to support a cooperative mechanism involving both NF(a) and NCl(a) such as energy pooling through the ${}^{3}\Pi_{2}$ state as the dominant mechanism for IF(B) production under the conditions of our experiment. Since we have not observed this intermediate state directly, however, we cannot rule out other cooperative mechanisms that may be based, for example, on ground-state intermediates in a high state of vibrational excitation.

The intensity of the IF(B-X) emission was found to scale linearly with CF₃I addition up to 500 mTorr, which is well in excess of any potential for F-atom generation in our experiment. Therefore, it is unlikely that the IF(X) resulted from the fast reaction⁵⁶

$$F + CF_3I \rightarrow CF_3 + IF$$
 (12)

because the yield of IF(B-X) emission would have saturated once the F atoms were titrated against the CF₃I. Since prior results tend to indicate a paucity of F atoms in our reactor, it appears that thermal or energy transfer induced disproportionation of CF₃I is a more likely source of ground-state IF. This mechanism, which

(55) Pritt, A. T.; Patel, D.; Benard, D. J. Chem. Phys. Lett. 1983, 97, 471. (56) Stern, L.; Wanner, J.; Walther, H. J. Chem. Phys. 1980, 72, 1128. does not require F atoms, would yield the observed linear dependence upon CF_3I addition. Disproportionation of the perfluoroiodide, however, is expected to be a very weak (low yield) source of the ground-state interhalogen, in which case the production of IF(B) may be throttled by IF(X) generation rather than the efficiency of pumping by NF(a) and NCl(a). Also if NF(a) is required to generate the IF(X) from CF_3I , then pumping to the B state can occur (consistent with our observations) solely due to the presence of NCl(a). Therefore, an effective thermal source of IF(X) will have to be developed and characterized before the mechanism and pump rates can be evaluated quantitatively.

Summary

Reaction of Cl_2 with moist NaN_3 efficiently generates ClN_3 , which has a barrier to dissociation of approximately 0.8 eV and a near gas kinetic rate of thermal excitation by collisions with the buffer gas. Thermal dissociation of ClN₃ occurs on the 1–10 μ s time scale in ~ 100 Torr of Ar gas buffer at temperatures near 1200 K. The products are primarily NCl(a) and N_2 , with a small fraction (<1%) as NCl(b). The radiative lifetime of NCl(a) is thought to be approximately 1.4 s and self-annihilation of NCl(a) may limit the kinetic lifetime of this species at high concentration. By use of a pulsed CO_2 laser and SF_6 as a sensitizer, transient concentrations of NCl(a) as large as 3×10^{15} /cm³ have been obtained. The NCl(a) molecules are capable of generating I* by resonant energy transfer (similar to the O₂-I interaction) and the I* may be used to upconvert NF(a) to NF(b). Cooperative pumping of IF(B) by NCl(a) and NF(a) appears to be limited by the availability of IF(X) due to a lack of F atoms and does not involve NF(b) as a precursor, but may be the result of an energy pooling mechanism that proceeds through the IF(${}^{3}\Pi_{2}$) state as an intermediate. Further studies are required to determine the potential of these and similar mechanisms for the generation of visible laser radiation from the electronic energy that is stored in the singlet metastable products of thermally dissociated halogen azides.

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Photofragmentation Pathways of a PMMA Model Compound under UV Excimer Laser Ablation Conditions

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A model compound for the polymer poly(methyl methacrylate) (PMMA) was synthesized and investigated under UV excimer laser photolysis of different wavelengths and pulse durations in hexane solution. Qualitative analysis of the photolysis products reveals a well-defined photochemical fragmentation pattern of the PMMA model system. Quantitative analysis shows that the major primary process in the photolysis of this type of molecules is the side-chain scission under formation of double bonds. Depending on the irradiation conditions, a quantum yield of $\Phi = 0.5 \pm 0.1$ is observed for 248-nm, 16-ns laser radiation. The high quantum yield and the strong analogy of the model system to the behavior of PMMA under 248-nm ablation show that the photochemical contribution to the ablation process at this wavelength is far from negligible.

Introduction

The ability of controlled material removal by UV excimer laser ablation^{1,2} has raised considerable interest due to its proven and potential applications in electronic manufacturing and surgery. A variety of materials ranging from polymers to biological tissue was successfully structured or cut by ablation showing little or no damage to the remaining material, and the achievable spatial resolution of excimer laser induced microstructures has been shown to be well below 1 μ m.³ While ablation has already found numerous applications in industry⁴ and surgery,⁵ a detailed un-

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