

Generation of N₃ in the thermal decomposition of NaN₃

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Gaseous azide radicals at concentrations up to 10^{13} molecules cm^{-3} appear to have been generated in a flow system in the thermal decomposition of solid NaN₃ at temperatures between 150 and 350°C. Between 150 and 250°C the activation energy for the decomposition is 0.80 ± 0.15 eV. The addition of small concentrations of oxygen atoms to the reactor excites NO γ -band chemiluminescence from the reaction $\text{O} + \text{N}_3 \xrightarrow{k_4} \text{NO} (A^2\Sigma^+) + \text{N}_2$. The γ -band emission may be used as a sensitive tracer for N₃ in kinetic measurements; k_4 was determined to be $(10 \pm 4) \times 10^{-12}$ cm^3 molecule⁻¹ s⁻¹. Large concentrations of O atoms quantitatively convert the N₃ to NO, and the resulting O/NO afterglow has been used to determine absolute concentrations of the N₃ radicals. Several other chemiluminescent emissions are observed, most notably the nitrogen first-positive emission excited in azide-radical recombination.

I. INTRODUCTION

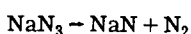
The azides are a class of endoergic compounds which appear to decompose into energy-carrying fragments. Thermal or photolytic decomposition of covalent azides generally leads to the formation of electronically excited singlet nitrenes, whereas decomposition of ionic azides is generally thought to produce the azide radical, although there has been little direct evidence to support this contention. The azide radical is highly endoergic ($\Delta H_f = 4.4$ eV),¹ and a number of its reactions have been shown to be chemiluminescent.¹ The purpose of this work was to investigate the thermal decomposition of solid ionic azides to determine if gaseous azide radicals were indeed products and to develop a clean system in which azide-radical chemistry could be studied.

The basic mode of thermal decomposition of ionic azides is thought to involve the dissociation of the azide ion into the azide radical and a free electron.² 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 an important factor in the explosive decomposition of many azides.

An alternative mechanism whereby decomposition of ionic azides yields molecular nitrogen and a metal nitrene MN, the pathway analogous to that observed in covalent azides, can be dismissed on the basis of energetics. Such a process is too endoergic to occur with much probability at temperatures as low as 200°C. We consider sodium azide as a case in point. Using techniques we have developed for estimating the thermochemistry of alkali sulfides,³ we have estimated the heat of formation of ground-state NaN to be 3.6 ± 1.5 eV. Since the heat of formation of NaN₃ is 0.23 eV,² the reaction



would be 3.4 eV endoergic to produce ground-state products. However, since NaN will have a triplet ground state, the reaction to ground-state products is spin forbidden. Thus, even more energy would be necessary to bring about a spin-allowed decomposition. This implies an activation energy for thermal decomposition $\geq 3.4 \pm 1.5$ eV. The observed activation energy is only 0.80 ± 0.15 eV (see below).

Nitrogen atoms cannot be formed in the thermal decomposition either directly or via azide-radical recombination. Decomposition of NaN₃ to give Na, N, and N₂ directly is 5.8 eV endoergic. Azide-radical recombination to yield N(⁴S), N(²D), and 2N₂(¹Σ_g⁺), the lowest energy spin-allowed products, is 3.4 eV endoergic.

There has been very little direct evidence to show whether the azide radicals recombine within the crystals, upon the crystal surfaces, or if they are liberated into the gas phase before recombination. de Panafieu *et al.*⁴ were able to observe small quantities of N₃ in a mass spectrometric study on the thermal decomposition of KN₃, but they were unable to determine if the predominant N₃ recombination was within the crystal or in the gas phase. Walker *et al.*^{5,6} were not able to observe any N₃ in their mass spectrometric study of NaN₃ decomposition, but then neither did they observe any Na, although their temperatures were clearly high enough to obtain volatilization of sodium. The only other evidence for N₃ production in ionic-azide decomposition comes from the thermal decomposition experiments of Audubert and co-workers,⁷⁻⁹ who observed an accompanying UV emission, the intensity of which was proportional to the rate of azide decomposition. This UV emission could have come from electronically excited nitrogen produced by the recombination of two azide radicals. In addition, the emission observed at ≈ 255 nm was enhanced when mercury was admitted to the system.⁸ This could have been produced from energy transfer from electronically excited nitrogen to mercury to excite the Hg 253.7 nm line.¹⁰ Based upon the arguments on energetics presented above, these observations could not come from excitation accompanying N-atom recombination. Audubert has caused some confusion on this point by calling his energy carrier "active nitrogen." His observations cannot be ascribed to what conventionally is called active nitrogen which is associated with the N-

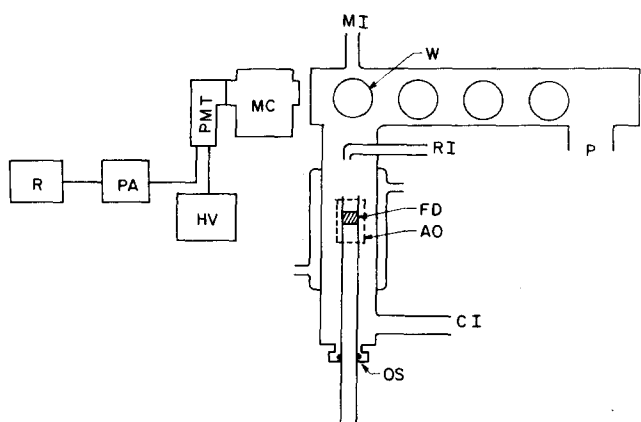


FIG. 1. Apparatus for studying azide-radical kinetics: AO, azide decomposition oven; FD, fritted disk on which azide rests; CI, carrier-gas inlet; RI, reagent gas inlet; MI, manometer inlet; OS, sliding o-ring seal to provide temporal variation with a fixed observation window W; P, to pump (Precision D-500); MC, Jarrell-Ash 0.25 m scanning monochromator; PMT, HTV R955 photomultiplier; HV, high voltage power supply; PA, Keithley 417S picoammeter; R, Heath SR 205 strip-chart recorder.

atom-recombination-generated Lewis-Rayleigh after-glow.

The results of our experiments indicate that azide radicals are a product of the thermal decomposition of NaN_3 at temperatures as low as 150°C . We have not been able to reproduce the UV emissions observed by Audubert, but have observed nitrogen first-positive emission, several still unidentified molecular emissions in the blue and UV, as well as very intense sodium D -line emission, all the result of NaN_3 decomposition in the absence of added reactants. The observations indicate that energy carriers are created in NaN_3 decomposition. Additional observations show that the energy carriers initially produced are most likely N_3 radicals.

II. EXPERIMENTAL

The flow tube built for this experiment (Fig. 1) is fairly conventional in design, but it incorporates a novel method of free-radical generation: thermal decomposition of a solid. 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 azide is decomposed 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. This allows for variation in the distance from the oven to the observation region, thus affording temporal variation. The oven is a 14 mm Pyrex sealing tube with a 10 mm fritted disk. 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 ac voltage supplied by a Variac. An iron-constantan thermocouple, placed against the fritted disk, measures the oven temperatures. 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 has maintained stable temperatures as high as 430°C over periods as long as several hours.

The experiments involved observation of electronically excited species along the axis of the observation region. 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. Photons emitted between 170 and 920 nm are detected with an HTV R955 photomultiplier, the output of which was fed to a Keithley 417S picoammeter, or in later experiments a PARC 1140 A/C quantum photometer.

The carrier gas flow ($\approx 1000 \mu\text{mol s}^{-1}$) and the flow through the azide oven ($\approx 10 \mu\text{mol s}^{-1}$) are metered into the system through rotameters which have been calibrated with a wet test meter. Reagent-gas flows (10^{-4} – $1 \mu\text{mol s}^{-1}$) are measured with capillary-oil flow meters which have been calibrated by measuring the change in pressure with time from a known volume. The reagents are stored in 5 l flasks integrated into the vacuum preparation 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 (McCarroll type) can be placed at either reagent inlet so that atomic reagents may be introduced either upstream or downstream of the oven. When the discharge cavity is placed on the downstream inlet, additional carrier gas flows through the sidearm in order to reduce the transit time from the discharge to the flow tube, thereby reducing atom recombination significantly.

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} . Flow tube pressures, measured with a silicon-oil manometer, are generally ≈ 3 torr and the bulk-flow velocity is about 1250 cm s^{-1} .

The sodium azide (J. T. Baker, practical grade) has a stated purity of $>95\% \text{ NaN}_3$. Elemental analysis indicated $100.1\% \pm 0.1\% \text{ NaN}_3$, although small amounts of volatile hydrocarbons were observed mass spectrometrically upon heating to 100°C . These impurity signals decayed upon prolonged heating under vacuum. The azide was therefore baked under vacuum at 150 – 200°C for several hours prior to beginning the experiments. Condensable gases NO and Cl_2 were purified by trap-to-trap distillation, while the other gases [He (99.995%), Ar (99.997%), and O_2 (99.99%)] were used directly from their cylinders.

III. RESULTS AND DISCUSSION

A. General observations on NaN_3 decomposition

Our qualitative observations on the decomposition of NaN_3 are in agreement with earlier studies^{5,6,9}. The sodium azide decomposed quickly at temperatures above

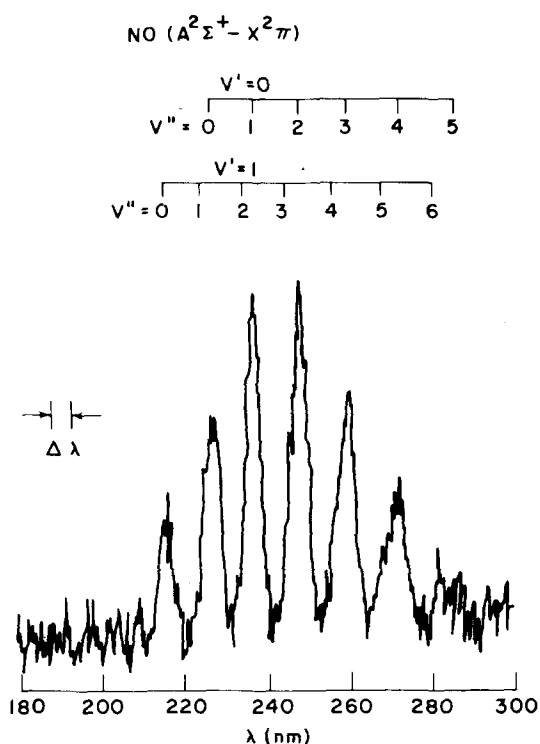


FIG. 2. Spectrum of the NO γ bands produced in the reaction between O and N₃ ($\Delta\lambda = 4$ nm).

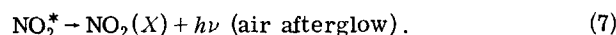
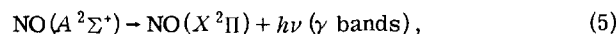
350 °C, as indicated by the rapid formation of a sodium mirror upon the walls of the reactor after the onset of decomposition; the decomposition commences after an incubation period which is longer at lower temperatures. At the higher temperatures (≥ 325 °C), the azide decomposition was relatively complete within about 20 min for amounts of NaN₃ on the order of 10 mmol (0.65 g). We could observe decomposition of the NaN₃ at temperatures below 150 °C after incubation times of several hours. At lower temperatures (< 250 °C), the rate of azide decomposition was constant 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.

B. Observations of N₃ generation

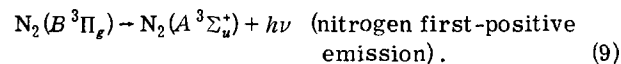
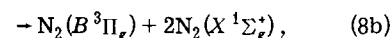
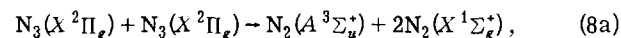
For oven temperatures above 150 °C, the addition of oxygen atoms to the reactor produced NO γ -band emission (Fig. 2) and the O/NO air afterglow.¹¹ The intensities of these emissions increased as the temperature was raised in the oven (with a concomitant increase in decomposition rate), and the emission disappeared when the oven was turned off. Therefore, one of the species responsible for these emissions is being produced in the azide oven. At low oxygen-atom concentrations ($\leq 10^{13}$ molecules cm⁻³), the intensity of the γ bands increases with increasing oxygen concentrations. However, at higher oxygen-atom concentrations, the γ -band intensity decreases presumably because the active species coming from the oven is being consumed by reaction with O during the 7.5 ms transit time between the injector and the observation region. The air-afterglow intensity increases as the O-atom concentration is increased for

all O-atom concentrations used in the experiments ($\leq 2 \times 10^{14}$ atoms cm⁻³).

The spectroscopic observations correspond to those made by Clark and Clyne^{1,12,13} in a system in which N₃ had been produced chemically. Thus, we conclude that the active species produced in the oven is the azide radical. Initially, Clark and Clyne reported observation of the NO β -band emission between 250 and 375 nm as well as the NO γ bands in the reaction between O and N₃. We did not observe the β -band emissions. However, recently, Clyne has reanalyzed his data and concurs with our observation.¹⁴ Both the spectroscopic and kinetic observations are compatible with a mechanism based upon the following reactions:



Because a good source of γ -band emission in the absence of β -band emission is the energy-transfer reaction between N₂ ($A^3\Sigma_u^+$) and NO,¹⁵ we did an experiment to investigate this possibility which demonstrated that the NO γ -band emission was excited directly in the O + N₃ reaction. N₂ ($A^3\Sigma_u^+$) could have been produced in our reactor in the bimolecular recombination of N₃:



Reactions (8a) and (8b) are the only energetically and spin-allowed pathways for N₃ recombination. 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 ($< 10^{12}$ molecules cm⁻³) that any N₂ ($A^3\Sigma_u^+$) in the reactor would not be appreciably quenched prior to entry into the observation region (a transit time of 7.5 ms),¹⁶ but sufficiently large that the strong NO γ -band emission should have been observable if the N₂ ($A^3\Sigma_u^+$) concentration were significant ($> 10^8$ molecules cm⁻³).

C. Kinetic observations

A kinetic model may be constructed from Reactions (4) and (5) to further test our observations. Under the assumption of constant N₃ concentration in the observation region, the rate equation for the formation and disappearance of electronically excited NO is

$$\frac{d[\text{NO}^*]}{dt} = k_4[\text{N}_3][\text{O}] - k_5[\text{NO}^*], \quad (10)$$

k_5 being the radiative-decay rate constant for NO ($A^2\Sigma^+$) (5×10^6 s⁻¹).^{17,18} Because the NO* radiates before it is pumped out of the observation region, its concentration can be assumed to be in steady state so that

$$I_{\text{NO}^*} = k_5[\text{NO}^*] = k_4[\text{N}_3][\text{O}], \quad (11)$$

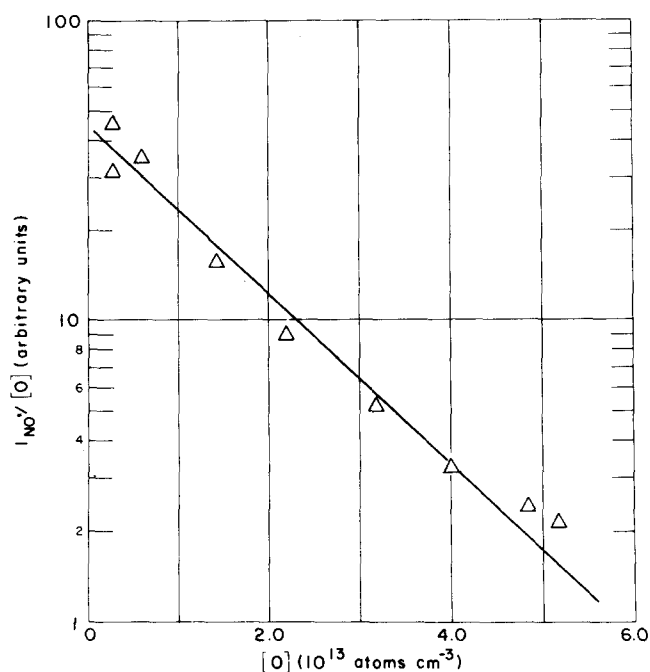


FIG. 3. Decay of $I_{\text{NO}^*}/[\text{O}]$ (proportional to azide radical concentration) as a function of atomic oxygen concentration ($\Delta t_{\text{eff}} = 7.5$ ms).

where I_{NO^*} is the intensity of the γ -band emission. Thus,

$$[\text{N}_3] \propto I_{\text{NO}^*}/[\text{O}]. \quad (12)$$

The concentrations of added reagents are sufficiently small that we may neglect quenching of the NO^* prior to radiation. Equation (12) shows that the NO^* γ -band emission may be used as a tracer to monitor azide radical concentrations in kinetic studies.

Experiments on O-atom kinetics 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 bimolecular recombination of the azide radicals, assuming the rate constant of Clark and Clyne¹³ for Reaction (8) of 5×10^{-12} cm^3 molecule⁻¹ s⁻¹ to be correct. Then the rate equation from Reaction (4) for $[\text{N}_3]$ is

$$\frac{d[\text{N}_3]}{dt} = -k_4[\text{N}_3][\text{O}]. \quad (13)$$

By choosing experimental conditions such that $[\text{O}] \gg [\text{N}_3]$ (pseudo-first order conditions), Eq. (13) may be solved by separation of variables to give

$$\ln \frac{[\text{N}_3]}{[\text{N}_3]_0} = -k_4[\text{O}]t, \quad (14)$$

where $[\text{N}_3]_0$ is the initial concentration of N_3 . For experiments in which the mixing time is constant, the rate constant k_4 may be determined by dividing the slope from a plot of $\ln[\text{N}_3]$ {or the natural logarithm of any quantity directly proportional to $[\text{N}_3]$, e.g., Eq. (12) versus $[\text{O}]$ } by the mixing time. For the case at hand, combining Eqs. (12) and (14) gives

$$\ln I_{\text{NO}^*}/[\text{O}] = \text{constant} - k_4[\text{O}]t. \quad (15)$$

The intensity of the NO^* γ bands were monitored as a function of $[\text{O}]$ and the resulting data are plotted according to Eq. (15) in Fig. 3.

The oxygen-atom concentration shown in Fig. 3 was calculated on the assumption of $50\% \pm 25\%$ dissociation in the discharge. Previous experience^{19,20} indicated that this assumption held provided the oxygen added to the discharge was highly diluted, i.e., $< 1\%$, as was the case here. Experiments in which the O-atom concentration was monitored by the O/NO air afterglow indicated that in the present apparatus the fractional O_2 dissociation as measured in the flow tube was $35\% \pm 15\%$ and was independent of O_2 flow rate over the range of flows used in the experiment (≤ 2 $\mu\text{mol s}^{-1}$). The slope of Fig. 3, corrected for 35% dissociation, and the mixing time of 7.5 ms gives $k_4 = 11 \times 10^{-12}$ cm^3 molecule⁻¹ s⁻¹. Two additional experiments in which the O-atom concentration was monitored gave $k_4 = 9.9 \times 10^{-12}$ and 8.0×10^{-12} cm^3 molecule⁻¹ s⁻¹ for mixing times of 5.4 and 4.8 ms, respectively. The average of the three experiments gives $k_4 = (10 \pm 4) \times 10^{-12}$ cm^3 molecule⁻¹ s⁻¹. The analysis leading to this rate constant assumes that the reaction between molecular oxygen and N_3 may be neglected. This assumption was confirmed in a subsequent experiment which showed negligible reduction in $[\text{N}_3]$ ($< 2\%$) for $[\text{O}_2] = 1.4 \times 10^{14}$ molecule cm^{-3} and an effective mixing time of 7.5 ms.

The analysis of the O-atom kinetics indicates that k_4 is sufficiently large that the addition of an excess of O atoms will drive Reaction (4) to completion within the 7.5 ms mixing time between the atom reagent inlet and the observation region. This suggests that the "radical freeze" method described by Clark and Clyne^{12,13} in their studies of NCl_2 may be used for measuring the N_3 concentrations in the reactor. Using this method, excess O atoms are added to the reactor which convert N_3 to NO , while the concentration of O atoms is little changed. The resulting intensity of the O/NO air afterglow is directly proportional to the concentration of NO produced¹¹ 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 is then equal to the concentration of N_3 generated in the thermal decomposition of the sodium azide in the oven.

Figure 4 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. Two other runs gave 0.68 and 1.04 eV, respectively. The average value of the four runs $[0.84 \pm 16$ (σ) eV] is smaller than the 1.64 eV^{21,22} obtained in other studies, but most of the latter

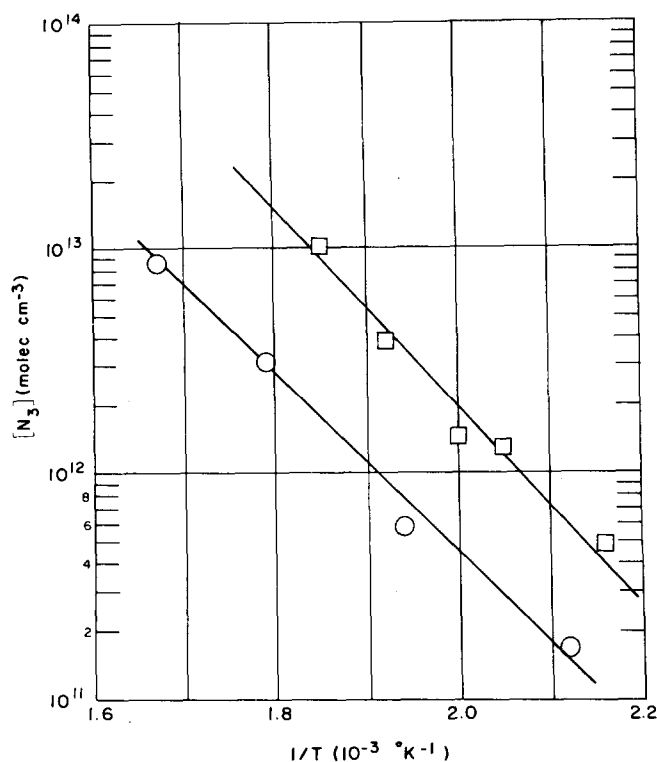


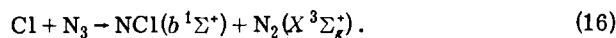
FIG. 4. Variation in absolute N_3 concentration with inverse temperature for two different runs.

values were obtained in a higher temperature regime. Jacobs and Kureishy²² 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.*²³ measured an activation energy for electrical conductivity in NaN_3 of about 0.65 eV for temperatures below 200 °C, increasing to 1.2 eV for temperatures up to about 240 °C. They assumed that the ionic conductivity could be related to the rate of decomposition. de Panafieu *et al.*⁴ have shown recently that the activation energy for the decomposition of KN_3 (which behaves similarly to NaN_3) differs significantly in different temperature ranges, becoming larger at higher temperatures. At relatively low decomposition temperatures (175–240 °C), they obtain a value of about 1.0 eV, fairly close to the value obtained here.

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. The results of five experiments in which the γ -band intensity was monitored as a function of temperature at constant O-atom concentration gave an activation energy of 0.72 ± 0.04 (σ) eV. Combining the results from the two techniques gives $E_a = 0.80 \pm 0.15$ eV.

D. Observations of chemiluminescence

The addition of Cl atoms to our reactor resulted in observation of the $\text{NCl}(b^1\Sigma^+ - X^3\Sigma^-)$ emission system. This chemiluminescent emission has also been observed by Clark and Clyne^{1,12,13} and results from the reaction



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

At a temperature slightly above 300 °C, somewhat higher than those used in the majority of our studies, but still sufficiently low that sodium volatilization is not too great, we observe, in the absence of added reagents, the $\text{N}_2(B^3\Pi_g - A^3\Sigma_u^+)$ first-positive system, and an additional unidentified band between 415 and 495 nm. Reaction (8), the bimolecular recombination of N_3 , is sufficiently exoergic to populate the $\text{N}_2(B^3\Pi_g)$ state up to $v=7$ or 8. At temperatures above 300 °C, the concentration of N_3 may be expected to be on the order of 10^{13} molecules cm^{-3} (Fig. 4). This is a sufficiently large concentration that the rate of reaction (8) will be significant if the rate constant of Clark and Clyne¹³ is correct.

The identification of the 415–495 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 $\text{N}_2(C^3\Pi_u - B^3\Pi_g)$ and the $\Delta v = -11$ through $\Delta v = -13$ sequences of the Vegard–Kaplan bands $\text{N}_2(A^3\Sigma_u^+ - X^1\Sigma_g^+)$. The bands certainly cannot be second-positive emission since there is not enough energy in the N_3 recombination to populate the $\text{N}_2(C^3\Pi_u)$ state and since much stronger transitions of that system, further to the blue, are not observed. The emission could arise from Vegard–Kaplan emission in high vibrational levels ($v' \geq 3$), although it seems fairly unlikely since this system is highly forbidden and therefore very difficult to observe.

At relatively high decomposition temperatures (≥ 350 °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 that of the Na D lines, the intensity of which is sufficient to be observed with the naked eye. The UV emissions are molecular (see Fig. 5), but 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. It cannot be Vegard–Kaplan emission because other strong bands of that system are absent.

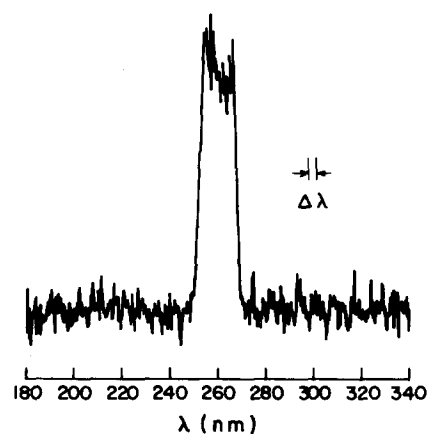


FIG. 5. UV emission produced in NaN_3 decomposition ($\Delta\lambda = 4$ nm).

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 the 260 nm emission emanates from a molecule containing sodium since the presence of Na seems to be required for observations of this emission. The emission does not correspond to known emissions from Na_2 .²⁴

IV. CONCLUSIONS

Our data strongly suggest that gaseous azide radicals are products of the thermal decomposition of solid ionic azides. This observation lends support to the generally accepted mechanism for decomposition of ionic azides.² Previously, belief in the production of azide radicals in the thermal decomposition of ionic azides had been based solely upon inference.

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. It has long been a matter of speculation that triplet states of nitrogen are formed in azide-radical recombination, but such emissions have not been observed previously during azide-radical recombination.

We have developed a clean system in which azide-radical reactions may be studied. Previously, the azide radical has been observed as a product of secondary reactions in the photolysis of the covalent azides HN_3 ,²⁵⁻³⁰ ClN_3 ,³⁰ and NCN_3 ,^{31,32} or as the product of the reactions between various atoms and ClN_3 or BrN_3 .^{1,11,12,33} None of these systems is particularly suitable for N_3 studies since a number of other reactive intermediates are always present to complicate the kinetics. In our system, we may produce N_3 in the absence of other reactive species, even being able to remain free from interference from sodium atoms at decomposition temperatures below about 250 °C. An additional advantage to this approach is the much greater ease of handling the stable species NaN_3 as compared to the highly toxic and explosive covalent azides previously employed.

The NO γ -band emission intensity from the $\text{O} + \text{N}_3$ reaction is a sensitive tracer for monitoring relative N_3 concentrations for kinetic studies. This allows much greater sensitivity than previously used absorption diagnostics. In addition, this fast reaction may be employed to convert N_3 to NO by a large excess of O atoms, so that the intensity of the resulting O/NO afterglow may be used to determine absolute N_3 concentrations. This will allow the direct measurement of the N_3 recombination rate constant.

V. ACKNOWLEDGMENTS

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