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Positive Ions in Nitric Oxide Afterglows

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Reported in this paper are results of measurements performed on a stationary nitric oxide afterglow. The nitric oxide was contained in a large gold-plated cylinder in which it was ionized by krypton resonance radiation. The ions from the afterglow were sampled through an electrically insulated orifice; it was observed that the potentials (in the mV range) applied to the orifice had a pronounced effect on the measured time constant of the afterglow decay. After the ions emerged from the sampling orifice, they were quantitatively detected by timeresolved mass spectrometry. An extensive study was made of the assumptions involved in the data-analysis model in order to establish the validity of the measurement techniques. In pure nitric oxide the only reaction observed over the pressure range investigated (10-300 mTorr) was $NO^+ + NO + NO \stackrel{k}{\rightarrow} NO^+ \cdot NO + NO$. The rate constant k was determined to be 5 ± 1 $\times 10^{-30}$ cm⁶/sec. Measurements were also made of the diffusion coefficients for NO⁺ and NO⁺• NO in nitric oxide gas. The afterglow plasma exhibits a sharp transition from positiveion-electron ambipolar-diffusion domination $D_{+,e}$ to positive-ion-negative-ion ambipolardiffusion domination D_+ _. The negative ion participating in this latter diffusion process is NO_2^- . These data represent the first reported observation of such a transition. For NO^+ the experimental values are $D_{\pm,e}p = 85 \pm 10 \text{ cm}^2$ Torr/sec and $D_{\pm,e}p = 42 \pm 5 \text{ cm}^2$ Torr/sec. Similarly, for NO⁺ NO the values are $D_{+,e}p = 84 \pm 13$ cm² Torr/sec and $D_{+,-}p = 41 \pm 5$ cm² Torr/sec.

I. INTRODUCTION

The techniques¹⁻¹¹ of observing the disappearance of charged particles in the afterglow of a gas discharge have been utilized for many years to study thermal-energy collision processes. In a stationary afterglow experiment, one observes the temporal variation of charged-particle densities following an ionizing pulse. The development of microwave techniques for absolute measurement of time varying electron densities has stimulated extensive stationary afterglow studies of electronion and electron-neutral interactions. In most of the investigations which employed microwave techniques the initial ionization density was sufficiently large that ion-electron recombination was the dominant electron-loss mechanism; the electron density decay was the principal analytic physical observable. Time-resolved mass analysis of the positive ions in the afterglow was first utilized to complement the microwave studies; its primary function was to identify the ions present in the afterglow and to ensure that the principal ion tracked the electron density decay. A number of different ionization sources have been utilized in afterglow experiments to produce the initial charged particles, including microwave breakdown, dc discharges, high energy β and γ irradiation, breakdown followed by Penning ionization, and photoionization. In this experiment, a photoionization source using selected wavelengths was chosen because such sources usually provide a minimum of undesirable initial species.

The primary result of an afterglow experiment is usually a reaction rate constant, which, in the case of a two-body process, is the product of the cross section and the relative particle velocity averaged over the relative velocity distribution of the interacting particles in the gas. For threebody reactions, where collisional stabilization of an unstable product is required and where particulars of the collision such as relevant cross sections and lifetimes are unknown, the use of a rate constant is a very practical way to convey information about the reaction. Furthermore, in a gas of specified composition and temperature, reaction rate constants may be used to describe the gross chemical properties of the gas.

The present paper contains a description of a stationary afterglow apparatus which was designed for the study of thermal-energy ion-molecule reactions; experimental results are reported for NO^+ ions in pure NO. The primary NO^+ ions are produced in a large ultrahigh-vacuum cavity by means of photoionization. Information on the individual ionic species in the afterglow is obtained by means of time-resolved mass spectrometry of the ions which pass through a sampling orifice in the cavity wall.

Initial charged-particle densities were sufficiently low that positive ion-electron recombination contributed negligibly to the plasma decay.

The remainder of this paper consists of description of the apparatus, data analysis, experimental results, evaluation of techniques, and error analysis. Wherever useful the present results are compared with those of other investigators.

II. DESCRIPTION OF APPARATUS

A schematic diagram of the apparatus is shown in Fig. 1. The afterglow cavity is a bakeable goldplated stainless-steel cylinder which is sealed by means of metal gaskets. The cavity has an 18 in. diameter and is 36 in. long. The cavity and differential pumping regions are pumped by 4-in. oil diffusion pumps equipped with water-cooled chevron baffles and zeolite traps. Typical base pressures following a 48-h, 200°C bake are ~10⁻⁹ Torr, with rate of rise less than 10^{-10} Torr/sec. The afterglow cavity can be isolated from its pumping station by means of an all-metal bakeable valve. Gas pressure in the cavity is mea-



FIG. 1. Schematic diagram of stationary afterglow apparatus.

sured with a capacitance manometer. Gas is admitted into the cavity through a servo-driven variable leak valve coupled to a feedback control system which regulates the cavity pressure to a value set by the capacitance manometer.

The primary NO⁺ ions are produced by photoionization of NO with krypton resonance radiation (123.6 and 116.5 nm) from a microwave-powered discharge lamp. The lamp body is of quartz with a 1-mm-thick MgF₂ window which transmits approximately 50% of the radiation at these wavelengths. The lamp is filled with krypton to a total pressure of ~1.5 Torr: microwave power is coupled into the lamp by means of an Evenson¹² cavity. The source of the microwave power is a standard 100-W, 2.45-gHz diathermy unit, which has been modified to permit microsecond pulsing as well as continuous operation. The intensity of the 123.6-nm radiation measured inside the afterglow chamber is ~ 10^{15} photons/sec: the 116.5-nm line is about 14% of that value. The vacuum ultraviolet spectrum of the lamp is quite clean: more than 98% of the total radiated energy between 200.0 and 115.0 nm (MgF₂ cutoff) is contained in the two krypton resonance lines.

For the purposes of this investigation the apparatus was operated at sufficiently low ion-number densities so that linear loss processes predominated. In order to minimize the time required for the ions to stabilize into a fundamental mode spatial distribution we irradiated the cavity with light having a radial spatial distribution close to a zeroth-order Bessel function. In the midplane of the chamber, where the ions were sampled, the radial distribution of the ionizing radiation was approximately a truncated cosine distribution, filling about 80% of the cavity. As will be demonstrated later, this distribution stabilizes in sufficient time to permit meaningful measurements to be made early in the afterglow.

Ions which diffused to the side wall of the cavity were sampled through a 0.60-mm-diam orifice in

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the cavity wall. The orifice is contained in a 6-cm-diam disc machined to match the contour of the cavity wall. The orifice plate can be electrically biased with respect to the cavity walls, and, as indicated in Fig. 1, the transient current to this plate can be measured with a computer of average transients. The rationale behind this design is the following. It is well known that both contact potential differences and surface charging can seriously affect the validity of sampling through an orifice. If the sampling orifice is an integral part of the cavity wall, then there are no experimental parameters which can be varied to verify directly the absence of discimination of the sampling system. If, however, the potential of the sampling orifice can be varied, then observation of the plasma decay as a function of orifice potential can lead to a useful estimate of possible uncertainties resulting from surface charging or contact potential differences. Moreover, the plasma decay as sensed by the orifice plate may be compared with the total ion plasma decay measured by the mass spectrometer. Agreement of these two assures the absence of discrimination in sampling the ion population through the orifice, differential pumping regions, and mass spectrometer. (The type of discrimination referred to here is not primarily mass discrimination, but discrimination based on ionic number density.) Results of varying the orifice potential will be given in a later section: the effect of this potential was found to be quite important.

The relatively high pressure in the afterglow cavity necessitates the use of differential pumping for the mass spectrometer. Two stages of differential pumping are employed in this apparatus; each affords a pressure reduction of $\sim 10^3$. The two stages of differential pumping are separated by a conical skimmer with a 1-mm-diam orifice in the tip. The skimmer orifice is separated from the orifice in the chamber wall by a distance of 3 cm. For nitric oxide, little agglomeration in the expansion through the first aperature is expected¹³ for pressures up to a few tenths of a Torr. The skimmer can be electrically floated off ground. and is normally operated in this fashion, both to enhance ion sampling efficiency and to reduce sampling discrimination. These points will be discussed in more detail in other sections of this paper.

The mass spectrometer is a General Electric monopole spectrometer, modified to permit operation with ions formed at ground potential. The ion optics on the spectrometer were rebuilt to permit more efficient operation with externally produced ions. Most of our data was taken at an ion-analysis energy of 40 eV, for which the ion transmission efficiency was quite satisfactory. Even at this energy, the spectrometer is capable of resolving adjacent mass peaks well beyond 200 amu. The electron impact ion source on the spectrometer was used to generate mass calibration spectra. When operated in a high-sensitivity mode, it was possible to observe positive ions at every mass peak over the mass range of interest. These ions were thus identified simply by counting mass peaks. In order to identify the mass peaks produced in NO by the Kr radiation one has only to compare with the calibration spectrum.

Those ions which passed through the mass spectrometer were detected with a 16-stage Ag-Mg multiplier operated in a single-particle pulse counting mode. Following amplification, shaping, and discrimination against low-level noise pulses, the ion signal was processed by a 1024-channel analyzer operated in a multiscaling mode. A master pulser simultaneously triggered the microwave source, the multiscaling sweep, and the computer of average transients. Repetitive pulsing of the discharge lamp permitted accumulation of a sufficient number of ions in each time channel to afford a statistically meaningful time history of the afterglow decay. The resulting ion buildup and decay history was then plotted out either linearly or logarithmically.

During the final vacuum processing of the apparatus, a thin film of gold ~ 100 nm thick was evaporated onto the walls of the afterglow cavity. The gold coat is intended to minimize potential differences in the cavity. Whenever the chamber was exposed to atmosphere, the gold was removed and a new layer deposited during the next vacuum processing operation.

III. ANALYSIS OF DATA

With this apparatus it is possible to determine reaction rates experimentally either from afterglow data or from data acquired during continuous ionization when the plasma is in equilibrium between production and loss processes. The two techniques involve different sets of assumptions, and, while the afterglow data analysis leads to more accurate rate constants, the analysis of the equilibrium plasma provides an important check on the validity of the afterglow data analysis.

A. Afterglow

The following analysis shall assume, for the sake of simplicity, that the ions are diffusing in a fundamental mode distribution during the afterglow. It is further assumed that all recombination losses were negligible. The validity of both of these assumptions has been demonstrated for late times in the afterglow.

If ion-electron ambipolar diffusion of NO⁺ and a reaction with loss frequency v_l were the dominant loss processes for NO⁺ ions, and if there were no sources for NO⁺ during the afterglow, then the continuity equation for NO^+ ions would be as follows:

$$\frac{\partial}{\partial t} \left[\mathrm{NO}^{+}(r,t) \right] = D_{a} \nabla^{2} \left[\mathrm{NO}^{+}(r,t) \right] - \nu_{l} \left[\mathrm{NO}^{+}(r,t) \right], \quad (1)$$

where the brackets [] denote number densities and D_a is the NO⁺ ion-electron ambipolar diffusion coefficient. For the case of a long cylindrical cavity of radius R and an initial NO⁺ concentration given by

$$[\mathrm{NO}^{+}(r,0)] = [\mathrm{NO}^{+}(0,0)] J_{0}(2.405 r/R), \qquad (2)$$

the solution of Eq. (1) is

$$[NO^{+}(r, t)] = [NO^{+}(0, 0)]J_{0}(2.405r/R)$$
$$\times \exp\{-(D_{a}P/\Lambda^{2}p + \nu_{l})t\}, \qquad (3)$$

where Λ is the characteristic diffusion length of the cavity, p is the total pressure, and NO⁺(0, 0) is the initial axial number density.

In this apparatus the direct physical observable is not the volume number density, but rather the NO^+ count rate at the mass spectrometer. If we assume that the NO^+ count rate is proportional to the NO^+ wall-current density and that the wall-current density is simply a diffusion current, driven by the ion density gradient, then it follows that

$$R(NO^{+}) \propto D_{a} [NO^{+}(0, 0)] \exp\{-(D_{a}p/\Lambda^{2}p + \nu_{l})t\}$$
$$\propto D_{a} [NO^{+}(0, 0)] e^{-\nu t}, \qquad (4)$$

where $R(NO^+)$ is the count rate of NO^+ ions exiting the mass filter, and ν represents the total NO^+ loss frequency.

Thus, under the stated assumptions, the ioncount rate is directly proportional to the ion number density in the afterglow cavity. This simple proportionality does not necessarily hold, however, in the event of a time-changing spatial distribution, surface-charging effect, or the application of a drawout voltage to the orifice plate. Experimental checks will be presented to establish the validity of each of the above assumptions.

Observation of the NO⁺ loss frequency ν as a function of pressure then yields both the ambipolar diffusion coefficient and the reaction loss frequency ν_l . If, for example, NO⁺ ions are lost through the reaction process

$$\mathrm{NO}^{+} + \mathrm{NO} + \mathrm{NO}^{\frac{k}{2}} \mathrm{NO}^{+} \cdot \mathrm{NO} + \mathrm{NO},$$
 (5)

with a reaction rate constant k in units of $\rm cm^6/sec,$ then

$$\nu_{I} = k \left[\text{NO} \right]^2 \,. \tag{6}$$

The p^{-1} and p^2 contributions to ν can be separated, and k can be determined. It should be noted that a rate constant obtained in this fashion is a rate constant for loss of NO⁺ ions. Even if all of the assumptions embodied above are verified, such a determination would be in error if there are sources or sinks for NO⁺ ions for which one has not accounted. Further, such a measurement provides no quantitative information concerning the products formed by the reactants. It is for this last reason that the "steadyglow" analysis described below was also employed.

B. Steadyglow

The steadyglow data analysis is best illustrated by a specific reaction, such as the clustering reaction in Eq. (5). If one assumes that the only source of NO⁺ · NO is from NO⁺ and that all ions are in a time-invariant spatial distribution, the continuity equation for NO⁺ · NO ions can be written in the form

$$d[\mathrm{NO}^{+} \cdot \mathrm{NO}]/dt = -\nu_{60}[\mathrm{NO}^{+} \cdot \mathrm{NO}] + \gamma[\mathrm{NO}^{+}].$$
(7)

The quantity ν_{60} represents the sum of all loss processes for NO⁺ · NO ions, and γ represents the gain frequency from NO⁺ ions. For continuous irradiation of the cavity, $d[\text{NO}^+ \cdot \text{NO}]/dt = 0$, and Eq. (7) can be rewritten

$$\gamma = \nu_{60} \{ [NO^{+} \cdot NO] / [NO^{+}] \}_{sg}$$
$$= \nu_{60} c^{-1} \{ R(NO^{+} \cdot NO) / R(NO^{+}) \}_{sg}, \qquad (8)$$

where sg implies steadyglow and c is the over-all detection efficiency of $NO^+ \cdot NO$ relative to NO^+ . The quantity ν_{60} in Eq. (8) is identical to v_{60} as determined from afterglow measurements of $NO^{\tau} \cdot NO$ decay under the following conditions: (i) the ionic number density is sufficiently low that linear loss mechanisms dominate, and (ii) the ions produced in the steadyglow conditions have a $J_{0}(2.405 r/R)$ distribution. This distribution is closely approximated by the spatial distribution of the ionizing radiation. Since both steadyglow and afterglow measurements are taken in ionic number-density regimes where the dominant loss processes are linear, the quantity ν_{60} can be measured in the afterglow. No assumptions are required concerning the nature of the loss processes involved for NO⁺ NO.

Since the steadyglow technique requires knowledge of the relative detection efficiency for ions of different mass, the rate constants so obtained are not as accurate as those determined by the afterglow technique. However, this shortcoming is offset by the fact that this measurement pro-

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vides an excellent check against a gross misinterpretation of the afterglow loss data. Assuming the absence of sampling difficulties, the interpretation of the afterglow data is in error only if there are loss processes for NO⁺ ions not accounted for in the analysis. Correspondingly, the steadyglow measurement is in error only if there are sources of NO⁺ · NO ions other than the one assumed. If the reaction rate constants measured by these two techniques agree within experimental uncertainties, then the conclusion is that the reaction loss process measured by the afterglow technique is proceeding primarily through the indicated channel.

IV. EXPERIMENTAL RESULTS

Over the pressure range of 10-200 mTorr, and at 293 K, the dominant positive ions present in pure NO are NO⁺ and the dimer NO⁺ · NO. These ion spectra are shown in Fig. 2. In this same pressure range NO₂⁻ dominates the negative ion spectrum by about a factor of 100. At pressures above 200 mTorr, however, reactions with trace amounts of water become increasingly important until at Torr the series of ions NO⁺ · H₂O, NO⁺ · 2H₂O, H₃O⁺ · 2H₂O, and H₃O⁺ · 3H₂O are of comparable intensity to NO⁺ · NO. These ion species will be discussed in a future publication.

The use of the ion sampling technique coupled with single-particle pulse counting and multichannel time analysis enables a large dynamic range of afterglow decay to be observed. For example, Fig. 3 depicts the time behavior of the sampled NO⁺-ion wall current at 20-mTorr pressure. The data represent a summation over ~10⁴ light pulses and cover more than six decades of decay. The maximum central-ion number density, while not directly measured, is estimated to be approximately 10⁷ ions/cm³. The early afterglow decay is clearly exponential, as expected from the simple theory of Sec. III. The



FIG. 2. Evolution of the mass spectrum as a function of increasing NO pressure. The total spectrum for each gas pressure is normalized to the same value.



FIG. 3. Typical NO^+ decay curve. The data are a summation over 10^4 ionizing pulses. Note that more than six decades of decay are observable. The "break" at 170 msec is a result of the transition of the afterglow from ion-electron ambipolar diffusion domination to positive-ion-negative-ion ambipolar-diffusion domination. The NO^+ decay is exponential before and after the transition, and the loss frequencies are in agreement with those predicted from such a transition.

loss frequency $\nu = 56 \text{ sec}^{-1}$ is the reciprocal time constant of the early afterglow decay. The rapidity with which the decay becomes a simple exponential decay following extinction of the photoionizing source indicates that the influence of higherorder diffusion modes is unimportant in this case.

The "break" in the NO⁺ wall current near 170 msec is associated with the transition of the afterglow plasma from positive ion-electron ambipolardiffusion domination to positive-ion-negative-ion ambipolar diffusion domination (see Appendix).

The structure in the wall current in the vicinity of the transition is a result of the following: (a) The sudden disappearance of electrons when the electron density became too small to sustain the electron-ion ambipolar-diffusion space-charge fields; and (b) the trapping of negative ions in the cavity by the electron-ion ambipolar-diffusion space-charge field.

The details of this transition are currently being investigated by M. D. Kregel in this laboratory. In the remainder of the text, the ion decay before and after this break shall be referred to as the early afterglow and late afterglow, respectively.

A. Afterglow Data

The experimental data for the pressure variation of the loss frequency of NO^+ ions in pure NO are shown in Fig. 4. The data shown were obtained with orifice-plate potentials varied between 0 and 100 mV negative with respect to the cavity wall. The observed decays were exponential over 1-4



FIG. 4. Variation of NO⁺ loss frequency in pure NO as a function of NO pressure. The closed circles represent early (ion-electron) afterglow data and the closed squares represent late (ion-ion) afterglow data. The dashed line is the sum of the asymptotic p^{-1} and p^2 lines.

decades. The lower pressure limit of 5 mTorr results both from increasing uncertainty concerning the effect of the orifice-plate potential and the fact that the total number of ion-molecule collisions in the cavity became too small to describe meaningfully by a statistical equilibrium process such as diffusion. The upper pressure limit of 200 mTorr results from the combination of rapid reactive loss of NO⁺ relative to diffusive loss and the increased time required for the ionic spatial distribution to stabilize into the fundamental mode distribution. (For a given ionic spatial distribution the stabilization time is inversely proportional to the diffusion coefficient, which in turn in inversely proportional to the pressure. Hence, the stabilization time is directly proportional to the pressure.) Over the indicated pressure range, the NO⁺ loss frequency was

$$\nu = a/p + bp^2 , \qquad (9)$$

implying that the dominant NO^+ loss processes were diffusion and a three-body reaction between NO^+ and two NO molecules. Since the only other significant ion observed in this pressure range was the dimer $NO^+ \cdot NO$, the indicated reaction process was

$$NO^{+} + NO + NO \stackrel{\mathcal{R}}{\rightarrow} NO^{+} \cdot NO + NO.$$
 (10)

This rate constant was evaluated from b and was found to be $5 \pm 1 \times 10^{-30}$ cm⁶/sec.

Since it was demonstrated that ambipolar diffusion was the diffusion process operative in the early afterglow, the observed diffusion loss frequency, together with the diffusion length¹⁴ of the cavity, provide sufficient information to determine the ion-electron ambipolar-diffusion coefficient. The result was $D_a p = 85 \text{ cm}^2 \text{ Torr}/$ sec, where D_a is related to the free-ion diffusion coefficient D_+ through the expression $D_a = D_+(1 + T_e/T_i)$, in which T_e and T_i represent the electron and ion temperatures, respectively. It is evident then that for the case of $T_e = T_i$, $D_a = 2D_+$. Late afterglow decays were also measured for NO⁺ ions in an effort to obtain information on ion-ion ambipolar diffusion. The analysis of Sec. III is applicable to this case if one substitutes the ion-ion ambipolar-diffusion coefficient $D_{+,-}$ for D_a (see Appendix).

In this case, unlike the previous example of electrons and ions, the two species which undergo diffusion are both ions with approximately the same free-diffusion coefficients. For these ions the space-charge field in the late afterglow will be small, and the ambipolar-diffusion coefficient will be essentially equal to the free-diffusion coefficient, i.e., $D_a = D_+$. If, in addition to the near equality of diffusion coefficients, the only ionic loss process is through diffusion and the electron and ion temperatures are equal, then the late afterglow loss frequency should be one-half the early afterglow loss frequency. That this is indeed the case is verified in Fig. 4, which shows the late afterglow D_{+} - $p = 42 \text{ cm}^2 \text{ Torr/sec.}$ This observation is an important verification of the absence of preferential electron heating in the afterglow. A discussion of the uncertainties associated with these measurements will be presented in a later section.

Afterglow measurements were also made for the $NO^+ \cdot NO$ dimer. A principal assumption in the afterglow analysis is that there were no important sources for the ion being observed, i.e., that the decay was representative of loss processes only. In the early afterglow, NO⁺ was negligible with respect to $NO^+ \cdot NO$ only for pressures greater than about 60 mTorr. At pressures greater than ~120 mTorr the early afterglow terminated too rapidly to permit accurate determination of the decay time. Thus, only a limited region of data was available for early afterglow measurement of the $NO^+ \cdot NO$ decay frequency. Data were extended down to 40 mTorr, however, by subtracting the contribution of NO^+ to the $NO^+ \cdot NO$ afterglow. The results obtained in this manner should correspond to the case in which $NO^+ \cdot NO$, in the absence of any sources, is lost through the diffusion process. As is indicated in Fig. 5, the correction brought the low-pressure data into correspondence with the data above 60 mTorr and therefore added credence to the latter data. The electron-ion ambipolar diffusion coefficient $D_a p$ (early afterglow) for $NO^+ \cdot NO$ was determined to be 84 cm² Torr/sec.

Late afterglow measurements of $NO^+ \cdot NO$ were also made for pressures greater than 30 mTorr, with NO⁺ an important source for NO⁺ ·NO. The



FIG. 5. $NO^+ \cdot NO$ loss frequency in pure NO. The high-pressure loss process represents a two-body reaction of $NO^+ \cdot NO$ with an unknown gas impurity.

relatively long time required for the NO⁺·NO spatial distribution to stabilize was not a problem in the late afterglow measurements, even at high pressures, for the late afterglow measurements may be extended to very late times. For example, Fig. 6 shows a typical decay of $NO^+ \cdot NO$ at 0.3 Torr. The light pulse is 14 msec wide, and the decay is a simple exponential from 30 msec to greater than 2.2 sec. The data represent 5 min of data accumulation time, or approximately 100 flashes of the photoionizing light source. All of the decay data for $NO^+ \cdot NO$ are summarized in Fig. 5. The late afterglow data are seen to be consistent with diffusive loss at low pressure and loss through a two-body reaction at higher pressure. The p^{-1} portion of the late afterglow data implies a diffusion coefficient $D_{+,-}p = 41 \text{ cm}^2$ Torr/sec for NO⁺ NO. It should be noted that the early afterglow diffusion coefficients are the same within experimental error for both NO⁺ and $NO^+ \cdot NO$, a rather surprising result. The same is also true for the late afterglow ion-ion diffusion coefficients. Furthermore, the data for both ions indicate that $D_a = 2D_{+,-}$, which is a result that one would expect from simple theory for the case in which both the positive and negative ions have approximately equal free-diffusion coefficients.

As mentioned earlier, impurity ions are not negligible in this high-pressure range. For example, a major impurity ion at M/e = 75 appears to be formed from NO⁺·NO; at 1 Torr the steadystate number density of M/e = 75 is just slightly less than that of NO⁺·NO. No evidence was seen for the trimer ion NO⁺·(NO)₂. Since the concentration of the impurity reactant is unknown, no measurement of the rate constant can be given. The observed loss can be accounted for, however, by an impurity of 1 ppm in the NO gas reacting with NO⁺·NO at a gas kinetic rate. If, instead, we assume (incorrectly) that all of the observed loss of NO⁺·NO proceeds through the channel

$$NO^{+}NO + NO \stackrel{k_1}{\rightarrow} NO^{+} (NO)_2$$
, (11)

then our data provide an upper bound on k_1 of 1.5 $\times 10^{-16}$ cm³/sec at 293 K, for the net forward rate constant. Judging from the absence of M/e = 90 in the ion spectrum, a probable upper bound on k_1 is at least a factor of 10 smaller.

B. Steadyglow Data

The count rates of NO^+ and $NO^+ \cdot NO$ ions were measured as a function of pressure under conditions of continuous irradiation. The loss frequency of $NO^+ \cdot NO$ was measured in the early afterglow, and these data were analyzed as outlined in the data-analysis section. The relative over-all sampling efficiency was assumed to be equal (c = 1) for NO⁺ and NO⁺ \cdot NO. The NO⁺ \cdot NO production frequency calculated in this fashion is shown in Fig. 7, together with the reaction portion of the NO+ loss frequency, as determined from afterglow data. The $NO^+ \cdot NO$ production frequency shows the same p^2 pressure dependence as the NO⁺ reaction loss frequency and is 15% smaller in absolute magnitude. The excellent agreement in shape and magnitude of these two curves provides assurance that the NO⁺ reaction is indeed proceeding in the channel indicated. The 15% difference could be ascribed easily to less efficient detection of $NO^+ \cdot NO$ than NO^+ , but, within the accuracy claimed by this steadyglow-measurement technique, such a correction would be scarcely justified, even if the efficiency could be independently measured.

In the case of the NO^+ clustering reaction, there was little doubt as to the NO^+ loss channel, and the steadyglow measurement only verified a fact that was already evident. However, the measurement also provided confirmation of the validity of the steadyglow-measurement technique in our



FIG. 6. Typical NO⁺•NO high-pressure decay. The late afterglow shows simple exponential decay to at least 2 sec. The plasma transition occurs too quickly to permit quantitative studies of the early afterglow decay.



FIG. 7. Comparison of afterglow and steadyglow data. The dashed line is the NO⁺ reaction loss frequency determined from afterglow data. The data points and solid line are the NO⁺ •NO production frequency determined from steadyglow data.

system and permits it to be used as a diagnostic tool in those cases where the reaction channels are not obvious. For example, when traces of H_2O are added to NO, a number of new ionic species are present in the photoionized afterglow,¹⁵ and the steadyglow technique is required to determine which of those new ions were formed from NO⁺.

V. EVALUATION OF EXPERIMENTAL TECHNIQUES

In an experiment of this type, the principal uncertainty lies not in the precision with which data can be obtained, but rather in the degree to which the experimental data match the physical model of the apparatus used in the data analysis. Accordingly, this section is addressed to the question of the applicability of the physical model, with results that are perhaps pertinent to other stationary afterglow experiments.

A. Sampling Efficiency

In the physical model employed in the analysis it is assumed that the count rate of mass-analyzed ions was directly proportional to the ion number density in the cavity. The validity of the assumption can be assured if the following three points are verified experimentally. One must demonstrate the following: (a) proportionality of the sampling probe (orifice plate) current to the ionic number density, (b) proportionality of the massanalyzed-ion count rate to the probe current, and (c) that only a negligible number of ions are changing identity in the sampling process, as, for example, in collisional breakup of loosely bound clusters in nonthermal collisions.

The last requirement can be satisfied with the observation that $NO^+ \cdot NO$ had no significant sources or sinks in the sampling system under the conditions of our measurements. The totally different time dependences of NO^+ and $NO^+ \cdot NO$ ions. together with the independence of their ratio with respect to changes in our sampling parameters. leave no doubt that the bulk of the $NO^+ \cdot NO$ ions were formed in the afterglow cavity and that few of them were broken up in the sampling process. At very large orifice-plate voltages, e.g., 5 V negative with respect to the cavity, a large portion of the $NO^+ \cdot NO$ ions were converted to NO^+ ions near the sampling region. Such conditions, however, were not typical of our experimental parameters. There is, however, an exception to this statement. At pressures greater than 0.1 Torr, where NO⁺ ions disappeared very rapidly in comparison with $NO^+ \cdot NO$ ions, the NO^+ decay tracked the $NO^+ \cdot NO$ decay when the NO^+ count rate had decreased to $\sim 10^{-3}$ of the NO⁺ \cdot NO count rate. This observation suggests either that NO+ and NO⁺ • NO had reached equilibrium concentration or that about 1 in 10^3 of the NO⁺ \cdot NO ions had broken up in the sampling process. While the inverse pressure dependence of the $NO^+/NO^+ \cdot NO$ equilibrium ratio tends to support the equilibrium hypothesis, we must admit the possibility of a small portion of the NO+ • NO ions being dissociated in the sampling process.

The question as to whether the mass-analyzed decay tracks the wall current can be answered in the following manner. With the orifice plate biased slightly negative so as to repel electrons, the orifice-plate current should track the massanalyzed plasma decay whenever one ion is dominant. Such a comparison is shown in Fig. 8, at a pressure of 20 mTorr, where NO⁺ is the dominant ion. The ion count rate and wall-current track in early and late afterglow, and even the details of the plasma transition, are in agreement. This particular comparison was obtained with the sampling probe 70 mV negative with respect to the cavity. Electron contributions to the wall current prevented comparisons with the probe voltage less negative than this value, but excellent agreement was also obtained for probe voltage up to -1 V. These results imply that there was no significant number density-dependent discrimination in the ion sampling through the orifice, the skimmer, and the mass spectrometer. These data, however, were taken with the skimmer floated 300 V negative with respect to the cavity. It was found that if the skimmer were not at least 50 V negative then the mass-analyzed decay, while still exponential, was faster than the probe decay for all probe potentials and hence not



FIG. 8. Comparison of mass analyzed ion decay with total positive-ion cavity wall current. This comparison was made under conditions such that NO^+ was the dom-inant positive ion. The wall current was normalized to the mass-analyzed decay curve at t = 10 msec.

representative of the wall current. All of the experimental checks mentioned in this paper apply to the case of -300 V on the skimmer. Without the capability of observing the total decay of the plasma by means of a probe, it would have been difficult to evaluate the effects of discrimination in the sampling process.

Once it was established that the ion count rate tracked the wall current, it was then necessary to demonstrate that the wall current was proportional to the volume number density of ions for the case of a time-invariant ionic spatial distribution. The establishment of the latter proportionality is necessary in order to validate the most hazardous assumptions implicit in the data-analysis model. The proportionality was verified in the following manner. Since the observed decays were exponential and the count rate R(n), tracked the wall current, then any sampling discrimination must be of the form

$$R(n) = a[n]^{O}, \tag{12}$$

where [n] denotes the number density of species n, and a and b may be functions of pressure, sampling probe potential or ionic species, but must be time-invariant. (The term time-invariant is intended to imply invariance over a pulsing period, but not necessarily over a longer interval of time. Surface charging could, for example, produce a slowly varying discrimination. This sort of discrimination would be detected in longterm stability checks.) If the time duration of the photoionizing light pulse is small in comparison with the time constant of the NO^+ decay, then the initial NO^+ concentration in the cavity is directly proportional to the ionizing pulse width. If the NO⁺ decay is observed at a given pressure for pulse widths W_1 and W_2 , which both satisfy the above criterion, then the two decay curves

should be parallel and their ratio at any time should be $(W_2/W_1)^b$. Observation of NO⁺ decay curves as a function of ionizing pulse width indicates that $b = 1.0 \pm 0.05$ under normal operating conditions; therefore this form of discrimination is not a major source of error.

The net result of these checks is the conclusion that, under normal operating conditions in our apparatus, the count rate for a mass-analyzed ionic species is directly proportional to the volume number density of that species. This criterion was satisfied for sampling probe potentials near the cavity wall potential, but, as Sec. V B indicates, not for a wide range of probe potentials.

B. Sampling Probe Potential

Even though the sampling orifice plate is machined to the contour of the cavity wall, it is properly considered to be a probe. It was found that the observed ion decays were sensitive functions of the probe-cavity potential. As an example, Fig. 9 depicts the NO⁺ loss frequency at 50 mTorr as a function of probe-cavity potential. The observed loss frequency changed by more than 90% as the probe-to-cavity potential was varied from -88 to +700 mV. Moreover, the observed decays were simple exponentials for at least three decades for all but the most positive probe potentials. Since the relatively small probe potentials could not significantly influence the volume loss process, these data indicate the presence of sampling discrimination of the form

$$R(n) = [n]^{f(V)},$$
(13)

where V is the probe-cavity potential difference.

(---)



FIG. 9. Effect of sampling orifice potential on observed NO^+ loss frequency. These data were obtained at 50 mTorr NO pressure. Negative orifice potentials are attractive for positive ions. The exact form of the data is pressure-dependent, and the interpretation of these data is presented in the text.

The checks of Sec. V A show that $f(V) \simeq 1.0$ for probe-cavity potentials from -50 to +50 mV, but these checks are not sufficiently precise to allow a determination of the "correct" potential. Accordingly, we choose to regard our data uncertain by an amount corresponding to the observed variation of loss frequency over the probe-cavity potential range of -50 to +50 mV. The exact form of the loss-frequency probe-voltage dependence is pressure-dependent, the effect becoming a larger source of uncertainty at lower pressures. It should be emphasized that the type of discrimination described in Sec. VA and VB yields exponential ionic decays, but with loss frequencies which differ from ionic volume decay loss frequency. Other less subtle forms of sampling discrimination may also be present, but can be readily detected as a result of nonexponential apparent decay rate. Some success in predicting the form of the variation is achieved by use of the probe-sheath theory developed by Schulz and Brown.¹⁶

Nakshbandi and Hasted⁹ have recently described a stationary afterglow apparatus which employed ion sampling through an orifice in a probe. The authors claim that the observation of an exponential ion decay with the mass spectrometer is a sufficient condition to ensure that sampling discrimination is absent and that the observed decay must necessarily be identical to the volume ionic decay. The discussion of Secs. V A and V B makes it clear that such a simple test does not justify their conclusion.

C. Discussion of Errors

The principal uncertainties in the data result from the effect of the probe voltage, applicability of the analysis model, random scatter in results, and pressure measurement. Other uncertainties, such as time-measurement accuracy $(\pm 0, 01\%)$. gas temperature $(\pm 0.5\%)$, linearity of the counting circuits, and the effect of noise counts, contribute negligibly to the over-all uncertainty. Gas heating by the ionizing pulse is a serious source of uncertainty in many stationary afterglow systems, but, as a result of the very low-energy input of the photoionization source (~ $5\mu J$ /pulse, pulse rate < 2/sec), such heating is not important in this apparatus. Many of these uncertainties were dependent upon the particular measurement involved and are described below.

D. NO⁺ Diffusion Coefficient

The NO⁺ ambipolar-diffusion coefficient was primarily determined from low-pressure data (5-50 mTorr), where the uncertainty due to the effect of the sampling probe was very important. A variation in probe voltage over the range from + 50 to - 50 mV introduced a possible error of ± 3%. As described in Secs. VA and V B, numerous checks have been applied in an attempt to ascertain the possible nonlinearity of the ion sampling process and the applicability of the data-analysis model. Our best estimate of the total uncertainty associated with these effects is obtained through a simple summation of the estimated maximum individual errors: from pressure measurement, ±4%; from probe voltage, ±3%; and from other nonlinear sampling effects, ±5%. Thus, for the NO⁺ ambipolar diffusion coefficient one obtains a total uncertainty of ±12%. This uncertainty yields a value for D_{ap} of 85 ± 10 cm² Torr/sec and for $D_{+, -p}$, 42±5 cm² Torr/sec.

E. NO⁺ Conversion to NO⁺•NO

The effect of sampling probe potential was smaller at the higher pressures (50–200 mTorr) used to determine the rate coefficient; the total error due to possible sampling nonlinearity and probe potential is estimated to be $\pm 7\%$. The reaction rate constant was calculated using the square of the absolute pressure, which contributes a possible uncertainty of $\pm 8\%$ in the rate constant. A summation of all of these uncertainties yields $k = 5.0 \pm 0.8 \times 10^{-30}$ cm⁶/sec for the three-body conversion of NO⁺ to NO⁺ • NO in pure NO.

F. NO⁺•NO Diffusion Coefficient

The electron-ion ambipolar diffusion coefficient of NO⁺ • NO is best determined in the early afterglow (before the plasma transition) after all sources of NO⁺ • NO are negligible. Unfortunately these requirements limit such a measurement to the pressure range from about 60 to 120 mTorr. In this limited range the observed NO⁺ • NO loss frequency was consistent with an ambipolar-diffusion coefficient $D_a p \simeq 84 \pm 13$ cm² Torr/sec. The uncertainty in this value was enlarged over that of $D_a p$ for NO⁺ because of the limited pressure range of the NO⁺ • NO measurement. The late afterglow data for NO⁺ • NO were found to be consistent with a diffusion coefficient $D_{+,-} p = 41 \pm 5$ cm² Torr/sec.

VI. DISCUSSION OF RESULTS

The present measurements of the ion-electron ambipolar-diffusion coefficient of NO⁺ ions $(D_a p)$ = 85 ± 10 cm² Torr/sec) in NO are in satisfactory agreement with those of Gunton and Shaw⁶ $(D_a p)$ = 83 ± 8 cm² Torr/sec) and Weller and Biondi¹⁰ $(D_a p) = 80 \pm 16$ cm² Torr/sec).

The NO⁺ • NO dimer-ion ambipolar-diffusion coefficient ($D_a p = 84 \pm 13 \text{ cm}^2 \text{ Torr/sec}$) in NO has not reported previously. The equality of the NO⁺ and NO⁺ • NO ambipolar-diffusion coefficients is

very surprising and is in marked contrast with the behavior of other cluster ions^{17, 18} (e.g., N_{2}^{+} , N_{4}^{+} , in N_{2} , or Ar^{+} , Ar_{2}^{+} in Ar), where resonant charge transfer reduces the parent-ion diffusion coefficient to approximately $\frac{2}{3}$ of the cluster-ion diffusion coefficient. Comparison of diffusion of NO⁺ in NO ($D_a p = 85 \text{ cm}^2 \text{ Torr/sec}$) to NO^+ in air¹⁹ ($D_a p \simeq 160 \text{ cm}^2 \text{ Torr/sec}$) shows a reduction of $D_a p$ typical of resonant charge transfer. If $D_a p$ for NO⁺ in air is used together with the mass dependence predicted by the Langevin theory²⁰ in order to estimate $D_a p$ for NO⁺ · NO in NO, the result is $D_a p \simeq 125 \text{ cm}^2 \text{ Torr/sec}$. Thus, it would appear that the observed $D_a p$ for NO⁺ · NO is smaller than that predicted for a nonreacting ion. It is possible that the relatively weak bonding energy of the dimer ion permits a significant amount of NO molecule interchange to take place in a collision between NO⁺ • NO and NO; an essentially equivalent process might involve the formation of a temporary $NO^+ \cdot (NO)_2$ complex. Either of these two mechanisms would reduce the dimer diffusion coefficient in a manner analogous to the resonant-charge-transfer case. However, we have no experimental means to test this hypothesis. In view of the unexpected results for NO⁺ · NO diffusion, extensive tests were undertaken in an attempt to invalidate the experimental data. Within the accuracy discussed in Sec. V, no reason has yet been found to question the validity of the $NO^+ \cdot NO$ ambipolar-diffusion coefficient.

The present data represent the only reported measurements known to us of the rate constant for formation of $NO^+ \cdot NO$ from NO^+ . The $NO^+ \cdot NO$ dimer has recently been observed by Weller and Biondi, ¹⁰ who measured the dissociative ionelectron recombination coefficient of $NO^+ \circ NO$ in a stationary afterglow apparatus. Gunton and Shaw, ⁶ however, report $[NO^+ \cdot NO]/[NO^+]$ ratios of 0.01 under conditions such that the use of our three-body rate constant implies that NO⁺ · NO should be the dominant positive ion. For example, Gunton and Shaw observed the pure NO afterglow for ~ 3 msec at a pressure of 1.5 Torr, and during this time only NO⁺ ions were detected. Our data imply a time constant of ~100 μ sec for conversion of NO^+ to NO^+ • NO under these conditions. Since Gunton and Shaw employed large (1-10 V) extraction potentials for their ion ananalysis, it appears likely that the NO⁺ ° NO ions were destroyed in their ion sampling process. In fact, they did observe the onset of destruction of N_4^+ at probe potentials of 1 V, while $NO^+ \cdot NO$ was still not detected. Since N_4^+ has a binding energy of $\sim 0.5 \text{ eV}$, this result would seem to indicate that the binding energy of NO⁺ • NO is considerably less than 0.5 eV.

Mahan and Person⁵ have investigated ion-ion recombination in NO-NO₂ mixtures in an apparatus lacking mass spectrometric ion identifica-

tion. They present arguments that the reacting ions are likely more complex than NO^+ and NO_{2}^- . In the pressure-time range of their measurements, the dominant positive ion must be at least as complex as $NO^+ \cdot NO$.

VII. CONCLUSIONS

A stationary afterglow apparatus has been developed and utilized to study ion-molecule reactions involving NO+ ions. A number of checks were performed to assess the validity of the data. In particular, it is essential to establish experimentally the relationship between the ionic volume number density and the sampled ion count rate. Insulating films on surfaces and contact potentials, as well as the ion sampling probe potential, may have an important effect on the functional form of this relationship. The NO⁺ ion decay in pure NO at 293 K over the pressure $% \left({{{\mathbf{N}}_{\mathbf{N}}}} \right)$ range 10-200 mTorr is consistent with ambipolar diffusion of $NO^{\!+}$ and three-body conversion of NO^+ to $NO^+ \cdot NO$. The experimental results for these processes are $D_a p = 85 \pm 10 \text{ cm}^2 \text{ Torr/sec}$ and $k = 5.0 \pm 0.8 \times 10^{-30} \text{ cm}^{6}/\text{sec.}$ The rate constant for dimer formation was determined both from loss of NO⁺ and from production of NO⁺ \cdot NO. The ambipolar-diffusion coefficient of NO⁺ • NO in NO is 84 ± 13 cm² Torr/sec at 293 K. The present measurements for ambipolar diffusion of NO⁺ in NO are in excellent agreement with previously published measurements. The rather large rate constant for formation of $NO^+ \cdot NO$ implies that in experiments involving NO at modest pressures, the dominant positive ion may well be NO⁺ • NO or even a more complex ion.

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APPENDIX: POSITIVE-ION-NEGATIVE-ION AMBIPOLAR DIFFUSION

An expression for the positive-ion-negative-ion ambipolar-diffusion coefficient $D_{+,-}$ can be derived in a manner completely analogous to that used by Oskam and Mittlestadt¹⁸ to derive the ionelectron ambipolar-diffusion coefficient D_a . The principal assumptions are near charge neutrality and equality of the ion and gas temperatures. The result is

$$D_{+,-} = 2D_{+}D_{-}/(D_{+}+D_{-}), \qquad (14)$$

where D_+ and D_- are the positive-and negativeion free-diffusion coefficients, respectively. We note that $D_{+,-}$ must take on a value intermediate between D_+ and D_- and that if $D_+=D_-$ then the ambipolar-diffusion process is effectively a freediffusion process.

Equation (14) is derived under the assumption that the charge non-neutrality required to generate the ambipolar-diffusion space-charge field is small compared with the total ion density. This assumption must fail as the total ion density decays, and the ion-ion ambipolar-diffusion decay will eventually undergo a transition to a freediffusion decay.

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We observe experimentally that in the late afterglow the dominant positive ions and negative ions, $NO^+ \cdot NO$ and NO_2^- , respectively, decay with time constants which differ by less than 2%; these data indicate that these two ion species are undergoing ion-ion ambipolar diffusion. The additional observation that

$$(D_a^p)_{NO^+} \cdot NO^{\cong (2D_+, -p)}_{NO^+} \cdot NO$$

serves to indicate that $D_{+,-}$ is approximately equal to the free-diffusion coefficient D_{+} and D_{-} .

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