AIP | The Journal of Chemical Physics

# Free Electrons in Active Nitrogen

W. B. Kunkel and A. L. Gardner

Citation: The Journal of Chemical Physics **37**, 1785 (1962); doi: 10.1063/1.1733369
View online: http://dx.doi.org/10.1063/1.1733369
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/37/8?ver=pdfcov
Published by the AIP Publishing

---

---

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 37, NUMBER 8 OCTOBER 15, 1962

# Free Electrons in Active Nitrogen*

W. B. KUNKEL AND A. L. GARDNER†
*University of California, Berkeley, California*

(Received June 8, 1962)

The resonance shift in an S-band cavity was used to measure the free-electron density $[n]$ in a continuous flow of rf-excited active nitrogen in the mm Hg pressure range. $[n]$ varied between $10^7$ and $6\times10^9$ cm$^{-3}$ and depended distinctly on the oxygen contamination. The ions formed presumably are $NO^+$. By admixing known small amounts of nitric oxide to the stream it could be demonstrated that the ionization rate indeed varied linearly with the amount of NO added. At high pressures and large $[n]$ the electron removal was by recombination, and at low pressures and small $[n]$ it was governed by ambipolar diffusion. The value of $Dp/\alpha$ was estimated at $10^9$ mm Hg/cm. Since the NO must be practically completely dissociated by the active nitrogen, the required large ionization rate indicates that the mechanism probably involves formation of excited nitrogen molecules as an intermediate step.

## INTRODUCTION

THERE is no doubt nowadays that the so-called long-lived active nitrogen consists primarily of nitrogen atoms in their ground state[1-3] and that the well-known Lewis–Rayleigh afterglow is the result of certain particular modes of recombination of these atoms.[4,5] This obstinate problem can therefore be considered as solved in principle and only certain details remain to be cleared up. One of the most baffling of the remaining questions concerns the electrical conductivity, which is frequently observed to exist in active nitrogen. It is certain, for instance, that in most cases this conductivity must be ascribed to ionization occurring in the volume rather than to electron release from surfaces. The density of free electrons measured in a specially arranged set of experiments we carried out some years ago was found to be closely correlated with the oxygen contamination of the gas, and it was obvious to suspect that ionization of nitric oxide by active nitrogen (chemi-ionization) was the source of conductivity.[6] The details of the process, however, remained obscure. In particular, it was discovered shortly afterward that nitric oxide was very rapidly destroyed by atomic nitrogen.[7,8] The rate constant for the proposed competing ionizing reaction was therefore required to be unreasonably high. Moreover, attempts to detect the nitric oxide ions by means of a mass spectrometer failed.[9] Therefore, we have hesitated to publish these findings in the open literature. Recently, interest in chemi-ionization in the gas phase has been renewed, however,[10,11] so that a brief description of our original experiments and results seems desirable after all.

## EXPERIMENTAL ARRANGEMENT

The arrangement used is readily explained with the help of Fig. 1. A constant flow of gas admitted through valve A and continuous rf excitation (14 Mc, 200 W) with external electrodes were used to produce a steady stream of active nitrogen in a long straight tube of about 3-cm diam. The afterglow luminosity could be monitored with a photomultiplier. The free-electron density as a function of time, i.e., as a function of distance from the discharge, was measured by means of a microwave cavity (S band) using the resonance-shift technique. In this respect the experiment resembled that of Benson.[12] However, the only metal exposed to the active nitrogen was the pump and its valve about 10 ft downstream from the discharge. It was therefore impossible for electrical currents to flow along the tube. Additional gases could be mixed into the stream through valve B and a capillary either upstream or downstream of the excitation region, depending on the position of the movable discharge chamber. The pressures were usually kept between 1 and 10 mm Hg, and the mean flow speeds typically ranged from 50 to 500 cm/sec. Further experimental details are not of importance to the present discussion. A complete description of the equipment and tech-

---

* Work supported jointly by the Office of Naval Research, the Office of Scientific Research, and the Wright Air Development Division.

† Present address: University of California Lawrence Radiation Laboratory, Livermore, California.

[1] M. A. Heald and R. Beringer, Phys. Rev. **96**, 645 (1954).

[2] R. V. Jones, W. Dobrowolsky, W. B. Kunkel, and C. D. Jeffries, Phys. Rev. **99**, 646 (1955).

[3] D. S. Jackson and H. I. Schiff, J. Chem. Phys. **23**, 2333 (1955).

[4] K. R. Jennings and J. W. Linnett, Quart. Revs. (London) **12**, 116 (1958).

[5] J. Berkowitz, W. A. Chupka, and G. B. Kistiakowsky, J. Chem. Phys. **25**, 457 (1956); G. B. Kistiakowsky and P. Warneck, *ibid.* **27**, 1417 (1957); K. D. Bayes and G. B. Kistiakowsky, *ibid.* **29**, 949 (1958); **32**, 992 (1960).

[6] A. L. Gardner, "Determination of Electron Density in Nitrogen Afterglows Using Microwave Methods," University of California Eng. Project Rept. HE-150-129 (1955). Also W. B. Kunkel and A. L. Gardner, Phys. Rev. **98**, 558 (1955).

[7] P. Harteck and S. Dondes, J. Chem. Phys. **27**, 546 (1957).

[8] G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys. **27**, 1141 (1957).

[9] W. B. Kunkel, Bull. Am. Phys. Soc. **2**, 87 (1957).

[10] C. F. Gatz, F. T. Smith, and H. Wise, J. Chem. Phys. **35**, 1500 (1961). Also F. T. Smith and C. F. Gatz, "Ionization in Afterburning Rocket Exhausts," Stanford Research Institute Technical Rept. BSD-TR-61-76 (1961).

[11] H. P. Broida and I. Tanaka, J. Chem. Phys. **36**, 236 (1962).

[12] J. M. Benson, J. Appl. Phys. **23**, 757 (1952).

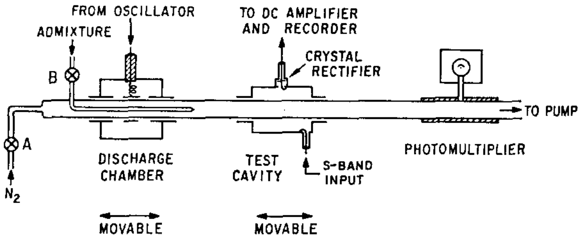

FIG. 1. Experimental arrangement.

niques used, as well as of some of the results has been given in a separate report.[6]

## GENERAL OBSERVATIONS

The appearance of the clearly visible afterglow indicated that the flow was laminar at all times. This was expected, of course, since the Reynolds number was never more than 100. Late times in the afterglow ($t>0.5$ sec) were studied using flow speeds less than 100 cm/sec. Under such conditions both the luminous intensity and the free-electron density were found to decay very nearly exponentially at the pressures used ($p\leq 6$ mm Hg). This indicated that under our operating conditions (untreated glass walls) the active nitrogen was quenched primarily by surface losses and it could be estimated that the probability of removal for nitrogen atoms was of the order of $10^{-4}$ per collision with the walls. Interestingly, and in agreement with many earlier findings, the decay rate depended on the gas composition. This was also true, of course, for the electron density as is apparent from the example shown in Fig. 2, in which small amounts of oxygen were added before the gas entered the excitation region. Unfortunately, for this reason data such as shown in Fig. 2 could not be used to separate the effect of oxygen contamination on the ionization phenomenon from its effect on the active nitrogen as a whole. All that could be ascertained was that the free-electron density correlated well with the Lewis–Rayleigh afterglow as long as some oxygen was present and known to be the only contamination of the gas.

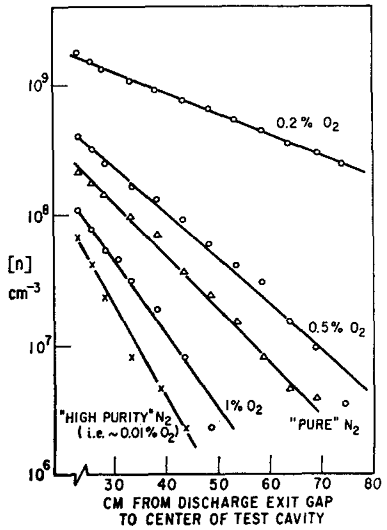

FIG. 2. Electron density vs distance from discharge in active nitrogen with various levels of oxygen contamination. Pressure: 4 mm Hg, flow speed 60 cm/sec.

It was found to be totally unjustified, for instance, to extrapolate the curves of Fig. 2 to zero time in order to obtain the "initial" state of ionization in the afterglow. By using higher flow speeds it could easily be demonstrated that during the first few tenths of a second both the luminosity and the electron density under our operating conditions deviated drastically from the exponential behavior observed at late times. In fact, as a rule both exhibited a maximum somewhere between 0.1 and 0.2 sec after the gas left the discharge region, very much as recently reported by Broida.[11] A similar behavior has at times been observed in static systems with pulsed discharges.[13] The effect is not surprising in our steady-flow system because during this time interval the gas temperature must be decreasing rapidly while the density is increasing in proportion; other excited components of the gas, of shorter lifetime, may still be contributing to the reactions in the gas; and the removal during the early stages may not be controlled by loss at the walls. The first effect of these is probably the most important one and is entirely adequate to explain the initial rise to a maximum. In Fig. 3, as an example, we show again the electron density as a function of time during the early stage of afterglow in which different amounts of oxygen were added to the flow of nitrogen upstream of the excitation region. It was also interesting to note that small amounts of nitric oxide gas, when added upstream of the discharge, had very similar effects on the electron density as molecular oxygen, two molecules of NO producing roughly the same result as one

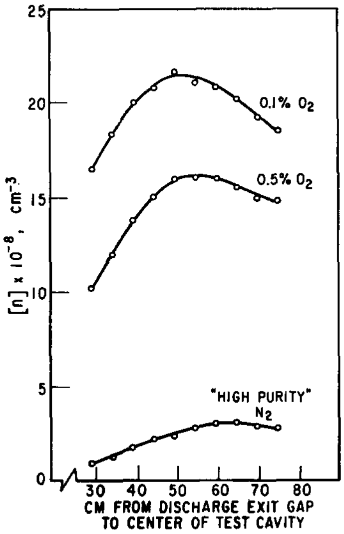

FIG. 3. Electron density vs distance from discharge in early stage of active nitrogen with various levels of oxygen contamination. Pressure: 4 mm Hg, flow speed 450 cm/sec.

---

[13] S. W. Kash, "A Study of the Decay of Nitrogen Afterglows," UCLA Institute of Geophysics Final Rept. N6 onr-27508 (1951).

molecule of $O_2$. We concluded from these observations that the oxygen contamination not only affected the discharge itself, of course, and the decay rate of active nitrogen, but probably also the ionization phenomenon directly. Surprisingly, roughly the same level of oxygen contamination that resulted in the slowest decay rate also produced the highest initial electron density in the afterglow. In our example at a pressure of 4 mm Hg this amount was found to be very nearly 0.2% of $O_2$. It appears likely, therefore, that these admixtures are totally dissociated in the discharge and that the parent substance responsible for the effect on decay and ionization in the afterglow is oxygen in the atomic state. Since in this investigation we were primarily interested in the ionization accompanying the afterglow, and not the mode of decay, the experiments discussed here will be limited to the early stage of the afterglow where the wall effects could be assumed to be relatively unimportant and where the atomic-nitrogen concentration was certain to be near its maximum value.

### ROLE OF NITRIC OXIDE

Whenever an appreciable contamination of oxygen is present in active nitrogen the emission bands of nitric oxide appear in the spectrum. Presumably, the excited molecules are formed in reactions such as[14,15]

$$N+O+M\rightarrow NO^*+M \qquad (1)$$

or conceivably in a two-step process ending with

$$N_2^*+O\rightarrow NO^*+N. \qquad (2)$$

In reaction (2) the nitric oxide may also be formed in the $X\,^2\Pi$ state, in which case, as far as energy is concerned, the $N_2^*$ need not be in a high-lying level. Furthermore, although the reaction is slow at room temperature and has an appreciable activation energy, molecular oxygen is known to be directly converted into nitric oxide[8,16]:

$$N+O_2\rightarrow NO+O. \qquad (3)$$

NO is probably also produced at a finite rate by atomic recombination at the walls.[17] None of these rates can be very rapid, however, because in conjunction with the known very fast reaction[7,8,15,16]

$$N+NO\rightarrow N_2+O \qquad (4)$$

even very small traces of oxygen would in that case be able to quench active nitrogen very rapidly. On the other hand, there is no doubt that a certain small amount of nitric oxide must be present in active nitrogen whenever the gas contains some oxygen as a contaminant.

It is, therefore, tempting to hypothesize that the free electrons are generated in the active nitrogen in one or several of the following ways:

$$N+N+NO\rightarrow N_2+NO^++e, \qquad (5)$$

or

$$N+N+M\rightarrow N_2^*+M \qquad (6)$$

followed by

$$N_2^*+NO\rightarrow N_2+NO^++e, \qquad (7)$$

or even by the three-body reaction

$$N_2^*+N+O\rightarrow N_2+NO^++e. \qquad (8)$$

In the last case, just as in reaction (2), the $N_2^*$ does not have to be a high-lying level; any one of the known electronically excited states of the nitrogen molecule would have sufficient energy to make this reaction possible. In this connection it should be mentioned that Kenty recently has reported evidence of chemi-ionization of barium and the existence of a long-lasting level of $N_2^*$ at about 8 eV.[18] As far as the energy is concerned, it is of course also possible to obtain ionized nitric oxide in reactions such as

$$N(^4S)+O^*(^1S)\rightarrow NO^++e, \qquad (9)$$

or

$$N^*(^2D)+O(^3P)\rightarrow NO^++e. \qquad (10)$$

As binary reactions the latter two are preferred in low-density gases such as considered here. But we do not think they are likely sources of ionization in our case because we are not aware of a mechanism that would produce the necessary excited atoms at a sufficient rate. The first three mechanisms can, however, not be readily distinguished and, in fact, all three may be operative.

With the help of the apparatus sketched in Fig. 1 it was very easy to demonstrate that the addition of either molecular oxygen or nitric oxide to a stream of active nitrogen indeed enhanced the ionization. The admixtures were first diluted with a substantial amount of pure nitrogen and introduced into the active stream several centimeters downstream of the discharge by means of valve B and the capillary shown. Care was taken that no ionization occurred inside the capillary. The results are given in Fig. 4. Clearly, molecular oxygen under these conditions is only slowly and incompletely converted, presumably by reaction (3), into the ionizable form of either nitric oxide or atomic oxygen. This is in full agreement with the observations by Kistiakowsky and Volpi.[8] It is also seen that the addition of NO gas results in a prompt increase of the free-electron density. However, since reaction (4) is so very rapid our experiments did not enable us to dis-

---

[14] Y. Tanaka, J. Chem. Phys. **22**, 2045 (1954).

[15] C. A. Barth, W. J. Schade, and J. Kaplan, J. Chem. Phys. **30**, 347 (1959).

[16] M. A. A. Clyne and B. A. Thrush, Proc. Soc. (London) **A261**, 259 (1961).

[17] J. T. Herron, J. Research Natl. Bur. Standards **65A**, 411 (1961); J. T. Herron, J. Chem. Phys. **35**, 1138 (1961).

[18] C. Kenty, J. Chem. Phys. **35**, 2267 (1961).

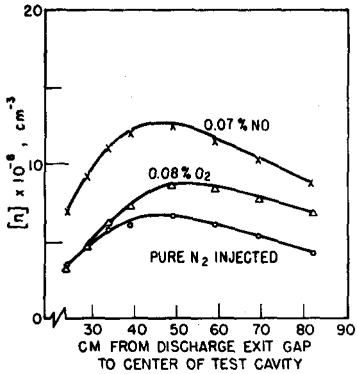

FIG. 4. Electron density vs distance from discharge in early stage of active nitrogen when $O_2$ or NO is added at 17 cm downstream of discharge. Pressure: 5 mm Hg, flow speed 370 cm/sec.

tinguish between the ionizing reactions (5) or (7) and (8).

## QUANTITATIVE ANALYSIS

Reactions (5) and (7) predict that the ionization rate should be proportional to the concentration of nitric oxide present in the stream. The same is true for reaction (8) if we assume, in addition, that reaction (4) in conjunction with the NO-producing mechanisms such as (1) and (2) maintain a nearly constant ratio of atomic oxygen and nitric oxide molecules. The existing electron density, on the other hand, is controlled also by the electron-removal rate. The predominant processes here are volume recombination, and ambipolar diffusion followed by recombination at the walls. Since we are dealing with steady-state flows only, the situation can be described formally by the following equation:

$$\mathbf{v}\cdot\nabla[n]=\nabla(D\nabla[n])-\alpha[n]^2+\beta[\mathrm{NO}], \qquad (11)$$

where $\mathbf{v}$ is the gas flow velocity, $[n]$ and [NO] denote the number densities of electrons and nitric oxide molecules, respectively, $D$ is the ambipolar diffusion coefficient, $\alpha$ is the recombination coefficient, and $\beta[\mathrm{NO}]$ expresses the ionization rate.

Equation (11), as it stands, is of course useless. For the analysis of our experiments, however, tremendous simplifications that allow fair quantitative estimates of the quantity of interest here, $\beta[\mathrm{NO}]$, seem justified. Recently, the coefficient $\alpha$ in photo-ionized room-temperature NO plasmas has been determined by several investigators and a value of $\alpha=10^{-6}$ cm³/sec seems to be ascertained to within a factor of 2.[19,20] The ambipolar diffusion coefficient for nitric oxide ions in nitrogen has not been measured yet, but, based on known values for similar systems, a guess of $D=100$ cm²/sec at 1 mm Hg pressure is probably not too much in error. Now, the observed mean electron densities were always $[n]>10^8$ cm⁻³ and varied only slowly in the direction of the flow while at the walls, of course, $[n]$ had to be zero. It follows that the left side of Eq. (11) in a first approximation may well be neglected and the diffusion on the right-hand side was practically only radial. In other words, the local ionization and de-ionization rates apparently were sufficiently rapid to control the electron density as a function of position along the direction of the flow. This is the first simplification.

Furthermore, at high gas pressures and high ionization levels the electron removal will be controlled by volume recombination, i.e., we can also neglect the first term on the right. In that case we should find

$$[n]^2=(\beta/\alpha)[\mathrm{NO}]. \qquad (12)$$

If, on the other hand, the electron removal was controlled by radial diffusion and recombination at the walls, we can neglect the second term on the right. Assuming for simplicity that neither $D$ nor $\beta[\mathrm{NO}]$ are functions of radial position, the solution then is

$$[n]=(\beta/4D)(R^2-r^2)[\mathrm{NO}], \qquad (13)$$

where $R$ is the radius of the tube. The average electron density in the tube is now given by

$$[n]=(\beta R^2/8D)[\mathrm{NO}]. \qquad (14)$$

Expression (14) is expected to hold for low electron densities and at low gas pressures.

When the electron removal rates by ambipolar diffusion and by volume recombination are comparable, Eq. (11) cannot be solved in closed form. Fortunately, the simplifying conditions under which either relation (12) or relation (14) applied were readily obtainable in our experiments. Keeping the gas flow and excitation conditions constant, the amount of nitric oxide, added at a fixed point downstream of the discharge, was varied and electron-density distributions as functions of axial position similar to those shown in Fig. 4 were

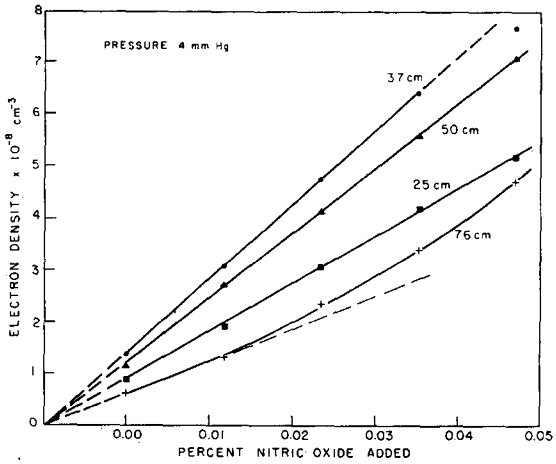

FIG. 5. Electron density, observed at various distances, vs amount of NO added at 17 cm downstream of discharge. Pressure: 4 mm Hg, flow speed 300 cm/sec.

---

[19] R. C. Gunton and E. C. Y. Inn, J. Chem. Phys. 35, 1896 (1961).

[20] J. P. Doering and B. H. Mahan, J. Chem. Phys. 36, 669 (1962).

determined. Representative results are shown in Fig. 5 and Fig. 6 where $[n]$ is plotted against the amount of nitric oxide added. The different curves refer to different points of observation along the tube, i.e., different ages of the afterglow. It is seen that, indeed, at a pressure of 4 mm Hg and electron densities well below $10^9$ cm$^{-3}$ linear relationships of the form (14) are usually obeyed whereas at 6 mm Hg and electron densities well above $10^9$ cm$^{-3}$ quadratic forms like (12) are indicated. This means that, according to these data, the ratio of diffusion to recombination coefficients must be estimated to be $Dp/\alpha \approx 10^9$ (mm Hg)/cm, i.e., about one order of magnitude larger than first expected. This may be considered fair agreement, particularly since the temperature of the gas in these experiments was probably considerably higher than it is under the conditions under which $\alpha$ and $D$ are usually measured.

So far, the observations described here seem to agree rather well with the expectations if the proposed mechanisms are indeed responsible for the ionization. The agreement may be fortuitous, however. It must be pointed out, for instance, that the straight lines in Fig. 5 and Fig. 6 can only result if the coefficient $\beta$ does not depend on the nitric oxide contamination. But, as was already shown in Fig. 2, the decay rate of the active nitrogen itself is affected by the oxygen content, small amounts of contamination increasing the lifetime presumably by rendering the tube walls slightly more inert. The nonlinear dependence of $[n]$ or $[n]^2$ on the amount of NO added at positions beyond 50 cm downstream from the discharge shown in Fig. 5 and Fig. 6 were probably caused by this effect. For the same reason, probably, it was also not possible to extend the measurements at 4 mm Hg pressure up to values where volume recombination becomes predominant so that Eq. (12) would apply. This was unfortunate, because in that case it would have been possible to evaluate the ratio $D/\alpha$ quite accurately. Conversely, the linear relationship (14) could not be produced properly at pressures higher than 4 mm Hg, presumably because our nitrogen was not pure enough.

As pointed out before, a much more serious difficulty in our interpretation arises from quantitative considerations. Reaction (4), which simultaneously removed nitric oxide and atomic nitrogen from the system, supposedly proceeds with the well-known very large rate constant $k_4$ while the active nitrogen itself was observed to decay with a certain time constant $\tau$. This immediately sets an upper limit for the number density of nitric oxide molecules [NO] that could possibly have existed in the mixture

$$[\mathrm{NO}] \leq (k_4\tau)^{-1}. \tag{15}$$

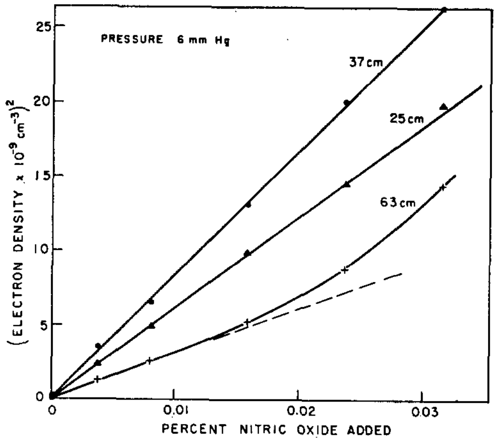

FIG. 6. Square of electron density, observed at various distances, vs amount of NO added at 17 cm downstream of discharge. Pressure: 6 mm Hg, flow speed 300 cm/sec.

The equality would apply if the removal of the nitrogen atoms were controlled by a chain of reactions ending with reaction (4) as the last step. This step could, for instance, be preceded by the formation of NO molecules via reaction (2) or via a type of wall recombination, but only the latter would result in an exponential decay of the active nitrogen. Reaction (1) is known to be too slow to be responsible for the observed half-life.[21] Obviously, the inequality in Eq. (15) is much more probable because it seems contradictory that the oxygen contamination should on the one hand control the decay rate in the manner of a catalyst and on the other be observed, below a certain maximum concentration at least, to lengthen the life of the afterglow.

Now, in general we know that $D\nabla^2[n] < 0$, hence $\beta[\mathrm{NO}] > \alpha[n]^2$ must always be true if $\mathbf{v}\cdot\nabla[n]$ is negligible. Therefore, in conjunction with Eq. (15) we conclude that certainly $\beta > k_4\tau\alpha[n]^2$ is always satisfied. This means, according to our model of ionization by the reactions (5), (7), and (8), we must require for the coefficient $\beta$ of Eq. (11) that

$$\beta \equiv k_5[\mathrm{N}]^2 + k_7[\mathrm{N}_2{}^*] + k_8[\mathrm{N}][\mathrm{N}_2{}^*][\mathrm{O}]\cdot k_4\tau > k_4\tau\alpha[n]^2, \tag{16}$$

where [N], $[\mathrm{N}_2{}^*]$, and [O] are again the number densities of the respective species. We may take for a numerical example a pair of values from Fig. 6, $p = 6$ mm Hg, e.g., $[n]^2 = 10^{19}$ cm$^{-6}$ and $[\mathrm{O}] = 3\times10^{13}$ cm$^{-3}$ [almost fully dissociated nitric oxide, in agreement with Eq. (15)]. Furthermore, we know $k_4 > 10^{-11}$ cm$^3$/sec, $\tau > 0.3$ sec, and $\alpha > 3\times10^{-7}$ cm$^3$/sec. If we now substitute the rather conservative guesses $[\mathrm{N}] \leq 10^{15}$ cm$^{-3}$ and $[\mathrm{N}_2{}^*] \leq 10^{13}$ cm$^{-3}$, Eq. (16) demands that either $k_5 > 10^{-29}$ cm$^6$/sec or $k_7 > 10^{-12}$ cm$^3$/sec or $k_8 > 10^{-29}$ cm$^6$/sec. Needless to say, these rate constants are much larger than would be expected except perhaps for $k_7$ which could be of the order indicated. It is therefore concluded that, if nitric oxide is indeed the substance ionized, reaction (7) is probably the predominant mechanism. But it is clear that more work will have to

---

[21] C. Mavroyannis and C. A. Winkler, Can. J. Chem. **39**, 1601 (1961).

be done on this problem before the matter can be settled with certainty. Fortunately, some new research along these lines is already in progress[11,22] and so far the new results seem to confirm our findings fully. In fact, it seems possible to use the chemi-ionization as a sensitive indicator of oxygen contamination in active nitrogen.

As a final comment we wish to point out that we have clear and unmistakable evidence that the free electrons are in no way involved in, and certainly not responsible for, the mechanism of the Lewis–Rayleigh afterglow emission as once had been suspected.[23] When the admixture of nitric oxide, introduced downstream of the discharge, was replaced by a minute trace of benzene vapor in an attempt to produce chemi-ionization of an organic molecule, the free-electron density unexpectedly was found to be suppressed completely (perhaps by attachment or by removal of the residual free oxygen). The afterglow, on the other hand, appeared unchanged or even enhanced in intensity and very strickingly lengthened by about one order of magnitude in duration! The emission bands of CN appeared very faintly and it could be demonstrated that a very durable wall coating was responsible for the long life. The effect persisted literally for hours after the benzene supply was shut off and could be wiped out quickly by flaming the glass wall or by running the discharge up and down along the tube. This discovery provides an exceedingly convenient method of keeping the glass walls "poisoned" indefinitely against the quenching of active nitrogen in a continuous flow system if the purity of the gas is not required to be exceptionally high, and if the free electrons are not needed.

---

[22] C. Gatz, F. T. Smith, and H. Wise, Bull. Am. Phys. Soc. **6**, 517 (1961).

[23] R. W. Nicholls, J. Chem. Phys. **20**, 1040 (1952).

---

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 37, NUMBER 8 OCTOBER 15, 1962

# High-Pressure Mass Spectrometric Study of Reactions of Rare Gases with $N_2$ and CO

M. S. B. Munson, F. H. Field, and J. L. Franklin
*Humble Oil & Refining Company, Research and Development, Baytown, Texas*

(Received February 6, 1962)

Studies have been made in a mass spectrometer at ionization chamber pressures of about 160 $\mu$ on mixtures of rare gases, R = He, Ne, Ar, Kr, and Xe, with $N_2$ or CO. The ions $R_2^+$, $ArN_2^+$, $KrN_2^+$, $XeN_2^+$, $ArCO^+$, $KrCO^+$, $XeCO^+$, $N_4^+$, and $C_2O_2^+$ were observed in these mixtures as a result of reactions of excited rare-gas atoms. The addition of Ar to $N_2$ enhances the formation of $N_4^+$ by reactions initiated by excited states of Ar; the addition of Ar or Kr to CO promotes the formation of $C_2O_2^+$ through reactions initiated by excited states of Ar and Kr. Rate constants were determined for the reactions

$$ArN_2^+ + N_2 = N_4^+ + Ar \qquad k = 1\times^{-10}\ \text{cc/molecule-sec}$$

$$KrCO^+ + CO = C_2O_2^+ + Kr \qquad k = 3\times 10^{-10}\ \text{cc/molecule-sec}$$

at a repeller field strength of 50 V/cm. Other combinations of rare gases with $N_2$ or CO show no such promotional effect on the formation of $N_4^+$ or $C_2O_2^+$. Ratios of the rate constants for the formation of $RN_2^+$ and $R_2^+$ in rare-gas–nitrogen mixtures and for the formation of $RCO^+$ and $R_2^+$ in rare-gas–carbon monoxide systems were also determined. At high pressures of $N_2$ or CO alone the formation of $N_4^+$ or $C_2O_2^+$ is observed, and the reaction is a bimolecular chemi-ionization involving highly excited $N_2$ or CO. At still higher pressures these ions are formed by termolecular ion–molecule processes.

At sufficiently high electron energies there are formed in binary mixtures of $N_2$ or CO with different rare gases the following ions: $RC^+$, $RN^+$, $C_2O^+$, $CO_2^+$ and $N_3^+$. The $N_3^+$ and $RN^+$ ions are formed by the reaction of excited nitrogen molecule ions with R and/or $N_2$, and the relative rates of these reactions were determined.

No compound ions between He or Ne and $N_2$ or CO were observed under any of the conditions of these experiments.

## INTRODUCTION

In the course of experiments in this laboratory on the reactions of rare-gas ions and excited rare-gas atoms it was observed that the addition of Ar to a moderately high pressure of $N_2$ caused the formation of an appreciable amount of an ion of mass 56 which was not observed in nitrogen alone under these conditions. This unexpected observation together with our general interest in the reactions of the rare gases led us to study the reactions of all the rare gases with nitrogen, and because of its expected similar behavior, carbon monoxide as well.

The higher ions of nitrogen, $N_3^+$ and $N_4^+$, were observed mass spectrometrically by Luhr[1] several years ago as a result of a discharge through nitrogen. Junk and Svec[2] have also detected $N_3^+$ and $N_4^+$ in a high-pressure mass spectrum of nitrogen. They found that $N_4^+$ has a second-power dependence upon nitrogen pressure, but they attribute the formation of $N_3^+$ to a surface reaction since they find a first-order pressure dependence. Saporoschenko[3] determined the appearance

---

[1] O. Luhr, Phys. Rev. **44**, 459 (1933).

[2] G. Junk and H. J. Svec, J. Am. Chem. Soc. **80**, 2908 (1960).

[3] M. Saporoschenko, Phys. Rev. **111**, 1550 (1958).