The $\text{O}(^{3}\text{P}) + \text{N}_2(^1\text{I}_g) \rightarrow \text{NO} + \text{N}_2$ and $\text{Se}(^{3}\text{P}) + \text{N}_3(^2\text{I}_g) \rightarrow \text{NSe} + \text{N}_2$ chemiluminescent reactions have been studied in a conventional discharge flow reactor using chemiluminescence detection of $\text{NO}(A^2\Sigma^+)$ and atomic resonance fluorescence detection of $\text{Se}(^1\text{P})$ to follow the rate of the reactions. The $\text{O} + \text{N}_3$ reaction produces electronically excited $\text{NO}(A^2\Sigma^+)$ in a nonthermal vibrational distribution of $v(0): 0.64$, $v(1): 0.31$, and $v(2): 0.05$. The high energy limit serves to place bounds on the heat of formation of $\text{N}_3$ indicating $107.8 > \Delta H_f > 101.3$ kcal mol$^{-1}$. The $\text{NO}(A \rightarrow X)$ photon yield and rate coefficient for the reaction were determined to be $\phi_{\text{NO} A \rightarrow X} = 0.3\%$ and $k_1 = (1.12 \pm 0.18) \times 10^{-11}$ cm$^3$ s$^{-1}$, respectively. The rate of the $\text{O}(^{3}\text{P}) + \text{HN}_3 \rightarrow \text{OH} + \text{N}_3$ reaction was also measured and found to be slow with $k_9 \leq 2 \times 10^{-13}$ cm$^3$ s$^{-1}$. The $\text{Se} + \text{N}_3$ reaction produces electronically excited $\text{NSe} (A^2\Pi_{1/2} s_{3/2})$ with a rate coefficient of $(6.4 \pm 2.4) \times 10^{-12}$ cm$^3$ s$^{-1}$. The photon yield for this reaction is also small: $\phi_{\text{NSe} A \rightarrow X} = 0.02\%$. The low yields of the excited products in the Group VI plus $\text{N}_3$ reactions are viewed in terms of weak angular orbital momentum constraints and a large number of reactant surfaces.
Chemiluminescent Reactions of Group VI Atoms (O(3P) and Se(3P)) with Azide Radicals

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The O(3P) + N(3P) → NO + N(2) and Se(3P) + N(3P) → NSe + N(2) chemiluminescent reactions have been studied in a conventional discharge flow reactor by using chemiluminescence detection of NO(A^3^S^+) and atomic resonance fluorescence detection of Se(3P) to follow the rate of the reactions. The O + N(2) reaction produces electronically excited NO(A^3^S^+) in a nonthermal vibrational distribution of v(0) = 0.64, v(1) = 0.31, and v(2) = 0.05. The high-energy limit serves to place bounds on the heat of formation of N(2) indicating 107.8 > AH_(2N(2)) > 101.3 kcal mol^-1. The NO(A -> X) photon yield and rate coefficient for the reaction were determined to be (1.12 ± 0.18) x 10^-11 cm^3 s^-1, respectively. The rate of the O(3P) + HN(3) reaction was also measured and found to be slow with k = 2 x 10^-13 cm^3 s^-1. The Se + N(2) reaction produces electronically excited NSe(A^3^II, 2I = 3) with a rate coefficient of (6.4 ± 2.4) x 10^-11 cm^3 s^-1. The photon yield for this reaction is also small: 0.3%. The low yields of the excited products in the group VI plus N(2) reactions are viewed in terms of weak angular orbital momentum constraints, a large number of reactant surfaces, and the potential for disposing a large fraction of the reaction exothermicity to ground-state products.

Introduction

Much recent work has been done on the chemiluminescent reactions of atomic species (R) with azide radicals (N(3)). These reactions typically produce excited-state nitrites or nitrenes which subsequently emit in the UV and visible regions. The high product specificity and large quantum yields observed in many of these reactions has been attributed to electron spin and/or orbital angular momentum constraints. Spin constraints have been found to be important in reactions of the group VII (halogens) atoms, and orbital constraints have been found to play a role in group V atom reactions. Since N(2) may be regarded as an excited N(2) atom loosely bound to N(2)(X), the extent to which orbital correlations are important depends upon the degree to which the reactive nitrogen of N(2) retains 2D character along the reaction coordinate; i.e., the NR product should correlate to N(2)D + R. Reactions of group VI atoms with N(2) have received less attention even though they are also of interest as chemiluminescent reactions capable of producing specific electronic states of group VI nitrides. The reactions of group VI atoms with N(2)

\[
\begin{align*}
\text{O(3P) + N(3P)} & \rightarrow \text{NO} + \text{N(2)} & -137 \text{ kcal mol}^{-1} \\
\text{S(3P) + N(3P)} & \rightarrow \text{N(2)} + \text{NS} & -102 \text{ kcal mol}^{-1} \\
\text{Se(3P) + N(3P)} & \rightarrow \text{N(2)} + \text{NSe} & -77 \text{ kcal mol}^{-1}
\end{align*}
\]

are sufficiently energetic to populate a number of electronic states of NO, NS, and NSe. As explained above, the degree of conservation of orbital angular momentum is defined by the correlation of the NR product to N(2)D + R(3P); i.e., the electron II excited states of NO and NS and the A^3^II state of NSe. The early studies on the O + N(2) reaction have indicated that the NO(A^3^S^+) state is not observed in reaction 1, which produced NO(A^3^S^+) exclusively from several energetically allowed states. Further, recent investigations of the S + N(2) reaction has shown that even though NS β-band emission (B^3^II -> X^3^II) is readily observed, the NS(3P) state is produced in very low yield. These results appear to indicate that, in marked contrast to the group V atom plus azide reactions, the orbital angular momentum correlations are much weaker for the group VI atom reactions and that these reactions may dispose a large fraction of their energy into the ground and other dark states.

In this paper we have extended our studies of the group VI azide reactions to include the reactions of O(3P) and Se(3P) with N(2) reporting measurements of the rate coefficients for the reactions 1 and 3 and spectroscopic observations on the chemiluminescence generated. The spectroscopic data is compared with earlier work and the overall trends in reactions of group VI atoms are examined. The strengths of the angular momentum correlations are compared to those of other azide reactions. The data are of interest with respect to a possible chemically or optically pumped laser since the excited group VI nitride diatomics have features which make them attractive laser candidates. Burrows and co-workers have already demonstrated an optically pumped NO(A -> X) laser.

Experimental Section

The experimental apparatus has been described in detail elsewhere. The experiments utilized a conventional discharge flow reactor with chemiluminescence or resonance fluorescence detection. The 50 cm long flow reactor was fabricated from 2.54 cm i. d. Pyrex tubing and had two side arms equipped with 2450-MHz microwave discharge cavities for atom production. Fluorine atoms were produced by a discharge through carrier gas/CF(4) or carrier gas/F(2). Nitrogen atoms were generated by passage of carrier gas/N(2) mixtures through the discharge. F and N atom number densities were determined by chemiluminescent titrations. To reduce F atom wall reactions, the flow tube was coated with halocarbon wax.

The flow tube contained a sliding injector for temporal resolution. Two different injectors were used. In the investigation of the O + N(2) and the O + HN(2) reactions, the injector was equipped with a microwave discharge cavity to provide for the production of oxygen atoms. To reduce background emissions emanating from the discharge of dilute He/O(2) mixtures, the cavity was positioned off the flow tube axis on a semi axis assembly which contained a Woods Horn light trap. In measurements of the rate coefficient for the O + HN(2) reaction, oxygen atoms were detected...
Chemiluminescent Reactions of Group VI Atoms

The rate constant for reaction 5 has not been reported, but on the basis of similar H-atom abstraction reactions, e.g., \( F + HS → HF + S, k = 5 \times 10^{-10} \text{cm}^3 \text{s}^{-1} \), it is expected to be large. Azide radicals were produced by the reaction of F atoms with HN\(_3\). In the studies of reactions 1 and 3, the HN\(_3\) entered the flow reactor either through the side arm across from the F atoms discharge or through the centermost injector, respectively.

The system was pumped by a Kinney KT-300 mechanical pump whose free-air displacement is 142 L/s. To ensure adequate evacuation, a Kinney KT-300 mechanical pump was employed in the investigation of the Se + N\(_2\) reaction. Dilute flows of H\(_2\)Se entered the flow reactor via the outermost tube of the double injector. Ground-state Se atoms were then generated by the reaction of F atoms with H\(_2\)Se:

\[
F + H_2Se → HF + HSe \quad k = 1.8 \times 10^{-10} \text{cm}^3 \text{s}^{-1}
\]

(4)

\[
F + HSe → HF + Se
\]

(5)

The system was pumped by a Kinney KT-300 mechanical pump whose free-air displacement is 142 L/s. To ensure adequate evacuation, a Kinney KT-300 mechanical pump was employed in the investigation of the Se + N\(_2\) reaction. Dilute flows of H\(_2\)Se entered the flow reactor via the outermost tube of the double injector. Ground-state Se atoms were then generated by the reaction of F atoms with H\(_2\)Se:

Emissions from electronically excited atoms and molecules were dispersed with a 0.25-m polychromator and detected with a cooled GaAs photomultiplier tube (PMT) (RCA C31034A).

Hydrazoic acid was synthesized by reacting stearic acid with NaN\(_3\) at 115 °C under vacuum. The gas was collected in 12-L glass bulbs and diluted with ultra-high-purity (UHP) He to obtain mixtures near 3% reactant concentration. Commercially obtained helium (UHP), O\(_2\) (UHP), N\(_2\) (UHP), F\(_2\) (5% in He), CF\(_4\) (99.95%), CI\(_2\) (10% in He), NO (99%), N\(_2\)O (99.5%), and H\(_2\)Se (98%) were used without further purification. However, during the course of the experiments it became evident that NO(A→X) (γ bands) background emission needed to be reduced such that it would not complicate the study of reaction 1. To this end a gas purifier (oxyclear) was installed in the He carrier gas line and, further, the He and F\(_2)/H\(_2\) flows were passed through liquid nitrogen cold traps. These measures reduced the NO(A→X) emission to extremely low levels.

Results

1a. Spectroscopy of the O/F/H\(_2\) Flame. The addition of small flows of HN\(_3\) to a stream containing F and O atoms, heavily diluted in He, gave rise to the spectrum shown in Figure 1. The spectrum is attributable to the \( v' = 0, 1, \) and 2 progressions from the A\(^{2} \Sigma^+ \rightarrow \chi^2 \Pi\) transition in NO. No evidence for emission from higher A state vibrational levels (i.e., \( v' > 2 \)), or from other electronically excited states of NO, namely \( B^2 \Pi \rightarrow \chi^2 \Pi\) emission, was obtained. The dependence of the NO(A) band system was checked as a function of reagent flows and was found to be strongly dependent on the CF\(_4\) or F\(_2\), HN\(_3\), and O\(_2\) flow rates. Removal of any of these reagents markedly reduced the γ-band emissions. However, when either the CF\(_4\) (or F\(_2\)) or the O\(_2\) flow was removed, a small background emission remained. This background was typically <5% of the original intensity.

In these experiments, the typical starting F atom and HN\(_3\) densities were \( \leq 1 \times 10^{13} \) atoms cm\(^{-3}\) and \( 3 \times 10^{13} \) molecules cm\(^{-3}\), respectively.
resonance transfer between N2 metastables is thought to occur. The quenching of N2(A) by HN3 has a reported rate constant \(^{13,14}\) in the range \((7-8) \times 10^{11} \text{ cm}^3 \text{s}^{-1}\) with a branching fraction of 3% to the A state. \(^{14}\) Given the relatively high densities of HN3 in the flow reactor, any N2(A) produced would be rapidly quenched and, as such, it is unlikely that energy transfer between N2(A) and NO to produce NO(A), known to be a relatively facile process, could account for the observed NO emission. However, to test this supposition, an experiment was performed to gauge N2(A) densities in the reactor. In the experiment, the O2 discharge was inactivated and a small flow of NO added through the injector. The NO density was high enough (approximately \(10^{12} \text{ molecules cm}^{-2}\)) to observe potentially strong NO(A) emission but not so large as to produce significant NO–NO(A) self-quenching. No increase in NO emission over background levels was observed, indicating low N2(A) densities in the reactor.

No other emissions were observed at wavelengths beyond 340 nm (aside from NF(b), mentioned above). Specifically, no emission from NF(a) and no nitrogen first positive or any air afterglow emission from the O + NO recombination reaction was apparent.

\[ \text{Se}(\text{P}) + \text{N}_2(\text{H}) \rightarrow \text{NSe} + \text{N}_2(\text{X}) \] (3)

The enthalpy change of the reaction can be calculated from standard heats of formation. \(^{17}\) Taking \(\Delta H(\text{NSe}) = 69.16 \text{ kcal}\)

\[ \Delta H(\text{NSe}) = 69.16 \text{ kcal} \]

Figure 2. Chemiluminescent spectrum of NSe(A1Π\(_{3/2,1/2}\)) produced by the H2Se/F/HN3 system. The transitions assigned to NSe(A2→X2), NH-(A2→X2), and NF(b1Σ→X1Σ) are indicated.
Figure 3. Typical time profile of the \( \gamma \)-band emission, (0,1) band. The initial densities of \( \text{O}, \text{F} \), and \( \text{HN}_3 \) were \( 8.5 \times 10^{12}, 4 \times 10^{11}, \) and \( 1 \times 10^{13} \) molecules cm\(^{-3} \), respectively. The closed circles are the individual data points and the line represents a nonlinear least squares fit to a function \( I = I_0 e^{-kt} \). A plot of the pseudo-first-order decay rate vs O-atom density is shown in upper right-hand corner. The slope of the line gives the second-order rate constant for the \( \text{O} + \text{N}_3 \) reaction.

\[ \Delta H(\text{Se}) = 48.4 \text{ kcal mol}^{-1} \] (where the dissociation energy of \( \text{NSe} \) has been used to calculate its heat of formation), and \( \Delta H_\text{N}_3(\text{N}_2) = 99.1 \text{ kcal mol}^{-1} \), the exothermicity of the reaction is calculated to be \(-78.3 \text{ kcal mol}^{-1} \). This represents enough energy to populate the \( \text{A}_1 \) state of \( \text{NSe} \) up to \( \nu' = 4 \). However, we have confirmed levels populated up to at least \( \nu' = 8 \). The discrepancy may be due to the uncertainties in the heat of formation of \( \text{N}_3 \).

Habdas et al.\(^{18} \) reported a substantially larger value for the \( \Delta H_\text{N}_3 \) of \( \text{N}_3 \) of 113 kcal mol\(^{-1} \). Using this value, we calculate a thermodynamic limit of \(-92.2 \text{ kcal mol}^{-1} \) for reaction 3. This represents enough energy to populate the \( \text{A}_1 \) state to \( \nu' = 12 \). However, population of \( \text{NSe}(\text{A}_1) \) above \( \nu' = 8 \) could not be confirmed due to the presence of \( \text{NH}(\text{A}-\text{X}) \) and \( \text{NO} \) \( \gamma \)-band emission in this spectral region.

Two quartet states, the \( \text{a}^3 \Pi \) and \( \text{b}^3 \Sigma^+ \), are believed to lie in close proximity to the \( \text{A}_1 \) and \( \text{A}_2 \) states. In a high-resolution study\(^{15} \) of the \( ^1\text{HNO} \text{Se} \) spectrum in the 330–580-nm region, Daumont, Jenouvrier, and Pascat have detected the presence of these close-lying states mainly through perturbations on the ro-vibrational manifold of the \( \text{A} \) states. In addition, they have also identified a weak transition thought to originate from the \( \text{b}^3 \Sigma^+ \) state. The resolution of the present experiments was not high enough to detect possible interaction from these quartet states.

2a. Kinetics of the \( \text{O} + \text{N}_3 \) and \( \text{O} + \text{HN}_3 \) Reactions. Time profiles of the \( \text{NO}(\text{A}) \) emission were measured by movement of the sliding injector (the \( \text{O} \) atom source) with respect to the fixed observation zone. A typical time profile recorded for the (0,1) band near 237.0 nm is shown in Figure 3 and is well fit by an exponential function. The decays were measured under pseudo-first-order conditions with \( \text{O} \) atoms in large excess over \( \text{N}_3 \) radicals. Since reaction 6 was used to produce the \( \text{N}_3 \) radicals, the starting \( \text{F} \) atom densities \( (\leq 4 \times 10^{11}) \) gave the initial \( \text{N}_3 \) densities. \( \text{O} \) and \( \text{F} \) atom concentrations were determined by titration with \( \text{NO}_2 \) and \( \text{Cl}_2 \), respectively.\(^{19,20} \) The lifetimes of the decays varied inversely with the \( \text{O} \) atom concentration and this behavior is identified with the rate of formation of \( \text{NO}(\text{A}) \) by the \( \text{O} + \text{N}_3 \) reaction. The rate coefficient for the reaction was determined by plotting the pseudo-first-order decay rate against the \( \text{O} \) atom density. The slope of the plot, shown in Figure 3, gives the rate constant \( k = (1.12 \pm 0.18) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \), where the error reflects the scatter in the data. This value is in good agreement with that reported by Piper, Krech, and Taylor.\(^{19} \) In their study of the thermal decomposition of \( \text{NaN}_3 \), they determined a less precise value of \( (2 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \).

The nonzero intercept indicates the occurrence of \( \text{N}_3 \) wall reactions. The \( \text{N}_3 \) wall removal rate of \( 39 \pm 15 \text{ s}^{-1} \) is similar to the value reported by David and Coombe\(^{13} \) who measured \( k_{\text{w}} = 46 \pm 0.04 \text{ s}^{-1} \) for a 3.5 cm i.d. PTFE flow reactor.

A series of rate measurements were performed to determine the importance of the reaction

\[ \text{O} + \text{HN}_3 \rightarrow \text{OH} + \text{N}_3 \quad \Delta H_0 = -22.2 \text{ kcal mol}^{-1} \] (9)

in the \( \text{O}/\text{F}/\text{HN}_3 \) chemical system. \( \text{O} \) atoms were detected\(^{19,20} \) by the chemiluminescent reaction that occurred when \( \text{NO} \) \( (3.2 \times 10^{12} \text{ molecules cm}^{-3}) \) was added through a titration port slightly upstream of the detection volume:

\[ \text{O} + \text{NO} \rightarrow \text{NO}_2^* \] (10)

\[ \text{NO}_2^* \rightarrow \text{NO}_2 + \gamma \text{h} \] (11)

The green-yellow "air afterglow" was detected by an RCA C31034 PMT.

The addition of large densities (approximately \( 10^9 \text{ atoms cm}^{-3} \)) of \( \text{O} \) atoms and \( \text{HN}_3 \) to the flow tube produced no visible emissions and no significant increase in \( \text{NO}(\gamma) \) band emissions over background levels.

The time decays of \( \text{O} \) atoms were measured by movement of the sliding injector (the \( \text{O} \) atoms source) with respect to the fixed observation zone. Measurements of the \( \text{O} \)-atom decays in the absence of \( \text{HN}_3 \) yielded a value for the \( \text{O} \)-atom wall recombination rate of \( \leq 3 \text{ s}^{-1} \). Addition of large pseudo-first-order densities of \( \text{HN}_3 \) in the range \( (1-10) \times 10^{13} \) to the flow reactor did not substantially increase the \( \text{O} \)-atom temporal decay over the \( \text{O} \)-atom wall loss values. Consequently, we report the rate constant for the \( \text{O} + \text{HN}_3 \) reaction as an upper limit, \( k \leq 2 \times 10^{13} \). MacDonald and Coombe\(^{11} \) have also measured a small rate constant for this reaction, giving an upper limit of \( k \leq 1 \times 10^{12} \text{ cm}^3 \text{ s}^{-1} \).

2b. Kinetics of the \( \text{Se} + \text{N}_3 \) Reaction. The rate constant for the \( \text{Se} + \text{N}_3 \) reaction was determined from the time decay of \( \text{Se} \) atoms in a stream of \( \text{N}_3 \) radicals. Very dilute \( \text{H}_2\text{Se} \) mixtures were entrained at the point of the outer injector into a \( \text{F} \) atom stream and the ensuing \( \text{H}-\text{atom abstraction reactions}, (4) \) and (5), generated free \( \text{Se} \) atoms at densities \( < 1 \times 10^{15} \text{ atoms cm}^{-3} \).

The \( \text{Se} \) atomic resonance line near 204 nm was used to monitor the decay of \( \text{Se} \) atoms in excess of \( \text{N}_3 \). \( \text{N}_3 \) densities were determined, as above, from the \( \text{HN}_3 \) flow rates. A response curve relating \( \text{Se} \) atom resonance fluorescence intensity to \( \text{H}_2\text{Se} \) flow rates was found to be linear over a wide range of \( \text{H}_2\text{Se} \) (hence, \( \text{Se} \) atom) concentrations. All kinetic decay curves were measured in the linear portion of the \( \text{Se} \) resonance fluorescence response.
Figure 5. Steady-state vibrational distribution in NO(A\(^*\Sigma^+\)) produced by the O + N\(_2\) reaction. If fit to a thermal distribution a vibrational temperature of 2594 K would be indicated. A typical decay is shown in Figure 4 and exhibits exponential behavior over several lifetimes. Figure 4 also shows a plot of the fluorescence decay rate against N\(_1\) density. The slope of the line gives the rate coefficient for the Se + N\(_1\) reaction, yielding \(k = (6.4 \pm 2.4) \times 10^{12} \text{ cm}^3 \text{s}^{-1}\). The intercept of 10 s\(^{-1}\) reveals a marginal wall loss of Se atoms on the halocarbon waxed surface.

3. NO(A) Vibrational Distribution. The radiative lifetime of NO(A) has been reported to be 215 ns out of \(v' = 0\). At He pressures of 2 Torr the molecule would suffer at most two collisions during its radiative lifetime. Hence, the intensity distributions from the NO spectrum should accurately reflect the nascent vibrational distribution. The upper state vibrational populations were determined from the corrected emission intensities (Figure 4) and the known Franck–Condon factors. The distribution is plotted as the fractional population of the \(v\) level against the vibration energy. From Figure 5 it is apparent that the distribution is nonthermal. As expected, no change in the distribution occurred when the bath gas pressure was varied in the 0.7–2 Torr range. The high-energy cutoff at \(v' = 2\) serves to place bounds on the heat of formation of N\(_2\), indicating: \(107.8 > \Delta H_f(\text{N}_2) > 101.3 \text{ kcal mol}^{-1}\). The lower boundary value is close to that reported by Clark and Clyne who determined \(\Delta H_f = 99.15 \pm 2.3 \text{ kcal mol}^{-1}\). The values reported by Habad et al. and by Pellerite et al. are above the upper limit. The data indicates that 21% of the excess energy is channeled into vibration.

As a check on the experimentally determined vibrational populations and to obtain information on rotational temperatures, a computer code was employed which fitted synthetic to experimental spectra. The calculation used the following equation to give the photon count \(P_{\nu}^{v'\nu'}\) for a vibration–rotation line in spontaneous emission

\[
P_{\nu}^{v'\nu'} = \frac{64\pi^3R^2S_{\nu}\nu}{3hKT_{\nu}} \exp\left[-\frac{B_{\nu}J(J + 1)}{kT_{\nu}}\right] \rho^3\varepsilon(o)R_{\nu}\nu'\nu']\phi(\nu'\nu')N_{\nu'}
\]

where \(B_{\nu}\) is the vibration level dependent rotation constant, \(S_{\nu}\) is the Hot–London factor, \(T_{\nu}\) is the rotational temperature, \(\rho^3\epsilon(o)\) is the frequency, \(R_{\nu}\) is the electronic transition moment, and \(N_{\nu'}\) is the population in level \(v'\). Since the Born–Oppenheimer approximation is applied in the calculation of the experimentally determined \(N_{\nu'}\) the transition moment integral takes the form \(\epsilon(o)\nu'\nu')R_{\nu}\nu'\nu'\). The fit of the synthetic to experimental spectra shown in Figure 1 supports the overall experimental \(N_{\nu'}\) determination. From analysis of line widths, the fit also indicates a rotational temperature of 1800 ± 600 K.

4. Quantum Yield of NO(A) and NSe(A). The yield of NO(A) and NSe(A) photons produced in the O/F/H\(_2\) and F/H\(_2\)Se/H\(_2\) systems, respectively, were determined by a procedure identical to one used previously. In brief, the air afterglow reaction is utilized to determine a calibration factor \(a\), which is a measure of the light collection efficiency of the detection system. The calibration factor may then be applied to measurements of the NO(A) or NSe(A) emission intensity. The photon flow is then determined from the volume integrated observed intensity as

\[
\phi = \frac{\text{photon flow at } N_j}{[N_j]} \times 100
\]

where \(N_j\) is the limiting reagent and is calculated assuming unit conversion of H\(_2\)N\(_2\) to N\(_2\) via reaction 10. Repetitive measurements of \(\phi\) and \(\beta\) were made and gave \(\phi_{\text{NO}} = 0.3\%\) and \(\phi_{\text{Se}} = 0.02\%\) with an uncertainty, characteristic of such measurements, of 50%.

Discussion

From the data, it appears that NO(A) and NSe(A) are generated by the O + N\(_2\) and N\(_2\) + F reactions, respectively. In both the O/F/H\(_2\) and H\(_2\)Se/F/H\(_2\) systems, the source of the N\(_2\) radicals is the rapid F + H\(_2\)N\(_2\) reaction. The upper limit obtained for the rate constant of the O + H\(_2\)N\(_2\) reaction indicates that it is a negligible source of N\(_2\) radicals and does not influence the kinetic measurements for reaction 1.

In both systems, the observation of NF(b–X) emission in the visible region reveals that a reaction between F atoms and N\(_2\) (7) occurs to some extent. In the O/F/H\(_2\) system, since high densities of H\(_2\)N\(_2\) were used, the majority of F atoms were consumed by the F + H\(_2\)N\(_2\) "titration reaction" (99.3% in 1 ms) and only very weak NF(b) emission was observed. However, in the H\(_2\)Se/F/H\(_2\) system F atoms were in excess of the H\(_2\)N\(_2\) density and the NSe spectrum is strongly overlapped by NF(b) chemiluminescence. The importance of the F + N\(_2\) reaction in this system depends upon which value of the rate constant for reaction 7 is used. Two widely differing values for this rate constant have been reported.

By using nitrogen first positive emission, produced by the N + N\(_2\) reaction, as a tracer for N\(_2\) radicals and by observing the change in this emission as a function of F atom density, David and Coombe have determined a value of \(k = (1.8 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}\) for reaction 7. Their measurements were made using a 3.5 cm i.d. PTFE discharge flow reactor with H\(_2\)N\(_2\) (hence N\(_2\)) densities near 10\(^3\) molecules cm\(^{-3}\). Habad and co-workers employed discharge flow methods in their measurements of the rate constant, although they used a much larger flow reactor (8 cm i.d. Pyrex tube coated with halocarbon wax) and lower H\(_2\)N\(_2\) densities, on the order of 7 \times 10\(^3\) molecules cm\(^{-3}\). By modeling the temporal behavior of the NF(a) chemiluminescence from reaction 7, they determined a significantly larger value of \((5 \pm 2) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}\) for the rate constant. For the F-atom densities employed in the Se + N\(_2\) kinetic experiments, the larger value indicates that the majority of N\(_2\) radicals would be converted to NF and N\(_3\) (99% conversion in 2 ms), the products of the F plus N\(_2\) reaction. If this were indeed the case, the observation of the NSe(A) chemiluminescence could no longer be attributed to the Se + N\(_2\) reaction; rather a reaction between Se atoms and NF must be hypothesized to account for the emission:

\[
\text{Se + NF} \rightarrow \text{NSe + F} \quad \Delta H_0 = -19.7 \text{ kcal mol}^{-1}
\]

Since reaction 12 is not sufficiently energetic to populate the A

\[\text{(26) Sloan, J. J.; Watson, D. G.; Wright, J. S. Chem. Phys. 1979, 43, 7.}\]
Chemiluminescent Reactions of Group VI Atoms

The production of NO(A) to reaction 1 and the air afterglow to the absence of recombinations of O atoms with NO reactions 10 and 11. A more detailed investigation of the reaction was performed by the latter group who utilized a unique thermal source to generate N\(_2\) radicals. The radicals, produced in a small oven by thermally decomposing Na\(_2\)NO, were mixed with small concentrations of O atoms and the resultant chemiluminescence was observed. The \(\gamma\)-band and air afterglow emissions observed were attributed to reaction 1 and the O + NO recombinant reaction, respectively. By monitoring the intensity of the \(\gamma\)-bands as a function of \([O]\), they determined a rate constant for reaction 1 which is in close agreement with the value determined in this work. Further, our general observations on the \(\gamma\)-band emission concur with those of these studies. One of the conclusions of our experimental work is the lack of NO\(_2\)* chemiluminescence. Since reaction 1 forms NO at densities near the initial N\(_2\) densities and since the initial O atom densities are given by the O\(_2\) flow rates and the fractional dissociation for O\(_2\) (near 50%) the relative amounts of NO and O atoms in the flow reactor can be estimated. These densities were near 1 \(\times\) 10\(^{12}\) molecules cm\(^{-3}\) and 2.5 \(\times\) 10\(^{12}\) atoms cm\(^{-3}\) for NO(A) intensities typical of these experiments. An experiment was performed to check the OMA sensitivity for detecting the NO\(_2\)* chemiluminescence under these conditions. All flows of gases except O\(_2\) (i.e., O atoms) and He were removed and a flow of NO introduced. The OMA response as a function of added NO was then monitored. The air afterglow was not detectable for NO concentrations below 1 \(\times\) 10\(^{12}\) molecules cm\(^{-3}\) which is well below the NO densities generated by the O + N\(_2\) reaction when operated under nominal flow conditions for the O/F/H\(_2\)N\(_2\) system.

The photon yields measured for the O + N\(_2\) and Se + N\(_2\) reactions represent the flow of NO(A-X) and NSe(A-X) photons, relative to the limiting N\(_2\) flow, respectively. Most likely, the branching fractions reported herein are larger since collisional quenching and removal of N\(_2\) by other processes has not been taken into account. An increase in yields of the excited diatomics NO\(_2\)(a) and N\(_2\)(a) has been observed in the F (or C1) + H\(_2\)N\(_2\) systems when gases normally considered collisional deactivators (e.g., CO\(_2\) and SF\(_6\)) have been added to the flow reactors. These gases are believed to act as stabilizers of the fragile N\(_2\) radical, capable of removing the internal excitation of the N\(_2\) where the internal modes have been excited by the heat of the reaction. The yields of the excited halide diatomics have been observed to double on addition of the stabilizer.

The yield determined for the O + N\(_2\) reaction of 0.3% is in good agreement with the value determined by Liu and Coomber who also employed the O + NO reaction to calibrate the light collection efficiency of their detection system and whose definition of photon flux and yield is identical with our own. By passing dilute O\(_2\)/He mixtures through a microwave discharge to produce the requisite O atoms, they determined \(\phi^{NO_X}\) = 0.44%. To check for possible systematic errors associated with O atom source chemistry they made additional measurements using the rapid 2F + H\(_2\)O reaction to generate the O atoms. This reaction method \(\phi = 0.42%\), indicating that the yield, as expected, was independent of the manner in which the O atoms were produced.

Table I compares the reactions of the group VI atoms with N\(_2\) radicals. Without exception the yields in these reactions are quite low and even if doubled they clearly do not approach other R + N\(_2\) reactions, such as the N + N\(_2\) reaction where spin and orbital constraints have been shown to be strong. As noted above, to the extent that angular momentum constraints are operative, these reactions are driven to produce states correlating to N(\(^{1}\)D) + R(\(^{3}\)P), i.e., NO(B), NS(B), and NSe(A). The reactions of the heavier atoms (S and Se) do produce the expected states, although, aside from the low-lying quartet states (a *H\(_{1\Sigma}\) and B*V\(_{2\Sigma}\)) which are typically only observed through spectral perturbations, the NS(B**) and NSe(A**) are the only accessible states within the energy limitations of reactions 2 and 3. In contrast, the NO(B**) states is not allowed in the O + N\(_2\) reaction which produces the

\[ (27) \text{Liu, X. Ph.D. Thesis, University of Denver, 1989.} \]
NO($A^2\Sigma^+\ast$) state exclusively from several energetically allowed states. These observations indicate that the orbital angular momentum constraints are not strong in the group VI reactions.

A central issue in the group VI atom plus $N_2$ reactions is the question of energy disposal. The low yields suggest that these reactions may distribute their exothermicities in a purely statistical fashion with no dynamical constraints. In order to evaluate this assumption a statistical model\(^\text{28}\) was used to predict the statistical or "prior" branching fractions for the reactions. The computed statistical branching fractions, shown in Table I, are small and as such are broadly consistent with what was observed experimentally. This would support the view that there are no strong dynamical correlations in these reactions. Further, this is consistent with the orbital correlation diagram for group VI atom plus $N_2$ reactions\(^\text{28}\) which indicates a large number of mixed doublet and quartet surfaces available to the (R(P)) + $N_2$($X^1\Sigma_g^\text{+}$) reactions. However, the O + $N_2$ reaction is clearly unique among the group VI atom reactions since it does not generate the $B^2\Pi$ state (even in the more energetic O($D^1\Pi$) + $N_2$($X^1\Sigma_g^\text{+}$) reaction the $\beta$ bands are not observed) and the measured yield of the A state is substantially larger than can be accounted for by the prior distribution.

\(^{28}\) The statistical branching ratios were calculated by a model given by Alexander, M. H.; Dugdigian, P. J. J. Chem. Phys. 1981, 13, 11. Equations 11 and 14 were used to estimate the "prior" branching fraction $k^\ast/k^\ast$.

\[ k^\ast/k^\ast = \frac{g_i\sum [E_i' - (G_{\ast} + g_{\ast} + 1)]/[(B_{\ast} + \beta_{\ast})^{1/2}]}{g_i\sum [E_i' - (G_{\ast} + g_{\ast} + 1)]/[(B_{\ast} + \beta_{\ast})^{1/2}]} \]

where $g_i$ is a statistical weight factor (multiplicities times A degeneracy) for the product electronic state and where $E_i'$ taken as 8440 cm\(^{-1}\) for NO(A), 10203 cm\(^{-1}\) for NO(B) and 8299 cm\(^{-1}\) for NO(C), and 40,709 cm\(^{-1}\) for NS(X), and 32,501 cm\(^{-1}\) for NSe(X) are the total translational, vibrational, and rotational energies of the NR + $N_2$ product channels, respectively. $G_{\ast}$, $g_{\ast}$, and $\beta_{\ast}$ are the rotational and orbital angular momentum constraints, and the potential in the brackets remain real. Using the known spectroscopic constants\(^\text{54}\) for NO, NO, NS, and NSe and the calculated values for $E_i'$ and $E_i''$ the "prior" branching fractions for reactions 1-3 were calculated and the results are shown in Table I.

\(^{29}\) Applying the orbital correlation rules, as originally set forth by Schuler (Schuler, K. E. J. Chem. Phys. 1952, 21(4), 624) to the R(P) + $N_2$($X^1\Sigma_g^\text{+}$) reactions yields a total of 12 surfaces (3$A^1\Pi + 3A^1\Sigma^\ast$, 3$A^1\Sigma^\ast + 3A^1\Sigma^\ast$). In contrast, the reaction of a highly excited $\Sigma^\ast$ atom with NSe($X^1\Sigma_g^\text{+}$) would be more constrained having only two surfaces (3$A^1\Pi + 3A^1\Sigma^\ast$).