CHEMISTRY LETTERS, pp. 777-780, 1986.

EXTERNAL MAGNETIC FIELD EFFECTS ON THE EMISSION INTENSITIES OF THE OH(A-X) AND CH(A-X) BANDS IN LOW PRESSURE C_2H_2/O_2 AND C_3H_8/O_2 FLAMES

Yoshio FUKUDA, Haruo ABE, Hisaharu HAYASHI,*
Takashi IMAMURA,[†] and Saburo NAGAKURA[†]
The Institute of Physical and Chemical Research, Wako, Saitama 351-01
[†]Institute for Molecular Science, Myodaiji, Okazaki 444

Magnetic field effects on emission intensities of the CH(A-X) and OH(A-X) emission were studied with low pressure C_2H_2/O_2 and C_3H_8/O_2 flames produced by a microwave discharge of O_2. When a magnetic field of 1.8 T was applied, the intensity of the CH(A-X) emission was reduced to 95% of that at zero field.

Recently, magnetic field effects on emission of some electronically excited radicals were observed with atmospheric flames.[1-3] To elucidate their detailed mechanism, we have studied chemiluminescence produced in discharge-flow systems.[4] We report here magnetic field effects on the CH(A-X) and OH(A-X) emission intensities produced by reactions of C_2H_2 and C_3H_8 in a discharge flow of O_2.

The experimental apparatus was described with detail in our previous paper.[4] A discharge-flow apparatus was set in a gap of an electromagnet. Its maximum and residual magnetic fields were measured to be 1.8 T and 3 mT, respectively. Hereafter, measurements under the residual magnetic field will be denoted as those at zero field.

Oxygen was discharged by microwave of 2450 MHz and C_2H_2 or C_3H_8 was mixed at about 50 cm downstream of the discharge. The emission intensities of the flames in the presence (I(H)) and absence (I(0)) of a magnetic field were measured.

The emission of both flames was proved to be produced only by reactions of neutral species from the following experimental results: Current of positive ions (i_+) and that of electrons and negative ions (i_-) at the observation region were detected by an ion probe. When a potential of -10 V was applied to ion-collector grids placed upstream, the values of i_+ and i_- were reduced to 1±1% and 10±10% of the values at 0 V, respectively. On the contrary, the observed emission intensities in the present study were independent of the potential within 1%.

To protect the microwave discharge from an applied magnetic field, a microwave cavity was placed within a shielding box made of iron plates 10 mm thick. The efficiency of the shielding box is considered to be sufficient because the ion current at the ion-collector grids was independent of an applied magnetic field within 0.1%. The efficiency for the detection system of chemiluminescence was also independent of the field strength within 1%. Namely, the observed magnetic field effects in the present study are completely due to non-ionic processes occurring in the discharge flow.

Figure 1 shows emission spectra observed with the C_2H_2/O_2 and C_3H_8/O_2 flames in the absence of a magnetic field. It is noticeable that the CH(A-X) emission is not observed with the present C_3H_8/O_2 flame whereas the emission can be observed with atmospheric C_3H_8/O_2 flames.[1)] Furthermore, the C_2(d-a) emission is not observed with both flames whereas the emission can be observed with the atmospheric flames of both fuels.[1,5)] These facts indicate that there are some differences in chemical processes occurring in the present discharge afterglow and atmospheric flames.

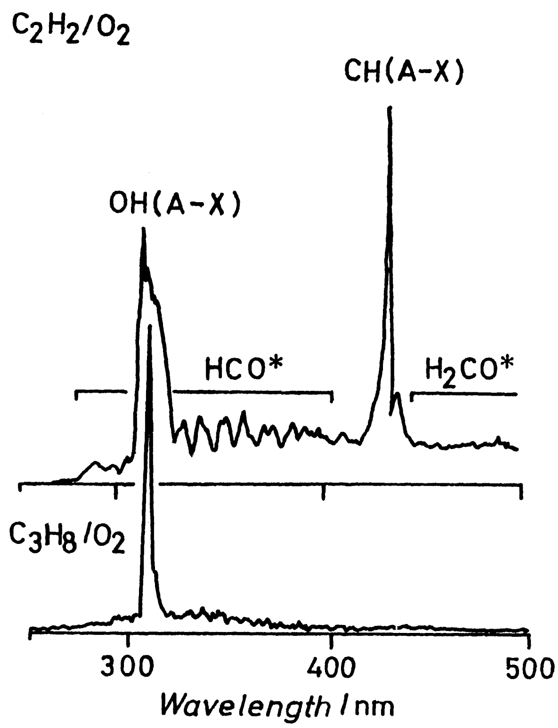

Fig. 1. Emission spectra observed with C_2H_2/O_2 (upper) and C_3H_8/O_2 (lower) flames in the absence of a magnetic field. Resolution is 1.6 nm. Pressures of O_2, C_2H_2, and C_3H_8 are 30, 3, and 3 Pa, respectively.

When a magnetic field of 1.8 T is applied, the emission intensities of CH(A-X) and H_2CO* produced in the C_2H_2/O_2 flame were found to be reduced by the field as shown in Figs. 2 and 3. As we can see from Fig. 2, there is little wavelength dependence of the I(H)/I(0) value upon the rotational structure of the CH(A-X) band.

Dependence of I(H)/I(0) on magnetic

field, H, was measured with the $C_2H_2(C_3H_8)/O_2$ flame at the band head of OH(A-X) emission, 310 nm, as shown in Fig. 3(4). From Figs. 3 and 4, the I(H)/I(0) values were proved to be independent of H within experimental errors. Because the emission intensity of HCO* at the vicinity of 310 nm was found to be independent of H, the intensities of the OH(A-X) emission produced in both flames are also considered to be independent of H.

The present findings show reverse tendencies to those observed with an atmospheric C_3H_8/O_2 flame.[1)] The intensity of the OH(A-X) emission in the atmospheric flame was found to be increased by a magnetic field whereas that of the CH(A-X)

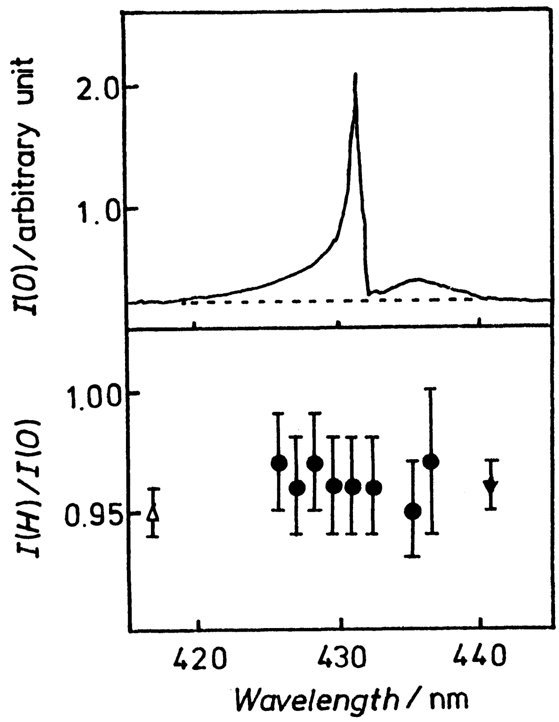

Fig. 2. Wavelength dependence of I(H)/I(0) of the CH(A-X) (●) and H_2CO^* emission (▲,▼) observed at 1.8 T with the C_2H_2/O_2 flame. I(H)/I(0) of the CH(A-X) emission was obtained by subtracting the H_2CO^* emission as indicated by a broken line. Resolution is 0.8 nm. Pressures are the same as those shown in Fig. 1. Errors are 2.5 times standard errors.

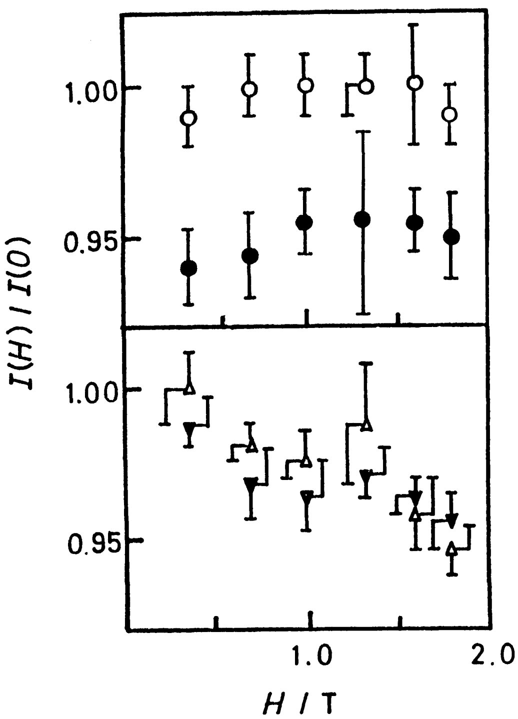

Fig. 3. Dependence of I(H)/I(0) on magnetic field, H, observed with C_2H_2/O_2 flame. Resolution is 3.3 nm. Pressures are the same as those shown in Fig. 1. ○, OH(A-X) at 310 nm; integrated intensity of CH(A-X) by subtracting emission of H_2CO^* as shown in Fig. 2; ▲,▼, emission of H_2CO^* at 417 and 441 nm, respectively.

emission not to be affected by the field. The lack of the magnetic field effect on the CH(A-X) emission in the atmospheric flame indicates that there is no magnetic field effect on the emission and quenching processes of CH(A) as in the case of the NO(B-X) emission.[4] In the present discharge flow of C_2H_2/O_2, the CH(A-X) emission was found to be decreased in intensity by a magnetic field. Therefore, some processes on formation of CH(A) in the present discharge flow are concluded to be affected by a magnetic field. In the present discharge flow of C_3H_8/O_2, the OH(A-X) emission was not found to be influenced by a magnetic field. On the other hand, a magnetic field was shown to affect the formation process of OH(A) in the atmospheric C_3H_8/O_2 flame.[1,2] The details of the mechanism of magnetic field effects upon formation of CH(A) and OH(A) in the discharge flow of O_2 and in the atmospheric C_3H_8/O_2 flame will be discussed later.

This work was supported by the Joint Studies Program (1984∿1985) of the Institute for Molecular Science. Authors thank Mr. Hisashi Yoshida at the Equipment Development Center of the Institute for Molecular Science for constructing an interface for the detection system.

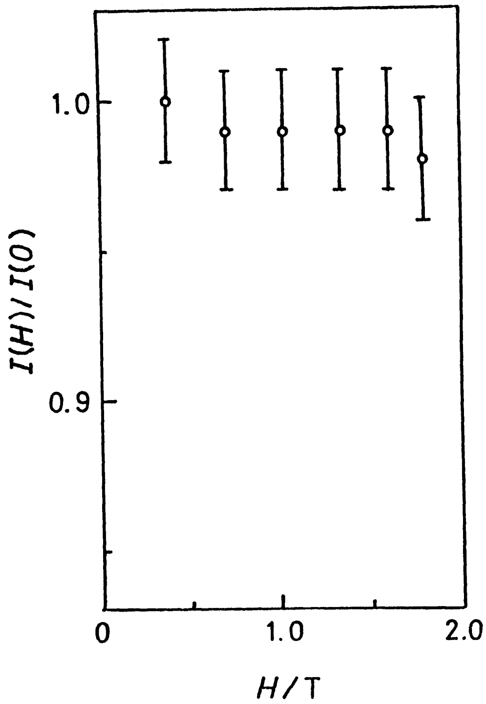

Fig. 4. The I(H)/I(0) dependence of the OH(A-X) emission at 310 nm on magnetic field, H, observed with the C_3H_8/O_2 flame. Resolution is 1.6 nm. Pressures are the same as those shown in Fig. 1.

References

1) H.Hayashi, Chem.Phys.Lett., 87, 113 (1982).
2) H.Hayashi, Nippon Kagaku Kaishi, 1984, 1753.
3) N.I.Wakayama, I.Ogasawara, and H.Hayashi, Chem.Phys.Lett., 105, 209 (1984).
4) Y.Fukuda, H.Hayashi, and S.Nagakura, Chem.Phys.Lett., 119, 480 (1985).
5) V.A.Fassel and D.W.Golightly, Anal.Chem., 39, 466 (1967).

(Received February 25, 1986)