Investigation of Induced Unimolecular Decomposition
for Development of Visible Chemical Lasers

Quarterly Progress Report

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ABSTRACT

This report summarizes progress during the third quarterly period of the subject contract. The logic developed in previous quarterly reports for studying the kinetics and spectroscopy of chemiluminescent azide radical reactions is summarized. The apparatus built for these studies is described in some detail. Preliminary observations of NO γ -band emission produced from the reaction of oxygen atoms with products of thermally decomposed sodium azide are taken as an indication that azide radicals are being produced in the thermal decomposition source. Additional observations are underway and future plans are discussed.

Summary

During this third quarterly period of Contract No. EY-76-C-02-2920.*000, the construction of the experimental apparatus was completed, its operation characterized and preliminary experiments begun. The apparatus is a flow reactor which was designed to permit (i) the production of N_3 radicals in a clean flow environment, (ii) the quantitative measurement of various kinetic rate constants of direct significance to the overall goal of this program, and (iii) the limited study of the spectroscopy of excited electronic states produced in the reactions.

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

During the next reporting period, data should be collected which will prove useful in evaluating azide decomposition as a source of electronically excited species for a potential laser device.

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Introduction

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

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

Review of Azide Chemistry

In two previous reports^{1,2} we have discussed the physics and chemistry of azides with particular emphasis upon the mechanisms of azide decomposition. With this information in mind an experimental program was designed and an apparatus built for the study of azide-radical reactions in the gas phase. The apparatus is now operational and preliminary tests have been made to explore its performance. In this report, we shall summarize the logic which preceeded the experimental design, describe the apparatus in some detail and discuss its performance characteristics. Lastly, we shall describe briefly some of the specific experiments we hope to perform.

Previous investigation has indicated that azides decompose in essentially two ways, depending upon the nature of the azide: (i) covalently bonded azides decompose to produce nitrenes, RN , generally in an excited singlet state (Table I); (ii) ionically bound solid azides generally decompose and produce a metal atom and an azide radical, N_3 (Table II). In covalent azide decomposition, excited states are produced directly, while in the solid decompositions, excited states are produced in chemiluminescent reactions between azide radicals themselves or other reactive species. Azide radicals may also be produced in the subsequent reaction of nitrenes with the parent azides. A number of reactions between azide radicals and atoms or other free radicals may be expected to give nitrenes.

Since azide radicals could play an important role in the decomposition of both ionically and covalently bonded azides, and nitrenes may be formed as a product in azide radical reactions, a system designed to study azide-radical chemistry would be most likely to yield the greatest amount of general information concerning azide decomposition. We have, therefore, built a gas-flow system which is suitable for studying a number of azide-radical reaction systems.

Azide radicals may be produced in essentially four ways (Table III):² (i) as a secondary product in the photolysis of covalent azides; (ii) direct photolysis of certain covalent azides such as tertiary organic azides; (iii) in certain chemical reactions, such as the reaction between chlorine azide and chlorine atoms; and (iv) in the thermal or photolytic decomposition of ionic

TABLE I

Decomposition Mechanism of Covalent Azides

A. General Case: RN_3

			Enthalpy Change
1. Forbidden ^a	$\text{RN}_3 (^1\text{A}_1) \xrightarrow[\text{or } \Delta]{h\nu} \text{RN} (^3\text{A}_1) + \text{N}_2 (\text{X}^1\Sigma_g^+)$		0.4 - 1.3 eV
2. Allowed	$\text{RN}_3 (^1\text{A}_1) \longrightarrow \text{RN}^* (^1\text{A}_1) + \text{N}_2 (\text{X}^1\Sigma_g^+)$		1.5 - 2.0 eV
3. Allowed ^a	$\text{RN}_3 (^1\text{A}_1) \longrightarrow \text{R} (^2\text{A}_1) + \text{N}_3 (\text{X}^2\Pi_g)$		~ 3.5 eV

B. Specific Example:

1. $\text{HN}_3 (^1\text{A}_1) \xrightarrow{h\nu}$	$\text{NH} (a^1\Delta) + \text{N}_2 (\text{X}^1\Sigma_g^+)$	1.96 eV.
	$\text{NH} (c^1\Pi_g) + \text{N}_2 (\text{X}^1\Sigma_g^+)$	5.77
	$\text{H} (^2\text{S}_{1/2}) + \text{N}_3 (\text{X}^2\Pi_g)$	3.55 eV ^b
2. $\text{NCN}_3 (^1\text{A}_1)^c \xrightarrow{h\nu}$	$\text{NCN} (a^1\Delta) + \text{N}_2 (\text{X}^1\Sigma_g^+)$	

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

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

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

TABLE II

The decomposition Mechanism of Ionic Azides

TABLE III

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.

azides. Our previous conclusion was that method (iv), the decomposition of ionic azides, was likely to prove the best source of azide radicals, since, in the other methods of production, reactive intermediates in addition to the azide radical would be present in the system. Therefore, we have designed a reactor in which N_3 radicals are formed by the thermal decomposition of ionic azides. The apparatus is sufficiently flexible, however, that modifications may be made readily, so that other radical formation techniques may be utilized.

Apparatus

The apparatus which has been built for this experiment is shown in Fig. 1. 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 viewing 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 has been blown. Nichrome wire has been wrapped around the tube from a few centimeters below to a few centimeters above the fritted disk, and heat is 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 contemplated experiments will involve spectroscopic analysis of excited products. The optical system designed for this analysis should give fairly good sensitivity with moderate resolution. The monochromator is a 0.25 m Jarrell-Ash instrument equipped with a stepping-motor

Fig. 1 - 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; OS, sliding o-ring seal to provide temporal variation with a fixed observation window; P, to pumps (Precision D-500); MC, Jarrell-Ash O, 25-m scanning monochromator; PMT, HTV R955 photomultiplier; HV, high voltage power supply; PA, Kiethly 417S picoammeter; R, Heath SR 205 strip chart recorder.

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 0.4 and 15 nm, respectively. Photons emitted between 170 and 920 nm may be detected with either an HTV R955 or RCA 4840 (210 - 850 nm) photomultipliers. The photomultipliers are operated at room temperature in the analog mode, a Kiethly 417S picoammeter being used to measure their output current. The picoammeter has a current suppression circuit so that dark current from the photomultipliers (on the order of 1 - 2 nA) may be nulled out. The wavelength calibration of the system was done by scanning the NO and N₂ emissions present in discharged air. The wavelength drive reads 24 nm low with the 300 nm grating and 54 nm low with the 600 nm grating. We plan additional calibration of the spectral response of the system by measuring the O/NO afterglow emission intensities.⁴ In order to eliminate problems with room-light interference, a light-tight enclosure has been constructed around the apparatus.

The observation region is constructed so that spectral observations may be made either along the axis of the flow tube, to enhance the light collection efficiency, or at any one of five windows spaced 10 cm apart in the observation region. This latter configuration allows temporal resolution of decaying emissions. Temporal resolution may also be achieved either 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 (100-100 $\mu\text{mols s}^{-1}$) are metered into the system through rotameters which have been calibrated with a wet test meter.⁵ It was found in the case of helium that the manufacturer's calibration curves were low by more than a factor of two at low flows.⁶ 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 are available to give a range of reagent flows in between 10^{-2} to 5 $\mu\text{mols s}^{-1}$. The reagents are purified prior to use and stored in 5 l storage flasks. One of the capillary-oil flow meters mixes reagents with the main carrier gas flow upstream of a 2.45 GHz microwave discharge cavity (Evenson type). Atoms such as O, H, F, or Cl are formed in the microwave discharge from the appropriate molecular reagents, O₂, H₂, CF₄, or Cl₂ respectively. 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.

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. Flow-tube pressures are measured with a silicon oil manometer which has a resolution of about 0.08 torr per mm.

Experiments

Preliminary experiments have been aimed at characterizing the operating conditions within the reactor. We have calibrated the flow meters and the wavelength indicator on the monochromator. In addition several preliminary experiments on azide decomposition have been attempted.

Some old and largely ignored experiments by the French worker, René Audubert,⁷ indicate that a number of solid inorganic azides, including NaN_3 , KN_3 , AgN_3 , TlN_3 and PbN_3 , emit photons in the region from 200 to 260 nm upon thermal decomposition. Furthermore, the rate of photon emission is apparently proportional to temperature, and therefore presumably proportional to the rate of azide decomposition. Audubert measured a crude spectrum of this emission (with a resolution of $\sim 7 \text{ nm}$) and found five bands within the spectral region scanned. However, this spectrum does not correspond particularly well to known emissions, so it is not clear what transitions are being observed. Nevertheless, the indications are, that merely by decomposing various ionic azides, one ought to be able to observe UV emission.

Our first two or three runs were directed towards trying to observe the emission of Audubert and, if possible, to assign the spectrum. Sodium azide, the most readily available and safest of the azides to handle, was chosen for these experiments. We have not been able to observe any emissions, although a systematic variation of conditions has not been attempted. It is possible that the emissions observed by Audubert resulted from excitations of impurities in his reactor with excited nitrogen formed from the recombination of azide radicals. This recombination reaction is 8.8 eV exoergic,⁸ so that both the $\text{N}_2(\text{A})$ and $\text{N}_2(\text{B})$ states may be formed. It is unlikely that Vegard-Kaplan

emission from the $N_2(A)$ state could be observed in a system containing Na atoms, but one might expect to see Na D-line emission (589 nm) from the energy-transfer reaction between $N_2(A)$ and Na.⁹ The nitrogen first positive emission (B-A) could be too far in the infrared for our detection system (the 0-0 transition is at 1050 nm). However, we scanned the spectral region from 200 to 850 nm, so that first positive emissions from $v' \geq 2$ should have been observable in addition to possible Na D-line emission.

The sodium azide appears to decompose quickly at temperatures above 350°C, because an Na mirror is formed rapidly upon the walls of the reactor after the onset of decomposition. The decomposition also appears to have an incubation period in qualitative agreement with some older studies.¹⁰⁻¹² 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 is deposited along the whole length of the flow tube. This material is fairly volatile, since it can be pumped away within an hour after the termination of azide decomposition. At the temperatures studied, the azide decomposition appears to be relatively complete within about 20 minutes for charges of NaN_3 on the order of 0.5 to 1.0 gram.

A more sensitive test for the presence of azide radicals in our flow tube is to look for emission following reaction between some reactive species such as O or Cl atoms and N_3 . Clark and Clyne have characterized several of these tracer emissions (Table IV).⁸ We have tried one experiment with O atoms and observed NO γ -band emission between 210 and 290 nm. This emission is what would be expected from the reaction between O and N_3 .⁸ However, we have not done enough work to rule out sources such as impurities in the argon carrier gas. The emission seen was weak so it is unlikely that the azide-radical concentration was very large. Thus, it is not surprising that no emissions were observed from excited nitrogen formed directly by azide-radical recombination. The observation of this emission, however, gives us a diagnostic to use in optimizing the operation of our system. We expect to be able to enhance our conditions sufficiently in the near future so that other chemiluminescent reactions of azide radicals may be observed and characterized.

TABLE IV

Chemiluminescent Reactions of N_3

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

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

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

Future Plans

Our preliminary experiments will be to characterize the chemiluminescent emissions resulting from the reactions of azide radicals with a number of atoms including O, H, N, Cl, and F. By comparing relative emission intensities from the different sources, we hope, at least semi-quantitatively, to obtain relative excitation rate coefficients for the various reactions. We shall also add several tracers, such as NO or Hg, to the reactor which give specific emissions in the presence of $N_2(A)^{13}$. NO may well be reactive towards N_3 and thereby prove a useful titrant for determining absolute azide-radical concentrations.

In conjunction with the above spectroscopic studies, we plan to try several different ionic azides, e.g. KN_3 and AgN_3 in addition to NaN_3 , to look for the most suitable candidate for controlled thermal decomposition studies. We may also try to measure thermal decomposition rates by measuring the rate of N_2 evolution as a function of time. The ideal azide would give a linear rate of decomposition with time.

Conclusions

We have completed the construction of a flow apparatus useful for studying the kinetics and spectroscopy of chemiluminescent azide-radical reactions. The apparatus is fully operational and several preliminary experiments involving the thermal decomposition of sodium azide have been tried. The observation of NO γ -band emission in an experiment in which O atoms were mixed with the products of NaN_3 decomposition, most likely indicates that azide radicals are indeed formed in the reactor. This is an important observation, because several mass spectrometric studies on NaN_3 decomposition failed to find evidence for the presence of azide radicals.^{10, 11} By the end of the next quarterly period, we should have begun to amass a body of data which should prove useful in directing future endeavors.

REFERENCES AND FOOTNOTES

1. L. G. Piper and R. L. Taylor, "Investigation of Induced Unimolecular Decomposition for Development of Visible Chemical Lasers", PSI TR-61, under Contract #EY-76-C-02-2920.*000 (1976).
2. L. G. Piper and R. L. Taylor, "Investigation of Induced Unimolecular Decomposition for Development of Visible Chemical Lasers", PSI TR-71, under Contract #EY-76-C-02-2920.*000 (1976).
3. H. W. Kroto, T. F. Morgan and H. H. Sheena, Trans. Faraday Soc. 66, 2237 (1970).
4. A. Fontijn, C. B. Meyer, and H. I. Schiff, J. Chem. Phys. 40, 64 (1964).
5. We wish to thank Dr. D. L. McFadden of Boston College for lending us the wet test meter.
6. Ace Glass, Vineland, New Jersey
7. R. Audubert and G. Calmar, J. de Chim. Phys. 54, 324 (1957) and references therein.
8. T. C. Clark and M. A. A. Clyne, Trans. Faraday Soc. 66, 877 (1970).
9. R. G. Gann, F. Kaufman and M. A. Biondi, Chem. Phys. Lett. 16, 380 (1972).
10. R. F. Walker, J. Phys. Chem. Solids, 29, 985 (1968).
11. R. F. Walker, N. Gane and F. P. Bowden, F. R. S., Proc. Roy. Soc. A294, 417 (1966).
12. R. Audubert and J. Robert, J. de Chim. Phys. 43, 127 (1946).
13. D. H. Stedman, J. A. Meyer and D. W. Setser, J. Chem. Phys. 48, 4320 (1968).