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COMMENT ON THE FAR-ULTRAVIOLET PHOTOLYSIS OF NITRIC OXIDE

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Comment on the Far-Ultraviolet Photolysis of Nitric Oxide

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In a recent paper,[1] Leiga and Taylor report the results of the photolysis of nitric oxide at three wavelengths in the vacuum ultraviolet. They demonstrate that for nitric oxide pressures in the range of 10 to 700 Torr, the quantum yield of nitrogen is approximately 0.4 for irradiation in the 1600-Å spectral region, and approximately 0.5 at 1470 and 1236 Å. Since the primary process at 1236 Å is photoionization of nitric oxide, they conclude from the relative insensitivity of the quantum yield to wavelength that the recombination of NO^+ with an electron leads to an excited nitric oxide molecule similar to ones formed by absorption of light at 1600 and 1470 Å. These excited molecules may be quenched, radiate, or as a result of a collision, decompose in N and O atoms. Leiga and Taylor suggest that the direct dissociative recombination reaction

$$NO^+ + e \rightarrow N + O, \qquad (1)$$

does not occur. The purpose of this comment is to show that under the conditions employed by Leiga and Taylor, Reaction (1) cannot be expected to be important, and consequently no conclusions as to whether or not it does ever occur should be drawn from this work. There is an alternate mechanism for

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photolysis in the photoionization region that is consistent with the observations of Leiga and Taylor, and which incorporates what is known about the behavior of electrons in nitric oxide.

Investigations[2,3] of the photoionization of nitric oxide with probes and microwave cavity resonance have demonstrated that the dominant electron-loss process is the attachment reaction

$$e + NO + NO \rightarrow NO^- + NO, \qquad (2)$$

when the pressure of nitric oxide is greater than a few torrecelli, and the ion concentration is no greater than 10^{10} ion/cc. From the reported lamp intensity,[1] the absorption coefficient of nitric oxide,[4] and approximate values for the ion-electron[2,3] or ion-ion[5] recombination coefficients for this system it is possible to estimate that the ion concentration in the experiments of Leiga and Taylor did not exceed approximately 5×10^9 ion/cc at a nitric oxide pressure of 10 Torr. This figure is consistent with our own[5] direct measurements of ion concentration in such photochemical systems. Even if the ion-electron dissociative recombination coefficient is as large[2,3] as 10^{-6} cc/ion·sec, and if the three-body electron attachment[3] coefficient is 4×10^{-31} $cc^3/ion^2 \cdot sec$, then electron attachment should be approximately 10 times as fast as ion-electron recombination at a nitric oxide pressure of 10 Torr. For greater nitric oxide pressures the ion concentration may approach 10^{10} cc^{-1}, because the light is absorbed in a shorter distance from the lamp window. At pressures below 100 Torr, however, electron attachment can be expected to be the dominant

electron-loss mechanism. For pressures much above 100 Torr, the fact that most of the light is absorbed in the first millimeter from the window may complicate interpretation of the experiments.

The existence of positive and negative gaseous ions offers an obvious mechanism for populating some of the lower excited electronic states of the nitric oxide molecule. At total pressures of 10 Torr and above, ions neutralize each other[5] by both two- and three-body processes that can lead to electronically excited states of the neutral fragments:

$$NO^+ + NO^- \ (+M) \rightarrow NO^* + NO \ (+M)$$

$$NO^+ + NO_2^- \ (+M) \rightarrow NO^* + NO_2 \ (+M)$$

Here we have recognized that some of the negative ions may be NO_2^-.

The maximum energy available to the products of such neutralization reactions is equal to the difference between the ionization energy and the electron affinity of the relevant neutrals. The electron affinities[6] of NO and NO_2 are 0.91 and 4.0 eV, respectively, and consequently the nitric oxide produced by charge transfer may have at most 8.3 eV of excitation energy. If most ion recombinations are of the three-body type, or if most involve NO_2^-, the excitation energy of the neutral may often be less than 8.3 eV. An excitation energy of 8.3 eV would correspond to absorption by nitric oxide of a photon of approximately 1490 Å. Thus, the results of Leiga and Taylor interpreted in this manner suggest that the products of mutual

neutralization reactions of ions in this system are electronically excited nitric oxide molecules that behave chemically in much the same manner as those formed by direct absorption of photons of wavelengths greater than 1236 Å.

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Footnotes

1. A. G. Leiga and H. A. Taylor, J. Chem. Phys. **42**, 2107 (1965).

2. R. C. Gunton and E. C. Y. Inn, J. Chem. Phys. **35**, 1896 (1961).

3. J. P. Doering and B. H. Mahan, J. Chem. Phys. **36**, 669 (1962).

4. M. Zelikoff, K. Watanabe, and E. Inn, AFCRC Tech. Rept. No. 53-23, A53.

5. B. H. Mahan and J. C. Person, J. Chem. Phys. **40**, 392 (1964).

6. A. L. Farragher, F. M. Page, and R. C. Wheeler, Discussions Faraday Soc. **37**, 203 (1964).

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