ACTIVE NITROGEN

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1968

PREFACE

Active nitrogen has been the subject of numerous experimental and theoretical investigations since 1865. The voluminous, often contradictory literature has been at least partially reviewed a number of times—at some length in 1929, 1939, 1945 (S. K. Mitra, "Active Nitrogen—A New Theory." Association for the Cultivation of Science, Calcutta, India, 1945), and, rather more briefly, in 1958, 1960, 1961 ("Encyclopedia Brittanica"), and 1963 (*Chemical Reviews*). The book, by Mitra, provides a comprehensive review of the experimental developments prior to 1945. Consequently, for the present discussion, reference is made to papers published before this date only if they are of particular relevance. An effort has been made, however, to take into account the subsequent pertinent literature until April, 1967. Since there has been, perhaps, a tendency for the chemist to ignore the important basic work on the physics of active nitrogen and for the physicist to pay scant attention to the rapidly developing knowledge of its chemical behavior, an attempt has also been made to bring together the physical and chemical aspects of this complex and interesting field of study.

The term "active nitrogen" has been taken to refer to any excited form of nitrogen, molecular or atomic, or a combination of these, of sufficient lifetime that it may be removed from the region in which it is formed, or, in a static system, remain long enough after the excitation is stopped to permit study of its physicochemical behavior, including the production of the various "afterglows." "Active nitrogen," so defined, has a limited number of excited species to which its characteristics may be attributed. Among these are, chiefly, ground state nitrogen atoms and excited molecules that may result from their recombination. These are, therefore, the species of main concern to the present review. However, recent studies on short-duration afterglows have required that attention be given also to the behavior of excited nitrogen atoms and nitrogen molecules of higher energy content, i.e., to the precursors of the second positive system of N_2 and the first negative system of N_2^+.

Information about the various species that might be present in active nitrogen has been drawn from any studies in which they have been identified, e.g., ion-molecule reactions, shock-tube experiments, studies on absorbed species and trapped radicals, etc. Active nitrogen and its behavior stand

revealed as more complex than generally recognized. Moreover, apparent contradictions in observations and interpretations are indicated as reflecting a greater sensitivity of the systems to experimental conditions than has generally been appreciated. As a consequence, assessment of much of the available data, at the present time, is likely to be arbitrary. The primary objective has been, therefore, the organization of as much relevant information on active nitrogen as possible in the hope that it might help to stimulate and facilitate further investigation of the subject.

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January 1968

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INTRODUCTION

I. A Brief Description of Active Nitrogen and Its Discovery

When molecular nitrogen is subjected to the action of an electrical discharge, under suitable conditions, the well-known yellow "nitrogen afterglow" is produced. In a flow system, the glow appears downstream from the discharge, and in a static system it may persist for some time after the discharge is terminated. In this condition, the gas is very reactive chemically, and is usually referred to as active nitrogen. Much of its reactivity may be attributed to the presence of ground state $N(^4S)$ atoms in the afterglow, the long lifetime of which is due largely to the relatively slow third-order, homogeneous recombination of the atoms in systems suitably "poisoned" against wall recombination.

Early studies on the electrochemistry of gases gave the first evidence that a chemically reactive form of nitrogen could be produced by passing an electrical discharge through nitrogen. In 1792, Lavoisier reported that oxides of nitrogen were formed when a spark was passed through air (*1*), while Berthelot, in 1869, found that hydrogen cyanide was produced by sparking a mixture of nitrogen and hydrocarbons (*2*).

The first report of a persistent luminescence in nitrogen at low pressures, following an energetic electrical discharge, appeared as long ago as 1865 (*3*). Subsequently, Warburg reported that air, subjected to an electric discharge at low pressure in a static system, emitted a bright, peach-colored glow which changed to a rich yellow, and persisted for several seconds after the discharge was discontinued (*4*). The first systematic study of the nitrogen afterglow was made in 1900 by E. P. Lewis, who confirmed its relatively long lifetime and identified its banded spectrum with that of molecular nitrogen (*5-7*).

Burke found later that the glow could also be produced with an electrodeless discharge (8).

In 1911, the Hon. R. J. Strutt (later, the third Lord Rayleigh*) presented the first of an outstanding series of papers in which he showed clearly that a chemically active modification of nitrogen was present in the afterglow (9-12). Accordingly, he referred to the glowing gas as "active nitrogen."

Strutt astutely suggested that many of the properties of active nitrogen could be attributed to the presence in it of *atomic* nitrogen. However, this postulate was not widely accepted until it was made the basis of an explanation of the afterglow by Sponer in 1925 (13). The yellow, long-lived afterglow, emitted by an unperturbed nitrogen molecule (14), is generally referred to as the Lewis-Rayleigh afterglow (15). It is now known to be due mainly to emission of the first positive band system, $N_2(B\ ^3\Pi_g) \rightarrow N_2(A\ ^3\Sigma_u^+)$, of the molecular nitrogen spectrum. However, other band systems do contribute to this emission, as well as to some shorter-lived nitrogen afterglows that correspond to other forms of "active nitrogen."

II. The Energy Content of Active Nitrogen and the Bond Dissociation Energy of N_2

Early in his investigations, Strutt concluded that active nitrogen did not contain an abnormally large amount of energy (16). Willey and Rideal later suggested, as a result of calorimetric studies, and from consideration of its reaction with nitric oxide, that active nitrogen, at a pressure of 10 torr, contained considerable concentrations of metastable molecules excited to about 2 eV (17, 18). On the other hand, band spectra in the extreme ultraviolet excited by active nitrogen (e.g., emission of bands of the fourth positive group of CO) led Knauss to suggest the presence of metastable nitrogen molecules with 9 to 10 eV of excess energy (19). In later experiments, Rayleigh observed that copper, silver, and platinum became red hot, and gold melted, downstream from an electrodeless discharge through nitrogen in a flow system at low pressure (20). He therefore modified his earlier views to conclude that energy as high as 10 eV was released for every molecule of nitrogen that passed through the discharge. He attributed the large average energy content to a large number of high-energy carriers in active nitrogen, in addition to atomic nitrogen. He also concluded that the maximum energy radiated in the afterglow, even under the most favorable

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* According to the obituary notice of John William Strutt (Lord Rayleigh) (8a), the peerage was first bestowed on his grandmother at the request of her husband, Col. Joseph Holden Strutt. At her death, it passed to their son, John James, during the lifetime of his father, and thence to his son, J. W. Strutt, father of R. J. Strutt.

conditions, was only of the order of 10^{-3} of the energy collected by the metal, and that emission in the visible or photographic infrared regions of the spectrum should be regarded as only a by-product of the main energy-releasing processes. Later evidence indicates that, when nitrogen atoms recombine, nonradiative processes accompany the radiative processes that are responsible for the afterglow (*21*).

Subsequent investigations have shown that much of the heat effect observed by Rayleigh was due to bombardment of the metals by electrons from the discharge (*22, 23*), and to reflection back to the metal of some of the infrared radiation emitted from it (*24*). Benson obtained a calorimetric value of 0.027 eV for the average heat content per molecule of N_2 in the active nitrogen stream (*23*). He estimated the concentration of active centers to be about one-sixth that deduced by Rayleigh from chemical evidence.

As Benson has outlined, the work of many experimenters helped to establish that the Lewis-Rayleigh afterglow contained no band system which could not be ascribed to an excited N_2 molecule formed during recombination of ground state atoms. However, uncertainty in the bond dissociation energy of the ground state molecule, $N_2(X\ ^1\Sigma_g{}^+)$, persisted until quite recently, and greatly obscured estimations of the energy content of active nitrogen. Only if the gas contained significant concentrations of excited nitrogen molecules of energy less than the dissociation energy of the normal N_2 molecule, would the energy content of active nitrogen in the Lewis-Rayleigh afterglow differ from the product of its atom content and the heat of formation of the $N(^4S)$ atom.

Until about 1950, four spectroscopically determined values (7.383, 8.573, 9.764, and 11.8 eV) had been proposed for the dissociation energy of ground state molecular nitrogen, with corresponding uncertainty in the heat of formation of the $N(^4S)$ atom. The lowest value was suggested by Herzberg on the basis of predissociations observed in molecular states of nitrogen, and was generally accepted for many years (*25-27*). As long ago as 1944, however, Gaydon pointed out (*28*) that the observed predissociation in the B $^3\Pi_g$ state of nitrogen (*29*) could be a result of recombination of $N(^4S)$ atoms through an intermediate, and supposedly repulsive, $^5\Sigma_g{}^+$ state of N_2. Such an explanation, which led to a dissociation energy of 9.764 eV (*28*), maintained the noncrossing rule for the potential energy curves of molecular states of nitrogen, which was violated (*30*) by the lower value of 7.383 eV. Extensive additional arguments were also offered for the higher value (*22, 31*). Indeed, as Mitra pointed out in the following year (*32*), a bond dissociation energy of 9.76 eV, coupled with the atomic recombination theory of Sponer (*13*), could explain most of the facts then known about active nitrogen. Nevertheless, the two spectroscopically determined values for $D(N_2)$, 7.383 and 9.764 eV, remained controversial.

Measurements of detonation velocities (*33*), and studies on the thermal decomposition of nitrogen (*34*), have produced strong evidence in favor of the larger value. This value was favored also by a new spectroscopically determined value for the dissociation limit of the B $^2\Pi_u{}^+$ state of $N_2{}^+$ (*35*), and by the observation of vibrational levels of the ground state of nitric oxide up to $v = 23$, which indicated a higher value for D(NO) than had been previously accepted (*36*). The argument would appear to be settled by the experiments of Frost and McDowell, who dissociated nitrogen with essentially monoenergetic electrons (*37*). They confirmed some earlier work of Clarke (*38*), and suggested that their experiments "lead unequivocally to the conclusion that the dissociation energy of the N_2 molecule is 9.756 eV." Other evidence has supported this result (*39–45*), and the value of 9.756 eV, or 225 kcal, for D(N_2), so long advocated by Gaydon, is now accepted without question. This value obviously sets a limit (somewhat less than 225 kcal) on the maximum energy content of any nitrogen molecule that may be formed by recombination of ground state N(^{4}S) atoms; it serves to define the energy content of most of the electronic levels of N_2; and, for purposes of developing thermochemical equations for chemical reactions initiated by ground state atoms, it establishes the heat of formation of N(^{4}S) atoms as 112.5 kcal mole^{-1}. It might be noted that the value of 9.756 eV approximates that ($\sim$9.6 eV) postulated many years ago from the spectra excited when metal vapors were introduced into the Lewis-Rayleigh afterglow (*46–49*).

III. Methods by Which Active Nitrogen May Be Produced

Active nitrogen is generally produced by an electric discharge through nitrogen, in the manner of the first experiments on active nitrogen (*3, 4, 6*). The condensed dc discharge, in which the voltage may momentarily build up to high values, has been particularly favored as a dissociating agent. It has the advantage that a continuous high voltage need not be maintained across the terminals. It is interesting, perhaps, that the activation of pure nitrogen may require an electron energy as high as 20 eV, which considerably exceeds the energy needed for dissociation, excitation, or even ionization of nitrogen (*50*). Small amounts of water have been demonstrated to facilitate corona discharges in nitrogen, oxygen, and air (*51*).

A Paschen curve has recently been published for pure nitrogen, for values of the product (pressure)(electrode spacing) from 0.1 to 20 torr, over a range from 200 to 4000 volts in breakdown potential (voltage required for a self-sustaining discharge) (*52*). Brandt has shown that, for a given discharge power, the degree of dissociation of N_2 depends on the electron temperature

in the discharge (*53*). He measured an activation energy of 15.6 ± 2.5 eV for the dissociation process.

A somewhat modified form of active nitrogen appears to have been produced to some extent many years ago by an uncondensed discharge through nitrogen containing 0.25% oxygen (*54*), or between aluminum electrodes in air at a pressure of 1.2 torr (*55*).

High-frequency electrodeless discharges have also been used for some time as a dissociating agent (*16, 56, 57*). This method avoids contamination of the gas by metal electrodes, and has been favored for experiments involving spectroscopic measurements. On the other hand, it does not appear to be capable of dissociating molecular nitrogen to as large an extent as the condensed discharge at moderately low pressure. With a high-frequency (10.25 Mc sec^{-1}) discharge through nitrogen, the afterglow intensity has been found to be a smooth function of pressure, voltage, and interelectrode distance for external sleeve-type electrodes (*58*). However, as with the corona discharge mentioned above, the degree of dissociation of N_2 in a microwave discharge appears to be determined largely by small amounts of impurities such as H_2O (*59*) or O_2, NO, and SF_6 (*60*). Modern techniques, such as "microwave-pulse-flash spectroscopy" (*61, 62*), and specially modified magnetic resonance (*63*) and mass spectrometric (*64, 64a*) techniques, should yield pertinent data on the effects of impurities and transient chemical species in electrical discharges.

Peyron has recently demonstrated that a resonant cavity technique may be quite efficient in producing the Lewis-Rayleigh afterglow in nitrogen over the pressure range 0.1 to 40 torr (*65*). A similar technique (pulsed and continuous wave) has been shown to produce microwave breakdown in nitrogen, as well as in air and oxygen, over the pressure range 0.01 to 100 torr (*66*).

Kenty and Turner produced "active nitrogen" with properties similar to that obtained with a condensed discharge, when they bombarded nitrogen with electrons of energy in excess of 10.8 ± 0.5 eV (*67*).

The characteristic yellow Lewis-Rayleigh afterglow may also be produced by an arc discharge, and this method has been used successfully to produce active nitrogen at pressures as high as one atmosphere (*68–71*).

A "plasma jet" containing large, nonequilibrium concentrations of ions and nitrogen atoms has recently been obtained by expanding the products from a continuous, high-pressure (up to one atmosphere), low-temperature nitrogen glow discharge through a supersonic nozzle into a low-pressure (1–100 torr) chamber (*72, 72a–c*). The supersonic stream has been shown to exhibit many of the properties associated with active nitrogen (*73*).

It has been confirmed that both ac and low-voltage dc continuous discharges may dissociate molecular nitrogen, and hence produce active

nitrogen, at pressures of about 50 torr (*74–76*). In the presence of an excess of argon as a plasma medium, a dc arc, operating under a power input of approximately 150 watts, was shown to be considerably more effective in dissociating N_2 than a source of alternating current 20 times as energetic (*76*).

The dissociation of molecular nitrogen may also be sensitized. For example, it has been induced by a collision of the second kind between nitrogen molecules and electronically excited krypton atoms possessing 10 eV of excess energy (*77–80*), and in three-body collisions of $He(2\ ^3S_1)$ atoms and two N_2 molecules (*81*). Molecular nitrogen is known to relax $Hg(6^3\ P_1)$ atoms with a cross section of $3.9 \times 10^{-16}\ cm^2$ (*82*), and to be excited in plasma jets by a collision of the second kind with metastable argon atoms containing either 11.55 or 11.72 eV of excess energy (*83*). However, the emission due to the trace of nitrogen in the flow system used showed only bands of the second positive system of nitrogen ($C\ ^3\Pi_u \rightarrow B\ ^3\Pi_g$, 11.14 eV excitation energy). Apparently no dissociation of the nitrogen resulted from this energy transfer. A suggestion that the observed spectra might be due to collisions of electrons with nitrogen molecules (84) has been rejected by Brewer and McGregor (*85*). Although excitation of nitrogen molecules on collision with excited, singlet argon atoms is an inefficient process (*86*), excitation of low-energy triplet states of the N_2 molecule by discharged argon has been confirmed (*87*). Metastable helium atoms produced by irradiation with soft X-rays may also excite N_2 molecules to the $B^3\Pi_g$ state (*87a*).

An "ozonizer-type" discharge (*88, 89*), or a heavy Tesla spark discharge (*90*) is also capable of dissociating N_2 at high pressures, with production of the Lewis-Rayleigh afterglow. However, under conditions of "mild excitation" these types of discharge produce emission different from that of the Lewis-Rayleigh afterglow (*91*). Indeed, they may lead to excitation of ground state nitrogen molecules without producing a significant extent of dissociation (*92, 93*). The recent work of Wilson and co-workers further illustrates that high-frequency "mild excitation" may produce "Tesla-type" luminescence, in which light emission results mainly from production of excited states, rather than dissociation of the molecules, in the discharge (*94*). They found that excitation in a simplified apparatus of their own design yielded nitrogen of a purple color over the pressure range 1.5 to 4.0 torr, with emission of 10 major peaks. There was no spectroscopic evidence for either the presence of nitrogen atoms in the discharge or emission of the first positive system of N_2, although the stable glow showed emission from the second positive system of N_2 and from various systems of N_2^+ (*95*).*

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* It is of interest to note that either a condensed or microwave discharge also produces a form of "active phosphorus" in the presence of argon as a carrier gas (*96*). This gas reacts beyond the discharge zone with hydrocarbons, ammonia, and hydrazine in a manner somewhat analogous to the behavior in active nitrogen.

Pannetier and co-workers have recently claimed that a form of active nitrogen, free from $N(^4S)$, and containing only metastable molecular species such as $N_2(A\ ^3\Sigma_u^+)$, may be produced by passing the yellow afterglow from a microwave discharge through two traps at 77°K *(97)*.*

Excitation of nitrogen by the shock-tube technique has been shown to produce emission in the infrared region due to the first positive system of N_2 *(98, 98a)*. Similar infrared emission has also been reported from shock-heated air *(99-101)*. If nitrogen atoms were produced, little recombination of them would be expected under the experimental conditions prevailing in these shock waves (thermal excitation by molecular collisions). It is probable that the short lifetime form of "active nitrogen" produced by such shock waves is due mainly to direct electronic excitation of nitrogen molecules. It has recently been reported, however, that at least part of the continuum infrared radiation from shock-heated air or nitrogen (6000°K-9000°K), at near atmospheric pressure, may be due to free scattering of electrons from nitrogen atoms and molecules *(102, 103)*, that is, "bremsstrahlung" *(104)*. Further data on the optical index of refraction of N_2, partially dissociated by a strong shock wave (Mach 22), have established a value of 1.13 ± 0.06 Å for the polarizability of ground state atomic nitrogen *(105)*. Ionization, as well as dissociation, of nitrogen may occur behind very strong shock waves *(106, 107, 107a)*. In strongly shocked systems at 6400°K, the rate constants for dissociation of N_2 were 14 times larger for collision with $N(^4S)$ than for collision with N_2, but decreased by a factor of about 2.5 when N_2 collided with Ar *(108)*. Wray has reported emission of both N_2 first positive and N_2^+ first negative bands from shock-heated $(N + N_2)$ mixtures *(109)*.

When traces of hydrocarbon were present in nitrogen subjected to a 32 cm shock wave, an afterglow of several seconds duration was produced near the glass walls *(110)*. This was presumed to be due to the violet and red systems of the excited CN radical, formed in a reaction of the hydrocarbon with nitrogen atoms produced by dissociative neutralization of N_2^+ with electrons present on the walls. Emission of CN violet and red bands from shocked $(CO + N_2)$ mixtures, over the temperature range 4000°K to 10,000°K, has been attributed to reaction of N atoms with CO *(111)*.

Under certain conditions, a visible, short-duration nitrogen afterglow may be emitted, in part at least, by species of higher energy content (>9.76 eV) than those responsible for the well-known Lewis-Rayleigh afterglow. These conditions include extended operation of the discharge *(74)*, rapid flow of the nitrogen *(112)*, electrode-type discharges *(74, 113)*, glow discharges *(114)*, and 2450 Mc electrodeless discharges *(112)*.

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* The authors refer to a metastable state with configuration $^3\Sigma_u^-$. It seems likely that it should be the A $^3\Sigma_u^+$ state, and it will be so designated in subsequent references to this paper.

Nitrogen in the upper atmosphere is dissociated, to some extent, by absorption of solar radiation, perhaps through a predissociation in the $a\,^1\Pi_g$ state *(115)*. Oldenberg pointed out *(24)* that the relatively small extent of N_2 decomposition apparent in the upper atmosphere *(116–118)* may be explained in terms of the Franck-Condon principle *(119, 120)*, since the internuclear distances are similar for the vibrational minima in the ground state, and in most of the electronically excited states, of the nitrogen molecule. A predissociation mechanism, however, necessarily involves a very low rate coefficient. As an alternative, Nicolet has proposed that, since nitrogen can be ionized in the ionospheric layers by ultraviolet radiation and X-rays, nitrogen atoms might be produced in the upper atmosphere by the dissociative recombination reaction $N_2^+ + e^- \rightarrow N + N$ *(121)*.

Dodonova has recently demonstrated that nitrogen may be activated by vacuum UV radiation from a hydrogen lamp *(122)*. Formation of HCN, after 8 to 10 hours irradiation, over the 1250 to 1700 Å region, of $(N_2 + CH_4)$ mixtures at a pressure of a few torr, indicated that some N atoms were probably produced. It appeared possible that significant concentrations of $N_2(a\,^1\Pi_g)$ and $N_2(A\,^3\Sigma_u^+)$ molecules might also be produced in this system.

The reaction $NO^+ + e^- \rightarrow N + O$ has been shown to be an important source of atomic nitrogen in shock-heated air *(123)*, and it may occur in NO subjected to far-UV photolysis *(124, 125)*. The dissociative recombination coefficient has been measured as $(5 \pm 2) \times 10^{-7}\,cm^3\,sec^{-1}$ *(125a)*.

Ion-atom interchange, such as $O^+ + N_2 \rightarrow NO^+ + N$ or $N_2^+ + O \rightarrow NO^+ + N$, could also be an important source of atomic nitrogen *(121, 126–130)*. The rate constant for the former reaction increases by a factor of about 20 when the N_2 molecules are vibrationally excited *(131)*. Studies in laboratory sources have indicated that atomic nitrogen may be produced in corresponding reactions of the positive ions of inert gases with N_2 *(128, 132, 133)*, and with nitrous oxide *(133, 134)*. It may also be produced in the reaction of nitrous oxide with N^+ *(135)* and O^- *(136)*, and in the reaction $N_2^+ + O_2 \rightarrow NO_2^+ + N$ *(137, 138)*. The absorption and photoionization coefficients of nitrogen (and oxygen), in the wavelength region 600–1000 Å, have been measured, and correlated with the penetration of solar radiation into the atmosphere *(139, 140)*.

The production of an active species by the α-ray irradiation of nitrogen has been known for many years *(141, 142)*, and recent work has proved that $N(^4S)$ atoms are produced in nitrogen irradiated with polonium-210 α-particles *(80, 143)*. The formation of oxides of nitrogen during the irradiation of $(N_2 + O_2)$ mixtures with the fission products of ^{235}U *(144–150)*, and with γ-radiation from ^{60}Co *(151)*, suggests that N atoms may be produced in these reactions. The formation of NH_3 in mixtures of N_2 and H_2 exposed to ^{60}Co γ-irradiation, or to proton irradiation, similarly suggests the formation

of some highly reactive, supposedly neutral, species of nitrogen (*150, 152, 153*). Ammonia production has also indicated the formation of $N(^4S)$ atoms from the reaction of excited $H(^2P)$ or $D(^2P)$ atoms with $N_2(X\ ^1\Sigma_g^+)$ during Lyman α-irradiation of $(H + N_2)$, or $(D + N_2)$, mixtures (*154, 155*). Nitrogen atoms may also be formed in shock-heated $(N_2 + H_2 + Ar)$ and $(NH_3 + Ar)$ mixtures by way of an $NH(A\ ^3\Pi)$ intermediate (*156*). The cross-over to form $N(^4S) + H(^2S)$ appeared to occur with a first-order rate constant of 3×10^5 sec^{-1}.

It has recently been reported that molecular nitrogen may be thermally activated by tungsten filaments at temperatures above 2000°K (*157, 158*). Dissociation of molecular nitrogen on the hot filament appears to be followed by partial desorption into the gas phase as atoms.

The production of nitrogen atoms is also possible by decomposition of N-containing compounds, rather than nitrogen itself. For example, nitrogen atoms were produced, accompanied by a yellow afterglow, when a condensed discharge was passed through argon containing about 1/10 its volume of NO or NH_3 (*159*). Electron paramagnetic resonance measurements on the products condensed from an electric discharge through NH_3 have confirmed that nitrogen atoms, as well as hydrogen atoms, are produced during the excitation process (*160*). Nitrogen atoms are also produced by decomposition of NH_3 induced by ionizing radiation from a wide-range radiolysis source (*160a*). The formation of HCN from a high-frequency electric discharge (40 Mc sec^{-1}) through a mixture of CH_4 and NH_3 (*161*), as well as from a mixture of CH_4 and N_2 (*162*), indicates that nitrogen atoms are also produced from ammonia under these conditions of excitation.

Nitrogen atoms may be produced in shock-heated (2000°–8000°K) nitric oxide, or oxygen-nitrogen mixtures, as a result of collision-induced decomposition of NO, or by reaction of oxygen atoms with NO or N_2 (*163–165*).

The photolysis of N_2O at 1236 Å has been found to form $N_2(B\ ^3\Pi_g)$ molecules directly, and these may then radiate the first positive system. It also produces a significant concentration of nitrogen atoms during a second primary mode of decomposition of the excited N_2O molecule (*166, 167, 167a*). The process leading to an excited N_2 molecule was later shown, by isotopic labeling, to be approximately 10 times as important as the production of nitrogen atoms (*168, 169*). It would seem, then, that the photolysis of N_2O at 1236 Å might provide a method for producing "active nitrogen" with a high initial $N_2(B\ ^3\Pi_g)$ content relative to that of $N(^4S)$. Photolysis of N_2O at wavelengths from 1236 to 1470 Å has been postulated to yield $N_2(A\ ^3\Sigma_u^+)$ molecules directly (*170*). Photolysis of N_2O at 1470 and 1830 Å has also been shown to proceed by the two primary processes, although the step leading to nitrogen atom production is considerably less prominent at these wavelengths (*169*). First positive emission has also been

detected from the argon afterglow in the presence of added nitrous oxide, presumably owing to the presence of $N_2(B\ ^3\Pi_g)$, following a collision of the second kind between N_2O and argon in the excited states $^3P_2$ or $^3P_0$ (*171*). It was suggested that $N(^4S)$ atoms might be produced in an alternative mode of decomposition of the excited N_2O molecule, with production of NO in the B $^2\Pi$ state. It is now established that N_2O^+ ions undergo a metastable dissociation to form NO^+ and N atoms (*172*).

It has recently been reported that nitrogen atoms may be produced in the *gas phase* during the catalytic decomposition of ammonia on platinum wires or iron filaments heated to about 1000°C (*173*), and by ionizing (neutron) radiation of NO_2 (*174*).

There is a good deal of evidence that the decomposition of azide-type compounds produces some form of active nitrogen from which emission may occur without the intervention of atomic nitrogen. Ultraviolet emission has been reported during the thermal, photochemical, and electrolytic decompositions of hydrazoic acid or its salts, in gaseous, liquid, or solid phases, and in aqueous solutions (*175, 176*). Observations on the spectra, and an apparent radiative half-life of 2.5 × 10^{-3} sec at atmospheric pressure for light emission during the electrolysis of solutions of sodium azide, indicated that the radiation was due to a form of active nitrogen different from that associated with the Lewis-Rayleigh afterglow. It has been suggested that the light emission might result from electronically excited molecules produced during a chain reaction in the decomposition process (*177*).

Other experiments have indicated that, at lower pressures (down to 20 torr), the active nitrogen produced during electrolysis of a solution of sodium azide may have an apparent half-life of the order of several seconds (*178*). At still lower pressures (10^{-4} torr), the active nitrogen produced during the thermal dissociation (265°C–275°C) of silver azide has been reported to have *two* values for the "true" radiative half-life (*179, 180*). Both values were much higher than that reported previously and depended on the state of the surface of the decay vessel: 40 sec for washed glass and 16 sec for a vessel coated with silver. In the absence of wall effects, the characteristic spectra (five bands in the ultraviolet region 1975 to 2550 Å), emitted during the decomposition of many azides, could be associated with various known transitions of the molecular nitrogen system (*180*). Most of these transitions were from energy levels higher than those usually associated with the Lewis-Rayleigh afterglow. In the presence of silver, the emission during the pyrolysis of AgN_3 had a lifetime of 16 sec, and was limited to a single band in the neighborhood of 2500 Å. It was concluded that the active nitrogen produced from the decomposition of azides possesses several levels of excitation characterized by specific deexcitation values on a silver surface.

The thermal decomposition of azides apparently produces a considerable

number of nitrogen molecules in excited states, capable of exciting emission from metallic vapors following a collision of the second kind (*181*). However, the thermal decomposition of barium, silver, or sodium azides in the presence of ethylene did not yield hydrogen cyanide (*182*). It appears, therefore, that if electronically excited nitrogen molecules are produced during the decomposition of the azides, they are not to be identified with the main chemically reactive species in active nitrogen produced by an electrical discharge through nitrogen.

Recent work on the kinetics of N_2 evolution during ultraviolet irradiation of solid sodium (*183, 184*) or barium (*185*) azides has indicated that the gas is evolved from active sites located deep within the crystallites, and that the azide ion, N_3^-, in an excited state, is the prime precursor of the nitrogen evolution. Absorption bands in the infrared spectrum, induced by ultraviolet irradiation of sodium azide single crystals at 77°K, appear to be caused by some configuration of vibrating nitrogen atoms, perhaps associated with a linear symmetric N_4 defect (*186*).

Electron spin resonance studies have provided some evidence that the irradiation of sodium azide with X-rays at liquid nitrogen temperature produces nitrogen atoms, which may be trapped in the crystal lattice (*187*). It is possible that the reaction involved is $N_3^- + h\nu \rightarrow N_2 + N + e^-$, where N_3^- may be electronically excited, that is, a triplet exciton (*188*). The presence of trapped nitrogen atoms has also been indicated by the emission of green phosphorescence (broad band near 5229 Å) from the solid (4°K and 20°K) products of the ultraviolet photolysis of HN_3, FN_3, ClN_3, and BrN_3 suspended in Ar and N_2 matrices (*189, 190*). At temperatures above 4.2°K, electron spin resonance studies suggested that nitrogen atoms in solid HN_3 may be produced as a result of photon absorption by NH radicals (*190a*).

The flash photolysis of HN_3, in the presence of inert gases, appears to yield a species that absorbs in the range 2670 to 2730 Å. Thrush has suggested that this might be N_3, corresponding to an energy level $N_2(X\ ^1\Sigma_g^+) + N(^2D)$, possibly produced by reactions of NH_2 or NH radicals with the parent HN_3 molecule (*191*). This gives some support to the proposal, made many years ago, that N_3 was an intermediate in the photolysis of hydrazoic acid (*192*). Jacox and Milligan have suggested that photolytically produced atomic fluorine can react with HN_3 at 14°K to yield N_3, which may then produce atomic nitrogen following photon absorption (*192a*). Welge has suggested that $N_2(A\ ^3\Sigma_u^+)$ molecules may be formed in the photodissociation of HN_3 at 1236 and 1470 Å (*170, 192b*).

The photolysis of aqueous azide solutions has been postulated to proceed by a chain mechanism, in which the chain carriers are the triplet state $N_2(A\ ^3\Sigma_u^+)$ molecules and an excited azide radical (probably in a quartet

state) with an energy content of 1.52 eV (*193*). The A-state nitrogen molecule appeared to have a lifetime of the order of 10^{-4} sec in solution.

Lichtin *et al.* have recently reported that discharged nitrogen retains its activity in chilled (0°–10°C) liquids (*193a*). It appears to react directly with iodide ion in acid solutions and fumaric acid in neutral solution, and to bring about, perhaps indirectly, the reduction of MnO_4^-, the ferrous → ferric, and ceric → cerous transformations.

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