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An ESR Study of Hydrogen Atoms in Methane-Air Flame

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In order to give a basis for the utilization of ESR in combustion chemical studies, both diffusion flames and premixed flames of a methane–air mixture have been studied by the flame-in-cavity ESR method. A pair of spectral lines separated by 51.0 mT due to H atoms and a very weak single line due to unidentified reaction intermediates have been recorded from combusting gases in a modified Bunsen burner. The H atoms in the diffusion flame give the spectral linewidth of 0.15 mT and populate a confined region near the luminous cone. In the premixed flame, the H atom concentration is the highest at the outside of the luminous inner cone (reaction zone), but it is distributed as long as 4 cm along the gas stream. The profile of the local concentration has been obtained by the deconvolution method from the observed dependence of the spectral intensity on the location of the flame in the resonant cavity. The maximum concentration can be estimated to be 2.4×10^{15} atoms/cm^3, which is much higher than the equilibrium concentration calculated from the flame temperature, 1200 K, and the oxygen excess ratio, 0.67. The spectral linewidth (0.01—0.04 mT) and the microwave power saturation of the H atoms depend on the location in the flame. These results strongly suggest that the line broadening and the spin relaxation are principally determined by the collision between the H atoms and the molecular oxygen.

Combustion in high-temperature flames is a complex reaction system which comprises branched-chain reactions carried by free atoms and free radicals as essential reaction intermediates.[1-4] These reaction intermediates have been studied by the optical absorption and emission spectrometric methods and incorporated in elucidating the flame structure.[1,5] Electron spin resonance (ESR) is a powerful technique for studying atomic and free radical intermediates in gas-phase reactions,[6,7] and it has been utilized, though not very extensively, for the study of combustion chemistry. Systematic studies have been reported by Russian workers,[8-21] who have succeeded in detecting the ESR spectra of several free atoms and free radicals from rarefied flames. Westenberg and Fristrom[22] and Eberius *et al.*[23] have studied H and O atoms generated in low-pressure C_2-hydrocarbon and hydrogen–air flat-flames by using the point-by-point sampling of combustion gases. Bennett *et al.*[24] have briefly communicated the detection of H atoms from hydrogen, methane, and propane free-burning flames under ordinary pressure set in an ESR resonant cavity (by the flame-in-cavity method). Later, Samoilov *et al.*[25-28] applied the flame-in-cavity method to study the kinetic aspects of H atoms, mostly in hydrogen–air free-burning flames, though they have not focussed their attention on the nature of the H atoms in the ESR observations. These studies as a whole show that the ESR technique is promising, but must still be developed for studying the intermediates in combustion reactions.

The present investigation is an extention of those by Bennett *et al.* and Samoilov *et al.* It is aimed at fully elucidating the ESR-spectroscopic nature of H atoms in methane–air free-burning flames by the flame-in-cavity method and giving a basis for utilizing this method for combustion-chemical studies. The methane–air flames are the simplest model of hydrocarbon combustion. The present experimental conditions allow us to detect only H atoms, because neither non-S-state atoms nor free radicals in the gas phase can be detected by ESR unless the pressure is so low that the collision broadening is effectively removed.[7,29] However, the study of the H atom concentration and distribution in the flames by themselves are interesting from the combustion-chemical point of view, since H atoms are known to be one of the major reaction intermediates in the fuel-rich combustion of hydrocarbons.[30]

Experimental

The burner used is a modified Bunsen burner, made of thin quartz tubes, the inner and outer tubes of which are 0.4 and 0.9 cm in diameter respectively. It was directly inserted into the cylindrical TE_{011} resonant cavity and fixed by means of a specially designed adapter. Cooling air could flow through a hole in the adapter when required. The burner could be moved up and down along the axis of the resonant cavity.

Methane of a 99.9% purity (research grade) was used as a fuel gas. Air flowed in from a conventional air compressor. These gases were controlled with a glass capillary-flow meter combined with a precise needle valve. Premixed flames were obtained by supplying methane–air mixed gas into the inner tube and then stabilized by letting secondary air flow into the outer tube. Diffusion flames were obtained by letting methane flow into the inner tube, and air into the outer tube. A rough estimate of the flame temperature was made by using a fine Pt–Rh thermocouple covered with quartz.

The ESR measurements were carried out with an X-band straight-detection-type spectrometer with a 100 kHz magnetic-field modulation. The resonant cavity was water-cooled when

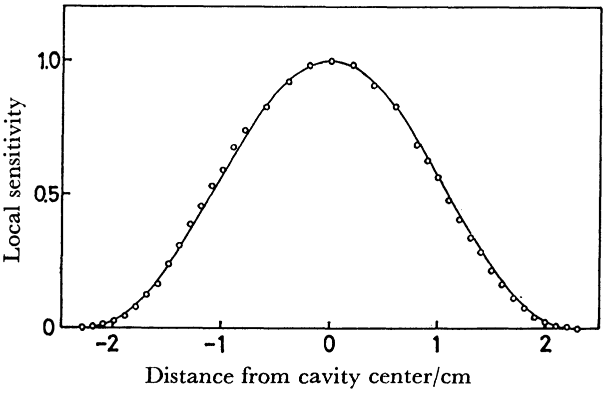

Fig. 1. Local sensitivity of ESR within the resonance cavity of TE_{011} mode.

the flame was set in it. The local sensitivity of the ESR within the resonant cavity was experimentally determined from the observed spectral intensity of a small piece of DPPH by moving it along the axis of the cavity. The sensitivity curve fit well with a sine-square function, as is shown in Fig. 1. The magnetic field inhomogeneity was checked by recording the sharp hyperfine lines of Fremy's salt in an aqueous solution; it was less than 0.002 mT within the effective volume in the cavity. The ESR saturation effect at a high microwave power level was studied at a 100 kHz magnetic-field modulation. The change in the power level was compensated for by an attenuator additionally set immediately before the crystal microwave detector, so that the crystal current was kept constant. This saturation measurement gives signals directly proportional to χ''.[31]

Results and Discussion

ESR Spectra from Diffusion Flames. A methane–air diffusion flame in a burner (with a flow rate of methane of 48 $cm^3 min^{-1}$ and one of air of, 490 $cm^3 min^{-1}$) formed a blue cone *ca.* 0.5 cm high and was stationary only for a limited methane/air ratio. The ESR signal recorded from this diffusion flame was composed of a pair of sharp lines with a separation of 51.0 mT around 330 mT, with a very sharp line at the center (g=2.005). The former is the spectrum due to H atoms. The latter spectrum was too weak for its nature to be studied, so that the entities responsible for this spectrum could not be identified. However, the inverted phase of the spectrum may be said to be due to the emission spectrum caused by the CIDEP effect of short-lived entities. Both the spectra were unquestionably due to unstable reaction intermediates in the flame, because they disappeared when the flame was extinguished.

The width (peak-to-peak of the derivative spectral curve) of the H atom spectrum was 0.15 mT; it remained unchanged when the burner was moved up and down along the cavity axis. In contrast, Bennett *et al.*[24] have reported the width of 0.08 mT for the H atoms in methane–air and propane–air diffusion flames. The difference in the width between the two observations is likely to result from the interaction of the H atoms with different concentrations of paramagnetic entities, such as carbons and soot compounds. The carbons and the soot compounds are the major products in the incomplete combustion of hydrocarbons, and they are generated in the reaction region of the diffusion flames.[32]

The intensity of the H-atom spectrum depended on the position of the burner in the cavity. The maximum intensity was obtained when the top of the luminous cone was situated at the center of the cavity. The variation in the intensity with the burner position almost completely followed the local sensitivity curve shown in Fig. 1. This indicates that the H atoms in the diffusion flame populate a limited region near the luminous cone, though the measurements were carried out for only a limited number of burner positions because of the poor signal-to-noise ratio.

ESR Spectra from Premixed Flames. The methane–air premixed flame, typically with a methane flow rate of 95 $cm^3 min^{-1}$, a primary air flow rate of 600 $cm^3 min^{-1}$, and a secondary air flow rate of 500 $cm^3 min^{-1}$, in the burner was composed of a bell-shaped, luminous inner-cone flame *ca.* 1 cm high and of a faint-blue outer-cone flame. The outer-cone flame seemed to be partially quenched chemically and/or thermally on the wall of the outer quartz tube. The ESR signal from the premixed flame (Fig. 2) was qualitatively the same as that from the diffusion flame; it was composed of a pair of sharp lines due to H atoms and a very weak central, single line due to unidentified entities.

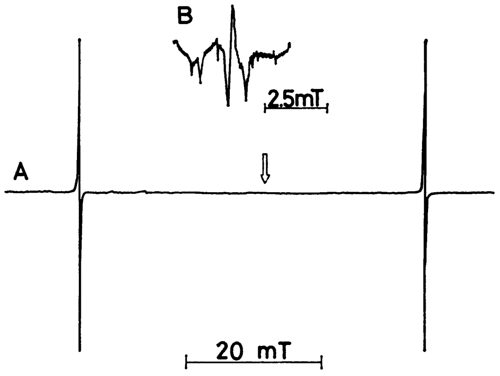

Fig. 2. ESR spectrum from a methane–air premixed flame (A) and the enlarged spectrum of the very weak signal whose resonance field is indicated by the arrow (B).

The linewidth and the intensity of the H atom spectrum varied depending on the position of the burner in the cavity. The microwave-power saturation behavior of the H-atom spectrum also depended on the burner position. These features of the premixed flame contrast with those of the diffusion flame.

The stationary premixed flame in the burner quartz tube could be obtained only within a limited methane/air composition range, that is, only for fuel-rich mixtures.

Concentration Profile of the H Atoms in the Premixed Flame. The intensity of the H-atom spectrum observed from the premixed flame is shown in Fig. 3 (open circles) as a function of the location of the burner in the cavity. The coordinate axis in the absolute concentration was

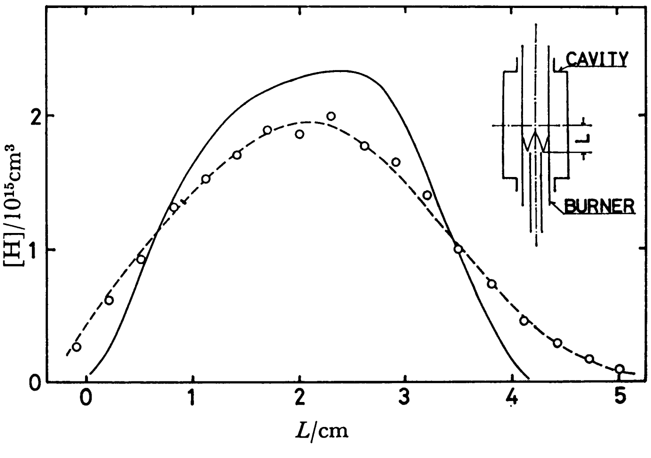

Fig. 3. The concentration profile of the hydrogen atom in a methane–air premixed flame: ○, observed signal intensities; solid line, true profile calculated by the deconvolution, dashed line, reconstructed apparent profile, where L is the distance between the cavity center and the top of the inner tube. (See Text for the details.).

calibrated with reference to the signal intensity of the molecular oxygen of the controlled concentration in the burner[7] by assuming that the H-atom concentration was uniform on a vertical cross-section plane of the burner. The maximum temperature was measured to be 1200 K, which was taken into account in the concentration calibration under the assumption that the temperature was uniform within the flame. The variation in the spectral intensity does not give the concentration profile of the H atom in the flame directly, because the local sensitivity curve of the resonant cavity (Fig. 1) causes the true concentration profile to deteriorate.

In order to get the true profile, the following deconvolution calculation was performed, using the Burger-Cittert method:[33]

$$g(L) = \int a(x)f(L-x)\mathrm{d}x, \tag{1}$$

where $g(L)$ is the observed intensity variation, $a(x)$, the local sensitivity curve (Fig. 1), and $f(L)$, the true concentration profile. The $f(L)$ thus calculated is apparently narrower than $g(L)$, as is shown in Fig. 3 (solid curve). The convergence of the deconvolution treatment was checked by reconstructing $g(L)$, which agreed well with the original data (the reconstructed $g(L)$ is shown by the dashed curve in Fig. 3). The maximum local concentration of the H atoms shifts slightly compared with the maximum signal intensity; it is located 2.5 cm down-stream from the top of the inner tube. Comparing this with the 1 cm height of the luminous inner cone, one can see that the H atoms are located mostly in the down-stream region of the premixed flame.

The above concentration profile was obtained from a Bunsen flame confined in a narrow tube, not from a flat flame (a one-dimensional flame), for which the theoretical calculation of the flame structure is much easier. However, the present results obtained by the flame-in-cavity method are qualitatively consistent with the H atom concentration profile expected from the point-by-point sampling study for flat flames.[22,23]

In the present study, the flame was stationarily obtained for the oxygen excess ratio, α, in the narrow range of 0.63—0.75. The maximum H-atom concentration, *ca.* 2.4×10^{15} atoms/cm^2, was found for $\alpha=0.67$ in the fuel-rich region. This concentration amounts to only 0.4% of the total combustion products, in qualitative agreement with the previous results.[26,34] The equilibrium concentration of the H atoms for $\alpha=0.67$ and $T=1200$ K can be calculated to be 2×10^{-7} % of the total combustion products.[35] The observed H atom concentration is much higher than the equilibrium concentration, as has previously been reported for hydrogen–air flames.[28]

Linewidth of the H Atoms in the Premixed Flame. The spectral linewidth of the H atoms decreased monotonously, as is shown in Fig. 4; the width was 0.04 mT for the H atoms near the top of the inner tube, while it approached the instrumental resolution limit, 0.01 mT, in the down stream region of the flame. The spectral line was much narrower than that in the diffusion flame, anyway.

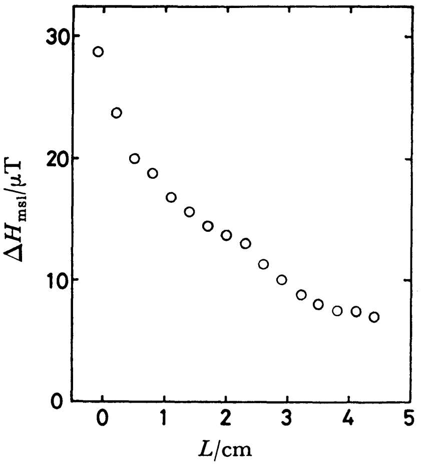

Fig. 4. The variation of the line width of the hydrogen atom in a methane–air premixed flame along the gas stream. L is the distance between the cavity center and the top of the inner tube.

The H atoms possess an angular momentum of only spin. The collision with paramagnetic entities causes the relaxation of the spin states of the H atoms. The linewidth is determined by spin-exchange interaction between the H atoms themselves, magnetic interaction with other paramagnetic entities, magnetic-field inhomogeneity, and a broadening due to high-frequency magnetic-field modulation.[29] Among these factors, the spin-exchange interaction is unimportant, because the variation in the linewidth (Fig. 4) does not run parallel with the concentration profile of the H atoms shown in Fig. 3. There exist a variety of paramagnetic entities in hydrocarbon combustion, *i.e.*, stable molecular oxygen, reactive atomic oxygen, and several free radical intermediates. However, the H atoms are much more abundant than the atomic and free radical intermediates in fuel-rich combustion, so that the interaction between the H atoms and other paramagnetic reaction intermediates contributes little to the line broadening of the H-atom spectrum. On the other hand, the concentration of the molecular oxygen far exceeds that of the reaction intermediates. The interaction with the molecular oxygen will result in the spectral line-broadening of the H atoms. Although Westenberg and de Haas[29] have demonstrated that the molecular oxygen has little effect on the line-broadening when the oxygen concentration is comparable with the H-atom concentration, the linewidth variation observed from the present premixed flame can be attributed to the local concentration of the molecular oxygen, which is consumed mainly in the reaction zone of the premixed laminar flame and which gradually decays in concentration afterwards.[34] The reaction zone of the Bunsen flames is the luminous inner-cone flame.[32]

The variation in the linewidth along the gas stream in flames has been observed for the H atoms in hydrogen–air flames. This has been attributed to the variation in the molecular-oxygen concentration in the flames.[25] In the hydrogen–air flames, the linewidth changes drastically at the stoichiometric mixture ratios from 0.015 to 0.25 mT when the air/fuel ratio is increased. This also suggests the significant contribution of the

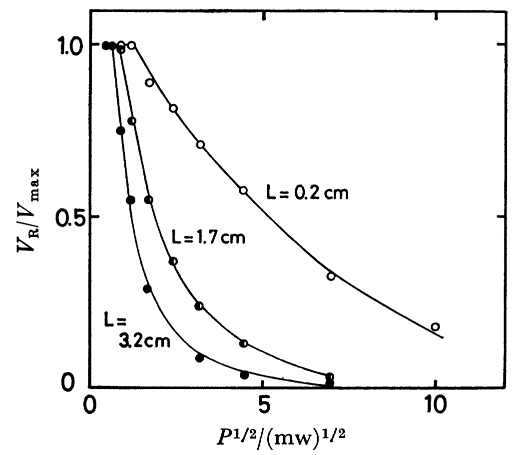

Fig. 5. Power saturation of the hydrogen atom in the different flame position of the methane–air premixed flame.

molecular oxygen to the line-broadening of the H atoms.[24)]

Microwave-power Saturation of the H-atom Spectrum in the Premixed Flame. With an increase in the microwave power incident into the resonant cavity, the spectral lines of the H atoms became broader and the spectral intensity decreased simultaneously. The saturation of the spectral intensity is shown in Fig. 5 by simply plotting the peak-to-peak height of the spectrum as a function of the square-root of the microwave power. Although the analysis of the saturation curves is essentially complex because of the high-frequency field modulation (rapid passage condition), the plotted intensity is recorded so as to be parallel with χ'', as was mentioned in the Experimental section.

It is obvious from Fig. 5 that the H atoms in the luminous inner cone (reaction zone) are comparatively little saturated, while those in the down-stream region in the flame are readily saturated, with the increase in the microwave power. According to Westenberg and de Haas,[29)] the spin-exchange collision between the H atoms and the molecular oxygen causes a remarkable reduction in the T_1 of the former. The observed dependence of the saturation behavior on the location in the flame is attributable to the local concentration of the molecular oxygen: the concentration initially decreases remarkably in the reaction zone, so that the T_1 of the H atoms becomes longer in down stream. This result is consistent with that of the linewidth variation.

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