AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **72**, 20 (1980); doi: 10.1063/1.438878
View online: http://dx.doi.org/10.1063/1.438878
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/72/1?ver=pdfcov
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Absolute rate constant for the chemiluminescent reaction of atomic oxygen with nitric oxide

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(Received 23 March 1979; accepted 14 August 1979)

The absolute rate constant for light emission from the NO–O reaction has been determined, as a function of wavelength, by using a standard brightness source, which has a surface of uniform brightness. The spectral distribution measured between 0.4 and 1.4 μm is in good agreement with those of the previous studies except for a little difference in the near infrared region. The influence from NO–O_3 chemiluminescence is demonstrated for atomic oxygen production from O_2 discharges.

INTRODUCTION

In recent years, chemiluminescent reactions have come under detailed investigation. Since the chemiluminescence is generally weak and there are great difficulties in calibrating detectors and determining optical geometries of emitting zones and detectors, it is not easy to measure the absolute emission rate even with highly advanced detection techniques. As was discussed by Fontijn *et al.*,[1] the NO–O chemiluminescent reaction is very useful as a standard reaction for calibrating the detection system when another unknown chemiluminescent reaction is to be studied using the same apparatus. Therefore, it is indispensable to obtain an accurate and trustworthy absolute emission rate constant for this chemiluminescent reaction.

The NO–O chemiluminescent reaction has been investigated by many workers.[1–11] After some long discussions about the mechanism of this chemiluminescence, it has been concluded that the emission intensity is independent of pressure above 1 torr.[9,10] The absolute emission rate constant is defined as $k = I/[\mathrm{NO}][\mathrm{O}]$ for the entire wavelength region, while sometimes it is described as a function of the wavelength and is denoted $k_\lambda (= I_\lambda / [\mathrm{NO}][\mathrm{O}])$.

The spectrum and absolute rate constant of this reaction reported by Fontijn *et al.* for the wavelength region between 0.4 and 1.4 μm are generally considered reliable and often adopted as a standard. Their absolute rate constant was measured using a method of chemical actinometry. Recently, a considerably stronger continuum emission than those of the earlier workers in the infrared region was reported by Stair and Kennealy,[6] Vanpee *et al.*,[7] and Golde *et al.*[8] Golde *et al.* reported considerable intensity at 1.51 μm using a detector calibrated against black body radiation. Woolsey *et al.*[11] obtained nine values of k_λ between 0.54 and 1.27 μm using a calibrating piston source, and their values were smaller than those of the previous data. The scattering of the reported values requires more accurate investigations in order to use it as a standard.

Moreover, there is another problem left. As most of the reported values for the NO–O reaction are obtained by using O atoms generated by direct discharge of O_2, the possibilities of influence from the reaction of ozone with NO should be considered, though most of the workers considered it to be negligible. The NO–O_3 chemiluminescence is a continuum extending from 0.6 to 3.2 μm with a maximum intensity at around 1.2 μm, and therefore, near the intensity maximum, even a small amount of O_3 may affect the value of k_λ.

The absolute rate constant and the spectral distribution of NO–O chemiluminescence were reinvestigated in this experiment. The titration of N atoms with NO[12] [designated as process (a) hereafter] was used for the production of the O atoms in order to avoid formation of O_3. The emission intensity resulting from O atoms generated by direct discharge of O_2 [designated as process (b)] was compared with that of process (a) to examine the influence of the NO–O_3 chemiluminescence. For the absolute calibration of the detectors, a standard brightness source which has a surface of uniform brightness was used; this source could be treated easily without the troublesome estimation of optical geometry.

EXPERIMENTAL

In process (a), N atoms are generated by a silent discharge in flowing N_2, NO is injected in the downstream, and the fast reaction $\mathrm{NO} + \mathrm{N} \rightarrow N_2 + \mathrm{O}$ produces atomic oxygen $\mathrm{O}(^3P)$. If the concentration of the injected NO is greater than that of N atoms, the chemiluminescent reaction $\mathrm{NO} + \mathrm{O} \rightarrow \mathrm{NO}_2 + h\nu$ takes place. The concentration of O atoms in this process is easily determined by means of the null point of the titration. The concentration of NO which can react with O atoms is equal to the difference between the injected $[\mathrm{NO}]_i$ and $[\mathrm{NO}]_0$ at the null point of the titration.

The apparatus used in this experiment is shown schematically in Fig. 1. The pressure of the flow system was controlled by needle valves and pumping by a rotary pump, and was measured by a Pirani gauge calibrated with a McLeod gauge. Nitrogen flowed through the water cooled ac silent discharge tube led via some bends to the 45 cm long, 4.7 cm diam. Pyrex reaction tube.

Nitric oxide was stored in reservoirs with a volume which could be selected ranging between 0.067 and 7.70 liter, including the bulbs and tubing volumes. As the partial pressure of NO in the flowing gas was below 0.05 torr, the total flow rate at around 1 torr was essentially unaffected by NO injection and was almost equal to the nitrogen flow rate. When the valve of the NO reservoir was opened to a certain aperture, the pressure of the reservoir decreased gradually, and thus the concentra-

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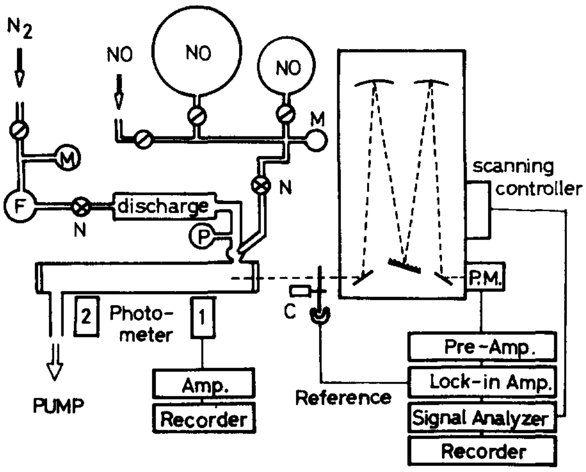

FIG. 1. Schematic diagram of the reaction flow system and the detection system: M, manometer; F, flowmeter; N, needle valve; P, Pirani gauge and McLeod gauge; C, chopper.

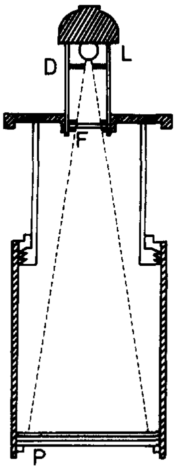

FIG. 3. Absolute brightness standard source: L, tungsten lamp; D, diaphragms; F, filter to convert the color temperature of light, P, opal glass plate.

tion of NO injected into the reaction tube varied with time. The concentration of the injected NO was obtained by measuring the rate of pressure decrease in the NO reservoir (dp/dt) and was proportional to $p_0V/Q \cdot (dp/dt)$, where p_0 is the total pressure, and Q is the total flow rate, and V is the volume of the NO reservoir.

The gases used in this study were N_2 of 99.999% purity, O_2 of 99.9% purity, and NO of 99.0% purity. N_2 and O_2 were used without further purification, while NO was purified by passing it through a trap filled with a molecular sieve.

The spectral intensity distribution was measured using a Czerny-Turner type 1 m monochromator equipped with a 600 grooves/mm grating, blazed at 1.0 μm. As the intensity was weak, the measurement was performed with resolutions of 4.7 Å between 0.35 and 0.9 μm, 30 Å between 0.7 and 1.0 μm, and 94 Å between 0.7 and 1.45 μm. The wide spectral range of the chemiluminescence required the use of three detectors (two types of photomultipliers and a dry-ice cooled PbS detector) with overlapping response regions. The output current of the photomultiplier was measured directly by a dc picoammeter. For the PbS detector, the emission was modulated at 150 Hz by a mechanical chopper, and the output signal was amplified by a lock-in amplifier. A 1024 channel analyzer was used to average the signals obtained from a large number of wavelength scans. Because of a long observation time, the experimental conditions (total pressure, [O], etc.) gradually changed. In order to cancel these drifts, the monochromator was scanned forwards and backwards alternately, and finally these data were averaged.

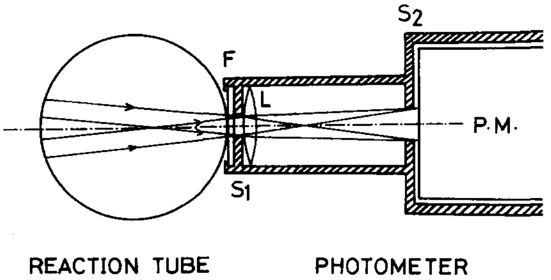

FIG. 2. Cross section of the reaction cell and photometer for measuring absolute intensity of the chemiluminescence: F, interference filter; L, lens; S_1 and S_2, slits to limit the viewing zone; P.M., photomultiplier.

The relative emission intensity was calibrated with a tungsten standard lamp. Since the spectrum of this lamp was determined only in the visible region, it was calculated from the table of De Vos[13] based on the emissivity of tungsten ribbon in the near infrared region.

In order to measure the absolute intensity of the chemiluminescence at one wavelength, a photometer was used which was constructed of an interference filter which had peak transmission at 5620 Å and a band width of 85 Å, a lens, a photomultiplier, and two collimating slits as shown in Fig. 2. The parallel light through the slit S_1, and the filter with a small angle to the optical axis was focused by a lens L on the slit S_2, and detected by a photomultiplier. The photometer was set so as to observe the chemiluminescence from the side of the reaction tube at a right angle to the gas stream. When the emission appears uniformly in the cross section of the reaction tube, the intensity detected by the photometer is proportional to the optical length along a line of sight in the emitting zone. Then the widths of slits were determined in such a way that the optical length was equal to the diameter of the reaction tube to within an error of 2%.

With this arrangement, the emission intensity of the chemiluminescence was measured and calibrated absolutely by means of the standard brightness source drawn in Fig. 3. The light from a tungsten lamp illuminates an opal glass plate, so that the plate has a uniform brightness. The absolute brightness of the surface had been determined previously by comparing with a diffuse surface (MgO plate) which was illuminated by a primary standard tungsten lamp.[14] Let the output current of the detection system for the chemiluminescence be i_c, and that of the standard source i_s; then the absolute intensity of the chemiluminescence $I(\lambda_0)$ is represented by

$$I(\lambda_0) = (i_c/i_s)B(\lambda_0)/L \ , \qquad (1)$$

where L is the diameter of the reaction tube and $B(\lambda_0)$ is

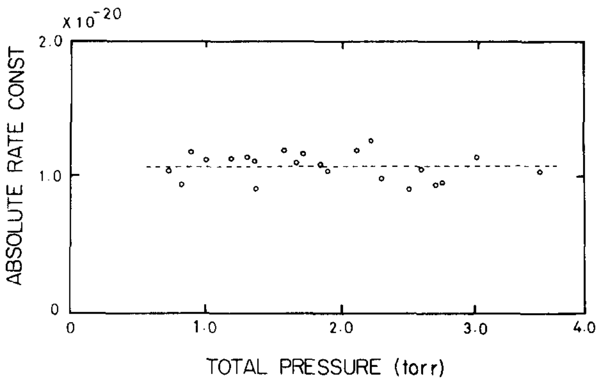

FIG. 4. Absolute rate constant k_λ at $\lambda = 5620$ Å plotted versus the total pressure in units of cm^3 molecule^{-1} sec^{-1} Å^{-1}.

the absolute brightness at λ_0 on the surface of the standard source. The uncertainty in measuring i_s was maintained below 1% and the uncertainty in $B(\lambda_0)$ is about 10%.

In order to compare the spectral distributions of the chemiluminescence from processes (a) and (b) at wavelengths λ_1, λ_2, and λ_3 (0.633, 1.08, and 1.20 μm, respectively), a photometer which consists of a PbS detector and three filters was used. Let the signals from the photometer be $i_a'(\lambda)$ and $i_b'(\lambda)$ in process (a) and (b), respectively. The spectral emission intensity in process (b) is then obtained by

$$I_b^r(\lambda) = [i_b'(\lambda)/i_a'(\lambda)]I_a^r(\lambda) \ , \qquad (2)$$

where $I_a^r(\lambda)$ is the spectral intensity of NO–O spectrum in process (a). The values of $I_b^r(\lambda)$ were normalized by putting $i_b'(\lambda_1) = i_a'(\lambda_1)$ at $\lambda_1 = 0.633$ μm, where the influence of the NO–O_3 emission could be negligible.

RESULTS AND DISCUSSION

The reason why the spectrum and the absolute emission intensity were measured by process (a) in this experiment is in order to avoid the production of O_3 and excited O_2. Using process (a), excited species of N_2, especially vibrationally excited species in the ground state, may be present. According to the absorption experiment of the yellow afterglow of N_2 by Tanaka *et al.*,[15] they were not able to observe any absorption bands from the vibrationally excited levels of N_2. Here it is therefore considered that the vibrational excitation transfer in the N_2 flow terminates very quickly and does not affect the NO-titration reaction which takes place far downstream of the N_2 flow.

Under the condition that the total pressure and [O] be maintained constant, the absolute intensities versus [NO] were plotted. When the absolute intensities were measured at various total pressures and flow rates, an additional photometer was used to monitor the intensity far downstream, and the data were used only when the intensity decrease between the two photometer positions was ≤ 10%. This procedure was used in order to confirm that the density of NO at the place where the absolute intensity was measured was same as that of the place where NO was injected, and in this case I vs [NO] plots indicated good linearity. The values of k_λ was obtained from the slope of the straight line thus obtained. Many data for k_λ were obtained under the various conditions of total pressure, and it was confirmed that the values of k_λ did not depend on the total pressure over the range of pressure used. They are shown in Fig. 4 as a function of the total pressure. The averaged value of k_λ is 1.07×10^{-20} cm^3 molecule^{-1} sec^{-1} Å^{-1} at 5620 Å, and from the dispersion in the data the standard deviation is calculated to be 11.2%. The accumulated uncertainty, which is due mainly to errors related to the intensity measurement, the estimation of [NO] and the absolute intensity calibration, is estimated to be about 30%.

The relative spectral distribution of NO–O chemiluminescence was measured under the condition that total pressure, [O], and [NO] are maintained constant. Overall spectral distribution is shown in Fig. 5, where error bars indicate the standard deviation in the many sets of data. The broken curve shows the spectrum reported by Fontijn *et al.*,[1] and the dotted curve shows the result of Vanpee *et al.*[7] They are normalized at the peak value in order to clarify the difference in the spectral shapes. It is obvious that the present result agrees with the previous data in the visible region, but near the infrared region, these spectra indicate different shapes. In this experiment, the emission could not be measured above 1.4 μm, because of the steep decrease in the transmission efficiency of the monochromator above 1.4 μm and strong absorption of H_2O and CO_2 in the atmosphere. Between 0.8 and 1.4 μm, the present spectrum shows a rather steeper decrease towards longer wavelength than that of Vanpee *et al.*, but it does not decrease as steeply as that of Fontijn *et al.* and yet still have some intensity at 1.4 μm. The spectrum has no distinct band structure below 1.4 μm, but between 0.7 and 1.2 μm, it is observed in this experiment that the spectrum is not entirely smooth but shows some bends.

In Fig. 6, the absolute rate constants are shown as a function of wavelength in comparison with the previous results. The present values are obtained from the spectral distribution in Fig. 5 by normalizing to the absolute value of k_λ at 5620 Å. In the visible region, the values

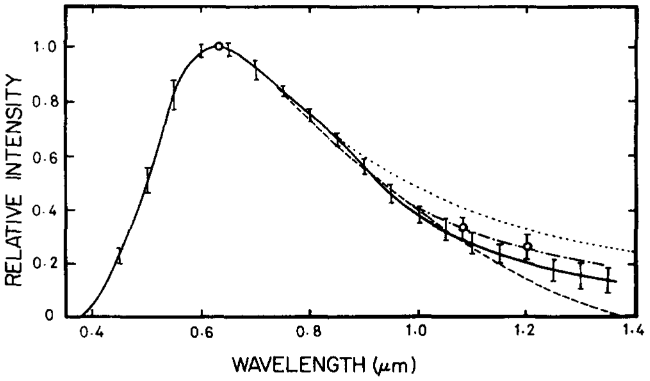

FIG. 5. Relative spectral distribution of NO–O chemiluminescence. The peak intensity was normalized to $I = 1.0$: ------, Fontijn *et al.*[1]; ······, Vanpee *et al.*[7]; ———, this work. The empty circles at $\lambda = 0.63$, 1.08, and 1.20 μm indicate the intensities of process (b) relative to process (a).

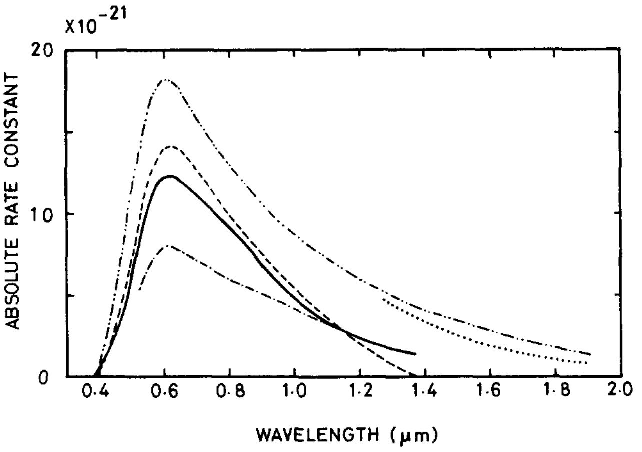

FIG. 6. Absolute rate constant k_λ plotted versus wavelength: ------, Fontijn *et al.*[1]; ······, Golde *et al.*[8]; -·-·-·-, Woolsey *et al.*[11]; -··-··-, Vanpee *et al.*[8]; ———, this work. The values of k_λ are plotted in units of cm^3 $molecule^{-1}$ sec^{-1} $Å^{-1}$.

of k_λ by Fontijn *et al.* and Woolsey *et al.* are different by about a factor of 2, and the present value lies intermediate between them. In the near infrared below 1.4 μm, the present value coincides with that of Woolsey *et al.* but is different from that of Golde *et al.* Since Vanpee *et al.* made the measurements at 367 °K, their absolute values were corrected to 296 °K by using the data of Clyne and Thrush[5] for the temperature dependence, as suggested by Vanpee *et al.*

The relative intensity $I_b^r(\lambda)$ in the direct O_2 discharge process [process (b)] was measured at the total pressure ranging from 0.7 to 3.0 torr, but it also showed no apparent dependence on the total pressure. The averaged values of $I_b^r(\lambda)$ are shown by empty circles in Fig. 5, where the error bars indicate the standard deviation of each set of measurements. The values of $I_b^r(\lambda)$ become large with increasing wavelength, and it indicates the same tendency as was found in the data of Vanpee *et al.*

The following reaction scheme is considered for NO–O chemiluminescence:

$$NO + O \rightarrow NO_2^* \qquad (k_1), \qquad (R1)$$

$$NO + O + M \rightarrow NO_2^* + M \qquad (k_2), \qquad (R2)$$

$$NO_2^* \rightarrow NO_2 + h\nu \qquad (k_3), \qquad (R3)$$

$$NO_2^* + M \rightarrow NO_2 + M' \qquad (k_4). \qquad (R4)$$

When O atoms are produced by direct discharge of O_2 [process (b)], $[O_3]$ is governed by the following reactions:

$$O + O_2 + O_2 \rightarrow O_3 + O_2 \qquad (k_5), \qquad (R5)$$

$$O + O_3 \rightarrow 2O_2 \qquad (k_6). \qquad (R6)$$

NO can therefore react with O_3 in addition to the above reactions with O atoms:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (k_7). \qquad (R7)$$

Clough and Thrush[16] studied the reaction of $NO + O_3$ and reported that 7% of Reaction (R7) yielded electronically excited NO_2^* from which the NO_2 continuum emission emanates.

In the steady state, the emission intensity in the process (b) is given using a rate constant k_7' for the process yielding NO_2^* in Reaction (R7) by

$$I_b' = k_3\{(k_1 + k_2[M])[NO][O] + k_7'[NO][O_3]\}/(k_3 + k_4[M]). \qquad (3)$$

The first and second terms in the numerator of Eq. (3) correspond to the NO–O chemiluminescence and the third to the NO–O_3 chemiluminescence. Each rate constant in Eq. (3) should be considered to depend on the wavelength of the emission, and now it is considered for simplicity that the coefficients of the first and the second terms in Eq. (3) have the wavelength dependence like that of the NO–O chemiluminescence shown in Fig. 6, and k_7' has similar wavelength dependence to that of NO–O_3 chemiluminescence reported by Clough and Thrush. The concentration of O_3 was evaluated from the differential equation from Reactions (R5) and (R6), using the previously reported rate constants.[17] According to Eq. (3), the relative intensities I_b' were calculated under various conditions of pressure, [O], [NO], and flow rates. The ratio of $I_b'(\lambda)/I_a^r(\lambda)$ scarcely depends on the pressure over the pressure range used in the present experiment. Typically, when the total pressure is 1.0 torr and $[O] = 0.01[O_2]$, the contribution of Reaction (R7) reached about 7% at 1.2 μm and about 10% at 1.5 μm, though the contribution is only less than 3% to the overall intensity. This nonnegligible effect on the spectrum is due to the spectral intensity distribution of NO–O_3 chemiluminescence which has its maximum intensity at 1.2 μm, where that of NO–O chemiluminescence is very weak. Thus, in the near infrared region, it is concluded that the absolute rate constant measured in process (b) contains some contribution from NO–O_3 chemiluminescence.

The values of k_λ by Vanpee *et al.* and Golde *et al.* in Fig. 5 are those obtained from the direct mixing of NO with the discharged O_2 [process (b)]. According to Vanpee *et al.*, two methods for generating the oxygen atoms were used, which are the same as the processes (a) and (b) in the present experiment, and when process (a) was used, they obtained almost the identical results as in the case of process (b). However, most of their experiments were carried out with process (b), because of the low intensity of the emission in process (a), and accordingly the data obtained by process (a) have a large uncertainty. Thus, the values of k_λ by Vanpee *et al.* might have been overestimated in the region beyond 1.0 μm.

Fontijn *et al.* obtained 6.4×10^{-17} cm^3 $molecule^{-1}$ sec^{-1} as the overall value for k in the wavelength region shorter than 1.4 μm. The corresponding value of Vanpee *et al.* is 9.7×10^{-17} cm^2 $molecule^{-1}$ sec^{-1} at 296 °K, and that of Woolsey *et al.* is 4.3×10^{-17} cm^2 $molecule^{-2}$ sec^{-1}, which is obtained by extrapolating between the 0.4 and 1.4 μm wavelength region, while the value of 5.6×10^{-17} cm^3 $molecule^{-1}$ sec^{-1} is obtained in this work. As the uncertainties of those values are about 30%, the present value is in good agreement with the previous values within their accuracies except that of Vanpee *et al.* The value of Vanpee *et al.* is rather large, but it should be considered that the temperature correction term by

Clyne and Thrush[5] is determined in the temperature range between 200 and 300 °K and also contains the uncertainty of about 30%.

More detailed investigations to confirm the standard reaction seems necessary in the near infrared region.

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