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FINAL TECHNICAL REPORT

CHEMICAL REACTIONS OF EXCITED NITROGEN ATOMS
FOR SHORT WAVELENGTH CHEMICAL LASERS

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EXECUTIVE SUMMARY

Two major goals of this program were to demonstrate clean, scalable chemical production of oxygen atoms (O) and cyanogen radicals (CN). These were to subsequently be used in the known efficient reaction of O and CN to produce $N(^2D)$. $N(^2D)$ contains $19,000\text{ cm}^{-1}$ of energy but is metastable and is not suitable as a laser. However, this metastability and the fact that reactions which start on excited state potential surfaces tend to produce excited products makes $N(^2D)$ attractive as a reagent in chemical reactions that produce excited state products that are suitable laser candidates.

Thus, our third goal was to study the reaction of $N(^2D)$ with a variety of halogen and oxygen atom containing species. The use of an excited reagent, system energetics and conservation of angular momenta all favor producing such interesting SWCL species as $NO(b)$, $NF(b)$, $NCl(b)$ and $NBr(b)$.

We were immediately successful in generation of oxygen atoms via our proposed two step process, $F + H_2O \rightarrow HF + OH$ followed by $F + OH \rightarrow HF + O$. Yields were 90% and there appear to be no processes preventing scaling production to any level of interest to SWCLs. However, we failed in production of CN radicals by our proposed method. Several early detection methods gave conflicting results but we eventually conclusively demonstrated that CN radicals were not produced in the reaction of F atoms and HCN. This created problems for our program, since generation and detection of CN was critical to all subsequent effort.

We explored the anomalous conversion of unknown products of the $F + HCN$ reaction by N atoms to C atoms as a potential source of CN via $C + NO/N_2O \rightarrow CN + O/NO$. We also explored the reaction of N atoms with C_2N_2 , both as a direct source of CN and as an indirect source via $N + CN \rightarrow N_2 + C$ and $C + NO/N_2O \rightarrow CN + O/NO$. We detected CN in all of these cases, both in spontaneous emission and by LIF. However, the production processes clearly were unsuitable for SWCLs.

In an effort to produce $N(^2D)$ by another process, we reacted NH_3 with F atoms, producing large amounts of electronically excited NH. This appears to produce $N(^2D)$ upon further reaction with F atoms. Evidence for this consists of observation of extremely high relative concentrations of $NF(b)$. Energetics of all processes considered dictates that this was produced by reaction of $N(^2D)$ with F_2 injected with the F atoms. We believe this system has high potential as an $NF(b)$ chemical laser and that elucidation of the detailed kinetic mechanism for production of $NF(b)$ is of fundamental interest and recommend it enthusiastically to basic researchers at more suitable institutions.

During the course of our efforts to produce CN via $C + NO/N_2O$, we utilized the $C + OCS \rightarrow CO + CS(a)$ reaction as a probe for C atoms. This reaction had been proposed to SDI/ISTO as a potential SWCL. To the best of our knowledge, this program was unsuccessful. Our work clearly shows that $CS(a)$ is indeed produced and that this system should remain a viable SWCL candidate for direct lasing of $CS(a)$ or as an energy transfer species.

After a one year hiatus, our program was restarted with a greatly reduced scope. We were successful in producing CN radicals in the reaction of Na atoms with ICN, BrCN, ClCN and $F_3C_3N_3$.

INTRODUCTION

This program was built upon the foundation of the known reaction of cyanide radicals, CN, and oxygen atoms, O, to produce carbon monoxide, CO, and metastable nitrogen atoms, $N(2p^3\ ^2D)$.¹ $N(^2D)$ yields are high, $\geq 85\%$.¹ This is not surprising considering that all of these species are, or are comprised of, elements in the first row of the periodic chart. Adiabatic reactions of such species tend to adhere rigidly to the principles of conservation of electron orbital and spin angular momenta. Thus, ground state $CN(X^2\Sigma^+)$ and $O(2p^4\ ^3P)$ are constrained to react on doublet and quartet potential energy surfaces. The doublet surface lowest in energy is ground state $NCO(X^2\Pi)$. This doublet surface also correlates to ground state $CO(X^1\Sigma^+)$ and excited $N(^2D)$, which cannot correlate to any of the quartet surfaces. On the other hand, ground state $N(2p^3\ ^4S)$ and $CO(X^1\Sigma^+)$ only correlate to NCO quartet surfaces, all of which are higher in energy than $O(^3P) + CN(X^2\Sigma^+)$. Thus, there are no energetically accessible and spin allowed reaction paths to permit production of $N(^4S)$ while there is at least one which is both spin allowed and energetically accessible. As a result, $N(^2D)$ yields should be as high as experiment has shown them to be.

It was our contention that $N(^2D)$ should react with a variety of molecules that contain weakly bonded halogen or oxygen atoms and produce electronically excited products that are suitable as lasers, i.e., $NO(B^2\Pi_r)$, $NF(b^1\Sigma)$, $NCl(b^1\Sigma)$ and $NBr(b^1\Sigma)$. If the molecule containing the oxygen (or halogen) atom is weakly bonded, then the reaction potential surface is only slightly perturbed from that for $N(^2D) + O(^3P)$ (or $X(2p^5\ ^2P_J)$) recombination and the residue of the oxygen (or halogen) atom donor serves as a convenient third body to carry off excess reaction energy. Thus, a major part of our effort was to screen several attractive oxygen atom or halogen atom donors to determine rate constants and product yields in reaction with $N(^2D)$. The other main part of our program was to demonstrate scalable chemical production of both O atoms and CN radicals for generation of $N(^2D)$.

Oxygen Atom Generation

Analysis of the energetics and known rate constants for the species involved in the reaction of F atoms and H_2O indicated that this should be an efficient O atom generator. Rate constants had been reported for the two sequential H atom abstraction reactions, (1) and (2), as well as the only significant interference, (3).

Reaction (3) was of concern because the introduction of O_2 into the flow permits undesirable side reactions, the most serious of which, reaction (4), would produce NCO which destroys $N(2p^3\ ^2D)$ by reaction (5).

F atoms could be generated, for our experiments, by microwave discharge of F_2 and CF_4 or, in a laser device, in an F_2 -rich F_2/H_2 combustor. However, when we attempted to generate O atoms by this chemistry using microwave discharge of CF_4 as the source of F atoms, we produced no oxygen atoms. We have subsequently concluded that this is due to any of a number of possible reactions of CF_n species with H_2O , OH or O, the most plausible of which is reaction (6), exothermic by approximately 2.6 eV. We experienced no such

difficulties when we used microwave discharge of F_2 as our source of F atoms. With a total flow of 430 SCCM producing 1 torr in the flow tube and a source of He make-up gas constantly adjusted to keep total pressure constant, we attained 90% dissociation of F_2 to produce 5.4 SCCM of F atoms ($N = 4.1 \times 10^{14} \text{ cm}^{-3}$) from 3 SCCM of F_2 . Into this we injected H_2O flows of 0.92 and 1.8 SCCM and measured, by titration with NO_2 , O atom flows of 0.79 and 1.7 SCCM ($N = 5.9 \times 10^{13}$ and $1.3 \times 10^{14} \text{ cm}^{-3}$) for yields of 86 and 94%, respectively. These numbers were obtained with factors of 3 and 1.5 more F atoms than required by stoichiometry. The value of 1.5 represents the limit of what we could attain due to the maximum flow of saturated H_2O solution allowed by the available flow controller and the minimum F_2 flow we could attain without its flow controller shutting off. The experimentally determined yields are higher than predicted by modeling from reported rate constants, indicating that uncertainties in the rate constants for reactions (2) and (3) have gone in favor of O atom production rather than O_2 production. We anticipate that no difficulties would be encountered in scaling O atom densities to much higher levels beyond that of generating higher concentrations of H_2O (attainable by heating.)

Cyanide Radical Production

While no rate constant had been reported when we proposed this program, the exothermicity of Reaction (7), 0.5 eV, and the known propensity of F

atoms to react by H atom abstraction led us to believe that this reaction would be a sure-fire CN radical source. We initially attempted to detect CN radicals formed in this reaction by multipass UV absorption. When we were not able to do so we expended considerable effort on improving our technique until we eventually concluded that either the uncertainties in extrapolating high temperature absorption data to room temperature rendered the technique unusable or else we were not producing CN. Since successful production and monitoring of CN was central to the success of our program, we initiated procurement of a nitrogen laser pumped dye laser system that would enable us to do laser-induced fluorescence on CN.

In the interim, we embarked on a series of experiments on the assumption that we were making CN but couldn't detect it. For these we injected O atoms (produced by titrating NO with N atoms from a microwave discharge) into a reacting flow of F and HCN to produce $N(^2D)$ by reaction (8). Large amounts of F and residual F_2 should have produced $NF(b^1\Sigma^+, a^1\Delta)$ via reaction (9).

Downstream injection of N_2O , NO_2 or Cl_2 (with care to minimize residual F atoms) could produce $\text{NO}(\text{B}^2\Pi_r)$ or $\text{NCl}(\text{b}^1\Sigma^+, \text{a}^1\Delta)$ via reactions (10), (11) or (12). We observed no excited products due to reactions (9)–(12), over a broad range of experimental conditions, indicating failure of reaction (7) to produce CN radicals or the existence of one or more fast loss processes.

Concurrently, we discovered that mixing F and HCN with active nitrogen (a mixture of ground state and excited state nitrogen atoms and molecules) results in a $\text{CN}(\text{B}^2\Sigma, \text{A}^2\Pi \rightarrow \text{X}^2\Sigma)$ flame followed by a long lived afterglow. Initially, we believed that the flame was caused by energy transfer from $\text{N}_2(\text{A}^3\Sigma_u^+)$ to CN, reaction (13), in competition with a loss mechanism for CN, reaction (14), and that the afterglow was N atom recombination, reaction (15).

(We further characterized the afterglow. This is described below.) The flame occurs both when HCN is injected into a mixture of F atoms and active nitrogen (i.e., active nitrogen is present as CN is formed) or when the active nitrogen is injected into the reacting flow of F and HCN, milliseconds down stream (i.e., active nitrogen is not introduced until well after the start and probable conclusion of the F + HCN reaction.) Various experiments verified that F atoms were required to be present and that N atoms in the active nitrogen were required. HCN and active nitrogen, without F atoms, produced only a very weak flame with no afterglow as did only $\text{N}_2(\text{A}^3\Sigma_u^+)$ (i.e., no N atoms) injected into a flow of reacting F + HCN. We attempted to estimate the F + HCN rate constant, k_7 , by injecting active nitrogen into the F + HCN reacting flow and monitoring $\text{CN}(\text{B}^2\Sigma, \text{A}^2\Pi \rightarrow \text{X}^2\Sigma)$ intensity at a point fixed relative to the active nitrogen injector. By varying the distance upstream of the active nitrogen injector at which we initiated the F + HCN reaction, we generated a profile of $\text{CN}(\text{B}^2\Sigma, \text{A}^2\Pi \rightarrow \text{X}^2\Sigma)$ intensity versus F + HCN reaction time. There were strong indications that the $\text{CN}(\text{B}^2\Sigma, \text{A}^2\Pi \rightarrow \text{X}^2\Sigma)$ intensity is not linearly related to $\text{CN}(\text{X}^2\Sigma)$ concentration. However, we believe the maximum we observed in the intensity profile should coincide with the maximum in a computer generated best-fit incorporating the F + HCN reaction and various loss processes. From this, we estimated $k_7 \approx 1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for the F + HCN reaction. This apparent low rate constant and the fact that products of the F + HCN reaction, presumably CN, were stable enough to be detectable by active nitrogen well downstream of their formation led us to construct a prereactor in which, by expansion of diameter of a section of flow tube, we added one second to the delay we could attain after mixing F and HCN. Within this section of slow moving gases the previously observed $\text{CN}(\text{B}^2\Sigma, \text{A}^2\Pi \rightarrow \text{X}^2\Sigma)$ flame collapsed to a few centimeters in the 4 inch diameter flow tube and was followed by approximately one foot (one second) of afterglow that changed from white to bluish white

over the length of the glow and then abruptly terminated in an orange "cap". The white to bluish white afterglow was due to atom recombination, i.e., reactions (15), (16) and (17). CN emission was clearly different from that

previously seen. $C_2(d^3\Pi_g \rightarrow a^3\Pi_u)$ Swan band emission peaked at the high v levels characteristic of the "high pressure bands" arising from carbon atom recombination into a dark quintet level and subsequent curve crossing to $C_2(d^3\Pi_g)$. Later in the program, the presence of atomic carbon was further demonstrated by injecting OCS into the blue-white end of the recombination glow and observing strong emission from $CS(a^3\Pi_r)$ at 362 nm, presumably by reaction (18), with simultaneous reduction in the intensities of the CN and C_2 emission bands

attributed to recombination processes.* As discussed above, the production of $CN(B^2\Sigma, A^2\Pi)$ by far downstream injection of active nitrogen into reacting F and HCN indicated formation of a product that was a precursor to $CN(B^2\Sigma, A^2\Pi)$. Other tests indicated that this could not be unreacted HCN. Energetics said it could not be FCN from reaction (7b). The production of C atoms from very

long lived species present in active nitrogen (presumably N atoms) with the $CN(B^2\Sigma, A^2\Pi)$ precursor (product of the F + HCN reaction) strongly supported the belief that reaction (7) produced CN which was destroyed by reaction (14), $N + CN \rightarrow N_2 + C$. We believed we were producing CN as proposed. This belief was further bolstered when Frost, et al.,¹² reported the rate constant for $F + HCN \rightarrow HF + CN$ to be $K_7(300K) = 3.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$.

However, despite the even more recent report of internal energy distributions of CN product from the F + HCN reaction by Johnston and Bersohn,¹³ we no longer believe that the room temperature reaction of thermal F atoms with HCN produces CN. Upon installation of a nitrogen laser pumped dye laser system, we were unable to detect any CN in any potentially accessible vibrational levels in the products of the reaction of F with HCN. When products of the F + HCN reaction were mixed with active nitrogen in the prereactor described above, we were able to detect $CN(X^2\Sigma)$ in the initial orange $CN(B^2\Sigma, A^2\Pi \rightarrow X^2\Sigma)$ flame. No $CN(X^2\Sigma)$ was detectable in the blue white afterglow region. Very strong CN LIF signals were obtained in the orange "cap" that terminated the afterglow region. But, from F + HCN alone, no signal. We do not believe that CN can be produced in a reaction and be undetectable while injection of

* It is worth noting that reaction of C with OCS, (18), was itself the subject of an SDIO/ISTO SWCL contract that, to the best of our knowledge, was unsuccessful because of lack of C atoms. We strongly support previous reports^{11,14} of the production of $CS(a^3\Pi_r)$ and recommend further study of this concept. We also recommend $4Na + CCl_4$ as a source of C atoms, known by us to produce intense $CS(a^3\Pi_r \rightarrow X^1\Sigma^+)$ emission when OCS is injected.

active nitrogen into the same mixture produces an afterglow that produces a strong signal more than one second later. We have detected CN produced in many different ways, described below, and are confident that if CN were produced by reaction (7), we would see it. We conclude that CN is not directly produced in the room temperature reaction of F and HCN. We believe that the $\text{HF}(v'=1)$ formation rate constant that Frost, et al.¹² measured was for a process other than reaction (7). [It is remotely possible that their filter system allowed photons from higher v levels to be monitored, i.e., $\text{HF}(v'>1 \rightarrow v''=v'-1)$, which might arise from other, more energetic HF producing processes. However, considering the reputation of those workers, there probably is not a facile explanation.] The more recent measurement of internal energy distribution of CN product from reaction (7) was made by 248 nm photodissociation of F_2 to obtain F atoms and probing the CN product by LIF under single collision conditions.¹³ F atoms produced in this way are extremely translationally hot and would not be relaxed under single collision conditions. Thus, there is no conflict between our results.

The failure of reaction (7) as a source of CN radicals was a major catastrophe for our program since we had based all subsequent reactions to generate and utilize $\text{N}(^2\text{D})$ upon its success. Accordingly, the remainder of the program, before and after our one year shutdown, was spent on attempts to find other sources of CN and to demonstrate the feasibility of reactions such as (9)-(12) that produced excited products suitable for SWCLs.

N Atom Generation

We initially explored N atom generation because of our need to have a stable supply during our experiments to use $\text{CN}(\text{B}^2\Sigma, \text{A}^2\Pi \rightarrow \text{X}^2\Sigma)$ emission as a $\text{CN}(\text{X}^2\Sigma)$ tracer in the reaction of F and HCN. We had observed that we obtained relatively high N atom densities shortly after gases were turned on and that production efficiency decreased during the course of our experiments. We subsequently determined that the primary cause was traces of F_2 in the N_2 supply lines. There are numerous reports in the literature that traces of O_2 or other species enhances the dissociation of N_2 in a microwave discharge. We subsequently determined that addition of less than one part per thousand F_2 in N_2 was capable of enhancing dissociation to incredible levels. Typically, we can convert greater than 5% of the energy in a 100 watt microwave discharge into broken N_2 bonds, which under our conditions gives c. 15 SCCM of N atoms and a number density of c. $1 \times 10^{15} \text{ cm}^{-3}$. We routinely generate and measure this level by titrating per reactions (19) and (20). It is

possible to do better. The mechanism responsible for this is unclear and it is interesting to note that N atom enhancement also occurs when F_2 is injected downstream of the discharge, instead. The process is certainly interesting and we recommend further investigation. It is also worth noting that the ability to produce high densities of N atoms also permits production of high densities of O atoms via reaction (19). We also utilized these high densities of N atoms to produce CN radicals and C atoms.

Production of CN Radicals by Reaction of N and C₂N₂

There have been numerous reports in the literature that CN(B²Σ, A²Π→X²Σ) emission results when C₂N₂ is injected into active nitrogen. In view of the high densities of nitrogen atoms we are able to produce and several fast or highly exothermic reactions, (21) - (28), we believed we should be able to make CN radicals with N and C₂N₂. The initiating mechanism is controversial - it is not clear whether reaction (21) or reaction (22) starts the process.

Our modeling, however, has shown that regardless of the initiation mechanism, the process ends up being a C atom catalyzed reaction consuming N atoms and C₂N₂ and producing C atoms, N₂ and cyanogen polymers. By varying the ratio of reactants, N and C₂N₂, we can affect the ratios of intermediates and, if the kinetics cooperates, it should be possible to produce lots of CN. We performed a series of experiments and, indeed, do make lots of CN, attaining CN LIF signals up to 3 orders of magnitude more intense than seen in the F + HCN + N system. As might be expected from the listed reactions, the system is extremely dirty and quickly coated the walls of the system with a carbon rich C/N polymer. However we nevertheless attempted to use this reaction to make N(²D). By increasing the amount of N atoms available and coinjecting NO with the C₂N₂ we planned to cogenerate O atoms by reaction (19), $N + NO \rightarrow N_2 + O$. In addition C atoms are known to react (29) with NO to produce

CN and O. Of course, NO and O could react with many of the other species in the system but analysis of the potential reactions indicates that they are benign and generally only affect efficiency. We anticipated detecting N(²D) by looking for emission from NCl(b¹Σ⁺) when Cl₂ was injected into the flow. However, when we turned on NO, we immediately observed a change from the typical dirty orange CN flame to a clean violet flame. We verified that the reaction no longer deposited polymer on clean walls. CN emission was now primarily due to intense CN(B²Σ→X²Σ) emission on Δv=0 near 388 nm with a strong contribution in the blue due to Δv=-1 near 422 nm and Δv=-2 near 461 nm. There was also weak CN(A²Π→X²Σ) emission in the yellow and red. We believe this strange behavior is due to direct chemical production of CN in

the $B^2\Sigma$ state, presumably involving $N(^2D)$ and another species such as C_2N or C_2 . Addition of Cl_2 to this system produced a strong yellow flame. With Cl_2 held constant, the flame increased in intensity as NO was turned off. The yellow was again due to CN emission, primarily from an unusual vibrational distribution in the the $A^2\Pi$ state, peaked near $v'=10$. [$CN(B^2\Sigma, v'=0)$ is resonant with $CN(A^2\Pi, v'=10)$]. It is also unfortunate that red $CN(A^2\Pi \rightarrow X^2\Sigma)$ bands overlapped possible emission from $NCl(b^1\Sigma^+)$. We were thus unable to determine whether $NCl(b^1\Sigma^+)$ was produced while NO was present (to produce O and $N(^2D)$). Plans to unravel this system and to try to produce $NO(B^2\Pi_r)$ in this system by replacing NO and Cl_2 with N_2O were abandoned when the contract was put on hold and resumed a year later at a reduced scope. We still believe that, were this reaction to be run, $NO(B^2\Pi_r)$ would be produced in the soup generated by mixing C_2N_2 , N and N_2O . Key products from the reaction of C_2N_2 and N are N , C and CN . These would interact with N_2O as follows:

Contingent upon some unknown rate constants, modeling indicates this reaction can proceed with reasonable efficiencies and the production of $NO(B^2\Pi_r)$ in reaction (10) is known. However, if one could start the reaction with C atoms as a reagent and avoid attempting to make $NO(B^2\Pi_r)$ [or $NCl(b^1\Sigma^+)$] in the middle of the $N + C_2N_2$ reaction mess, one could be more efficient.

Production of CN by Reaction of C and NO or N_2O

Late in the program, after we had clearly demonstrated the presence of atomic carbon in the reaction of HCN , F , and N atoms by the observations of "high pressure" Swan Band emission and by reaction (18), we expanded C atom production to the $C_2N_2 + N$ atom system in an attempt to clean it up. To do this, we attempted to run the reaction very rich in N atoms so as to drive it towards C atoms + residual N atoms. We were relatively successful in that we able to obtain strong $CS(a)$ emission spectra when OCS was injected.

We were in the process of determining whether we would be able to produce a clean flow of N and C atoms when shutdown occurred. This effort was not resumed when we restarted. We believe the $HCN + F + N$ system is the cleanest source of C atoms, but C atom density is very low. The $N + C_2N_2$ system is not nearly as clean but we believe higher C atom densities are possible. Also, as we had already seen for the $N + C_2N_2$ reaction system, injection of NO results in a clean reaction. Accordingly, we believe that this system would have demonstrated that the chemistry was all in place to produce a SWCL as proposed. However, the kinetics were so ugly (and unknown) that it is very unlikely that we would be able to sort them out, much less optimize them for a SWCL. Accordingly, we determined that finding a new source for CN radicals was essential if anyone was to actually demonstrate a SWCL based on O atom/ CN radical/ $N(^2D)$ chemistry.

Production of CN by Effect of Active Nitrogen of Cyanogen Halides.

In order to evaluate other reactions as CN generators, we needed to have a readily available source of CN radicals to permit tuning and aligning our LIF laser. Preferably, this would be one that didn't require a full second of reaction time in a large prereactor and did not render the flow tube opaque. Fortunately, we discovered that injection of active nitrogen into flows of ClCN, BrCN and ICN resulted in clean, long-lived $\text{CN}(\text{B}^2\Sigma, \text{A}^2\Pi \rightarrow \text{X}^2\Sigma)$ flames that provide excellent $\text{CN}(\text{B}^2\Sigma \rightarrow \text{X})$ LIF signals on the $\Delta v = -1$ sequence. We observed, for all three precursors, $\text{CN}(\text{B}^2\Sigma, v' \leq 3)$. There is insufficient energy in $\text{N}_2(\text{A}^3\Sigma_u^+)$ to directly produce these levels from the cyanogen halides and, if produced in a two step process, we would expect higher vibrational levels to be present, even allowing for the large Franck-Condon Shift in $\text{N}_2(\text{A}^3\Sigma_u^+)$. Regardless of the pump mechanism, this is an outstanding source of CN radicals for tuning, aligning and other wise checking out instruments for CN spectroscopy.

Production of CN Radicals by Reaction of Cyanogen Halides with Sodium.

We had previously initiated the use of Broida-type ovens to generate Na atoms under another program to study reactions with halocarbons. Experience gained there led us to design a version with preheated carrier gas and stainless steel screen "wicking". A series of calibration runs in which we varied preheater or heater voltages and carrier or sweep gas flows and compositions allowed us to generate a family of plots of these variables vs temperature that, in conjunction with sodium (or other alkali metal) vapor pressure vs temperature curves, permitted us some degree of control over sodium concentrations in the reaction region. We then injected a series of cyanide/halogen compounds into the flow of Na atoms and probed for formation of cyanide radicals formed in reactions (31)-(34).

In all cases, except for the reaction of Na with FCN, the undesirable reaction channel that forms NaCN is more exothermic than the channel forming CN radicals. The free enthalpies for formation of CN radicals from ClCN and ICN indicate that the reactions should not occur. Only for BrCN and FCN does thermodynamics predict formation of CN product and in the case of BrCN, CN production must compete with a channel that is approximately 7 times more exothermic.

Despite this gloomy outlook, we observed very strong CN LIF signals from ClCN, BrCN and ICN reacting with Na. We have concluded that yields increase in the order ICN, BrCN and ClCN, although this is very tentative since

conditions from one reaction to another were not reproducible regarding actual amounts of cyanogen halide available for reaction. Heat from the sodium oven causes decomposition of cyanogen halides and we are not certain we were able to entirely eliminate this as a factor. In addition cyanogen iodide has a very low vapor pressure and purified samples were very dilute mixtures in argon. We can not be certain that these low concentrations were not significantly further reduced by adsorption on, or reaction with, the delivery system. We were unable to make measurements of absolute CN yields. However, CN LIF signals were very strong, comparable to those from the N atom + C₂N₂ flames. We do believe the undesirable channel producing NaCN is also open. Weak Na emission (3p ²P_{3/2,1/2} → 3s ²S_{1/2}) is visible at the point of cyanogen halide injection. The only reaction with sufficient energy that could conceivably be occurring might result from halogen atoms produced by reactions (31b), (32b), (33b) or (34b). Only very small amounts of Na₂ are present in our system, but these could react with the halogen atoms in reaction (35),

which is exothermic enough to produce excited Na. We also attempted to synthesize FCN to run reaction (31a) which, because of the endothermicity of the undesirable channel, was the most promising CN generation reaction. Unfortunately, we were not able to obtain the precursors required for the easier synthetic routes and were forced to attempt to make FCN by decomposition of cyanuric trifluoride, F₃C₃N₃, a six member ring polymer of FCN, and by decomposition of trifluoro acetonitrile, CF₃CN. Discharge decomposition of F₃C₃N₃ and CF₃CN provided us only with an inert fluorocarbon and N₂ so we were unable to compare the production of CN from FCN with the other cyanogen halides. However, we have discovered that Na vapor reacts directly with F₃C₃N₃ to give the strongest CN LIF signals of any of the cyanogen/halogen compounds. (CF₃CN does not react directly with Na. Products of the interaction of active nitrogen and CF₃CN do react with Na, presumably because, by comparison to CF₄, the initial abstraction by Na of an F atom from CF₃CN is endothermic.) This area is ripe for further investigation. (If one does so, one should be aware of the fact that ClCN and, presumably, all cyanogen halides are remarkably efficient at turning vacuum pump oil into a high viscosity polymer. This can easily and safely be avoided by wrapping the outlet end of the flow tube in a heating tape.)

Production of NF(b)

While blocked from producing N(²D) via the O + CN reaction, we examined an alternate approach. By analogy to the H + NF₂ reaction, known to produce NF(a¹Δ, b¹Σ⁺) and N(²D) via reactions (36) and (37), we attempted to produce NF(b¹Σ⁺) by a similar sequence followed by reaction of N(²D) with F₂.

There are a very large number of cross reactions possible in this system, but modeling with known rate constants and estimates of unknowns showed us that excited product yields could be very good. Experimentally, we observed an apparently faint greenish white flame. Spectra of this flame show that much, if not most, of the light emitted by this flame is on the $\text{NH}(\text{A}^3\Pi_i \rightarrow \text{X}^3\Sigma)$ $\Delta v=0$ and $\Delta v=-1$ sequences near 336 nm and 375 nm, respectively, and on $\text{NH}(\text{c}^1\Pi \rightarrow \text{a}^1\Delta)$ $\Delta v=0$ and $\Delta v=-1$ sequences near 325 and 363 nm, respectively. Additional contributions, in the visible, come from $\text{N}_2(\text{B}^2\Sigma \rightarrow \text{A}^2\Pi)$ emission (possibly from reactions of nitrogen atoms with NH^* or cross reactions of NH^*) and, most importantly, from $\text{NF}(\text{b}^1\Sigma^+, v' \leq 2)$. The only energetically feasible mechanism we can identify for chemical production of $\text{NF}(\text{b}^1\Sigma^+)$ is the reaction of $\text{N}(^2\text{D})$ with residual F_2 from the microwave discharge production of F atoms. By correcting the observed intensities on the various transitions for the differences in radiative lifetimes, we estimate that the concentration of $\text{NF}(\text{b}^1\Sigma^+)$ is about three order of magnitude higher than that of other species. It is also apparent that, at the density of F atoms available, almost all $\text{NH}(\text{A}^3\Pi_i)$ and $\text{NH}(\text{c}^1\Pi)$ decay radiatively, not reactively. Therefore, we conclude that the $\text{NF}(\text{b}^1\Sigma^+)$ precursor is some other excited state, probably metastable $\text{NH}(\text{a}^1\Delta)$. It is also apparent that it would be possible to beat the $\text{NH}(\text{A}^3\Pi_i)$ and $\text{NH}(\text{b}^1\Sigma^+)$ radiative rates with F atoms densities on the order of 1 torr and, thus, utilize these excited species as additional sources of excited NF species. We believe this system has very high potential as a source of $\text{NF}(\text{b}^1\Sigma^+)$ and should be further explored.

Summary of Accomplishments

Accomplishments of this program include the following:

1. Scalable, chemical generation of oxygen atoms by reaction of fluorine atoms and water vapor.
2. Production of nitrogen atom densities of $1 \times 10^{15} \text{ cm}^{-3}$ with 5% electrical efficiency by injecting trace amounts of fluorine into microwave discharged nitrogen.
3. Production of cyanide radicals by reaction of high densities of N atoms with cyanogen.
4. Production of carbon atoms by reaction of nitrogen atoms with cyanogen or with fluorine atoms and hydrogen cyanide.
5. Confirmation that the reaction of carbon atoms and carbonyl sulfide produces $\text{CS}(\text{a}^3\Pi_r)$, as predicted by conservation of electron spin and orbital angular momenta and as proposed by others under another SWCL program.
6. Production of cyanide radicals by injection of cyanogen halides into active nitrogen and use as spectroscopic calibration source.
7. Demonstration that sodium atoms react with cyanogen chloride, bromide and iodide and with cyanuric trifluoride to produce cyanide radicals.
8. Demonstration of the potential utility of the fluorine atom plus ammonia reaction system in the production of $\text{NF}(\text{b}^1\Sigma^+)$ via $\text{N}(^2\text{D}) + \text{F}_2$.

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SIGNATURE PAGE

20 December 1989

(Date)

A handwritten signature in dark ink, appearing to read 'William L. Nikolai', written over a horizontal line.

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A handwritten signature in dark ink, appearing to read 'Don Gardiner', written over a horizontal line.

Donald S. Gardiner, Manager
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