CHEMISTRY LETTERS, pp.309-312, 1972. Published by the Chemical Society of Japan

STUDY OF CHEMILUMINESCENCE BY MEANS OF CROSSED BEAMS: NITRIC OXIDE – OXYGEN ATOM SYSTEM

Takamasa IBARAKI, Isao KUSUNOKI, and Kumasaburo KODERA
Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto

NO-O chemiluminescence was studied by means of crossed molecular beams. Anomalously bright light emissions have been observed with low temperature NO beams. It is considered that the chemiluminescence is caused by the two-body collisions between NO dimers and O atoms. Radiation cross section is estimated to be about 2 x 10^{-15} cm^2.

In recent years, the chemiluminescence in nitric oxide – oxygen atom system has been studied widely and the mechanism involving a three-body recombination has been proposed.[1,2] The experiments were extended to the low pressure region and it was found that, along with a three-body recombination, a two-body radiative recombination, $NO + O \longrightarrow NO_2 + h\nu$, also occurs.[3,4]

On the other hand, the enhanced light emission rate in the reaction of adiabatically expanded nitric oxide and atomic oxygen, which was observed in the rocket survey in the upper atmosphere, has been studied in wind tunnel experiments and explained by the two-body collision between a nitric oxide cluster formed by the adiabatic expansion and an oxygen atom, (headglow).

In this study, a crossed beem technique has been employed to study the reaction under the condition where no three-body collision can occur. By means of this technique, it is possible to measure directly the cross section of light emission by two-body collisions, and also the life time of reaction intermediate can be determined directly in a condition free from collisional quenching.

EXPERIMENTAL

The experimental apparatus consists of a source chamber and a reaction chamber as is shown in Fig. 1. O atomic beam was formed by passing O_2 gas through a microwave cavity (2450 MHz) and effusing from a glass tube of ca. 0.5 mm diameter and ca. 5mm length, then collimated into a beam by a slit of 0.5 mm width at the entrance of the reaction chamber.

NO molecular beam source made of pyrex glass can be cooled with liquid nitrogen. The beam was formed by effusing NO through the glass tube of ca. 0.5 mm diameter and ca. 5 mm length. No collimating slit was used for this beam. To make low temperature NO molecular beams, after certain amount of NO was trapped in solid state inside the source by cooling with liquid nitrogen, it was sublimed rapidly by blowing out the liquid nitrogen from the trap. The temperature of sublimation was considered to

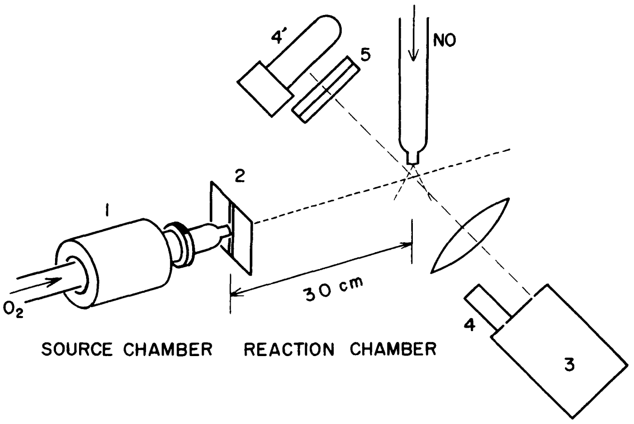

Fig. 1. Schematic of the crossed molecular beam system for chemiluminescence study.
1: microwave cavity,
2: collimating slit,
3: monochromater,
4,4': photomultiplier,
5: filters

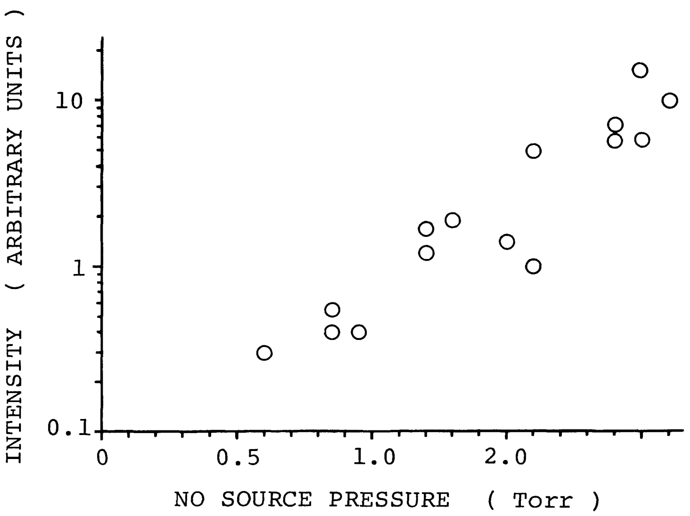

Fig. 2. Dependence of the over all light intensity on the pressure of the cold NO gas in the source.

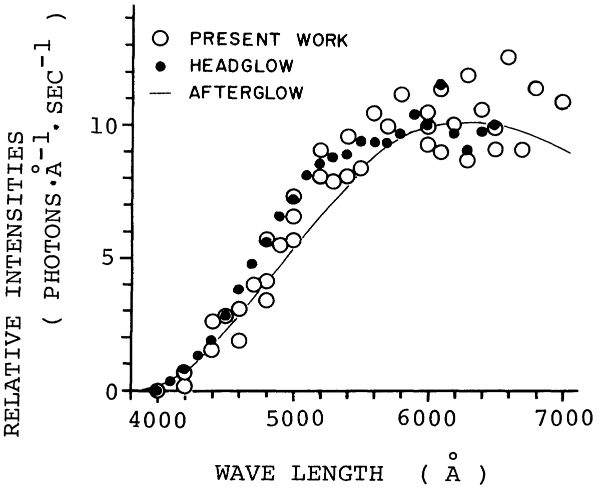

Fig. 3. Spectrum of the chemiluminescence.
Headglow from Ref. 5
Afterglow from Ref. 2

be below −150°C.

Emission spectrum was obtained using a grating monochromater CT-25 of Japan spectroscopic. Co. at low resolution with a photomultiplier R374 of Hamamatsu TV Co.

Since the low temperature NO beam was not in stationary flow but was intermittent, another photomultiplier (Toshiba, MS-9S) was used to monitor the changing intensities of the radiations. The wave length of monitored radiation was limited about 5500 Å by the combination of an interference filter KL-55 and a colored glass filter V-O 53 of Toshiba Kasei Co.

The spectral sensitivity was calibrated with a standard lamp in the same optical system used.

RESULTS AND DISCUSSION

The light emission by two-body collisions between NO and O could not be observed at the intersections of the molecular beams, however, anomalously bright light emissions have been observed with NO beams generated from cooled NO source. Similar bright light emissions have been observed in the gas phase ($\sim 10^{-4}$ Torr) near the liquid nitrogen cooled surfaces. The both emissions have nearly the same spectral distribution as the air afterglow or the headglow.

Figure 2 shows the over all light intensities against pressures of the cold NO gas in the source. Below 1.5 Torr, the background pressure of the reaction chamber was kept within the range of 10^{-5} Torr. To measure the spectral distributions of the radiation by the monochromater, the source pressure was increased to ca. 10 Torr to get enough intensity. By this increase of the source pressure, a temporary increase of the background pressure to the range of 10^{-3} Torr was observed.

The spectral distribution is shown in Fig. 3. The intensity is normalized to a value of 10 photons emitted per Ångstrom unit per second at 6000 Å. The normal NO-O afterglow spectrum obtained by Fontijn, Meyer, and Schiff[2] and the headglow spectrum obtained by Golomb and Good[5] are shown together. There is no significant difference between these spectra and ours. Therefore, it is considered that these radiations arise from the same electronic state of the product.

Assuming the mechanism, $NO + O \longrightarrow NO_2 + h\nu$, the cross section of the chemiluminescence for the wave length 4000 to 6500 Å is estimated to be $\sigma \approx 2\mathrm{x}10^{-19}\ \mathrm{cm}^2$ for a presumed O concentration of a few per cent. The value is remarkably larger than that of two-body mechanism obtained by Becker, Groth, and Thran[4]; $\sigma \approx 2\mathrm{x}10^{-22} - 2\mathrm{x}10^{-23}\ \mathrm{cm}^2$ estimated from their rate constant $k \approx 10^{-18} - 10^{-19}\ \mathrm{cm}^3\mathrm{molecule}^{-1}\ \mathrm{sec}^{-1}$.

Therefore, it is considered that not the monomer but the dimer of NO contributes to the chemiluminescence as in the case of headglow. The dimer might be produced by the low temperature equilibrium or by the sublimation from the condensed NO in the source, or both.

The existence of dimers at low temperatures has been established by Dinerman and Ewing[7] and the dimerization constant K ($2NO \rightleftarrows N_2O_2$) has been estimated from the deviation of the second virial coefficient of NO from that of monomer at low temperatures by Guggenheim[8] and Scot[9]; i.e., $\ln(K/\mathrm{atm}) = -15.44+1320°K/T$ and $\ln(K/\mathrm{atm}) = -10.90+752°K/T$, respectively.

Assuming that the NO pressure is 1 Torr and its temperature is 100°K in the source, and using the K of Guggenheim, ratio $[N_2O_2]/[NO]$ is estimated to be about $1x10^{-4}$. From this value the radiation cross section for NO dimer and O atom is estimated to be $\sigma \approx 2x10^{-15}$ cm^2. The value agrees with that of the headglow obtained by Golomb and Good, i.e., $\sigma \approx 6x10^{-15}$ — $6x10^{-16}$ cm^2 estimated from $k \approx 3x10^{-11}$ — $6x10^{-16}$ cm^2sec^{-1} for 4000 — 6500 Å.

From the above result, it is considered that the anomalously bright chemiluminescence observed in the crossed beem is caused by the two-body collisions between NO dimers and O atoms.

The radiation in the gas phase near cooled surface is considerably brighter than normal NO-O afterglow and seems to be originated from the same mechanism as in the crossed beam. At present, it is not clear whether the dimers are produced by the temperature equilibrium or directly from the sublimation of the solid NO. Further study will be continued.

The authors are grateful to the Ministry of Education and Toray Science Foundation for a grant-in-aid, by which this study was partly supported.

REFERENCES

1) H.P.Broida, H.I.Schiff, and T.M.Sugden, Trans.Faraday Soc., 57, 259 (1961).
2) A.Fontijn, C.B.Meyer, and H.I.Schiff, J.Chem.Phys., 40, 64 (1964).
3) R.R.Reeves, P.Harteck, and W.H.Chace, J.Chem.Phys., 41, 764 (1964).
4) K.H.Becker, W.Groth, and D.Thran, Chem.Phys.Letters, 6, 583 (1970).
5) D.Golomb and R.E.Good, J.Chem.Phys., 49, 4176 (1968).
6) M.Vanpee and W.R.Kineyko, J.Chem.Phys., 52, 1619 (1970).
7) C.E.Dinerman and G.E.Ewing, J.Chem.Phys., 53, 626 (1970).
8) E.A.Guggenheim, Mol.Phys., 10, 401 (1966), ibid., 11, 403 (1966).
9) R.L.Scott, Mol.Phys. 11, 399 (1966).

(Received February 17, 1972)