Mass Spectrometric Study of the Effects of Nitric Oxide and Other Additives on "Purified" Active Nitrogen

John T. Herron

A mass spectrometric study has been made of the interaction of NO and other additives with "purified" active nitrogen. The observed increase in N atom partial pressure when NO is added is interpreted in terms of a change in the accommodation coefficient of the N atoms.

The metastable N_2 species which can be detected with the mass spectrometer can be deactivated with N_2O or NH_3, but not with NO, O_2, or NF_3.

1. Introduction

Young and Sharpless [1][1] have stated that the excited species present in active nitrogen, such as those contributing to the pink nitrogen afterglow [2], can destroy nitric oxide and hence lead to a false value for the atom concentration as measured by the NO titration technique [3]. Young, Sharpless, and Stringham [4] have given some detailed results on the effect of adding a variety of compounds both before and after passing nitrogen through a microwave discharge. The magnitude of the effects observed seems to depend on the initial purity of the nitrogen. In untreated "prepurified" grade nitrogen they are not significant.

The recent emphasis on high purity gases, particularly in the study of atomic recombination reactions makes it mandatory that we have a clear understanding of the nature of the interaction of NO and other additives with highly purified active nitrogen.

I wish to report here a mass spectrometric study of the interaction of NO and other additives with active nitrogen.

2. Experimental Procedures

The instrument and associated reactors have been described elsewhere [5].

Matheson "prepurified" grade nitrogen was taken at 19.7 psi through copper lines, a glass flowmeter (attached with short Tygon sleeves), and a metal needle valve into the low pressure flow system. On the high pressure side the gas could be passed through a copper

coil held at -78 °C, while on the low pressure side it could be passed through a glass coil held at -196 °C before entering the discharge zone (2450 MH electrodeless discharge). The total pressure was varied from 2 to 6 torr [6] at linear flow rates of about 1000 cm/sec.

Reactant gases could be added just before the discharge or at various points after the discharge. The sampling orifice of the mass spectrometer was downstream of the reactant inlets.

The partial pressure of the additives was followed in the usual manner using 58 eV electrons. The relative partial pressures of atomic N and O were measured at reduced electron energies (25 eV nominal) as previously described [5, 7]. The relative partial pressure of metastable N_2 was followed at 17 eV (nominal).

3. Effects of Additives on the N Atom Partial Pressure

The method of purification used here was not as elaborate as that used in references [1] and [4], and in general the effects observed were proportionally less. Nonetheless, the same general phenomena were observed; the addition of NO, O_2, NH_3, NF_3, or SF_6 in varying proportions before the discharge led to about a threefold increase in the partial pressure of the N atoms detected by the mass spectrometer. If added after the discharge, the additives, with the exception of SF_6 which had little or no effect, caused about a twofold increase in the N atom partial pressure.

The lower two curves of figure 1 show the relative partial pressures of N and O atoms (in terms of ion current) as a function of the initial partial pressure of NO added after the discharge. It is noteworthy that O atoms are detectable over the entire range.
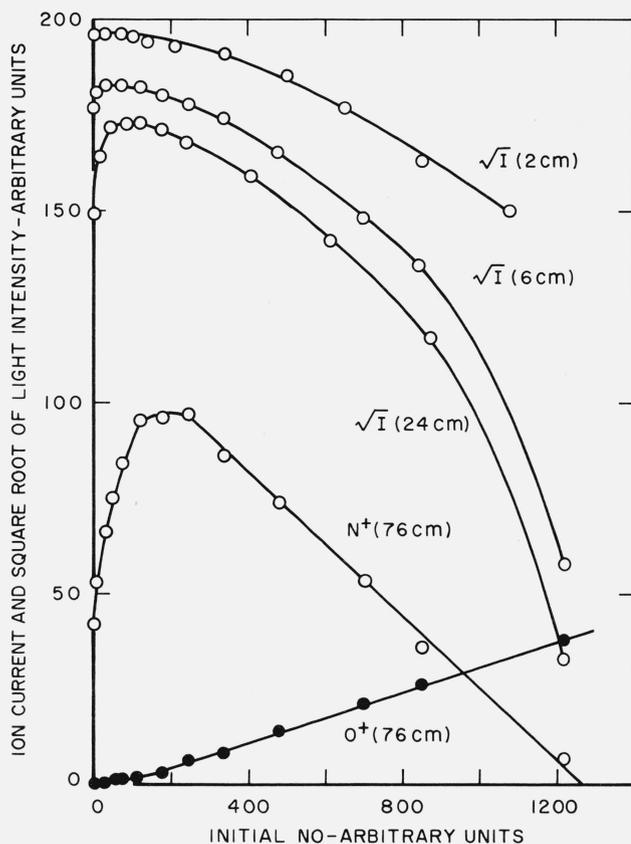
FIGURE 1. *Relative N and O atom partial pressure from mass spectrometric and photometric measurements as a function of the initial NO partial pressure, at various distances from the NO inlet.*

The photometric measurements are not corrected for emission from the NO* formed in the reaction of N with O. (NO inlet located 20 cm below the discharge zone. Total pressure 3 torr.)

Oxygen atoms were also detected when O_2 was added after the discharge. If the O_2 was partially decomposed in a discharge before addition, then only about 1/3 as much O_2 was required to maximize the N atom partial pressure. When ^{15}NO was used as an additive, the maximum amount of ^{15}N produced (at any point) was no greater than 0.4 percent of the ^{14}N originally present. This indicates that, barring some improbable reactions, NO is not decomposed by active nitrogen, but rather reacts via $N + NO \rightarrow N_2 + O$, confirming previous studies on untreated active nitrogen [7, 8].

Some additional experiments were made using a photomultiplier to monitor the nitrogen afterglow intensity (proportional to $[N]^2$) at various points along the reactor when NO was added after the discharge. These data are shown in figure 1. The nonlinearity of $\sqrt{I}$ curves is caused by emission from NO formed by the reaction of N and O atoms [9]. Figure 1 is a composite curve, and there is no absolute connection between each set of data.

No striking difference was observed when reactants were added before, directly into, or after the pink nitrogen afterglow.

4. Effects of Additives on Metastable N_2 Molecules

Foner and Hudson [10] have shown that metastable N_2 molecules in active nitrogen can be detected by means of mass spectrometry. By working at reduced electron energies (17 eV nominal) it was possible in the present work to detect an increase in the ion current at m/e 28 when the discharge was turned on.

If the metastable was generated only in the discharge zone, then its decay in the presence of an additive can be described by the reactions:

$$N_2^* + A \xrightarrow{k_1} \text{products} \tag{1}$$

$$N_2^* \xrightarrow{k_2} N_2 \tag{2}$$
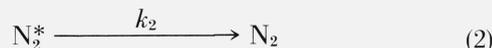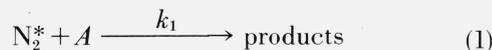
Reaction (2) may be influenced by the wall, or may simply represent the radiative decay of the metastable state.

The overall rate of disappearance of N_2^* can be written as:

$$-\frac{d[N_2^*]}{dt} = k_1[N_2^*][A] + k_2[N_2^*]$$

Since $[A]$ is constant under the conditions described here

$$-\frac{d[N_2^*]}{[N_2^*]} = k_1[A]dt + k_2dt$$

$$\text{or } \log[N_2^*]_t = -\frac{k_1 t}{2.303}[A] - \frac{k_2 t}{2.303}.$$

Here $[N_2^*]_t$ is the relative partial pressure of the metastable species at a fixed time t.

The effects of adding NH_3 or N_2O to active nitrogen are striking. A plot of $\log[N_2^*]_t$ versus $[A]$ for these additives is shown in figure 2 (in terms of partial pressure). It is obvious that the simple kinetic scheme is inadequate.
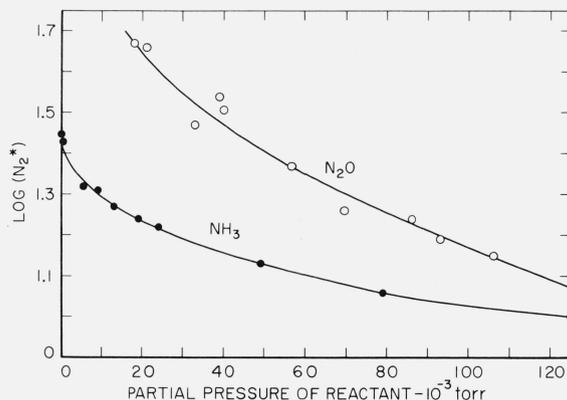
FIGURE 2. *Relative partial pressure of metastable N_2 as a function of the partial pressure of NH_3 and N_2O additives (total pressure 3 torr).*
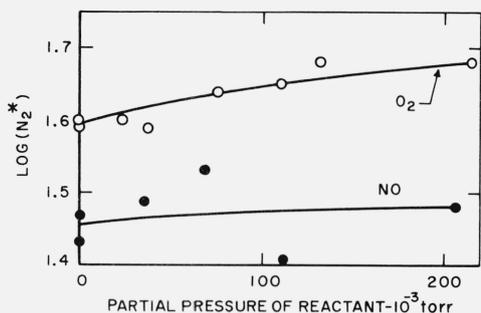
FIGURE 3. *Relative partial pressure of metastable* N_2 *as a function of the partial pressure of NO and* O_2 *additives (total pressure 3 torr).*

The addition of O_2 or NO caused a shift in the base line for N_2^+ so that small effects are difficult to determine. A plot of $\log [N_2^*]_t$ versus $[A]$ for these additives is shown in figure 3. It would appear that neither of them appreciably deactivates the metastable species [11]. The same observation was made for NF_3.

5. Discussion

Examination of figure 1 shows that the maximizing effect of NO on the N atom partial pressure increases as the distance between the point of addition and the point of detection is increased. Since the $NO + N$ reaction is so rapid that all the NO would be consumed within a distance of about 5 cm from the point at which it was added in the flow system used in this work, it is unlikely that NO itself could be connected with effects observed further downstream. It is more likely that O atoms are the responsible species. This is supported by the observation that partially decomposed O_2 is more effective than ordinary O_2 in maximizing the N atom partial pressure.

If a catalytic reaction between O atoms and some N atom precursor is invoked, the reaction is either relatively slow, or the precursor concentration must increase with distance (time). The latter possibility seems highly improbable, while the former would predict a shift in the position of the N atom maximum to higher initial NO partial pressure as the distance was reduced and not to lower initial NO partial pressure as observed.

A better explanation for the shapes of these curves is a change in the rate of disappearance of N atoms on the walls occasioned by a change in the accommodation coefficient. The latter effect is probably due to "poisoning" of the walls with oxygen atoms. This explains the nonlinearity of the O^+ curve up to the point of maximum N^+. Once the walls are saturated with O atoms, the N atom partial pressure begins to decrease linearly and the O atom partial pressure to increase linearly.

The greater rate of recombination of atoms on the walls would also explain the fact that the walls become extremely hot in the case of purified active nitrogen. Enhanced wall activity may also play a significant part in the formation of the "pink" afterglow, since the

latter is best obtained in purified active nitrogen and is dependent on wall parameters.

The importance of wall effects was directly observable under certain conditions. Thus, if the reactor was first cleaned with HF, a considerable reduction was observed in both afterglow intensity and detectable N atoms. However, a band about 3 mm deep was observed to form on the walls of the tube about 15 cm from the discharge, and then slowly to move down the tube (at about 3 cm/min). The nitrogen afterglow was distinctly more intense on the upstream side of the band. Addition of O_2 to the discharge intensified this effect. When the O_2 was shut off, the walls took on a dull red glow.

Although the effects of the other additives used has not been studied in any detail, a similar wall poisoning mechanism is applicable, involving either the additive or its reaction products.

There appeared to be no connection between the maximizing of the N atom partial pressure and the magnitude of metastable N_2 partial pressure. The only pertinent observation here was that the metastable partial pressure was somewhat larger in purified nitrogen.

6. Conclusion

The number of parameters and complexity of the mechanisms involved makes it difficult to draw firm conclusions about the nature of active nitrogen. It is suggested however, that wall effects play an important part in the "catalytic" production of nitrogen atoms, and in the production of the "pink" afterglow. Further it is observed that the catalytic effect is not connected with those metastable N_2 molecules detectable by mass spectrometry, and that the latter are not appreciably affected by the addition of nitric oxide.

7. References and Notes

[1] R. A. Young and R. L. Sharpless, Disc. Faraday Soc. **33**, 228 (1962).
[2] J. P. Kaplan, Phys. Rev. **42**, 807 (1932); G. E. Beale, Jr., and H. P. Broida, J. Chem. Phys. **31**, 1030 (1959).
[3] G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys. **27**, 1141 (1957).
[4] R. A. Young, R. L. Sharpless, and R. Stringham, J. Chem. Phys. **40**, 117 (1964).
[5] F. S. Klein and J. T. Herron, J. Chem. Phys. **41**, 1285 (1964).
[6] A torr is defined as 1/760 of normal atmospheric pressure.
[7] J. T. Herron, J. Chem. Phys. **33**, 1273 (1960).
[8] R. A. Back and J. Y. P. Mui, J. Phys. Chem. **66**, 1362 (1962).
[9] In separate experiments at distances of 2 cm and 24 cm from the NO inlet, the light intensity was monitored using an orange filter to remove most of the NO β emission. The use of the filter made the curves more linear beyond the maximum, but had no significant effect on the position of the maximum.
[10] S. N. Foner and R. L. Hudson, J. Chem. Phys. **37**, 1662 (1962).
[11] The reaction $N + NO \rightarrow N_2 + O$ leads to the formation of N_2 predominantly in the 4th or higher vibrational levels (D. E. Morgan, L. F. Phillips, and H. I. Schiff, Disc. Faraday Soc. **33**, 118 (1962) and therefore might contribute to the measured metastable peak. In separate experiments the $N^{14}N^{15*}$ generated by the reaction of $N^{15}O$ with N has been studied. The magnitude of this contribution was about 5 percent of that produced directly in active nitrogen.

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