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# Vacuum Ultraviolet Photochemistry. Part IV. NO at 1236 Å

MURRAY ZELIKOFF AND LEONARD M. ASCHENBRAND

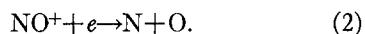
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(Received December 5, 1955)

Dissociative recombination of  $\text{NO}^+$  ions with electrons was shown to take place when NO is irradiated with krypton resonance radiation at 1236 Å. Application of a dc voltage across the reaction cell produces an increased rate of decomposition by electron or positive ion bombardment of neutral NO molecules.

## I. INTRODUCTION

THE dissociative recombination of electrons and  $\text{NO}^+$  ions has been discussed by Mitra and Jones<sup>1</sup> from a theoretical standpoint as a possible process taking place in the upper atmosphere. No experimental data regarding the magnitude of the recombination coefficient is available, nor has there been any evidence other than theoretical that such a process can in fact occur at all. Until recently, the lack of knowledge of the photoionization efficiency of nitric oxide has discouraged any attempt to demonstrate experimentally that such a recombination can take place. The work of Watanabe<sup>2,3</sup> and his co-workers has shown that the ionization potential of NO is 9.23 eV (1343 Å) and that at about 1250 Å the ionization efficiency becomes 100% within experimental error ( $\pm 10\%$ ). This means that practically all photons of  $\lambda < 1250$  Å (except where the ionization efficiency is less than 100%) being absorbed by NO would lead at least in the first step to  $\text{NO}^+ + e$  and that dissociation observed experimentally can originate only from recombination. Furthermore, the results of Marmo<sup>4</sup> on NO absorption show that if a dissociation continuum does exist at all in this region, it is very weak and almost certainly absent between 1100 and 1300 Å. Thus:



This paper will present the results of experiments designed to show that Eqs. (1) and (2) do, in fact, occur.

## II. EXPERIMENTAL

The lamp used in these experiments was quite similar to that described by Harteck and Oppenheimer.<sup>5</sup> The gas filling consisted of a mixture of 2 to 3 mm (Hg) neon and about  $50 \mu$  krypton. The light beam was emitted through a lithium fluoride window into a Pyrex reaction vessel which contained two electrodes. Figure 1 shows

the arrangement. The electrodes were of carbon powder coated on the inside of the reaction vessel using a water suspension. The manifold contained the pumping system, NO filling and sampling arrangement. After exposure of the NO for several minutes, a sample was taken and analyzed on a Consolidated Engineering Corporation analytical mass spectrometer (Model 21-103). In some cases, a voltage was applied during the period of irradiation, and the current measured with the arrangement shown in Fig. 1. Here also, a sample was taken and analyzed.

The light intensity was estimated using  $\text{N}_2\text{O}$  as actinometer. Both gases,  $\text{N}_2\text{O}$  and NO, were purified by bulb-to-bulb distillation from liquid nitrogen. Mass spectrometer checks showed their purity to be at least 99.9%.

## III. DATA AND DISCUSSION

In order to establish that the only radiation absorbed in significant amounts by NO could lead only to ionization, the spectral purity with respect to krypton was checked by photographing the discharge with a Hilger E-2 quartz spectrograph. At least 90% of the discharge was found due to neon and krypton. Since the neon resonance lines are not transmitted by lithium fluoride, the only significant light absorbed by NO could be that due to the krypton resonance line at 1236 Å. Even the small amount of light at 1165 Å (due also to Kr) would lead also to ionization, although here there may be preionization.

The use of  $\text{N}_2\text{O}$  as actinometer requires some discussion. The quantum yield of  $\text{N}_2\text{O}$  photolysis has been

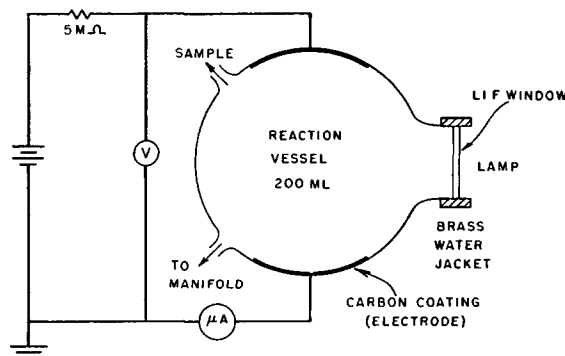


FIG. 1.

<sup>1</sup> A. P. Mitra and R. E. Jones, Scientific Report No. 44, Ionosphere Research Laboratory, Pennsylvania State College, March 25, 1953.

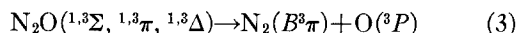
<sup>2</sup> Watanabe, Marmo, and Inn, Phys. Rev. **91**, 1155 (1953).

<sup>3</sup> K. Watanabe, J. Chem. Phys. **22**, 1564 (1954).

<sup>4</sup> F. F. Marmo, J. Opt. Soc. Am. **43**, 756 (1953).

<sup>5</sup> P. Harteck and F. Oppenheimer, Z. physik. Chem. **B16**, 77 (1932).

found to be about 1.7 at 1470 Å<sup>6</sup> and at 1849 Å.<sup>7</sup> Referring to the absorption spectrum of N<sub>2</sub>O in the vacuum ultraviolet,<sup>8</sup> one finds that 1236 Å falls in a region of continuous absorption. From the potential energy diagram, it appears that absorption of 1236 Å by N<sub>2</sub>O can lead to



or



Since no chain mechanism is likely, it may be supposed that either Eqs. (3) or (4) (or both) followed by subsequent steps involving N<sub>2</sub>O and the products (NO\*, N<sub>2</sub>\*, O, N) would result in a quantum yield of about 2 or 3. Thus, for a semiquantitative purpose, N<sub>2</sub>O is a satisfactory actinometer at 1236 Å.

Having shown that the lamp used was, for the purpose of these experiments, essentially monochromatic and that the light absorbed by NO led only to ionization, several NO exposures were made and appreciable decomposition occurred in each case. In order to demonstrate directly that electrons are involved in the decomposition, dc voltages were applied across the reaction cell. Table I shows some of the observations.

The amount of decomposition in runs 1 to 5 is essentially constant within the experimental error of the measurements. Thus, at the voltages used, the electrons cannot be withdrawn in amounts large enough to reduce the percentage decomposition. This may be attributed to the speed of recombination of ions and electrons. The observed current indicates that approximately  $5 \times 10^{12}$  electrons per second were removed from the reaction cell. Since the crude actinometer (N<sub>2</sub>O) indicated that at least  $5 \times 10^{14}$  quanta/sec were absorbed by the NO and that, hence, the same number of electrons/sec were produced, the maximum effect that could be expected on the percentage decomposition is one percent of the *amount decomposing*. Thus, the observations are not surprising.

Since the low voltages used produced no observable effect on the NO photolysis, one might suppose that higher voltages would increase the decomposition by electron or ion bombardment of the neutral molecules. Accordingly, a group of measurements was made in which the voltage was varied through a fifteen minute

TABLE I. Results of NO photolysis at 1236 Å.

Run No.	P <sub>NO</sub> (mm)	Volts	Current in $\mu\text{A}$	Exposure time in min	% Decomposition
1	1.4	0	0	15	11 $\pm$ 1
2	1.4	0	0	15	11 $\pm$ 1
3	1.4	22.5	0.26	15	10.5 $\pm$ 1
4	1.4	45	0.38	15	10 $\pm$ 1
5	1.4	0	0	15	10 $\pm$ 1

<sup>6</sup> M. Zelikoff and L. M. Aschenbrand, J. Chem. Phys. **22**, 1680 (1954).

<sup>7</sup> M. Zelikoff and L. M. Aschenbrand, J. Chem. Phys. **22**, 1685 (1954).

<sup>8</sup> Zelikoff, Watanabe, and Inn, J. Chem. Phys. **21**, 1643 (1953).

TABLE II. Effect of applied dc voltage on NO photolysis at 1236 Å.

Run No. P <sub>NO</sub> (mm) Exposure time in min	1 0.43 15		2 1.40 15		3 3.25 15	
	Volts	Current ( $\mu\text{A}$ )	Volts	Current ( $\mu\text{A}$ )	Volts	Current ( $\mu\text{A}$ )
	70	1.0	70	1.2	70	1.0
	75	1.4			75	1.05
	80	1.45	80	1.5		
	85	1.6				
	90	1.8	90	1.65		
	100	1.85	100	1.9	100	1.4
	125	2.5	125	2.5	125	1.8
	150	3.2	150	3.1	150	2.2
	175	3.9	175	3.7	175	2.6
	200	4.6	200	4.4	200	3.1
	225	5.3	225	5.1	225	3.5
	*250	6.8	250	6.0	250	4.1
			300	8.1	300	4.6
			350	10.5	350	5.8
			*360	12.0	360	6.1
					*380	6.4
% Light absorbed	60		70		85	
% Decomposition	~20		~20		~20	

period and the decomposition measured. Table II shows some of these results. It is evident from observation of this table that the applied voltage brings about a large increase in the percentage decomposition. Here it is important to observe that 20% decomposition for  $p_{\text{NO}} = 3.25$  mm means much more NO decomposing than 20% for the lower pressures. The percentage of absorbed light is calculated from  $I_0/I = \exp(-kx)$  where  $k = 58 \text{ cm}^{-1(4)}$  and  $x$  is the absorbing path length in cm reduced to 0°C and one atmosphere pressure.  $I_0$  and  $I$  represent the intensity of light entering and leaving the cell.

The starred values of the voltage in Table II are those at which electrical breakdown of the NO occurred and discharge began. At this point the current increase with voltage became much more rapid. At any point, the current in the reaction cell fell to zero when the lamp was switched off. Attempts to produce reaction without the lamp on and with the voltage below the breakdown potential failed. Thus, we have shown that acceleration by the applied voltage of electrons or ions initially produced by absorption of 1236 Å is responsible for an increase in decomposition rate. Presumably, this requires a higher voltage than those shown in Table I. This is probably due to the ability of the electrons or ions to gain enough energy to produce effective bombardment of neutral NO before they recombine. This ability would be enhanced at higher voltages. It is worth noting that for a given voltage, at least in the pressure range studied, the current decreases with increasing pressure. Thus the recombination rate may be pressure dependent, and at low pressures is not as effective in reducing the current as at higher pressures. One must note carefully here that this effect cannot with certainty be ascribed solely to recombination, since the voltage applied may produce other, somewhat more complex processes.

#### IV. CONCLUSIONS

The absorption of 1236 Å by NO leads only to ionization, and the resulting decomposition is due to recom-

bination of  $\text{NO}^+$  ions and electrons. Nothing can be said quantitatively about the magnitude of the recombination coefficient, although the rate is apparently pressure dependent. The nature of the processes occurring in NO under simultaneous irradiation by

1236 Å and applied voltage is too complex to be subjected at this time to quantitative interpretation. A detailed study of quantum yields as well as reaction rates will be necessary before any reliable estimates of the recombination coefficient can be given.

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## Experimental Proof for the Existence of Nonthermal Rotational Distributions of OH ( $^2\Sigma^+$ ) in Flames\*

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(Received November 15, 1955)

Experiments have been carried out to determine whether nonthermal rotational distributions in the  $^2\Sigma^+$  electronic state of OH observed in certain flames are caused by self-absorption. A study of emission (single and double path) and absorption by OH between 3064 Å and 3350 Å in atmospheric and low-pressure flames has shown that self-absorption is negligible in at least two cases in which nonthermal distributions are found. This leads to the conclusion that anomalous "temperatures" of OH measured previously in hydrocarbon flames at low pressure and in highly diluted flames at atmospheric pressure are real.

### INTRODUCTION

APPARENT nonthermal rotational distributions of electronically-excited OH ( $^2\Sigma^+$ ) in hydrocarbon flames have been observed by several investigators.<sup>1-4</sup> Penner<sup>5-7</sup> has emphasized the possibility that these observations could result from effects of self-absorption. In various detailed calculations he has shown how the observed distributions closely resemble those expected when self-absorption is large. Recently we have measured<sup>4</sup> the OH absorption in a low pressure acetylene-oxygen flame. The amount of absorption was far too small to cause the observed nonthermal distribution. Because of the importance of the question of the existence of nonthermal distributions of energy, we have repeated measurements on two flames—at low pressure<sup>1</sup> and at one atmosphere<sup>3</sup>—which have shown a nonthermal distribution of OH in emission. For comparison we also have made measurements on several flames which appear to be in equilibrium and have large self-absorption. Emission measurements have been made with both single and double paths.<sup>8</sup> Absorption measurements have been made using a narrow, discrete

line source<sup>9</sup> so that the results would not depend upon the available resolving power.

"Temperatures"† generally are determined from emission spectra by assuming a Boltzmann distribution and by using the equation<sup>10</sup>

$$\ln[I_{K'K''}/A_{K'K''}\nu_{K'K''}^4] = \ln C - E_{K'}/kT. \quad (1)$$

This equation is valid only when the peak absorption of the lines is sufficiently small.<sup>5</sup>  $I_{K'K''}$  is the intensity of the transition at the frequency  $\nu_{K'K''}$ ,  $A_{K'K''}$  is the transition probability,  $E_{K'}$  is the energy of the initial state,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $C$  is a constant. An expression similar to Eq. (1) holds for absorption measurements.<sup>9</sup> "Temperatures" are obtained directly from the reciprocal of the slope of a graph of  $\ln[I_{K'K''}/A_{K'K''}\nu_{K'K''}^4]$  vs  $E_{K'}$ . If the distribution is not Boltzmann, the plotted points do not fall on a straight line and it is not possible, to measure the "temperature" strictly. However, it is convenient to use a straight line through a portion of the points (e.g.,  $K'=10$  to  $K'=20$ ) to indicate the extent of the departure from equilibrium. Lack of a straight line does not necessarily indicate a non-Boltzmann distribution. Large self-absorption can produce a nonlinear plot even when the distribution is Boltzmann.<sup>11</sup> In cases for which Eq. (1) is not valid be-

\* This research was supported by the U. S. Air Force through the Office of Scientific Research of the Air Research and Development Command.

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<sup>2</sup> Penner, Gilbert, and Weber, J. Chem. Phys. 20, 522 (1952).

<sup>3</sup> W. R. Kane and H. P. Broida, J. Chem. Phys. 21, 347 (1953).

<sup>4</sup> H. P. Broida and H. J. Kostkowski, J. Chem. Phys. 23, 754 (1955).

<sup>5</sup> S. S. Penner, J. Chem. Phys. 20, 507 (1952).

<sup>6</sup> S. S. Penner, J. Chem. Phys. 21, 31 (1953).

<sup>7</sup> S. S. Penner, J. Chem. Phys. 21, 686 (1953).

<sup>8</sup> B. H. Elliot and S. S. Penner, J. Chem. Phys. 22, 101 (1954).

<sup>9</sup> H. J. Kostkowski and H. P. Broida, J. Opt. Soc. Am. 46, 246 (1956).

† Quotation marks are used to indicate that the measured "temperature" does not necessarily correspond to the equilibrium temperature.

<sup>10</sup> E.g., H. P. Broida, *International Temperature Symposium (1954)* (Reinhold Publishing Corporation, New York, 1955), Vol. 2, "Temperature, Its Measurement and Control in Science and Industry."