Investigation of Induced Unimolecular Decomposition
for Development of Visible Chemical Lasers

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ABSTRACT

This report summarizes the results of a study of azide decomposition for possible application in a visible chemical laser under the Dept. of Energy Contract No. EY-76-C-02-2920*000. Task 1 of the subject contract involved thorough review of the chemical literature pertaining to azide decomposition. Covalently bonded azides decompose directly into an electronically excited nitrene (RN) and ground-state molecular nitrogen. Ionic azides decompose to metal atoms and azide radicals. The azide radicals subsequently recombine to form electronically excited nitrogen molecules.

Task 2, the experimental phase of this program involved the study of azide-radical reactions. A flow reactor was built in which large concentrations (up to 10^{13} molec cm^{-3}) of N_3 could be produced from the thermal decomposition of NaN_3 . The kinetics of and chemiluminescent products from several reactions of N_3 have been studied, and a method for obtaining absolute concentrations of N_3 is described.

The potential utility of azide decomposition for the production of excited electronic states suitable for a laser device, and further areas of research germane to this goal are discussed briefly.

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I. INTRODUCTION

It has been clearly established that a long term need exists for an efficient, short-wavelength laser device for laser fusion application. The general characteristics of such a laser device are: large energy ($\geq 10^5$ joules), short pulse duration (≤ 1 nsec), short wavelength ($\lambda \geq 3000 \text{ \AA}$), modest repetition rate (~ 10 Hz), overall high efficiency (1 - 10%), and low cost. The requirements of a large device and the short pulse combine to suggest that the device configuration is most likely an oscillator/amplifier chain in which the amplifier acts as an energy-storage medium. The most critical feature of the amplifier medium are a small optical cross section ($\sim 10^{-20} \text{ cm}^2$) for stimulated emission and a relatively long energy storage time ($\sim 1 \mu\text{sec}$). 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 energy storage 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 goal of this program to investigate enough of the fundamental issues to provide the data necessary to evaluate the utilization of the 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 survey was necessary because there was no modern review which discussed the reaction mechanisms of azides emphasizing the state-specific mechanisms. Furthermore, this survey was important in order to provide the necessary background upon which

to plan efficiently an experimental program (Task 2). The results of this experimental program together with all other available information are 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).

II. REVIEW OF STATE-SPECIFIC KINETICS OF AZIDES

A. General

The azides are a class of compounds which contain a terminal substituent consisting of three nitrogen atoms linked together; this group is called the azide or azido group. Azide compounds exhibit a number of chemical and physical properties which are similar to those of halogen-containing compounds, especially bromine compounds.¹ This similarity places the azides in a group of compounds known as pseudohalides, other members being compounds of CN, CNO, NCO, SCN, etc. There are, of course, important differences between azides and halides, primarily because of the polyatomic nature of the azido substituent. As in the case of halides, there are azide compounds which are ionic in nature, and others containing covalent bonds. This bonding nature is reflected not only in the bond between the N_3 group and the rest of the molecule, but also within the azide group itself. The azide ion is linear and symmetric with a bond length $\sim 1.186 \text{ \AA}$.² In contrast, the azide group in the covalent azides is asymmetric (although linear in the ground electronic state); the bond between the central nitrogen atom and the nitrogen connected to the remainder of the molecule is somewhat longer ($\sim 1.24 \text{ \AA}$) and much weaker ($D \sim 0.4 - 1.3 \text{ eV}$) than the other N-N bond (length $\sim 1.12 \text{ \AA}$, $D \sim 6 - 9 \text{ eV}$) in the group.¹ The bond between the azide group and the rest of the molecule is intermediate in character between these two extremes ($D \sim 3.5 \text{ eV}$). Figure 1 and Table I summarize these characteristics of azide structure and thermodynamics. It is the weakness of the $RN-N_2$ bond with respect to the other bonds in the molecule which determines the primary mode of decomposition of the covalent azides. We will discuss the mechanisms for decomposition of the covalent and ionic azides below.

Azide Radical

Azide Ion

Rubidium Azide (ionic)

Hydrazoic Acid (covalent)

Methyl Azide (covalent)

Fig. 1 Geometry of the Azide Radical, the Azide Ion, and Selected Azide Compounds.

TABLE I

BOND DISSOCIATION ENERGIES OF SELECTED AZIDES (eV)

Compound	$\underline{D(R-N_3)^a}$	$\underline{D(RN-N_2)}$
HN_3	3.9 ± 0.35	0.39 ± 0.09^b
ClN_3	1.61 ± 0.17^c	0.61^c
BrN_3	1.55 ± 0.19^c	0.98^c
CH_3N_3	3.7 ± 0.35^d	
NCN_3	4.15 ± 0.10^d	0.30 ± 0.09^a
$C_6H_5N_3$ (phenyl azide)	3.75 ± 0.22	
c- $C_5H_7N_3$ (cyclopentyl azide)	3.2 ± 0.3	
c- $C_6H_9N_3$ (cyclohexyl azide)	3.45 ± 0.3	

a. H. Okabe and M. Lenzi, J. Chem. Phys. 47, 5241 (1967).

b. J. L. Franklin, V. H. Dibeler, R. M. Reese and M. Krauss, J. Am. Chem. Soc. 80, 298 (1958).

c. Our calculations are based upon the results of T. C. Clark and M. A. A. Clyne, Trans. Faraday. Soc. 66, 877 (1970), C. Paillard, et al. C. R. Acad. Sci. Paris t. 264, 1721 (1967), and G. Dupré, et al. C. R. Acad. Sci. Paris t. 273, 445 (1971). For the halogen azides, dissociation to ground-state XN and N_2 is exothermic. The molecules are bound because this dissociation is to the first $^1\Sigma^+$ state.

d. M. Chiang and R. Wheeler, Can. J. Chem. 46, 3785 (1968).

The heats of formation of a number of azides have been determined from their heats of combustion or heats of decomposition. The values are tabulated in Refs. 3 and 4. The formation of the organic azides is a moderately endoergic process with the heats of formation in the region 1.3 - 3.5 eV. The heats of formation of ionic azides and heavy-metal azides range from slightly exothermic ($\text{Ba}(\text{N}_3)_2 \Delta H_f^\circ = -0.22 \text{ eV}$, $\text{CsN}_3 \Delta H_f^\circ = -0.01 \text{ eV}$) to highly endothermic ($\text{Hg}(\text{N}_3)_2 \Delta H_f^\circ \approx 6.15 \text{ eV}$). Most of the azide compounds have positive heats of formation (endothermic).

The heat of formation of the azide radical was initially determined by combining the heat of formation of the negative ion with values of the electron affinity of the azide radical (ionization potential of the ion).^{4,5} Consideration of the thermodynamic properties of ionic crystals has led to values of 1.51^{4,5} and 1.47⁶ eV for the heat of formation of the azide ion. The electron affinity of the azide radical is commonly accepted to be 3.03 eV^{4,5} although a more recent study has placed it at 3.47 eV.⁷ Based upon these values, the heat of formation of the azide radical becomes about 4.52 or 4.96 eV depending upon the value chosen for the electron affinity of the azide radical.

Subsequent to these studies, Clark and Clyne observed chemiluminescence from NO and N_2 produced in the reactions between O and N atoms and the N_3 radical:⁸

Based upon the maximum observed excitation in the two spectra, they suggested a value of 4.3 eV for the heat of formation of the gaseous azide radical, in relatively good agreement with the value deduced above based upon the lower electron affinity. Actually, the experiments of Clark and Clyne give a lower

limit to the heat of formation, but their results are not expected to be in error by more than about 0.1 eV. A mean value of 4.4 ± 0.15 eV for $\Delta H_f(N_3)$ encompasses all the data.

Most organic azides of low molecular weight, and a large number of inorganic azides are quite unstable, indeed many are explosive.^{9,10} The physical properties of azides have been investigated to determine potential utility as explosives or as explosive initiators. Hydrazoic acid, HN_3 , and its salts are highly toxic, so that extra precautions must be taken in handling these compounds.^{9,10} Hydrazoic acid is equivalent to hydrogen cyanide in terms of toxicity. Inhalation of small concentrations of its vapor produces headaches and dizziness and clogging of the mucous membranes. Injection of small amounts of sodium azide into mammals produces spasms and the symptoms of heart and lung paralysis. Fortunately, the effects of small doses of azides seem to be reversible, and there does not seem to be evidence of cumulative damage to the physiological system.^{9,10}

A number of reviews have been written on the physics and chemistry of azides,^{1, 3-5, 10-15} although none are particularly current. Much of the recent work on azides has focused upon the induced decomposition of organic azides to provide intermediates which can be exploited for novel syntheses. This work is not, in general, germane to the concerns of the present study and, thus, will be substantially ignored.

B. Covalent Azides

The covalent azides are most easily discussed when divided into three groups: aromatic, non-aromatic including non-metallic inorganic azides, and organometallic azides. The non-aromatic azides share a common spectrum and pattern of decomposition, while the aromatic azides exhibit variations in these properties.¹² The organometallic azides have not been studied in sufficient detail to allow more than cursory speculations.

1. Non Aromatic

The non-aromatic azides exhibit a spectrum which is determined primarily by the azide group itself. Thus, there is a fairly weak absorption at around 285 nm with an absorption coefficient $\epsilon \sim 25\text{--}30 \text{ l mol}^{-1} \text{ cm}^{-1}$, and a much stronger absorption band peaking around 215 nm ($\epsilon \sim 500 \text{ l mol}^{-1} \text{ cm}^{-1}$). In azides containing a carbonyl group, and in HN_3 and ClN_3 , the weaker band is slightly blue shifted and slightly stronger than indicated.^{12, 16, 17} However, the basic spectrum is essentially the same. Theoretical considerations indicate that these transitions involve electrons localized in the azide group.¹

The decompositions of these compounds are governed primarily by the extreme weakness of the RN-N_2 bond ($\sim 0.4\text{--}1.3 \text{ eV}$) compared to the R-N_3 bond ($\sim 3.5 \text{ eV}$). Thus the primary products of decomposition are molecular nitrogen and the RN radical, known as a nitrene:

The ground-electronic state of the nitrene is a triplet, but decomposition to a triplet nitrene and the singlet ground-state nitrogen molecule is spin forbidden. Thus, decomposition to the electronically excited, singlet nitrene is expected in both photolytic and thermal decompositions. Table II summarizes these relationships.

Most of the evidence supporting the contention that the primary photolytic products from covalent azide photolysis are electronically excited singlet nitrene and ground-state nitrogen is indirect; however, two systems, HN_3 ²⁰⁻³⁹ and NCN_3 ⁴⁰⁻⁴⁶ have been studied in sufficient detail, and with sufficient time resolution that the results of these studies may be considered to be unequivocal. In several other systems, the evidence strongly favors the hypothesis that singlet nitrene is the primary product.

TABLE II
PATHWAYS FOR DECOMPOSITION OF COVALENT AZIDES

	Reaction	Enthalpy Change
I. Specific Case: HN_3		
1. Forbidden	$\text{HN}_3 (^1\text{A}') \rightarrow \text{NH} (\text{X}^3\Sigma^-) + \text{N}_2 (\text{X}^1\Sigma_g^+)$	0.39 ^a
2. Allowed	$\text{HN}_3 (^1\text{A}') \rightarrow \text{NH} (a^1\Delta) + \text{N}_2 (\text{X}^1\Sigma_g^+)$	1.96 eV ^b
3. Allowed	$\text{HN}_3 (^1\text{A}') \rightarrow \text{H} (^2\text{S}_{1/2}) + \text{N}_3 (\text{X}^2\Pi_g)$	3.58 eV
II. General Case: RN_3		
4. Forbidden	$\text{RN}_3 (^1\text{A}_1) \rightarrow \text{RN} (^3\text{A}_1) + \text{N}_2 (\text{X}^1\Sigma_g^+)$	0.4 - 1.3 eV
5. Allowed	$\text{RN}_3 (^1\text{A}_1) \rightarrow \text{RN} (^1\text{A}_1) + \text{N}_2 (\text{X}^1\Sigma_g^+)$	1.5 - 2.0 eV ^c
6. Allowed	$\text{RN}_3 (^1\text{A}_1) \rightarrow \text{R} (^2\text{A}_1) + \text{N}_3 (\text{X}^2\Pi_g)$	~ 3.5 eV

a. There is some uncertainty over this bond energy. The value of 0.39 eV has been derived experimentally.¹⁸ However, if the currently accepted value for $\Delta H_f^\circ (\text{NH}) = 3.9 \text{ eV}$ ¹⁹ is valid, then the bond energy would be 0.78 eV.

b. Recent experiments have established that the singlet-to-triplet term energy of NH is 1.57 eV.⁹⁰ If the HN-N₂ bond energy is 0.78 eV then the enthalpy change for this process would be 2.35 eV.

c. This range of values is based upon the activation energies found in the thermal decomposition of organic azides (see Ref. 13).

The photolysis of NH_3 has been studied by a number of people over a number of years,²⁰⁻³⁹ but only recently have the experiments been performed with sufficiently low partial pressures of HN_3 and sufficient time resolution to give unequivocal results on the identification of the primary products.³⁴⁻³⁷ Using broad-band photolysis, Paur and Bair have studied the system with an absorption diagnostic.³⁴⁻³⁶ The major product from the photolysis was NH ($a^1\Delta$). They also saw evidence for formation of NH ($c^1\pi$) (which is spin allowed and possible for wavelengths shorter than 215 nm) and NH ($A^3\pi$) (which is spin forbidden, but energetically feasible for wavelengths shorter than 303 nm). Neither product amounted to more than 1% of the total photolysis products. The NH ($c^1\pi$) was probably formed directly, but the time resolution of their experiments was not sufficient to determine if the triplet NH could be formed directly, or via secondary reactions such as:

a process which is known to occur.⁴⁷ The $\text{N}_2 (\text{A}^3\Sigma_u^+)$ could have been formed in the system by the recombination of N_3 radicals, which are also present as photolysis products. That N_3 is formed from secondary reactions, probably

is clear from the work of Paur and Bair. They are not, however, able to exclude some direct formation of N_3 via the reaction:

Indeed several researchers claim that this reaction is a primary photolysis channel.^{25, 31, 38}

In a much cleaner experiment, McDonald et. al.³⁷ have photolyzed HN_3 at 266 nm using a frequency quadrupled Nd^{+3} YAG laser, and using laser-induced fluorescence as a diagnostic. They claim that over 99% of the primary photolysis is through channel 2, Table II, although they did not look for N_3 or H to confirm the absence of reaction (6). It is also their contention that the NH_2 formed in reaction (5) is electronically excited. This is in contrast to the work of Paur and Blair who were unable to observe NH_2 fluorescence in their reactor.

The photolysis of NCN_3 ⁴⁰⁻⁴⁶ has not been studied with quite the precision of NH_3 , but again the results are unequivocal that the dominant process is:

At the earliest times after the photolysis flash the major product has been shown to be the singlet NCN radical which subsequently decays either via emission or reaction.^{42,46} Other observed products include NCN ($A^3\Pi$), N_3 , and CN.⁴⁶ It is clear that the predominant channel for the formation of these products is via secondary reactions because the populations of these species augment with time after the photolysis flash.^{42,46} Unfortunately, the detailed kinetics have not been studied, so that the reaction scheme subsequent to photolysis has not been worked out.

The photolysis of CH_3N_3 has been studied by several workers,⁴⁸⁻⁵⁰ but unfortunately not in a low pressure, time-resolved system. Both Currie and Darwent⁴⁹ and Getoff et. al.,⁵⁰ have shown that the quantum yield for nitrogen production in pure azide is about 2, but that this yield is reduced markedly if free radical scavengers are added to the reactor. Currie and Darwent, however, claimed the N_2 quantum yield increased to shorter wavelengths, whereas the results of Getoff, et. al. show the quantum yield to be independent of wavelength.

The quantum yield of 2 may be explained by reactions:

and

That the CH_3N formed in reaction (8) is in the electronically excited singlet state is supported by additional work by Getoff et. al.⁵⁰ with mercury-photosensitized decomposition of methyl azide:

In the sensitized reaction, the CH_3N should be in a triplet state, and Getoff et. al. have shown that the secondary processes from the sensitized reaction are different. In particular, the quantum yield for nitrogen formation is unity, implying that reaction (9) does not occur if the CH_3N radical is in the triplet state. O'Dell and Darwent,⁵¹ in a study on the thermal decomposition of CH_3N_3 , observed the product yields to be markedly different from those obtained in the photolytic decomposition. They assumed that this difference results from the generation of triplet CH_3N in the thermal reaction. However, different secondary reaction channels may become important at the higher temperatures used in the thermal decomposition, so that the thermal and photolytic mechanisms may not be in conflict. Finally, Getoff et. al.⁵⁰ felt that about 10% of the photolytic decomposition followed the reaction:

whereas Currie and Darwent⁴⁹ felt that this channel was totally unimportant. Supporting the contention of Currie and Darwent is the failure of Thrush²² to observe the N_3 radical in absorption following flash photolysis of methyl azide.

Several other observations also support the hypothesis that singlet nitrenes are the primary fragments from covalent azide decomposition. Analysis of products from thermal decomposition of mixtures of ethyl azidoformate ($N_3-C-O-C_2H_5$)⁵²⁻⁵⁵ or NCN_3 ⁵⁶ with olefins shows stereospecific addition to the olefinic double bond. This behavior is expected of a singlet radical but not a triplet. In photolytic decompositions of ethylazidoformate,⁵⁷⁻⁵⁹ product analysis indicates about 30% of the products come from non-stereospecific addition, indicating that at the higher energies involved in the photolysis, intersystem crossing from singlet to triplet states of the azide is efficient. Finally, in the thermal decomposition of ClN_3 ,⁶⁰ emission has been observed from NCl ($b^1\Sigma^+$). This emission could arise in the primary decomposition step, since dissociation of ClN_3 to give NCl ($b^1\Sigma^+$) + N_2 requires only 0.61 eV of energy. The breaking of a bond this weak is clearly possible in thermal decompositions at 400°C.

The results of experiments proposing alternative mechanisms to the ones given above are inconclusive, since most studies on azide decomposition have been done in the liquid phase and have involved analysis of final products resulting from the decomposition. Thus, the inference of intermediates or lack thereof is largely a speculative process. As previously mentioned the difference between photolytically⁴⁹ and thermally⁵¹ produced products in the decomposition of methyl azide was rationalized in terms of formation of triplet methyl nitrene in the thermal decomposition.⁵¹ In addition, there is a body of opinion which holds that the thermal decomposition of alkyl azides does not result in the formation of a nitrene intermediate; rather that the elimination of nitrogen is a concerted process.¹³ These ideas are based upon the observation that most organic azide decompositions in solution result in migration of a substituent from the parent group in the compound to the nitrene nitrogen:¹³

However, none of these experiments is sufficiently clean to provide unequivocal results.

Evidence for the formation of excited N_2 in the decomposition of covalent azides is secondary in nature. Okabe, in his photolytic study of HN_3 ,³² observed ill-defined emissions in the region between 500 and 1000 nm and, in addition, NH ($\text{A}^3\pi$) which he showed was produced by secondary reactions. The infra-red emissions could occur from the N_2 ($\text{B}^3\pi_g$) electronic state, while the triplet NH could be produced by energy transfer from N_2 ($\text{A}^3\Sigma_u^+$) to HN_3 .³⁰ Welge's study of the photolysis of HN_3 ²⁸ showed production of NH ($\text{A}^3\pi$), NO γ -band emissions and emission from Hg at 253.7 nm when these latter two species were added to the gaseous mixture. It is well known that N_2 ($\text{A}^3\Sigma_u^+$) readily excites both of these latter emissions.⁴⁷ Okabe and Mele⁴⁵ observed emission from NCN ($\text{A}^3\pi$) in a photolytic study of NCN_3 and showed that the most likely precursor of this triplet emission was the interaction of N_2 ($\text{A}^3\Sigma_u^+$) with NCN_3 , a process which is known to occur:⁶¹

If triplet states of nitrogen are formed, it is not clear whether they are formed in the direct photolysis, which is spin allowed and energetically feasible for $\lambda \leq 185$ nm for HN_3 and NCN_3 , or indirectly from the recombination of two azide radicals, a process which is both spin allowed and energetically feasible:

The N_3 radical has been observed directly (by its characteristic absorption spectrum around 272 nm) in the gas-phase photolyses of HN_3 ,^{22,31,34-36,38,62} ClN_3 ,⁶² and NCN_3 .^{41,46} In addition, the N_3 radical has been inferred to have been formed in the photolytic decomposition of (i) CH_3N_3 in the gas phase,⁵⁰ (ii) tertiary organic azides in solution,¹³ (iii) the azides of the halogens F, Cl, and Br in low-temperature inert matrices,⁶³ and (iv) in photolyses of azide ions in solution.^{64,65} Some controversy still exists, however, whether the N_3 radical is formed in a primary photolytic step, or whether it is the product of secondary reactions. Further studies with good time resolution are needed to resolve this point.

In summary, the primary species resulting from the induced decomposition of non-aromatic, covalent azides is a singlet nitrene and molecular nitrogen. In some cases there may be a minor channel to produce the N_3 radical. In only the simplest cases (NH ⁶⁶ and NCN ⁴³) has the nitrene been characterized spectroscopically, and only in the case of NH is the excitation energy of the singlet nitrene known. The singlet/triplet splitting in NH is 1.57 eV.⁹⁰ In the NCN radical, Schoen suggests a value between 4.1 and 5.2 eV.⁴² Clearly, further studies would be fruitful to unravel the energetics and state-specific mechanism of the primary decomposition process.

2. Aromatic

Unlike the alkyl azides, the aromatic azides have an absorption spectrum characteristic of the parent aromatic group.¹² Thus the photolytic decomposition of the aromatic azides involves essentially a flow of energy from the main molecule into the side chain where the weak RN-N_2 bond resides. It is therefore a sub-class of the phenomenon known as aromatic side-chain decomposition,⁶⁷ a type of unimolecular decomposition of photolytically

activated molecule. Studies on the photo-induced decomposition of aromatic azides at low temperatures in inert matrices indicate that there is a mixture of singlet and triplet nitrene produced in the primary decomposition.⁶⁷

Studies in solution at temperatures between 10°C - 50°C give the same product quantum yields as were obtained in the low temperature matrices.⁶⁷

Thus, as in the case of non-aromatic photolysis, aromatic photolysis does not involve thermal dissociation of an excited state.

3. Organometallic

One final class of covalent azides are the organometallic azides.¹⁴

These azides may be further subdivided into two classes, those organometallic azides which upon decomposing give up all nitrogen in the azide group, and those which give up only 2/3 of the azido nitrogen (i. e. , decompose to $RN + N_2$). The latter group comprises the derivatives of B, Si, Ge, P and As, while the former group consists of the remaining organometallic azides.

There is no information on the photolysis or pyrolysis of these compounds to yield detailed information on the state-specific primary products of decomposition.

4. Summary for Covalent Azides

The data presently available on the decomposition of covalent azides suggests that the formation of electronically excited states in good yield may be realized in the decomposition of the non-aromatic azides. In contrast, the aromatic azides may not be so fruitful a class of compounds for study, since large yields of ground-state triplet nitrenes appear to be formed in the decomposition of these species. For the organometallic azides, only those which decompose to give up all azido nitrogen are likely to produce good yields of electronically excited states, and then only if the primary decomposition step produces large quantities of the N_3 radical, and if the subsequent recombination of the N_3 radical is shown to be an efficient source of electronically excited nitrogen molecules (reaction (14)).

C. Ionic Azides

The ionic azides are the non-volatile solids comprised of metals from the alkali and alkaline earth groups as well as the azides of Ag, Cu, Pb, Tl (I), and NH_4^+ .^{3,68} Many of these solids are thermally and mechanically unstable. The azide ion in these solids is generally symmetric, although recent studies have shown small asymmetrical structures in heavy-metal azides.⁶⁹ The thermal and photolytic decompositions of many of these azides have been studied in some detail over a number of years and several facts are well established:³ (i) these azides decompose to liberate all of the nitrogen as the azide ion N_3^- ; (ii) decomposition appears to take place at the surface of the crystals or along dislocations in the crystal planes;⁷⁰⁻⁷² (iii) the thermal stability of these azides increases as the ionization potential of the cation decreases (e. g., $\text{KN}_3 > \text{TlN}_3 > \text{AgN}_3$);^{73,74} (iv) after an initial, rapid liberation of nitrogen from the azide, which may be just desorption of gases from the crystal, there is an incubation period, the time of which varies inversely with the temperature of the sample, before the main decomposition sets in;^{71,72,75-77} (v) the rates of decomposition after the incubation period appear in many instances to be linear in time,^{70-72,75,76} and (vi) the log of the rate of decomposition in this linear region varies linearly with inverse temperature.^{70,76-78}

The decomposition data yield activation energies about 2 eV for monovalent azides and around 1 eV for the divalent azides.³ In some instances it has been shown that the activation energy of a given azide changes upon entering different temperature regions.^{70,77-79} In decompositions of a few of the divalent azides, metal nitrides have been found, but these are thought to be formed in secondary reactions.

The basic mode of decomposition of ionic azides is thought to involve the dissociation of the azide ion into the azide radical and a free electron.³ This may be effected either thermally or photolytically. The electrons then recombine with the cations, or more readily with a cation which is associated with a cluster of free metal atoms; and the azide radicals recombine to form free nitrogen with the evolution of large amounts of energy:

The great amounts of energy liberated in the azide radical recombination is surely a factor involved in their explosive decomposition. The inverse correlation between the thermal stability of the azides and the ionization potential of the cation is consistent with the proposed mechanism, because metals with a higher ionization potential will more readily attach electrons, thus reducing the probability of recombination between the azide radicals and the free electrons.^{73, 74} Therefore, the rate of N_3 liberation will be enhanced.

Some old and largely ignored experiments by the French worker René Audubert,^{75, 76, 79, 80} indicate that the thermal decomposition of a number of inorganic azides, including NaN_3 , KN_3 , AgN_3 , TlN_3 , and PbN_6 , results in the observation of photon emission in the region between 200 to 260 nm. Furthermore, the rate of photon emission apparently varies inversely with temperature, and is therefore presumably proportional to the rate of azide decomposition. Audubert measured a crude spectrum of this emission — with a resolution of ~ 7 nm — and found five bands.⁷⁹ This spectrum does not correspond particularly well to known emissions, so it is not clear what transitions are being observed. Presumably, the spectrum results either from a chemiluminescent reaction of an impurity species in Audubert's reactor with the azide radical, or from excitation

of impurities by electronically excited nitrogen formed from azide radical recombination. Audubert's spectrum most closely resembles—although not very well—the NO γ -band emissions which are excited from the interaction of N_2 ($A^3\Sigma_u^+$) with NO. NO has been shown to be formed in systems containing N_2 ($A^3\Sigma_u^+$) and O_2 or air.⁸¹ Additional evidence that the precursor might be N_2 ($A^3\Sigma_u^+$) is that Audubert noticed an augmentation in emission at around 255 nm when he allowed mercury into his system. The excitation of Hg 254 nm emission by N_2 ($A^3\Sigma_u^+$) has been firmly established.⁴⁷ As the decompositions proceeded, most of the bands observed by Audubert disappeared, and only a relatively broad emission peaking at 260 nm remained.⁷⁹ The identity of this emission is uncertain. The spectrum observed by Audubert was independent of azide cation, and was also observed by him in anodic oxidation of several azide salts and of HN_3 in solution.

In a few cases, the decompositions have been studied with mass spectrometric detection under conditions of ultra-high vacuum. Studies on the decomposition of KN_3 did find mass peaks corresponding to K and N_3 ,⁷⁰ but the experimentors were unable to discuss these findings quantitatively. Studies with NaN_3 , on the other hand, showed no Na nor N_3 given off under normal conditions.^{71,72}

The production of electronically excited states from the ionic azides depends primarily upon the ease with which N_3 radicals may be liberated into the gas phase in the decomposition of these solids and on the subsequent kinetics of N_3 radical reactions. Clark and Clyne have produced N_3 in a flow system chemically, e. g.,

and observed chemiluminescence from the species ClN , BrN , NO and N_2 ⁸ when Cl , Br , O , or N atoms respectively were added to the flow reactor.

Unfortunately, they were unable to measure directly rate constants for these reactions. They felt that the reaction between Cl and N_3 was fairly slow ($k < 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) while the reaction between N_3 and N or O atoms was somewhat faster ($k > 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$). Using indirect methods to extract N_3 concentrations, Clark estimated that the rate constant for the reaction between Cl and N_3 was $\sim 2 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and that for bimolecular N_3 recombination the rate constant was $\sim 5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. Indirect evidence by Combourieu et. al., however indicates a rate constant for $\text{Cl} + N_3$ to be greater than $4 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.⁸³ Thrush observed the bimolecular decay of N_3 radicals in the gas phase but was not able to describe the kinetics quantitatively. He felt that the reaction proceeded with a "low collision efficiency".²² Hayon and co-workers have observed the bimolecular decay of N_3 in solution and have inferred that the decay proceeds at a nearly diffusion-limited rate ($2k = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$).^{64,65} The fairly rapid reaction between azide radicals in solution compared to their apparent behavior in the gas phase may be rationalized in terms of stereochemistry. In a study of N_3^- electrolysis, using center-labeled azide, ($^{14}\text{N}-^{15}\text{N}-^{14}\text{N}$), yields of $^{14}\text{N}_2$ and $^{14}\text{N}^{15}\text{N}$ were obtained in a 1:2 ratio but no $^{15}\text{N}_2$ was observed.⁸⁴ From this observation, it may be inferred that the intermediate would be cyclic or linear in nature:

In solution, of course, the effective collision time is much longer than in the gas phase, so that geometrical requirements will be less stringent.

D. Review Summary

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). The available evidence 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 and upon their spectroscopy, neither of which are well characterized.

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 ($\Delta H_f = 4.4 \text{ eV}$),⁸ many of whose reactions have been shown to be chemiluminescent⁸ (Table III). 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.^{34-37,46} Thus the azide radical may also be the most important energy carrying species in the decomposition of certain covalent azides.

TABLE III

REACTIONS OCCURRING IN AZIDE SYSTEMS WHICH MAY
PRODUCE ELECTRONIC EXCITATION IN ONE OF THE PRODUCTS

Reaction	Possible or Known Products	Excitation Energy ^a , eV
$2N_3 \rightarrow N_2^* + 2N_2$	$N_2(A^3\Sigma_u^+)$ or $N_2(B^3\Pi_g)$	6.3 7.4
$Cl + N_3 \rightarrow NCl^* + N_2$	$NCl(b^1\Sigma^+)^b$	1.86
$Br + N_3 \rightarrow NBr^* + N_2$	$NBr(A^1\Sigma^+)^b$	1.83
$O + N_3 \rightarrow NO^* + N_2$	$NO(A^2\Sigma^+)^b, NO(B^2\Pi)^b$	5.45, 5.7
$N + N_3 \rightarrow N_2^* + N_2$	$N_2(B^3\Pi_g)^b$	7.4
$RN_3 \xrightarrow{h\nu \text{ or } \Delta} RN^* + N_2$	$NH(a^1\Delta)^c$ $NH(c^1\Pi)^d$ $NCN(a^1\Delta)^e$ $RN(a^1\Delta)$	1.57 5.45 4.1 - 5.2 1.3 - 2.6

a. The energies of excitation represent the energies of the 0,0 transition, i. e., the minimum excitation in the molecule.

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

c. J. R. McDonald, R. G. Miller, and A. B. Baronowski, *Chem. Phys. Lett.* **51**, 57 (1977).

d. H. Okabe, *J. Chem. Phys.* **49**, 2726 (1968), and K. H. Welge, *J. Chem. Phys.* **45**, 4373 (1966).

e. H. W. Kroto, *J. Chem. Phys.* **44**, 831 (1966), and L. J. Schoen, *J. Chem. Phys.* **45**, 2773 (1966).

III. EXPERIMENT

A. Introduction

The discussion of azide-decomposition mechanisms 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 was produced either in the primary decomposition step of ionic azides or in secondary reactions following decomposition of covalent azides. Evaluation of the proceeding information in terms of potential laser devices indicates that both the spectroscopy and kinetics of singlet nitrenes must be understood, and detailed knowledge of the products and kinetics of azide-radical reactions must be acquired.

We chose the experimental study of azide-radical reactions in the initial experiments for the following reasons: Firstly, 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. Therefore, many of the major kinetic and spectroscopic aspects of azide decomposition for laser utilization are amenable to investigation in a system built to study azide-radical reactions.

Having made the decision to study the reactions of the azide radical, it became necessary to develop a system in which the relevant species and kinetics could be observed. There are four methods by which the azide radical may be formed (see Table IV): (i) as a secondary product in the

TABLE IV
METHODS OF N₃ PRODUCTION

A. As a secondary product in covalent azide decomposition

B. Direct Decomposition of tertiary covalent azides ^d

C. Chemical Production

2. Specific: see Table V

D. Ionic Decomposition ^e

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 N₃ in photolyzed ClN₃.

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.

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 ionic azides. The first two methods contain the drawback that other reactive species in addition to the azide radical will be present in the system, which might complicate the kinetics. Azide radicals produced by method (i), however, have been observed in absorption.^{22, 31, 34-36, 46, 67}

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 between ground-state species which could 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 reactions between Cl and N_3 is slow as has been indicated by Clark and Clyne,^{8, 82} or fast as it is thought to be by Combourieu and co-workers.⁸³ Other reactions not listed may work, but no other quantitative information exists, so that finding a suitable chemical source for azide radicals could have become a lengthy trial-and-error procedure. However, chemical methods have been shown to produce N_3 ,⁸ so they might prove useful in future experiments.

The fourth possibility listed above, i. e., the thermal or photolytic decomposition of ionic azides is a method on which direct information was sparse, but it is also the method which afforded the best opportunity to develop a completely clean system in which to study azide-radical kinetics. There are potentially no other reactive species present in the reactor. It is known that large quantities of nitrogen gas are evolved when the ionic azides are decomposed.³ This has always been assumed to arise from the bimolecular

TABLE V
CHEMICAL PRODUCTION OF N₃ AND
COMPETING DESTRUCTION REACTIONS

Reaction	Rate Constant (cm ³ molec ⁻¹ s ⁻¹)
A. Formation Reactions	
ClN ₃ + Cl	3.7 x 10 ⁻¹² ^a
H	> 2 x 10 ⁻¹³ ^b
O	c
N	c
Br N ₃ + Br	c
HN ₃ + H	1.1 x 10 ⁻¹⁴ ^d
N	5 x 10 ⁻¹⁵ ^d
B. Destruction Reactions	
N ₃ + Cl	> 4 x 10 ⁻¹² ^a
Cl ₂ , ClN ₃	2.2 x 10 ⁻¹⁴ ^e
	"slow" ^{a,c}
Br	c
N	c
O	c
HN ₃	2.2 x 10 ⁻¹¹ ^f
N ₃	~ 3 x 10 ⁻¹⁰ ^g
	5 x 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 $X = O, N$. Based upon their observations, we estimate that $k_{X + ClN_3} > 1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ 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).

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. It is also known that the decomposition of alkali azides in a flowing system is a good method for the production of alkali atoms.⁸⁵ By analogy, one would expect that the other decomposition product, i. e., N_3 , could also be formed readily. Small quantities of the azide radical have been observed mass spectrometrically in the thermal decomposition of potassium azide,⁷⁰ but no quantitative estimates of the yield have been made. Finally, the observations of UV emission by Audubert^{75,79,80} in the thermal decomposition of a number of ionic azides indicates that energy carrying species are liberated in the decomposition. The most logical candidates for this emission are species produced indirectly by 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 was little direct evidence that the thermal or photolytic decomposition of ionic azides did indeed produce significant concentrations of azide radicals, the indirect evidence indicated that this approach would work; and, furthermore, that there would be no other reactive species in the reactor. The alkali atoms formed in the decomposition would be pumped rapidly 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 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 could be derived from the understanding of condensed-phase decomposition.

Azide-radical kinetics may be studied most conveniently in a flow system which provides for efficient evolution of N_3 into the gas phase by sweeping the azide radicals 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 occurring 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.^{82,86}

B. Apparatus

The apparatus which was built for this experiment is shown in Figs. 2-5. It is constructed from 25 mm i.d. pyrex in two sections which separate the experimental regions. The vertical section contains the source and reaction regions while the observation region comprises the horizontal section. The two sections are connected by an o-ring joint, so that they may be replaced by other configurations if different sources or geometries need to be tried. Azide radicals are formed in a small oven mounted on the end of a 1/2 in. o.d. pyrex tube which may slide coaxially within the source section. The oven is a piece of 12 mm pyrex tubing into which a 10 mm fritted disk was blown. Nichrome wire was wrapped around the tube from a few centimeters below to a few centimeters above the fritted disk, and heat was produced from a variable a. c. voltage supplied by a variac. An iron-constantan thermocouple, placed against the fritted disk, measures the oven temperature. The solid azide rests upon the fritted disk. A small flow of helium or argon carrier gas passes through the frit to enhance the evolution of azide radicals from the surface of the decomposing solid. The oven is capable of operating at temperatures up to 500°C, and in operation has maintained stable temperatures of as high as 425°C over periods as long as several hours.

The majority of the experiments involved spectroscopic analysis of excited products. The f/3.5 optical system combined good collection efficiency with modest resolution. The monochromator is a 0.25 m Jarrell-Ash instrument equipped with a stepping-motor scanning drive, two interchangeable gratings blazed at 300 and 600 nm, and fixed slits of widths 0.15, 0.3, 1, 3 and 5 mm for resolutions between 0.5 and 16 nm, respectively. Photons

Fig. 2 Apparatus for Studying Azide-Radical Kinetics.

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

Fig. 3 Overall View of the Azide Decomposition Apparatus Showing the Flow Tube, Vacuum Prep and Handling Line and the Monochromator.

Fig. 4 Close-Up View of the Flow Tube and Monochromator. The azide decomposition oven can be seen inside the vertical section of the flow tube.

Fig. 5 Close-Up View of the Vacuum Prep Line Showing Gas Purification Traps and Gas Storage Bulbs.

emitted between 170 and 920 nm were detected with either an HTV R955 or RCA 4840 (210 - 850 nm) photomultiplier. The photomultipliers were operated at room temperature in the analog mode, a Keithly 417S picoammeter being used to measure their output current. The picoammeter has a current suppression circuit so that dark current from the photomultiplier (on the order of 1 - 2 nA) could be nulled out. The wavelength calibration of the system was done by scanning the NO and N₂ emissions present in discharged air. In the later stages of the experiment, a PARC 1140 A/C quantum photometer⁸⁷ was used to measure PMT output, and the PMT housing was water cooled. These modification improved our sensitivity by about an order of magnitude. In order to eliminate problems with room-light interference, a light-tight enclosure was constructed around the apparatus.

The observation region was constructed so that spectral observations could be made either along the axis of the flow tube, to enhance the light collection efficiency, or normal to the flow-tube axis at any one of five windows spaced 10 cm apart in the observation region. This latter configuration allowed temporal resolution of decaying emissions. Temporal resolution was also achieved by moving the oven, and thereby changing the distance from the oven mouth to the observation region (15 - 40 cm), or by throttling the pump on the system which reduces the flow velocity.

The carrier gas flow (100-3000 $\mu\text{mols s}^{-1}$) and the flow through the azide oven (10-100 $\mu\text{mols s}^{-1}$) are metered into the system through rotameters which have been calibrated with a wet test meter.⁸⁸ This calibration is necessary because, in the case of helium, the manufacturer's calibration curves were low by more than a factor of two at low flows.⁸⁹ Reagent-gas flows are measured with capillary-oil flow meters which have been calibrated by measuring the change in pressure with time from a known volume. A number of capillaries of different sizes were available to give a range of reagent flows in between 10^{-2} to 5 $\mu\text{mols s}^{-1}$. The reagents were stored in

5 l flasks integrated into the vacuum prep-line. One of the capillary-oil flow meters mixes reagents with the main carrier-gas flow prior to their entry into the flow tube. The other reagent flow meter is connected to a fixed inlet downstream from the azide oven and about 8.5 cm upstream of the observation region. A 2.45 GHz microwave discharge cavity (Evenson type) could be placed at either reagent inlet so that atomic reagents could be introduced either upstream or down stream of the oven. When the discharge cavity is placed on the downstream inlet, an additional flow of carrier gas passes through the side arm in order to reduce the time of flow from the discharge to the flow tube, and thereby reduce significantly atom recombination.

The flow tube is pumped by a Precision D-500 mechanical pump which has an effective pumping speed in the reactor of 375 l min^{-1} , essentially independent of pressure between 2 and 12 torr. The bulk-flow velocity, therefore, is about 1250 cm s^{-1} which will permit a maximum temporal resolution of about 0.8 ms per cm. This temporal resolution is suitable for rate constants between 10^{-14} and $10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. Flow-tube pressures are measured with a silicon oil manometer which has a resolution of about 0.08 torr per mm of oil.

C. Experiments

1. General Observations on NaN_3 Decomposition

Most of our experiments were done using NaN_3 as the source of azide radicals. Our qualitative observations on the decomposition of this salt are in agreement with earlier studies:^{71, 72, 76} the sodium azide decomposed quickly at temperatures above 350°C , as indicated by the rapid formation of a sodium mirror upon the walls of the reactor after the onset of decomposition; the decomposition commences after an incubation period which is longer at lower temperatures. In addition to the Na mirror formed on the walls of the flow tube from

0 to 5 cm downstream of the azide oven, a reddish-brown material was desposited along the whole length of the flow tube. This material was fairly volatile, since it could be pumped away within an hour after the termination of azide decomposition. At the higher temperatures ($\geq 330^{\circ}\text{C}$), the azide decomposition was relatively complete within about 20 minutes for amounts of NaN_3 on the order of 10 m moles (0.65 gram). We can observe decomposition of the NaN_3 at temperatures below 200°C after incubation times of several hours. At lower temperatures ($< 250^{\circ}\text{C}$) the rate of azide decomposition was relatively constant in time for periods longer than an hour. Because of this constant and relatively slow rate of decomposition, most experiments were done in the low temperature region. Another advantage of low temperature operation is that the sodium does not evaporate from the oven, thus leaving the reactor walls clean. A coating of metallic sodium on the reactor walls catalyzes surface recombination of the azide radicals and reduces the effective N_3 concentration in the reaction and observation regions.

2. Diagnostics for N_3 Generation

Our major diagnostic for the presence of N_3 in the reactor has been the observation of NO γ -band emission and the O/NO air afterglow⁹¹ when O atoms were added to the reactor. These emissions arise from reactions (19) and (20):

A spectrum of the NO γ -bands excited in Reaction (19) is shown in Fig. 6. The intensities of these emissions increased as the temperature was raised in the oven, and the emission disappeared when the oven was turned off. Thus, one of the species responsible for these emissions is being produced in the azide oven. Clark and Clyne⁸ claim that the reaction between O and N_3 ought to produce the NO β -band emissions between 250 and 375 nm as well as the NO γ -bands. We have not observed the β -band emissions. Therefore, we sought

Fig. 6 Spectrum of the NO γ -bands Produced in the Reaction Between O and N_3 ($\Delta \lambda = 4$ nm).

other information to support our view that the NO γ -band emission was excited directly in the $O + N_3$ reaction. One very good source of γ -band emission in the relative absence of β -band emission is the energy-transfer reaction between $N_2(A^3\Sigma_u^+)$ and NO.^{47, 92} $N_2(A^3\Sigma_u^+)$ could have been produced in our reactor in the bimolecular recombination of N_3 , or in the atom discharge with impurities in the helium or argon diluent. Two observations effectively rule out the possibility that the source of the γ -bands is $N_2(A^3\Sigma_u^+) + NO$. When the discharge is turned off, and a small amount of NO is added to the reactor upstream of the oven, no emissions are observed. The concentration of added NO was sufficiently small that any $N_2(A^3\Sigma_u^+)$ in the reactor would not be appreciably quenched prior to entry into the observation region, but sufficiently large that the strong NO γ -band emission should have been observable if the $N_2(A^3\Sigma_u^+)$ concentration was significant. Additional confirmation comes from observations on the quenching of the γ -band emission produced from the $O + N_3$ reaction by added NO. Figure 7 shows the semi-logarithmic decay of NO emission as a function of added NO for a mixing time of about 12.5 msec. The observed semi-logarithmic decay is linear as expected, and the slope of the decay gives a rate constant of $1.8 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. The rate constant for quenching $N_2(A^3\Sigma_u^+)$ by NO is $1.1 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.⁹³ While our measured rate constant is preliminary, and therefore uncertain by as much as a factor of 2, the factor of 60 difference between our measured rate constant, and that measured by Meyer, et al. for the quenching of $N_2(A^3\Sigma_u^+)$ by NO is well outside the combined experimental error. We feel that the measured quenching rate constant represents the process:

We are uncertain why we were unable to observe the NO β -bands from the $O + N_3$ reaction, but note that in a preliminary communication of their

Fig. 7 Decay of NO γ -Band Fluorescence (Proportional to Azide Radical Concentration) as a Function of Added NO Concentration. ($\Delta t_{\text{eff}} = 12.5 \text{ ms}$)

work, Clark and Clyne mention only the observation of the γ -bands.⁸⁶ It is possible that the major product channel for the $O + N_3$ reaction is to produce NO ($A^2\Sigma^+$), and that since the production of the NO ($B^2\Pi$) state is a much less significant process, the resulting weaker emission from these levels is below our present detection limits.

Figure 8 shows the change in intensity of the NO γ -bands as a function of atomic oxygen concentration. At low oxygen addition rates the intensity increases with oxygen concentration whereas at the higher oxygen concentrations, the γ -band intensity decreases. As there is a delay of about 7.5 ms between the atom inlet and the observation region, we feel that the decrease in emission intensity indicates removal of N_3 by O atoms (reaction 19). Under the assumption of relatively constant N_3 concentration in the observation region, we have:

$$\frac{d[NO^*]}{dt} = k_{O+N_3} [N_3] [O] - k_{rad} [NO^*] \quad (22)$$

The concentrations of added reagents is sufficiently small that we may neglect quenching of the NO^* prior to radiation. Thus, the excited NO is in steady state and we may write:

$$I_{NO^*} = k_{rad} [NO^*] = k_{O+N_3} [N_3] [O] \quad (23)$$

so that $[N_3] \propto I_{NO^*}/[O] \quad (24)$

The experiments were performed at a low decomposition temperature (188°C) which corresponds to a fairly low concentration of N_3 in the reactor, less than 10^{12} molecules cm^{-3} (see below). Thus, we may neglect second order

Fig. 8 Variation in Intensity of the NO γ -bands as a Function of Atomic Oxygen Concentration. ($\Delta t_{\text{eff}} = 7.5$ ms)

bimolecular recombination of the azide radicals, and loss processes for N_3 prior to entry into the observation region will be pseudo first order:

$$\ln \frac{[N_3]}{[N_3]_0} = -k_{O+N_3} [O] t \quad (25)$$

Using relation (24) above to give the N_3 concentration in the observation region, we obtain:

$$\ln \left\{ I_{NO^*}/[O] \right\} = \text{constant} - k_{O+N_3} [O] t \quad (26)$$

Therefore, a plot of $\ln \left\{ \frac{I_{NO^*}}{[O]} \right\}$ vs. $[O]$ should give a straight line with a slope of $k_{O+N_3} t$. Such a plot is shown in Fig. 9. As we were not set up to monitor the O atom concentration in our reactor, we have calculated concentrations assuming $50 \pm 25\%$ dissociation of the O_2 added. It is our previous experience^{94,95} that this assumption is generally valid when the oxygen added to the discharge is highly dilute, i. e. $< 1\%$, as was the case here. Given the slope from Fig. 9 and the mixing time of 7.5 ms we calculate a rate constant for reaction (19) of $8.4^{+8}_{-3} \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. The analysis leading to this rate constant assumes that the reaction between molecular oxygen and N_3 may be neglected. This is probably a good assumption but will be checked in future studies.

The preceeding analysis indicates that reaction (19) is sufficiently fast that we may drive the reaction to completion within the 7.5 ms mixing time between the atom reagent inlet and the observation region, provided that a sufficient excess of O atoms are injected into the reactor. This suggests a method for measuring the N_3 concentrations in the reactor.⁸⁶ When excess O atoms are added to the reactor, the N_3 will be converted

Fig. 9 Decay of Azide Radical Concentration as a Function of Atomic Oxygen Concentration. ($\Delta t_{\text{eff}} = 7.5 \text{ ms}$)

to NO, while the concentration of O atoms will be little changed. The resulting intensity of the O/NO air afterglow will be directly proportional to the concentration of NO produced⁹¹ and hence to the concentration of N_3 consumed. Upon turning off the oven, one may then add NO to the reactor until the O/NO intensity returns to its previous value. The concentration of added NO at the point of equal intensity will then be equal to the concentration of N_3 generated in the thermal decomposition of the sodium azide in the oven.

Figure 10 shows a plot of the log of the N_3 concentrations inferred by the above method as a function of the inverse oven temperature for two different runs. The difference in magnitude of azide radical concentration as a function of temperature between the two different runs may be attributed to a number of experimental parameters which are difficult to maintain constant from run to run, such as the effective surface area and mass of the decomposing solid. The slopes of the lines give activation energies for the decomposition process of 0.75 and 0.88 eV for the data points denoted by circles and squares respectively. The average value of the two runs, 0.81 eV is somewhat smaller than the 1.64 eV^{77,78} obtained in other studies, but most of the latter values were obtained in a higher temperature regime. De Panafieu et al.⁷⁰ have shown recently that the activation energy for the decomposition of KN_3 differs significantly in different temperature ranges, becoming larger at higher temperatures. At relatively low decomposition temperatures 180-240°C, they obtain a value of about 1.0 eV, fairly close to the value obtained here. Jacobs and Kureishy⁷⁸ have shown that the activation energy for NaN_3 decomposition may vary somewhat with the method of sample preparation and extent of decomposition. A sample precipitated from a slightly alkaline solution (pH 9) gave an activation energy of about 0.95 eV in the range of 5-50% decomposition. Torkar et. al.⁹⁶ measured an activation energy for electrical conductivity in NaN_3 of about 0.65 eV for temperatures below 195°C, increasing to 1.2 eV for higher temperatures up to about 240°C. They assumed that the ionic conductivity could be related to the rate of decomposition.

Fig. 10 Variation in Absolute N_3 Concentration with Inverse Temperature for Two Different Runs.

At low temperatures, corresponding to low N_3 production rates, the intensity of the NO γ -bands will also be proportional to the rate of N_3 production. Plots of γ -band intensity at constant O-atom concentrations against $1/T$ give similar activation to energies those obtained from the slopes in Fig. 10.

3. Observations of Chemiluminescence

The addition of Cl atoms to our reactor resulted in observation of the NCl ($b^1\Sigma^+ \rightarrow X^3\Sigma^-$) emission system (Fig. 11). This chemiluminescent emission has also been observed by Clark and Clyne⁸ and results from the reaction:

As the intensity of this relatively forbidden transition was weak, and the corrosive nature of Cl_2 created gas handling problems in our apparatus, we did not pursue this observation in detail.

At a temperature slightly above $300^\circ C$, somewhat higher than those used in the bulk of our studies, but still sufficiently low that sodium volatilization is not too great, we observe, in the absence of any added reagents, two visible emissions, one between 415 and 495 nm, peaking at about 455 nm, and the other between about 550 and 750 nm, peaking at about 650 nm (Fig. 12). Although we have not been able to obtain sufficient intensity to scan these emission under conditions of high resolution, we feel confident in identifying the emission peaking at 650 nm as the $N_2(B^3\Pi_g - A^3\Sigma_u^+)$ first-positive system. The $\Delta v=2$ through $\Delta v=5$ sequences of this system are strong in this region of the spectrum, with the $\Delta v=3$ sequence, extending to the blue from 688 nm, being the strongest. Reaction (14), the bimolecular recombination of N_3 , is sufficiently exoergic, to populate the $N_2(B^3\Pi_g)$ state up to $v=7$ or 8. At temperatures above $300^\circ C$, the concentration of N_3 may be expected to be on the order of 10^{13} molec cm^{-3} (Fig. 10). This is a sufficiently large

Fig. 11 NCl Chemiluminescence from the Reaction
Between Cl and N_3 .

Fig. 12 Molecular emission excited in the recombination of azide radicals. The longer wavelength band is nitrogen first positive, the band in the blue is unidentified. The break in the scan reflects a change of grating. ($\Delta\lambda = 16 \text{ nm}$)

concentration that the rate of Reaction 14 will be significant if the rate constant of Clark and Clyne⁸² is correct. The identification of the 455 nm emission shall have to await higher resolution studies. The only emission systems of nitrogen in this region are the $\Delta v = -4$ through $\Delta v = -6$ sequences of the second-positive system ($N_2 C^3\pi_u - B^3\pi_g$) and the $\Delta v = -11$ through $\Delta v = -13$ sequences of the Vegard-Kaplan bands, $N_2(A^3\Sigma_u^+ - 1^1\Sigma_g^+)$. The bands certainly cannot be second-positive emissions since there is not enough energy in the N_3 recombination to populate the $N_2(C^3\pi_u)$ state and since much stronger transitions of that system, further to the blue, are not observed. That the emission arises from Vegard-Kaplan emission in high vibrational levels, may not be ruled out, although it seems fairly unlikely since this system is highly forbidden and therefore very difficult to observe.

At relatively high decomposition temperatures ($\geq 350^\circ\text{C}$), with only Helium carrier gas in the reactor, we were able to observe emissions at 260, 294, and 589 nm. The emission at 589 nm is of course the Na D-lines, the intensity from which is sufficient to be observed with the naked eye. A photograph of this is shown in Fig. 13. The uv emissions are shown in Figs. 14 and 15. We have not been able to obtain sufficient intensity with the present apparatus to scan these emissions under high enough resolution to identify the radiating states. Figure 14 shows, however, that the 260 nm emission is molecular in nature, since the full width at half maximum of this band is 16 nm whereas the spectral resolution of the data is 4 nm. There is also some evidence of structure to the band. At later stages of Audubert's experiment,⁷⁹ when metal atoms had coated the walls of his reactor, the initial five bands observed by him had disappeared and only a band at 260 nm remained. Although we have not seen Audubert's initial five bands, we do apparently observe the 260 nm band. In a few experiments at high temperature in which KN_3 was substituted for NaN_3 , we did not observe the 260 nm emission. We did however observe quite strong emission at 768 nm corresponding to the first resonance transition in potassium. It may be that

Fig. 13 Na-D Line Emission Excited in High Temperature Decomposition of NaN_3 . The photograph was taken at $f/1.8$ with a one minute exposure time using Kodacolor 400 film (ASA 400). The glow extends about 11 cm from the mouth of the oven.

Fig. 14 UV Emissions Produced in NaN_3 Decomposition.
($\Delta\lambda = 16 \text{ nm}$)

Fig. 15 UV Emission Produced in NaN_3 Decomposition
($\Delta \lambda = 4 \text{ nm}$).

emission emanates from a molecule containing sodium since the presence of Na seems to be required for observation of this emission. The emission does not correspond to known emissions from Na_2 ⁹⁷. It may involve a sodium nitride molecule.

The 260 nm emission shows clearly that energy carriers containing at least 5 eV are produced in ionic azide decomposition. Since we have observed nitrogen first-positive emission, the energy carriers are most likely $\text{N}_2(\text{A}^3\Sigma_u^+)$ or $\text{N}_2(\text{B}^3\Pi_g)$ produced from azide radical recombination. The alkali-atom resonance lines can be excited either by $\text{N}_2(\text{A}^3\Sigma_u^+)$ ⁹⁸ or by nitrogen in highly excited vibrational levels of the ground electronic state.⁹⁹

D. Experimental Summary

We have demonstrated that azide radicals, in sufficiently large yields to be useful for kinetic studies in a flow system, may be produced in the thermal decomposition of ionic azides. This technique produces azide radicals in a clean environment in which azide-radical reactions may be studied free from competing reactive species. The observation of good yields of azide radicals in the thermal decomposition of ionic azides confirms the proposed mechanism for ionic decomposition.³ Heretofore, the production of azide radicals in thermal decomposition of ionic azides had been based upon inference rather than upon direct observation.

We have observed chemiluminescent emission resulting from the reaction between O and Cl atoms and N_3 and have shown how the NO emission intensity from the $\text{O} + \text{N}_3$ reaction may be used as a tracer to monitor relative N_3 concentrations. This tracer technique was used to measure rate constants for the reactions of O and NO with N_3 . In addition, by converting N_3 to NO by a large excess of O atoms, we have shown how the intensity of the resulting O/NO afterglow may be used to determine absolute N_3 concentrations.

Our experiments show that the recombination of azide radicals produces nitrogen first-positive emission and another, as yet unidentified band system between 415 and 495 nm. At higher decomposition temperatures, when the sodium becomes volatile and enters the gas stream, the excited nitrogen from the N_3 recombination transfers its energy to atomic sodium (and potassium in the case of KN_3 decomposition) and to another as yet unidentified species which emits at 260 and 293 nm.

The original goals of the experimental program designed for this contract were to develop a system in which the kinetics and chemiluminescent products of azide radical reactions could be studied, and to begin to study some of these processes. We feel that we have met these goals. We plan to continue further experiments on this system in a subsequent ERDA contract.

IV. CONCLUSIONS

This program has provided several significant technical results of value for eventual application for laser device technology. First, the thermal decomposition mechanism of ionic azides has been essentially verified, and the evolution of gaseous azide radicals demonstrated. In addition, the observation of various chemiluminescent emissions, such as the Na resonance line, indicates that the decomposition process generates energy carriers, presumably azide radicals, which can enter into a variety of reactions which lead to excited electronic states.

The above two facts do not provide enough information to design a laser, but they do suggest future, potentially interesting, avenues of research. The ability to produce a gas laser from condensed phase fuel offers considerable interest for many civilian and military applications. Solid azides, typical of many explosives, contain ~ 2 kJ/gm of available energy. Even the release of a small percentage of this energy as coherent photons could provide a compact laser device.

Azide compounds can be incorporated into chemical matrices, such as solid propellants, which could potentially provide a means to control thermal decomposition of a large surface area to produce a large concentration of azide radicals. Of course, it must first be established that such a chemical decomposition can be accomplished without changing the reaction mechanism of the ionic azide. In addition, ionic azides might be decomposed by passage of a pulsed electric current to produce controlled initiation of large volumes of material. Since photolytic decomposition of ionic azides is believed to proceed by the same mechanism as pyrolysis, pulsed electric or photolytic decomposition of significant volumes of material seems possible, although practical problems need to be considered.

Finally, the very rich chemistry of azide compounds and their products, which appear on the basis of the most recent evidence to lead to

a variety of electronically excited fragments, some of which are formed in good yield and are potentially interesting energy storage media, provides the motivation for additional research in this area. In a parallel program PSI is presently investigating the wavelength-selected photolysis of gaseous azides, such as HN_3 , as a potential source of metastable electronic species such as nitrenes. This program will make use of some of the information and techniques developed under this completed program and will provide additional insight into the practicality of employing controlled decomposition of energy-rich compounds, such as azides, for laser-device application.

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