PSI TR-71

Investigation of Induced Unimolecular Decomposition for Development of Visible Chemical Lasers

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ABSTRACT

This report summarizes progress during the second quarterly period of the subject contract. The methods available for the production of excited electronic states following azide decomposition are summarized. It is concluded that an experiment designed to study the kinetics of and branching ratios for electronically excited products from azide radical reactions will be most productive in elucidating excitation mechanisms for potential chemical lasers. A flow reactor is described in which these studies may be undertaken. The major feature of this apparatus is a clean azide radical source based upon the thermal decomposition of solid, ionic azides. The construction of the experimental apparatus has been started.

Summary

During this second quarterly period of Contract No. EY-76-C-02-2920.*000, the design of an experiment was completed, the relevant equipment ordered, and the apparatus is now under construction. An experiment was selected which permits (i) the production of N_3 radicals in a clean flow environment, (ii) the quantitative measurement of various kinetic rate constants of direct significance to the overall goal of this program, and (iii) the limited study of the spectroscopy of excited electronic states produced in the reactions.

This experiment was designed after careful consideration of the many kinetic and spectroscopic issues concerning azide chemistry which were elucidated during the investigation of Task 1, Literature Survey of Azides. The experiment selected is fairly general in nature and should provide a considerable amount of data on issues of direct importance to the application of azide chemistry to the production of an efficient, scalable short wavelength laser. Also, the experiment can be readily modified, e.g., with photolysis initiation of selected gaseous azide compounds, at a later stage of this investigation.

During the next reporting period, the experiment should become operational and initial data will be acquired. In addition, the laser modeling task will be started.

LIST OF TABLES

TABLE OF CONTENTS

Introduction

The following report summarizes technical progress during the second quarterly period of ERDA Contract No. EY-76-C-02-2920.*000, "Investigation of Induced Molecular Decomposition for Development of Visible Chemical Lasers". It has been clearly established that a long term need exists for efficient, short wavelength laser devices for laser fusion application. It is the goal of the research program described herein to investigate a class of compounds, azides, which in principle, could provide a source of excitation for a short wavelength chemical laser. Azides are a class of energy-rich molecules which can be decomposed via a variety of means, i.e., thermally, photolytically, and chemically, into a number of possible exothermic reaction channels. There is substantial evidence that for many azides certain reaction channels lead to excited electronic state products. However, much of the state-specific kinetics, branching ratios, spectroscopy, energetics, etc. are not known in sufficient detail. It is the initial goal of this program to investigate enough of the fundamental issues to provide the data necessary to evaluate the utilization of azides in a visible chemical laser.

This research effort is divided into several tasks. Task 1 involved a thorough review of the extensive technical literature concerning azides, emphasizing reaction mechanisms and kinetics. This first task was reviewed in detail in the first Quarterly Progress Report.[1] The results of Task 1 are a necessary foundation for Task 2, the planning and execution of an experimental program to study decomposition channels of selected azides. The major activity of the second quarterly period has been to plan the experimental program and to design and construct an experimental apparatus. The results of this experimental program together with all other available information will be evaluated to determine the possible utilization of azides or azide-like molecules in a short wavelength chemical laser (Task 3). Finally, since the fundamental data obtained in this study can provide more complete understanding of reaction mechanisms for induced decomposition, it is planned to interact with theoretical efforts in this area (Task 4).

In the First Quarterly Progress Report,[1] we reviewed the technical literature relating to the physics and chemistry of azides, with particular emphasis upon the mechanisms of decomposition of azides. The effort during this past reporting period has been aimed at the development of an experimental program which will give detailed information on the energy carrying products of azide decomposition necessary for use in a potential laser device. The initial experiments have been designed, and an apparatus is being assembled. In this report, we shall outline briefly the important features relating to azide decomposition which have been selected for study in the experimental phase of the program. Lastly, we shall describe the apparatus which we have designed for these preliminary experiments.

<u>Summary of Task 1</u>

The class of compounds known as azides may be subdivided into two groups, covalent and ionic. The covalent azides comprise the organic and organometallic compounds and the inorganic azides of non-metals such as hydrazoic acid and the halogen azides. The ionic azides are salts of the alkali and alkaline earth elements and a few heavy metals such as lead, thallium, and silver. These two groups have different decomposition mechanisms which will affect the form in which electronic excitation may be produced following decomposition.

The covalent azides decompose to give a nitrene (an RN radical) and molecular nitrogen (see Table I, cases A1 and A2). Much of the evidence available indicates that for simple azides both photolytic and thermal decomposition give almost exclusively a nitrene in the first excited singlet state (Table I, A2). Thus, the induced decomposition of covalently bonded, organic azides contains the potential for rapid production of large concentrations of electronically excited products. The practical utilization of these systems in laser devices depends primarily upon the reactivity of the excited nitrenes as well as upon their spectroscopy.

The ionic azides decompose to give the azide radical. This occurs because the primary step in the decomposition involves the dissociation of the azide ion in the crystal lattice into a free electron and the azide radical (see Table II). The azide radical is a highly endoergic species ($\Delta H_f = 4.4$ eV)[2], many of whose reactions have been shown to be chemiluminescent[2] (Table III).

TABLE I

Decomposition Mechanism of Covalent Azides

A. General Case: RN_3

			Enthalpy Change
1.	Forbidden[a]	$RN_3\ (^1A_1) \xrightarrow[\text{or } \Delta]{h\nu} RN\ (^3A_1) + N_2\ (X^1\Sigma_g^+)$	0.4 - 1.3 eV
2.	Allowed	$RN_3\ (^1A_1) \longrightarrow RN^*\ (^1A_1) + N_2\ (X^1\Sigma_g^+)$	1.5 - 2.0 eV
3.	Allowed[a]	$RN_3\ (^1A_1) \longrightarrow R\ (^2A_1) + N_3\ (X^2\pi_g)$	~ 3.5 eV

B. Specific Example:

1.	$HN_3\ (^1A_1) \xrightarrow{h\nu}$	$NH\ (a\ ^1\Delta) + N_2\ (X^1\Sigma_g^+)$	1.96 eV
		$NH\ (c\ ^1\pi_g) + N_2\ (X^1\Sigma_g^+)$	5.77
		$H\ (^2S_{1/2}) + N_3\ (X^2\pi_g)$	3.55 eV[b]
2.	$NCN_3\ (^1A_1)$[c] $\xrightarrow{h\nu}$	$NCN\ (a\ ^1\Delta) + N_2\ (X^1\Sigma_g^+)$	

a. If this pathway occurs, it will be of minor significance compared to pathway 2.

b. This channel accounts for at most 10% of the total decomposition. No experiment has presented unequivocal evidence either for or against this pathway.

c. Kroto et al.[3] have shown that all of the N_3 produced in NCN_3 photolysis is the result of secondary processes.

TABLE II

The decomposition Mechanism of Ionic Azides

$(M^+ N^-_3)$

$$N_3^- \xrightarrow[\text{or } \Delta]{h\nu} N_3 + e^- \tag{1}$$

$$M^+ + (M)_n + e^- \longrightarrow (M)_{n+1} \tag{2}$$

$$2\,N_3 \longrightarrow 3N_2 + 8.8\text{ eV} \tag{3}$$

TABLE III

Chemiluminescent Reactions of N_3

$$X + N_3 \rightarrow XN^* + N_2$$

Reactant Species X	Observed Products (XN^*)	Excitation Energy (eV)
N_3	$N_2\ (A\ ^3\Sigma_u^+)$ or $N_2\ (B\ ^3\Pi_g)$[a]	6.3, 7.4
Cl	$NCl\ (b\ ^1\Sigma^+)$[b]	1.86
Br	$NBr\ (A\ ^1\Sigma^+)$[b]	1.83
O	$NO\ (A\ ^2\Sigma^+)$, $NO\ (B\ ^2\Pi)$[b]	5.45, 5.7
N	$N_2\ (B\ ^3\Pi_g)$[b]	7.4

[a] K. H. Welge, J. Chem. Phys. 45, 166 (1966) and Ref. 1.

[b] T. C. Clark and M. A. A. Clyne, Trans. Faraday Soc. 66, 877 (1970).

Thus, the production of electronically excited species in the decomposition of ionic azides will be determined by reactions of the azide radical subsequent to its liberation from the parent azide in the primary decomposition step.

In a few covalently bonded azides, the primary decomposition may involve the production of the azide radical (Table I, A3). This class includes certain of the organometallic azides and perhaps tertiary organic azides. In addition, secondary reactions between nitrenes and the parent azide have been shown to produce the azide radical.[3,4] Thus the study of azide radical kinetics is also relevant to the production of electronically excited species in the decomposition of covalent azides.

Summary of Task 2

The brief discussion above shows that electronically excited species may be produced in the induced decomposition of azides in essentially two ways, either in the direct decomposition of covalently bonded compounds to produce excited singlet nitrenes, or in the reactions of the azide radical which has been produced either in the primary decomposition step of ionic azides or in secondary reactions following decomposition of covalent azides. In order to evaluate the first reaction scheme, in terms of potential laser devices, we need to understand the spectroscopy and kinetics of singlet nitrenes. For the second method of excited-state production, a detailed knowledge of the products and kinetics of azide radical reactions is required.

We have concluded that the experimental study of azide radical reactions is a more fruitful avenue to follow in the initial experiments. The study of azide radical kinetics is more general in nature, since the azide radical is the important species from the standpoint of extracting chemical energy in all of the ionic decompositions. Secondly, the azide radical could be an important energy carrying species in the covalent decompositions due to rapid reaction between the electronically excited singlet nitrene and the parent azide. Finally, a number of simple nitrenes may be formed in reactions between atoms or free radicals and the azide radical, thus giving a source of nitrenes for spectroscopic or kinetic studies. Thus, most of the major kinetic and spectroscopic aspects of azide decomposition for laser utilization are amenable to investigation in a system based on azide radical reactions.

Accepting this decision to study the reactions of the azide radical, it is necessary to develop a system in which the relevant species and kinetics may be observed. There are four methods by which the azide radical may be formed (see Table IV): (i) as a secondary product in the photolysis of covalent azides; (ii) direct photolysis of certain covalent azides such as tertiary organic azides; (iii) chemical production, such as in the reaction between chlorine atoms and chlorine azide; and (iv) the thermal or photolytic decomposition of inorganic azides. The first two methods contain the drawback that reactive species in addition to the azide radical will be present in the system, which will complicate the kinetics. Azide radicals produced by method(i), however, have been observed in absorption.[5,6]

In order to produce azide radicals via chemical methods, a rapid reaction is required; but reactants and products from the primary reaction must not react rapidly with azide radical. Table V summarizes the known reactions which will produce the azide radical, and of the azide radical with the primary reactants. Of the reactions listed, only that between Cl atoms and ClN_3 appears to be sufficiently fast to be potentially useful for N_3 production. The utility of this reaction depends upon whether the subsequent reaction between Cl and N_3 is slow as has been indicated by Clark and Clyne,[2,7] or fast as it is thought to be by Combourieu and co-workers.[8] Other reactions not listed may work, but no other quantative information exists so that finding a suitable chemical source for azide radicals could become a lengthy trial-and-error procedure. However, chemical methods have been shown to produce N_3,[2] so they may not be dismissed completely from further consideration.

The fourth possibility listed above, i.e., the thermal or photolytic decomposition of ionic azides is a method on which direct information is sparce, but it is also the method which affords the best opportunity to develop a completely clean system in which to study azide radical kinetics. There are potentially no other reactive species in the reactor. It is known that large quantities of nitrogen gas are evolved when the ionic azides are decomposed.[9] This has always been assumed to arise from the bimolecular recombination of the azide radical which is the primary species assumed to result from the decomposition; however, little direct evidence exists to support this view.

TABLE IV

Methods of N_3 Production

A. As a secondary product in covalent azide decomposition

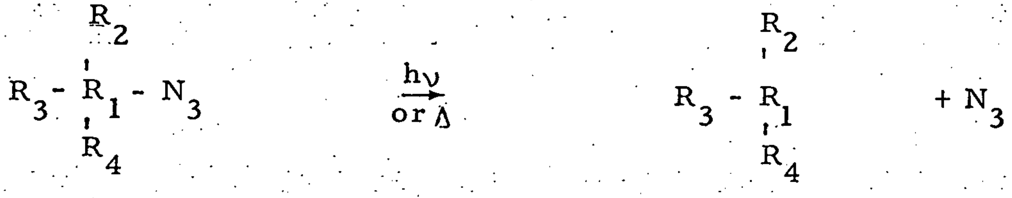
1. General: $RN^{*}({}^{1}A_{1}) + RN_3 \longrightarrow R_2N + N_3$

2. Specific: $NH\,(a^{1}\Delta) + HN_3 \longrightarrow NH_2 + N_3$ $K \sim 9 \times 10^{-11}\ \mathrm{cm^{3}\,molec^{-1}\,s^{-1}}$[a]

b. $NCN\ (a^{1}\Delta) + NCN_3 \longrightarrow N_3 +$ "other products"[b]

c. $NCl^{*} + ClN_3 \longrightarrow NCl_2 + N_3$[c]

B. Direct Decomposition of tertiary covalent azides[d]



$$R_3 - \underset{R_4}{\overset{R_2}{R_1}} - N_3 \xrightarrow[\text{or } \Delta]{h\nu} R_3 - \underset{R_4}{\overset{R_2}{R_1}} + N_3$$

C. Chemical Production

1. General: $X + RN_3 \longrightarrow RX + N_3$

2. Specific: see Table V

D. Ionic Decomposition[e]

$$N_3^{-} \xrightarrow[\text{or } \Delta]{h\nu} N_3 + e^{-}$$

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a. R. J. Paur and E. J Bair, Int. J. Chem Kinet. 8, 139 (1976).

b. H. W. Kroto, T. F. Morgan and H. H. Sheena, Trans. Faraday Soc. 66, 2237 (1970).

c. Inferred from the observation of N_3 in photolyzed ClN_3.

A. E. Douglas and W. J. Jones, Can. J. Phys. 43, 221 (1965).

d. The evidence for this process is indirect. R. A. Abramovitch and E. P. Kyba in The Chemistry of the Azido Group, S. Patai, ed., New York: John Wiley, 221-329 (1971).

e. See Table II.

TABLE V

Chemical Production of N_3 and Competing Destruction Reactions

	Reaction	Rate Constant (cm^3 $molec^{-1}$ s^{-1})
A.	Formation Reactions[a]	
	ClN_3 + Cl	3.7×10^{-12}[a]
	H	$\gtrsim 2 \times 10^{-13}$[b]
	O	c
	N	c
	Br N_3 + Br	c
	HN_3 + H	$1{\cdot}1 \times 10^{-14}$[d]
	N	5×10^{-15}[d]
B.	Destruction Reactions	
	N_3 + Cl	$>4 \times 10^{-12}$[a] $2{\cdot}2 \times 10^{-14}$[e]
	Cl_2, ClN_3	"slow" [a,c]
	Br	c
	N	c
	O	c
	HN_3	$2{\cdot}2 \times 10^{-11}$[f]
	N_3	$\sim 3 \times 10^{-10}$[g] 5×10^{-12}[e]

a. J. Combourieu, G. Le Bras, G. Poulet, and J. L. Jourdain, XVIth Int. Comb. Symp. Boston (1976).

b. The rate constant given is for reaction to form vibrational levels V = 1 and 2 of HCl(X) W. W. Rice and R. J. Jensen, J. Phys. Chem. 76, 805 (1972).

TABLE V (Con't)

c. T. C. Clark and M. A. A. Clyne, Trans. Faraday Soc. 66, 877 (1970). Because these authors could not observe N_3 in the O, N + ClN_3 systems in contrast to the situation in the Cl(Br) + Cl (Br) N_3 systems, they infer that $k_{X + N_3} > k_{X + ClN_3}$ for X = Cl, Br. Based upon their observations, we estimate that $k_{X + ClN_3} > 1 \times 10^{-12}$ cm^3 molec^{-1} s^{-1} for all X.

d. G. Le Bras and J Combourieu, Int. J. Chem. Kinet, 5, 559(1973).

e. T. C. Clark, Ph.D. Thesis, Queen Mary College (Univ. of London), London, U. K. (1969).

f. R. J. Paur and E. J. Bair, Int. J. Chem. Kinet. 8, 139 (1976).

g. R. J. Paur, Ph. D. Thesis, Indiana University, Bloomington, Indiana (1973).

It is also known that the decomposition of alkali azides in a flowing system is a good method for the production of alkali atoms.[10] By analogy, one would expect that the other decomposition product, i.e. N_3, would also be formed readily. Small quantities of the azide radical have been observed mass spectrometrically in the thermal decomposition of potassium azide,[11] but no quantative estimates of the yield have been made. Finally, in a series of experiments encompassing several decades, Audubert[12] showed that several ultraviolet bands between 190 and 260 nm could be observed in the thermal decomposition of a number of ionic azides. The crude spectrum which he was able to measure (his resolution was no better than about 5 nm) was independent of the cation in the azide salt. The most logical candidates for this emission are species produced either directly from the recombination of azide radicals (e.g. N_2 ($A\ ^3\Sigma_u^+$)) or indirectly in reactions of the various species present in air with the azide radical or with metastable nitrogen formed in the recombination of the azide radical. Thus, although there is very little direct evidence that the thermal or photolytic decomposition of ionic azides does indeed produce significant concentrations of azide radicals, the indirect evidence indicates that this approach should work; and, furthermore, there should be no other reactive species in the reactor. The alkali atoms formed in the decomposition will be rapidly pumped by the vessel walls. In any case alkali atoms should not be reactive towards the azide radical since the more easily handled ionic azides are composed of metals which do not form stable nitrides. Thus, we have decided to try to produce azide radicals for subsequent study by the decomposition of ionic azides. An additional advantage arising from the study of ionic decomposition is the potential benefit for eventual laser application which may be derived from the understanding of condensed-phase decomposition.

Azide radical kinetics may be studied most conveniently in a flow system which provides a more efficient evolution of N_3 into the gas phase because the azide radicals may be swept away from the surface of the decomposing salt by a flow of gas. This permits a separation of the azide radical source from the observation region, which, in turn, eliminates mechanistic complications occuring in a system in which all reagents are mixed in the same region. Furthermore, a flow system simplifies the analysis with respect to time resolution and gaseous reagent mixing, and, in addition, offers the opportunity to determine absolute azide radical concentrations by chemical titration techniques.[13]

The flow system which we have designed for our initial experiments is shown in Fig. 1. The azide radicals are to be liberated in the thermal decomposition of sodium azide at temperatures between 300 and 400°C. The sodium azide rests upon a pyrex fritted disk which has been blown into a section of pyrex tubing wrapped with heating wires. A small flow of inert gas passes through the fritted disk and sweeps the azide radicals out of the oven and into the main flow tube. Spectroscopic observations may be made either along the axis of the horizontal flow tube in order to enhance light collection efficiency, or at a number of windows normal to the axis of the horizontal tube. This latter configuration allows temporal resolution, as the spectrometer used for detection may be moved readily from one observation window to another. The azide-oven tube enters the vertical section of the flow tube through a sliding o-ring seal. Therefore, time resolution also may be achieved by changing the position of the azide oven relative to a fixed observation position. Reagents to be used in studying reactions of azide radicals with other species may be introduced either with the bulk gas flow which enters near the bottom of the vertical tube, or through the reagent inlet centered along the axis of the vertical section at its top. The system is pumped by a 500 $l\ min^{-1}$ mechanical pump (Precision D500) which, after allowing for conductance losses, will give a bulk flow velocity of about 10^3 $cm\ s^{-1}$ in the 25 mm i.d. flow tube. Thus the time resolution will be on the order of a millisecond which is suitable for measuring rate constants between 10^{-14} and 10^{-11} $cm^3\ molec^{-1}\ s^{-1}$.

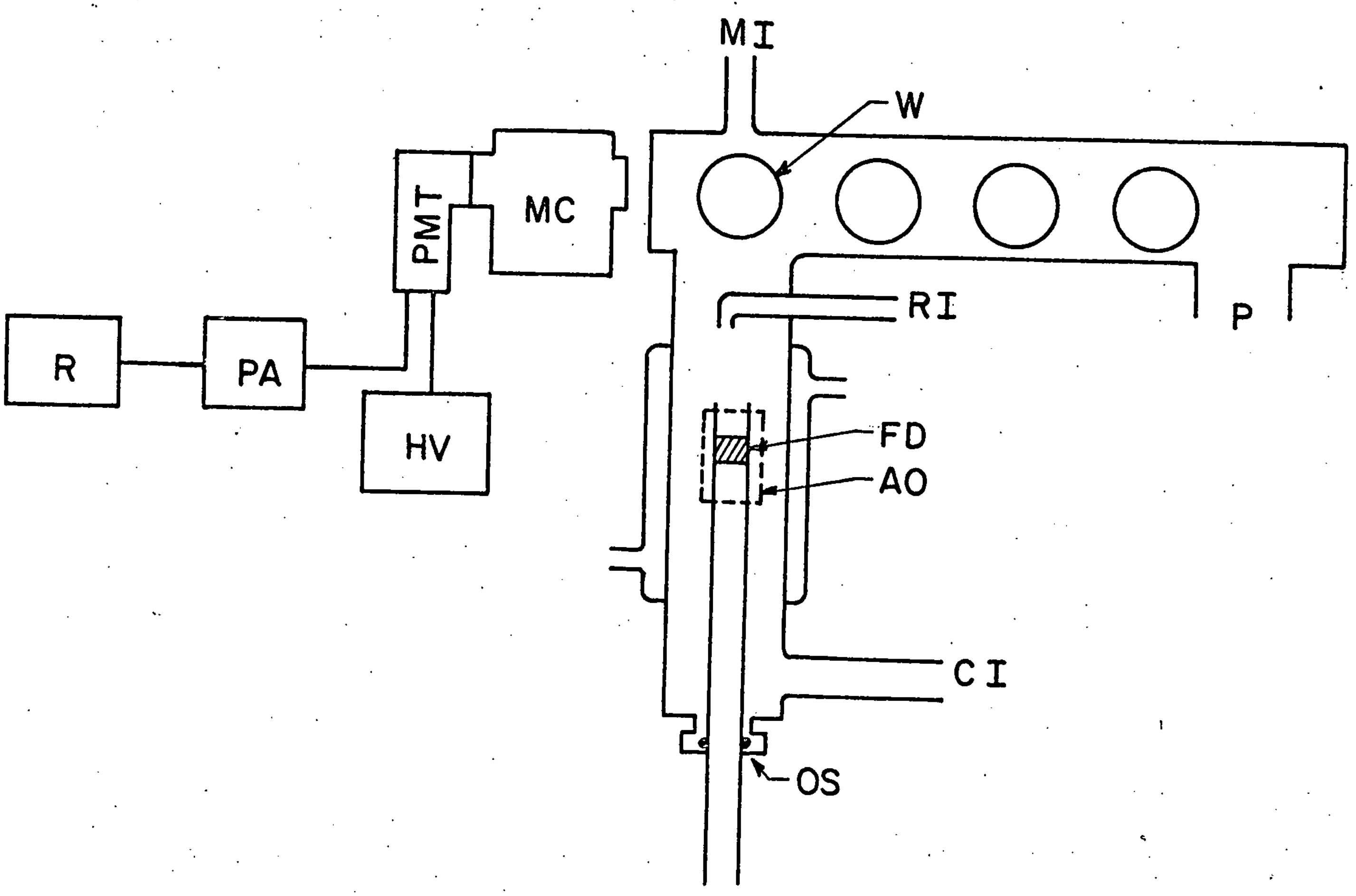

Fig. 1

Our spectroscopic system consists of a 0.25 m Jarrell-Ash monochromator which has been equipped with a scanning drive, and an HTV R955 photomultiplier (multiakali photocathode with extended red sensitivity and quartz envelope for extended ultraviolet transmission; useful range 170-900nm). Output from the photomultiplier will be read by a Kiethly 417S picoammeter which has provision for suppressing the PMT dark current. The picoammeter output will be recorded by a Heath SR205 strip-chart recorder.

The initial experiments will be aimed at determining some of the excited-state products resulting from the interaction of N_3 with itself and with other species. In addition to seeking unequivocal confirmation of earlier results,[2] we shall be able for the first time to determine the excited products from the bimolecular azide-radical recombination, and shall look for new chemiluminescent excitations, such as the formation of NF $(a^1\Delta)$, NF $(b^1\Sigma^+)$ and NH $(b^1\Sigma^+)$ from the interactions of F and H atoms with N_3. Atoms will be produced in a microwave discharge outside the flow tube. We shall calibrate our optical system by means of the O/NO method,[14] and thereby be able to determine photon yields from the various chemiluminescent reactions, given the absolute concentrations of N_3 in the system which shall be determined by titration techniques.

Kinetic studies require a knowledge of the N_3 concentration, both in a relative sense, for reactions with atoms and other free radicals, and in an absolute sense, for the determination of the bimolecular recombination rate constant, a rate constant about which there is more than a two order of magnitude disagreement.[7,15] The azide-radical may be detected in absorption around 272 nm,[5,6] probably by laser-induced fluorescence at 272nm, or by a tracer which gives a characteristic emission spectrum.[2,7,13] Oxygen atoms have been used before as a tracer; the diagnostic emission spectrum being that of the NO γ-and β-bands.[2] Oxygen atoms have the additional unique feature that they may be used as a titrant to obtain absolute concentrations.[7] The product NO will react with the excess O atoms to give the air afterglow emission, the intensity of which will be proportional to the NO, and thereby N_3, concentration. We plan, however, to search for reactions between N_3 and stable-but-reacive species such as NO which might be suitable for titration reactions. The advantage of using NO is that the titrant concentrations may then be determined directly, rather than indirectly as in the case of O atoms which require a subsequent titration reaction. The initial kinetic experiments will use the tracer technique to monitor the N_3 concentration, and rate constants will be determined for a number of species which react with N_3. Particular emphasis will be placed upon those atoms and molecules involved in chemiluminescent reactions.

We have completed the design of the apparatus and have ordered, and in most instances received, the necessary components. We have contracted with a glass blower to build the apparatus described above, (Fig 1), and the completed assembly is due by the middle of November. In addition we have begun to set up the rest of the experimental apparatus, including a glass vacuum line for the handling of gases. By the end of the next quarterly period, we shall be accumulating data on the azide—radical reaction systems discussed above.

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FIGURE CAPTION

Fig. 1. Apparatus for studying azide radical knietics:

AO, azide decomposition oven; FD, fritted disk on which azide rests; CI, carrier gas inlet; RI, reagent gas inlet; OS, sliding o-ring seal to provide temporal variation with a fixed observation point; MI, manometer inlet; W, quartz observation window; P, to pumps (Precision D-500); MC, Jarrell-Ash 0.25-m scanning monochromator; PMT, HTV R955 photomultiplier; HV, high voltage power supply; PA, Kiethly 417S picoammeter; R, Heath SR 205 strip chart recorder.