Investigation of Induced Unimolecular Decomposition for Development of Visible Chemical Lasers

Quarterly Progress Report

for Period 1 May 1976 - 1 August 1976

L. G. Piper and R. L. Taylor

Physical Sciences Inc.
Woburn, Massachusetts 01801

August 1976

Prepared for
ERDA
under Contract No. E(11-1) -2920

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

ABSTRACT

This report summarizes progress during the first quarterly period of the subject contract. Task 1, a technical review of the azide literature, has essentially been completed. A number of interesting reactions of azides which potentially lead to electronic excitation have been identified. However, uncertainties in state-specific mechanisms, branching ratios, and rate constants do exist. To evaluate the potential of azide chemistry for a short wavelength laser, an experiment is being designed to determine some of the critical, but unknown, information and data.

TABLE OF CONTENTS

Introduction

The following report summarizes technical progress during the first quarterly period of ERDA Contract No. E(11-1)-2920, "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 involves a thorough review of the extensive technical literature concerning azides, emphasizing reaction mechanisms and kinetics. This survey is necessary because there is no recent review which discusses the reaction mechanisms of azides emphasizing the state-specific mechanisms. Furthermore, this survey is important in order to provide the necessary background upon which to efficiently plan an experimental program (Task 2). The results of this experimental program together with all other availalbe 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).

During this quarterly period, Task 1 has essentially been completed, and the results of this survey are summarized in this progress report. It is planned subsequently to provide a more complete and detailed description of this literature survey and evaluation in a separate report. Task 1 has indicated several important questions which require further experimental study. During the next quarterly period, an experimental program will be developed and undertaken which addresses some of these technical issues.

Summary of Task 1

1. 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 bromides and azides, 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 ~ 1.186 Å.[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 (~ 1.24 Å) and much weaker (D ~ 0.4 - 1.3 eV) than the other N-N bond (length ~ 1.12 Å, D ~ 6 - 9 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 ~ 3.5 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

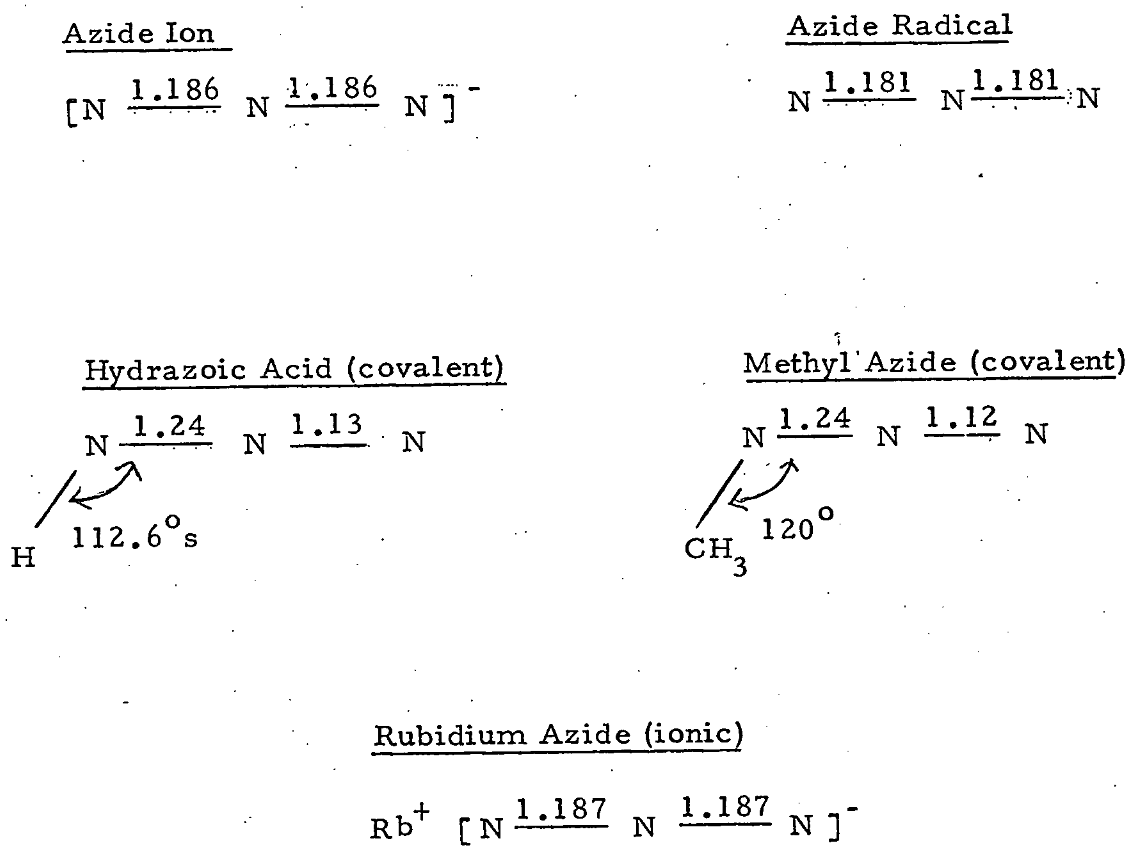


Fig. 1 Geometry of the azide ion, the azide radical, and selected azide compounds.

Table I. Bond Dissociation Energies of Selected Azides (eV)

Compound	$D(R\text{-}N_3)$[a]	$D(RN\text{-}N_2)$
HN_3	3.9 ± 0.35	0.39 ± 0.09[b]
CH_3N_3	3.7 ± 0.35[c]	
NCN_3	4.15 ± 0.10[c]	0.30 ± 0.09[a]
$C_6H_5N_3$ (pheny 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. M. Chiang and R. Wheeler, Can. J. Chem. 46, 3785 (1968) modes of decomposition of the covalent azides. We will discuss the mechanisms for decomposition of the covalent and ionic azides below.

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 ($Ba(N_3)_2 \Delta H_f^o = -0.22$ eV, $CsN_3 \Delta H_f^o = -0.01$ eV) to highly endothermic ($Hg(N_3)_2 \Delta H_f^o = 6.15$ eV). Most of the azide compounds have positive heats of formation (endothermic).

The heat of formation of the azide radical has been 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 1.47[6] 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 4.54 or 4.98 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]

$$O(^3P_J) + N_3(^2\Pi_g) \rightarrow NO^*(A^2\Sigma^+ \text{ and } B^2\Pi) + N_2(X^1\Sigma_g^+) \qquad (1)$$

$$N(^4S) + N_3(^2\Pi_g) \rightarrow N_2^*(B^3\Pi_g) + N_2(X^1\Sigma_g^+) \qquad (2)$$

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.

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 an 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.

2. 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.

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 $\epsilon \sim 25\text{-}30\ 1\ mol^{-1}cm^{-1}$,and a much stronger absorption band peaking around 215 nm ($\epsilon \sim 500\ 1\ mol^{-1}cm^{-1}$).

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 ($\sim 0.4 - 1.3$ eV) compared to the $R-N_3$ bond (~ 3.5 eV). Thus the primary products of decomposition are molecular nitrogen and the RN radical, known as a nitrene:

$$RN_3 \xrightarrow[\text{or } \Delta]{h\nu} RN + N_2 \qquad (3)$$

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.

A number of experiments have shown that formation of singlet nitrene is the primary product in covalent azide decomposition. Emission has been observed from singlet NH produced in the gas-phase photolysis of HN_3 by vacuum ultraviolet radiation.[21-23] Herzberg has apparently observed absorption by the lowest singlet state of NH following the photolysis of HN_3.[24] Kroto showed that,whereas the absorption of the lowest singlet state of NCN, produced in the photolysis of NCN_3, was at a maximum immediately after the photolytic flash, absorption from the triplet ground state of NCN augmented with time after the flash.[25] Schoen observed the primary formation of singlet NCN produced by photolysis of NCN_3 in a nitrogen matrix at 20.4°K with subsequent decay to the triplet.[26] Nitrenes produced from the thermal decomposition of ethyl azidoformate ($N_3 - \overset{O}{\overset{/\!/}{C}} - O - C_2H_5$) have been shown to add stereospecifically to double bonds in unsaturated hydrocarbons. This behavior is expected of a singlet radical, but not a triplet.[27]

Table II. Pathways for Decomposition of Covalent Azides

		Reaction	Enthalpy Change
I. Specific Case: HN_3			
1.	Forbidden	$HN_3\ (^1A') \rightarrow NH\ (X\,^3\Sigma^-) + N_2(X\,^1\Sigma_g^+)$	0.39[a]
2.	Allowed	$HN_3\ (^1A') \rightarrow NH\ (a\,^1\Delta) + N_2\ (X\,^1\Sigma_g^+)$	1.96 eV[b]
3.	Allowed	$HN_3\ (^1A') \rightarrow H\ (^2S_{1/2}) + N_3(X\,^2\Pi_g)$	3.55 eV
II. General Case: RN_3			
4.	Forbidden	$RN_3\ (^1A_1) \rightarrow RN\ (^3A_1) + N_2\ (X\,^1\Sigma_g^+)$	0.4 - 1.3 eV
5.	Allowed	$RN_3\ (^1A_1) \rightarrow RN\ (^1A_1) + N_2\ (X\,^1\Sigma_g^+)$	1.5 - 2.0 eV[c]
6.	Allowed	$RN_3\ (^1A_1) \rightarrow R\ (^2A_1) + N_3\ (X\,^2\Pi_g)$	~ 3.5 eV

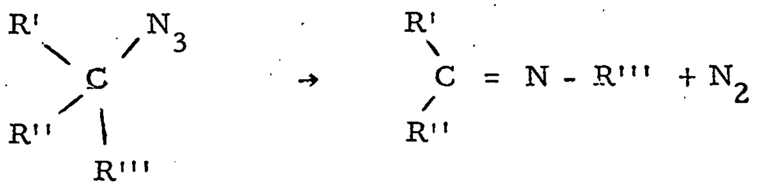
---

[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 ΔH_f^o (NH) = 3.9 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.[20] If the HN-N_2 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 results of experiments proposing alternative mechanisms to the one 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. The products from the photolytic decomposition[28] of methyl azide, CH_3N_3, are apparently different from the products resulting from thermal decomposition.[29] It was suggested that this difference could be rationalized in terms of formation of triplet methyl nitrene in the thermal decomposition.[29] In fact, 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]



Product analysis from the photolytic decomposition of ethyl azidoformate indicated that 30% of the primary nitrene products were in the triplet state.[27] This is in contrast to the results of the thermal decomposition study of ethyl azidoformate mentioned above, but it does indicate that intersystem crossing in the excited singlet state of the azide is a relatively efficient process.

Evidence for the formation of excited N_2 in the decomposition of covalent azides is secondary in nature. Okabe observed ill-defined emissions in the region between 500 and 1000 nm and, in addition, NH ($A^3\Pi_i$) which he showed was produced by secondary reactions.[21] The infra-red emissions could occur from the nitrogen($B^3\Pi_g$)electron state, while the triplet NH could be produced by energy transfer from $N_2(A^3\Sigma_u^+)$ either to NH or to HN_3.[30] Welge[23] also studied the photolysis of HN_3 and observed, in addition to NH ($A^3\Pi_i$), NO γ-band emission and emission from Hg at 253.7 nm when these latter two species were added to the gaseous mixture. It is well known that $N_2(A^3\Sigma_u^+)$ readily excites both of these latter emissions.[30] Okabe and Mele observed emission from NCN ($A^3\Pi$) in a photolysis study of NCN_3 and showed that the most likely precursor of this triplet emission was the interaction of $N_2(A^3\Sigma_u^+)$ with NCN_3.[31]

$$N_2\ (A)\ +\ NCN_3\ \rightarrow\ NCN\ (A^3\Pi)\ +\ 2N_2(X) \qquad (5)$$

If triplet states of nitrogen are formed, it is not clear whether they are formed in the direct photolysis, or indirectly from the recombination of two azide radicals, a process which is both spin allowed and energetically feasible.

$$2N_3\ \rightarrow\ N_2^*\ (A^3\Sigma_u^+\ \text{or}\ B^3\Pi_g)\ +\ 2N_2\ +\ \Delta E \qquad (6)$$

One final mechanistic aspect of the decomposition of covalent azides is that the N_3 radical has been observed directly (by its characteristic absorption spectrum around 272 nm) in the gas-phase photolyses of HN_3[32,33], ClN_3[33], and NCN_3[25]. 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[34], (ii) tertiary organic azides in solution[13], and (iii) the azides of the halogens F, Cl, and Br in low-temperature inert matrices.[35] 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 need 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 appears to be a minor channel to produce the N_3 radical. In only the simplest cases (NH[36] and NCN[37]) has this 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[20]. In the NCN radical, Schoen suggests a value between 4.1 and 5.2 eV[26]. Clearly, further studies would be fruitful to unravel the energetics and state-specific mechanism of the primary decomposition process.

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[38], a type of unimolecular decomposition of a 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.[38] Studies in solution at temperatures between 10°C - 50°C give the same product quantum yields as were obtained in the low temperature matrices.[38] Thus, as in the case of non-aromatic photolysis, aromatic photolysis does not involve thermal dissociation of an excited state.

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.

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 that group 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 6).

3. Ionic Azides

The ionic azides are generally non-volatile and thermally and mechanically unstable 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, 39] The azide ion in these solids is generally symmetric, although recent studies have shown small asymmetrical structures in heavy-metal azides.[40] 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; (iii) the thermal stability of these azides appears to correlate inversely with the ionization potential of the cation (e.g., $KN_3 > TlN_3 > AgN_3$), and (iv) ultraviolet emission (200 - 250 nm) may be observed which is proportional to the rate of decomposition.[41,42] In some decompositions, metal nitrides have been found, but these nitrides are thought to be formed in secondary reactions.[3]

The basic mode of decomposition 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.

$$N_3^- \xrightarrow[\text{or } h\nu]{\Delta} N_3 + e^- \qquad (7)$$

$$M^+ + (M)_n + e^- \rightarrow (M)_{n+1} \qquad (8)$$

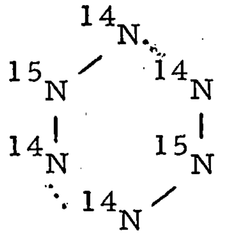
$$2N_3 \rightarrow 3N_2 + 8.8 \text{ eV} \qquad (9)$$

The great amounts of energy liberated in the azide radical recombination is surely a factor involved in their explosive decomposition. The correlation of the thermal stability of the azides with respect to 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.

The observation of ultraviolet emission accompanying the decomposition of the azides is also in accord with the large amounts of energy liberated in azide radical recombination, since the recombination to produce an excited nitrogen molecule in either the $A^3\Sigma_u^+$ or $B^3\Pi_g$ state is both energetically feasible and spin allowed. Indeed, the luminescence studies indicate an augmentation in emission at about 255 nm when Hg vapor was introduced into the system.[42] This is probably due to the efficient excitation of Hg 253.7 nm radiation by N_2 $(A^3\Sigma_u^+)$.[30] Unfortunately, only a crude spectrum of this emission has been determined,and it is not possible to decide with any degree of certainty what states are responsible for the emission, nor what the precursor(s) of the excitation might be.[41] The observed spectrum is independent of azide cation and has also been observed 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, but the experimentors were unable to discuss these findings quantitatively.[43] Studies with NaN_3, on the other hand, showed no Na nor N_3 given off under normal conditions.[44,45]

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 observed chemiluminescence from the species ClN, BrN, NO and N_2 when Cl, Br, O, or N atoms respectively were added to a flow system containing N_3 radicals.[8] Unfortunately, they were unable to extract quantitative information on the kinetics of these reactions. They felt that the reaction between Cl and N_3 was fairly slow ($k < 10^{-13}$ cm^3 molec^{-1} s^{-1}) while the reaction between N_3 and N or O atoms was somewhat faster ($k > 10^{-12}$ cm^3 molec^{-1} s^{-1}). Thrush observed the bimolecular decay of N_3 radicals in the gas phase but was not able to describe the kinetics quantitatively. He observed that the reaction proceeded with a "low collision efficiency".[32] 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 ($2k = 9 \times 10^9$ l mol^{-1} s^{-1}).[46,47] 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, ($^{14}N - {}^{15}N - {}^{14}N$), yields of $^{14}N_2$ and $^{14}N{-}^{15}N$ were obtained in a 1:2 ratio but no $^{15}N_2$ was observed.[48] From this observation, it may be inferred that the intermediate would be cyclic or linear in nature.



or $^{14}N - {}^{15}N - {}^{14}N \ldots {}^{14}N - {}^{15}N - {}^{14}N$

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

Task 2: Experimental Program

The information discussed above indicates that there are three potential sources of electronic excitation following the induced decomposition of azides: (i) the bimolecular recombination of azide radicals; (ii) the chemiluminescent reaction between reactive species, e.g., atoms and azide radicals; and (iii) the direct formation of the metastable singlet nitrene in the decomposition of organic azides. Table III summarizes these findings. The first two sources of excitation require a good source of N_3 radicals, and a better knowledge of the kinetics

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
$2N_3 \rightarrow N_2^* + 2N_2$	$N_2(A^3\Sigma_u^+)$	6.3
	or $N_2(B^3\Pi_g)$	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
$RN_3 \xrightarrow[\text{or } \Delta]{h\nu} RN^* + N_2$	$NH\ (a^1\Delta)$[c]	1.57
	$NH\ (c^1\Pi)$[d]	5.45
	$NCN\ (a^1\Delta)$[e]	4.1 - 5.2
	$RN\ (a^1\Delta)$	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. G. Herzberg, private communication to H.W. Kroto, Ref. 22

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) of this species. N_3 radicals may apparently be produced in unknown yields in the thermal or photolytic decomposition of the solid ionic azides, in small yields from the photolytic decomposition of covalent azides of low molecular weight, e.g., HN_3, NCN_3, CH_3N_3, but perhaps in good yields from the photolytic decomposition of the halogen azides or carbonyl azide,(there is no direct quantitative information in the case of these latter compounds), and by certain chemical reactions such as that between Cl atoms and ClN_3 [17]

$$Cl + ClN_3 \rightarrow Cl_2 + N_3, k \geqslant 10^{-12}\ cm^3 molec^{-1} s^{-1} \qquad (10)$$

The azide radical may be observed directly by resonance absorption at 272 nm,[32,33] so that in principle there is no reason why quantitative studies on azide radical kinetics may not be pursued. The studies could be undertaken either in a flow or static system designed to achieve good time resolution.

A study of the production of singlet nitrene will first require a better characterization of the energy content of these species, and for all nitrenes save NH and NCN, the spectroscopy. Experiments also need to be done to determine the lifetime and energy-transfer characteristics of these nitrene species. These studies would be most conveniently done in a flash-photolysis system.

The induced decomposition of azides appears to be a favorable route for the production of electronically excited states in good yields. However, most of the available information is rather superficial in nature,so that much work will be required before assessment may be made of these systems as possible sources of energy for a visible or short wavelength laser.

Summary

Task 1 has essentially been completed. As previously suggested, the results of this review show that azide compounds and their reactions provide a rich source of possibilities as an energy source for a visible laser. Of course, the formation of an excited electronic state or the occurrence of light emission are not alone sufficient to produce a chemical laser device. Much work remains to be done to provide specific rate constants, spectroscopic data, branching ratios, etc. in order to evaluate the expectations of a laser device based on azide chemistry.

During the next quarterly period, the important technical questions indicated by the survey will be evaluated and a logical, cost effective experimental program planned. The experiment(s) will most probably involve time and wavelength resolved photodecomposition of selected azides in the gas phase with identification of reaction products, branching ratios, and rate constants. Some spectroscopic studies may also be necessary to provide diagnostic interpretation and thermochemical data.. An experiment involving condensed phase decomposition may also be considered, as obvious practical advantages accrue to a laser device based on a condensed phase fuel.

REFERENCES

1. A. Treinin, "General and Theoretical Aspects [of the Azido Group]", in <u>The Chemistry of the Azido Group</u>, S. Patai, ed., New York: John Wiley, 1-53 (1971).

2. C. S. Choi and E. Prince, J. Chem. Phys. <u>64</u>, 4520 (1976).

3. A. D. Yoffe, "The Inorganic Azides", in <u>Developments in Inorganic Nitrogen Chemistry</u>, C. B. Colburn, ed., London: Elsevier, 72-149 (1966).

4. B. L. Evans, A. D. Yoffe and P. Gray, Chem. Revs. <u>59</u>, 515 (1959).

5. P. Gray, Quarterly Reviews <u>18</u>, 441 (1964).

6. H. P. Dixon, H. D. B. Jenkins and T. C. Waddington, Chem. Phys. Lett. <u>10</u>, 600 (1971).

7. I. Burak and A. Treinin, J. Chem. Phys. <u>39</u>, 189 (1963).

8. T. C. Clark and M. A. A. Clyne, Trans. Faraday Soc. <u>66</u>, 877 (1970).

9. M. E. C. Biffin, J. Miller and D. B. Paul in <u>The Chemistry of the Azido Group</u>, S. Patai, ed., New York: John Wiley, 61-62 (1971).

10. L. F. Audrieth, Chem. Rev. <u>15</u>, 169 (1934).

11. S. Patai, ed., <u>The Chemistry of the Azido Group</u>, New York: John Wiley (1971). Of primary interests here are chapters 1 and 8 and to a lesser extent Ch. 5. (Refs. 1, 12 and 13).

12. A. Reiser and H. M. Wagner, "The Photochemistry of the Azido Group", <u>ibid.</u>, 441-501 (1971).

13. R. A. Abramovitch and E. P. Kyba, "Decomposition of Organic Azides", <u>ibid.</u>, 221-329.

14. J. S. Thayer, Organomet. Chem. Revs. <u>1</u>, 157 (1966).

15. M. F. Lappert and H. Pyszora, "Pseudohalides of Group IIIB and IVB Elements", in <u>Adv. Inorg. Chem. and Radiochem.</u> <u>9</u>, 133 (1966).

16. J. R. McDonald, J. W. Rabalais and S. P. McGlynn, J. Chem. Phys. <u>52</u>, 1332 (1970).

REFERENCES (Cont'd)

17. T. C. Clark and M. A. A. Clyne, Trans. Faraday Soc. 65, 2994 (1969).

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

19. W. J. Stevens, J. Chem. Phys. 58, 1264 (1973) and references therein.

20. A. Gilles, J. Masanet and C. Vermeil, Chem. Phys. Lett. 25, 346 (1974).

21. H. Okabe, J. Chem. Phys. 49, 2726 (1968).

22. K. H. Welge, J. Chem. Phys. 45, 4373 (1966).

23. K. H. Welge, J. Chem. Phys. 45, 166 (1966).

24. G. Herzberg, private communication to H. W. Kroto, Ref. 25.

25. H. W. Kroto, J. Chem. Phys. 44, 831 (1966).

26. L. J. Schoen, J. Chem. Phys. 45, 2773 (1966).

27. Various experiments by W. Lwowski and co-workers as reported in Ref. 12.

28. C. L. Currie and B. deB. Darwent, Can J. Chem. 41, 1552 (1963).

29. M. S. O'dell, Jr., and B. deB. Darwent, Can J. Chem. 48, 1140 (1970).

30. D. H. Stedman and D. W. Setser, Chem. Phys. Lett. 2, 542 (1968).

31. H. Okabe and A. Mele, J. Chem. Phys. 51, 2100 (1969).

32. B. A. Thrush, Proc. Roy. Soc. (London) A235, 143 (1956).

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

34. N. Getoff, R. Laupert and R. N. Schindler, Z. Phys. Chem. 70, 70 (1970).

35. D. E. Milligan and M. E. Jacox, J. Chem. Phys. 40, 2461 (1964).

36. J. M. Lents, J. Quant. Spectrosc. Radiat.Transfer, 13, 297 (1973).

37. H. Kroto, Can. J. Phys. 45, 1439 (1967).

38. A. Reiser and R. Marley, Trans. Faraday. Soc. 64, 1806 (1968).

39. Some recent data indicates that there is substantial covalent character to the bonding of the heavy-metal azides. see. R. J. Colton and J. W. Rabalais, J. Chem. Phys. 64, 3481 (1976).

40. References 11-15 in Ref. 39.

41. R. Audubert and G. Calmar, J. Chim. Phys. 54, 324 (1957).

42. R. Audubert, J. Chim. Phys. 49, 31 (1952).

43. A. de Panafieu, B. S. H. Royce and T. Russel, J. Chem. Phys. 64, 1473 (1976).

44. R. F. Walker, N. Bane, and F. P. Bowden, Proc. Roy. Soc. (London) A294, 417 (1966).

45. R. F. Walker, J. Phys. Chem. Solids 29, 985 (1968).

46. E. Hayon and M. Simic, J. Am. Chem. Soc. 92, 7486 (1970).

47. A. Treinin and E. Hayon, J. Chem. Phys. 50, 538 (1969).

48. K. Clusius and H. Schumacher, Helv. Chem. Acta 41, 972 (1958).