Absolute Rate Constant Measurements for the Radiative Combination of Atomic Oxygen with Nitric Oxide

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The spectral radiant intensity and the absolute rate constant of the NO-O chemiluminescent reaction have been determined over the wavelength region 3875–20,000 Å. A direct method of intensity calibration making use of an NBS Standard light source was employed. In order to eliminate any possible interferences due to wall effects, the reaction was investigated in a freejet. The spectral intensity distribution curve, which extended in the infrared up to 20,000 Å, was independent of pressures from 0.1 to 1 torr and was found to be identical whether oxygen atoms were produced from discharged O_2 or from the reaction $N(^4S) + NO(^2\pi) = N_2(^1\Sigma) + O(^3P)$. Additional measurements of the NO-O glow, performed in a hydrogen flame at 10 torr pressure indicated a substantial shift of the intensity maximum toward longer wavelengths with increasing temperature. Four independent rate constant determinations were performed over the observed spectral range of the glow and gave an average value of 6.8×10^{-17} cm^3 molecule^{-1} sec^{-1} at 367°K with a probable error of ±35%.

Introduction

THIS paper reports the redetermination of the rate constant of an important chemiluminescent reaction. It confirms earlier work that used different experimental techniques. The importance of the NO-O chemiluminescent reaction stems from its use as a laboratory standard for chemiluminescence[1] and from its recent applications in atmospheric physics. For instance Golomb et al.,[2] determined the atomic oxygen concentration in the upper atmosphere by analyzing the radiation intensity of chemiluminous nitric oxide trails deposited into the atmosphere from rocket experiments. The quantitative investigation of the NO-O chemiluminescence is also of general interest in connection with the interpretation of observable phenomena occurring during missile re-entry in the gas phase flow around and behind the vehicle.

The first accurate rate constant determination of this reaction was due to Fontijn and Schiff.[3] Prior to their work virtually no rate data were available for chemiluminescent reactions with an accuracy greater than an order of magnitude. In their first investigation Fontijn and Schiff[3] determined the absolute quantum yield of the reaction for the spectral range 3875–6200 Å by a method of chemical actonometry. They used as a standard a solution of 0.15 M-K_3 $Fe(C_2O_4)_3$ of which the quantum efficiency had been determined accurately by Hatchard and Parker.[4] In their final study Fontijn, Meyer, and Schiff[1] determined the emission intensity spectral distribution and found the emission to extend in the infrared up to at least 1.4 μ. On the basis of these data the actinometer measurements were extended over the observed emission range (3875–14,000 Å), and the absolute rate constant over this range was calculated and found to be 6.4×10^{-17} cm^3 molecule sec^{-1}.

In the present work the reaction was investigated in a premixed freejet. The jet defined a homogeneous zone of reaction which was observed with a spectrometer of large aperture. Absolute spectral emission intensities of the zone of reaction were determined by direct comparison with an NBS spectral light source. The quantum yield over the observed emission spectrum was measured, and the absolute rate constant of the reaction was determined.

Definition of Absolute Rate Constant

It has been established that the intensity of radiation (photons emitted per unit time and unit volume) of the reaction

$$NO + O = NO_2 + hv$$

is given by

$$I = k[O][NO]$$

where k is the effective rate constant leading to the radiation. The actual process is believed to be more complex than that indicated by the single reaction above; these mechanisms have been discussed in earlier work.[5,6] The constant k has been found to be independent of pressure from 60 μ up to 1–2 mm Hg,[5] and no effect of a third body could be detected for a number of gases including Ar, CO_2, H_2, N_2O, O_2, and CF_4.[7] Our experiments were performed within these ranges of pressure and composition where k is essentially constant.

The photon emission within the wavelength range $\lambda_1 - \lambda_2$ of the continuum is given by

$$I = \int_{\lambda_1}^{\lambda_2} I_\lambda d\lambda$$

where I_λ is the spectral radiant density at wavelength λ (photons emitted per unit time, unit volume and unit wavelength interval). The rate constant is then given by

$$k = \int_{\lambda_1}^{\lambda_2} (I_\lambda/[O][NO])d\lambda$$

For an optically thin and uniform source, I_λ is related to the measured spectral radiance N_λ (erg sec^{-1} sterad^{-1} cm^{-2} μ^{-1}) by the formula

$$I_\lambda = (4\pi/d)\ N_\lambda/hv$$

where d is the path length (here taken as the diameter of the jet), h is the Planck constant, and v is the frequency of the photons emitted.

From the measured path length, spectral radiance, oxygen atom and nitric oxide concentrations the quantity $I_\lambda/[O]$ $[NO]$ can be deduced and plotted as function of λ. The

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Received December 22, 1969; revision received April 27, 1970. Work supported by Advanced Research Projects Agency.

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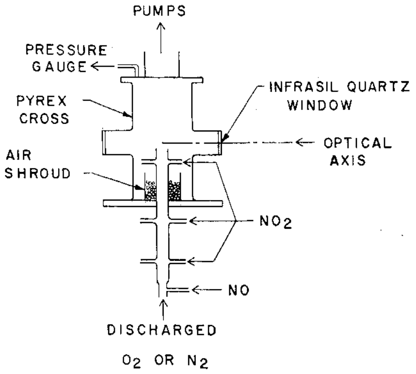

Fig. 1 Schematic diagram of experimental arrangement.

integral under this curve gives the rate constant of the reaction within the desired wavelength interval.

Experimental

Flow System

The NO-O reaction was studied by two methods which differed in the manner of generating the oxygen atoms. The first method was a direct mixing of NO with atomic oxygen from a discharge tube. The second was a two-step process where nitrogen was dissociated in the discharge tube and mixed with excess NO. This leads to the fast initial reaction

$$N(^4S) + NO(^2\pi) = N_2(^1\Sigma) + (O^3P) \qquad (1)$$

and results in a supply of ground state atomic oxygen for the NO-O reaction.

The reacting gases were premixed in a Pyrex flow tube of about 70 cm in length and 28 mm in diameter (Fig. 1) before entering a vacuum chamber where they formed a freejet. The jet was surrounded by a shroud of air in order to avoid recirculation of the active gases in the chamber. The total pressure in the vacuum chamber was maintained at constant pressure near 1 torr with a Heraeus Roots Pump VP-R-L-1000 A of 650 ft^3/min capacity at 1 mm Hg backed up by a single-stage pump of 100 ft^3/min capacity. In these experiments an average stream velocity in the order of 50 m/sec was adequate to maintain a freejet with negligible spreading over the region of observation (1–2 cm above the exit plane). This in turn required a relatively high atom flow in the order of 100 μmoles/sec. It was found that these requirements were best met by using a glow discharge with inside electrodes. The discharge tube including the electrodes was immersed in a constant temperature bath. Degrees of dissociation of 50% with a total O_2 flow up to 1000 μmoles/sec could be maintained for hours without any appreciable change in the rate of production of oxygen atoms. The yield of nitrogen atoms from molecular N_2 was found to be somewhat lower.

The flow tube was fitted with a number of inlets. The first inlet (used for the introduction of NO) was located at the upstream end of the tube. Three other inlets were located along the tube at 20-cm intervals for the introduction of NO_2 which was used for the titration of oxygen atoms.

The total pressure in the vacuum chamber was measured with a calibrated MacLeod gauge. The temperature of the gas stream was measured by a thermocouple shielded with a thin-walled quartz capillary. Partial pressures of nitric oxide and other added gases (p) were determined by measuring the flow rate of added gas (Fμ moles/sec), the total flow rate in the tube (Σ Fμ moles/sec) and the total pressure in the chamber p_t; p is then given by $p = p_t/\Sigma F$. Partial pressures of oxygen atoms were determined by titration with nitrogen dioxide. All gases were obtained from the Matheson Gas Company, and all were stated to be at least 99.8% pure.

Light Emission Measurements

The chief difficulty encountered was the low-radiation intensity of the source. However, since the NO-O radiation is essentially a continuum, the spectral resolution was not a critical factor and a prism instrument of large aperture was found adequate for these measurements.

The radiation was investigated with an F/6 Perkin-Elmer Monochromator (Type 12C) equipped with a Fluorite prism. The linear dispersion of this instrument was around 300 Å/mm in the visible and 2000 Å/mm in the near infrared. Spectral radiances were obtained at spectral slit widths of 0.01 to 0.1 μ in the 0.3–1 μ wavelength range and at 0.1 to 0.2 μ in the region from 1 to 3 μ. The detectors used were a 1P28 photomultiplier covering wavelengths from 3000 to 6500 Å, a 7102 phototube from 6000 Å to 1.5 μ, and a PbS detector from 0.9 to 3 μ.

The optical arrangement is shown in Fig. 2. The reaction zone is viewed through an infrasil lens of 15 cm focal length which focuses a 1 to 1 image onto the entrance slit of the spectrometer. The limiting aperture at the lens provides approximately 80% illumination of the spectrometer. The surface opposite to the observation window was coated with a radiation absorber in order to minimize errors due to reflected or scattered light.

Calibration Optics

The absolute intensity calibration was performed by focusing the filament of an NBS lamp (Spectral Radiant Intensity Lamp) on the entrance slit of the spectrometer using the same optics as those in the NO-O emission measurements. Since the spectral intensity of the glow was generally 4–5 orders of magnitude lower than that of the standard lamp, the brightness of the filament image was attenuated in order to bring the calibration signal within the range of linear response of the detector. This was done by using two neutral density filters placed in front of the lens. The combined transmittance of these filters (about 0.3%) was measured in situ and determined as a function of wavelength. In addition to these filters a duplicate of the infrasil window was placed in the optical path in order to account for the transmission losses through this window.

In order to cover the whole spectral range from 0.4 to 2 μ it was necessary to use two standard lamps. One was calibrated at 2200°K and gave the spectral radiance in the range from 2700 to 5000 Å. The second lamp, calibrated at 1700°K, gave the spectral radiance in the range of 5000 Å to 2.6 μ. The spectrometer and its associated optics were mounted on a rotating table to allow convenient viewing of either the source or the standard lamp. An absolute intensity calibration was performed immediately after each run to insure that all gain settings, optical alignments etc., were constant.

Experimental Results and Discussion

Preliminary Experiments

A number of experiments were first made in order to investigate the general flow characteristics of the freejet. With

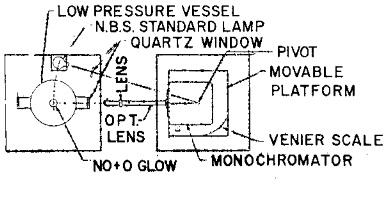

Fig. 2 View of the optical arrangement used for absolute intensity calibration.

oxygen in the discharge tube and NO added at the upstream end of the flow tube a bright NO-O glow was visible along the length of the flow tube. Without the air shroud the active gases recirculated and the chamber also became luminous. With the air shroud a luminous column was obtained which exhibited very little spreading over a distance of about 15 mm above the exit plane. A radial spectral intensity profile (λ = 5500 Å) taken at 15 mm above the exit plane for a jet of average linear velocity of 40 m/sec and stabilized at 1 torr is shown in Fig. 3. It is shown that the emission intensity is 20% of the maximum value for a radial distance equal to the radius of the tube. Very little light is emitted beyond this point, and the intensity drops practically to zero at a distance equal to 1.2 radii. If correction is taken for the path length, a reasonably flat profile is obtained up to $r = 0.8$ radius. Because of the insignificant spreading of the jet at the station of measurement no correction for marginal effects was taken into account, and the jet was assimilated to a uniform source with diameter equal to the exit diameter.

In a following experiment light absorption measurements at λ = 5500 Å were performed in order to evaluate possible effects due to self absorption of the gases. In all cases the absorption was within the range of experimental error estimated at ±0.5%.

Intensity Spectral Distribution of the NO-O Glow

Figure 4 reproduces the results obtained for the spectral radiant intensity in experiments where atomic oxygen was produced from discharged O_2. Similar results were obtained in an N_2 carrier with oxygen atoms produced from the nitrogen atom titration reaction. The different data points correspond to the measurements obtained with the different detectors and agree in general within 6% if the overlap is not carried outside the reasonable range of detector sensitivity. The spectral distribution curve obtained by Fontijn, Meyer, and Schiff is compared with our data in Fig. 4. It is shown that the long wavelength end of our curve does lie somewhat above the curve of Fontijn, Meyer, and Schiff. This is probably due to a difference in instrumental sensitivity as indicated by the recent work of Stair[8] who has shown that the NO-O continuum extended to at least 3.7 μ.

Two other series of experiments on the NO-O spectral distribution were performed at room temperature in order to investigate the effects of composition and pressure. The spectral radiant intensity curves in an argon atmosphere at 1 torr and in an oxygen atmosphere at 0.1 torr were found to be identical to the curve shown in Fig. 4.

In order to investigate the temperature effect on the spectral intensity distribution a number of experiments were performed in a flame atmosphere. These flames were stabilized at reduced pressure at 10 torr on a flat flame burner 4 in. in diameter.[9] Oxygen-rich and stoichiometric hydrogen-oxygen flames were used. The NO-O glow was produced by adding a few percent NO to the mixture before combustion. Under these experimental conditions the NO-O glow was observed as a green column surmounting the reaction zone. The spectral distribution of the glow was determined in the visible and in the near infrared up to 0.75 μ. Above this wavelength the infrared radiation due to the water bands became predominant.

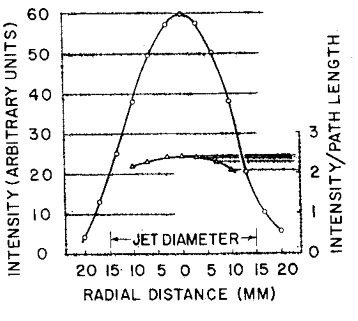

Fig. 3 Spectral intensity radial profile of NO-O chemiluminescence in free gaseous jet; λ = 5500 Å; linear velocity, 40 m/sec; distance from exit plane, 15 mm.

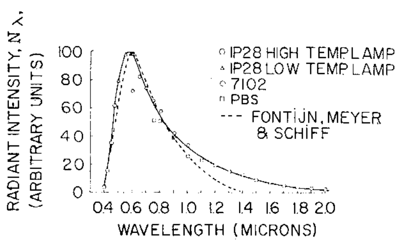

Fig. 4 Spectral intensity distribution of the NO-O glow. Relative intensities normalized to Nλ = 100 at intensity maximum; Oxygen atoms are produced by direct dissociation 0_2.

The results obtained in a stoichiometric and in an oxygen-rich flame are shown in Fig. 5A and 5B, respectively. It can be seen that there is no appreciable change in the spectral distribution due to differences in composition between the two flames. However a comparison between the flame results and the results obtained in the discharge flow experiments indicates a shift of the intensity maximum toward longer wavelengths with increasing temperature. It is of interest to note that the short wavelength limit of the glow remained unaffected by a temperature change.

Absolute Rate Constant

Four absolute independent rate constant determinations were performed at a pressure in the order of 1 torr. The first three experiments were made in an oxygen carrier in which the oxygen atoms were prepared from the dissociation of pure oxygen in the glow discharge. Experiment IV (see Table 1) was made in a nitrogen carrier with oxygen atoms prepared from the nitrogen atom titration reaction.

The oxygen atom concentration in the freejet was determined by measuring the decay of oxygen atoms in the flow tube and by extrapolating the decay curve obtained up to the point corresponding to the station of observation (15 mm above the exit plane). Some difficulties were originally encountered in the NO_2 titration used for the determination of oxygen atoms. In the first experiments the end point of the titration was determined visually, and this gave rise to some subjective results. In the final procedure the titration was followed quantitatively by measuring the light intensity near the exit plane. Typical titration curves obtained in this fashion are shown in Fig. 6. If the $NO_2 + O = NO + O_2$ titration reaction were infinitely fast, these curves would end at the NO_2 axis with a definite slope. However the titration curve shows an inflection point at the end. This effect is more pronounced for the titration corresponding to the 12.5-cm station, at which less time was available for the titration reaction to go to completion. The ideal end point

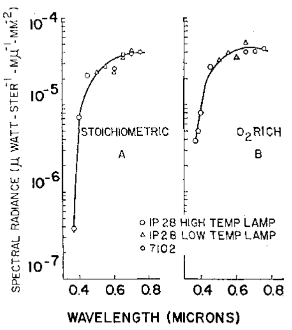

Fig. 5 Spectral intensity distribution of the NO-O glow: A) in stoichiometric H_2/O_2 flame at 10 torr, T = 1900°K (Li reversal); B) in oxygen rich H_2/O_2 flame at 10 torr, T not measured.

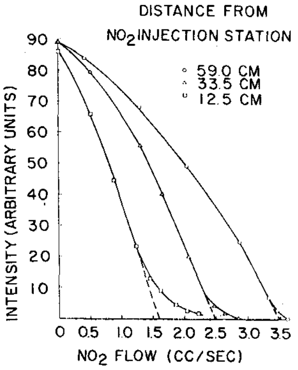

Fig. 6 Typical titration plots for $NO_2 + O = NO + O_2$.

of the titration (which would be observed if the $NO_2 + O$ reaction were infinitely fast) is then given by the intercept of the tangent at the inflection point with the NO_2 axis.

Under the conditions of our experiments about 50% of the oxygen atoms initially dissociated disappeared by recombination processes in the flow tube. In general, the percentage of O atoms in the freejet was about 4%. It is estimated that the atom concentrations in the jet were determined with an error of less than 5%. The main error was due to the extrapolations involved in the titrations and in the decay curves.

The results of the rate constant determinations over the spectral range 3875–20,000 Å are given in Table 1. It is shown that experiment IV, in which the oxygen atoms were prepared from the nitrogen atom titration reaction, gives an exceptionally high value for the rate constant. However, it is uncertain if this result is attributable to the different mode of preparation of atomic oxygen. Because of the low yield of atoms in the discharged N_2, the concentration of atomic oxygen and, as a consequence, the radiation intensity were about one order of magnitude lower in experiment IV than in the experiments where O was prepared by direct dissociation of O_2. The precision of the measurements in experiment IV was therefore reduced, and this might explain the observed discrepancy.

The data taken over all four experiments are summarized in Fig. 7 where the quantity $I_\lambda/[O][NO]$ has been plotted as function of λ. This quantity has the dimension of a "rate constant per unit wavelength interval," and the integral under the curve gives the rate constant of the chemiluminescent reaction. The vertical bars indicate the maximum spread observed over 4 to 6 data points at a given wavelength, and the circle points give the arithmetic mean of these data points. The scatter of the data falls roughly between the envelope shown, and the rate constant over the wavelength interval 3875–20,000 Å is given by $k = 6.8(\pm 1.2) \times 10^{-17}$ cm^3 $molecule^{-1}$ sec^{-1}, where the error figure relates to the precision of experiments and does not include systematic errors. Among these a ±5% possible error may be caused by inaccuracies in the calibration of the standard lamp.[10] The NBS calibration gave the spectral radiance of the filament for selective wavelengths as function of lamp current. We used the lamp in conjunction with an EG and G Model 590-11 Power Supply which regulated the current to ±0.25%. Geometrical errors were reduced to a minimum by viewing the radiation standard and the reaction zone through the same optics. The main geometrical error is due to the fact that the reaction zone is an extended source with a definite path length. It can be shown that under our experimental conditions errors due to this factor are roughly given by $E = r/2(2f + 2)$ where r is the radius of the jet and f the focal length of the condensing lens. Values of $r = 1.4$ cm and $f = 15$ cm give an estimated error of ±2.2%. The transmittance of the neutral density filters were measured in situ as a function of wavelength. If we allow for a possible error of ±2% in the transmittance of each neutral density filter and for a 5% error in the measurement of the oxygen atom concentration, the rate constant is given with a total error of the order of ±35%.

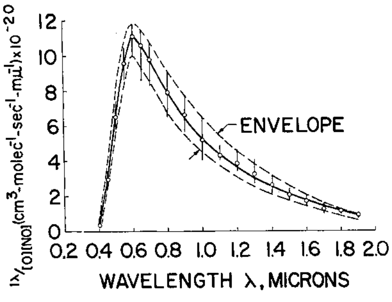

Fig. 7 Absolute rate constant for NO-O radiative combination.

In order to compare our data with the previous determination of Fontijn, Meyer, and Schiff, we have to recall that their rate constant was given for a lower temperature (296°K) and for a shorter wavelength interval. Making the wavelength correction, we find for k a value of 5.97×10^{-17} cm^3 $molecule^{-1}$ sec^{-1} at an average temperature of 367°K. For the temperature correction we make use of the data of Clyne and Thrush[11] who investigated the temperature dependence of the rate constant between 200 and 300°K. Their data are expressed in the form

$$k = 3 \times 10^{16} \exp \frac{+1500 \pm 400}{RT} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

Taking the temperature coefficient deduced from this expression and reducing our data to 296°K, we find for k a value of 9.7×10^{-17} cm^3 $molecule^{-1}$ sec^{-1}. This value is to be compared to the value of 6.4×10^{-17} cm^3 $molecule^{-1}$ sec^{-1} obtained by Fontijn, Meyer, and Schiff. Considering the different methods employed in the two investigations and the inherent difficulties in performing absolute reaction rate measurements, these two values are in reasonable agreement.

To complete this discussion, mention should be made of the enhanced light emission effect that is observed when adiabatically expanded $NO^{(2,12,13)}$ is used. Fontijn and Rosner[14] have forwarded an explanation of this effect which was recently substantiated experimentally by Golomb and Good.[15] These latter authors found that the enhanced light emission is in direct relationship with dimer concentration in the expanding NO jet. Because our experiments were performed in a freejet, one could at first glance attribute our larger measured quantum yield (compared to Fontijn, Meyer, and Schiff's results) to partial polymerization of NO. Although the possibility of cluster formation in our experiments cannot be ruled out entirely, it must be emphasized that the freejet itself was of subsonic velocity. It is therefore quite improbable that the temperature in the jet could have

Table 1 Absolute rate constant for the radiative combination of atomic oxygen with nitric oxide

	Experiment			
	I	I-A	III	IV
Pressure (torr)	1.02	1.145	0.947	1.245
Temperature (°K)	353	357	363	394
Concentration (molecule-cm³) × 10^{15}				
(O_2)	18.4	22.5	16.2	...
(N_2)	...	...	...	20.5
(NO)	6.45	4.20	7.70	9.25
(O)	1.34	1.94	1.73	0.248
Rate constant (cm^3-$molecule^{-1}$-sec^{-1}) × 10^{-17}	6.03	6.40	6.41	7.64

$$k = \int_{0.38\mu}^{2.0\mu} k_\lambda d\lambda$$

dropped below the saturation curve. It is also unlikely that clusters eventually formed upstream of the flow tube could have survived and be present at the station of measurement.

Conclusions

The NO-O(^{3}P) radiative combination has been investigated in a free gaseous jet in order to obtain results independent of heterogeneous effects. The spectral intensity distribution was determined over the wavelength region 3875–20,000 Å and was characterized in the infrared end by a slow decay curve of exponential shape. This distribution was found to be independent of composition in the pressure range 0.1–1.5 torr for O_2, N_2 and Ar atmospheres. The rate constant of the reaction was determined over the observed spectral range 3875–20,000 Å and was found to be 6.8×10^{-17} cm^3 molecule^{-1} sec^{-1} at 367°K with a probable error of ±35%.

The reaction was also investigated at high temperature in a hydrogen-oxygen flame atmosphere. Reliable results could be obtained in the range 3875–7000 Å, but above this wavelength the water bands and other sources of radiations made the measurements uncertain. Nevertheless, the results indicated a shift toward longer wavelengths of the intensity maximum with increasing temperature. Our rate measurements confirm within the limit of accuracy the previous results of Fontijn, Meyer, and Schiff.

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