  Bull. Chem. Soc. Jpn., 56, 2559—2561 (1983) 

# ESR Studies of Bunsen-type Methane-Air Flames. I. Effects of the Entrainment and Diffusion of Secondary Air on the Chemical Reactions in the Flame

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(Received January 5, 1983)

H atoms in a Bunsen-type methane-air flame have been studied by observing their ESR signals at different flow rates of $O_2$ and $N_2$ in a synthetic secondary air. The optical emissions from excited CH, $C_2$, and OH radicals in the same flame have been also studied. It has been found that an increased $O_2$ flow rate produces changes in the intensity of the ESR and emission signals, and that it also increases the burning velocity in the inner-cone flame. An increased $N_2$ flow rate, on the other hand, has almost no effect on the flame. The inner-cone of a Bunsen-type flame is, therefore, not a completely premixed flame; it is affected chemically by the secondary air.

A Bunsen flame is roughly characterized as a double flame: an inner, premixed flame propagating through the combustible gas mixture(usually fuel-rich) against the gas stream, and an outer, diffusion flame where further combustion of the gas mixture is assisted by the surrounding secondary air. Secondary air plays an important role in stabilizing a Bunsen flame.[1] Its entrainment and diffusion into the flame have great effects on the flame characteristics and flame chemistry, but these effects have not yet been elucidated.

Electron spin resonance(ESR) has been proved to be a convenient means for observing atomic and free radical intermediates in combustion reactions.[2-5] Recently we ourselves have reported an ESR study of methane combustion where the nature of the H atom ESR signal and the spatial distribution of H atoms were studied by inserting a flame burning under ambient pressure directly into the resonant cavity.[3] Although such a flame-in-cavity method allows neither the detection of species other than H atoms(because of the collisional broadening of the resonance lines) nor a detailed examination of the distribution of the H atoms, it is a convenient and useful method for studying the chemical aspects of flames by observing the dependence of the total H-atom concentration on the burning conditions. Our previous investigation has, therefore, now been extended to get a picture of the chemical effects of the entrainment and diffusion of secondary air by examining the H-atom concentrations at different flow rates and compositions of a mixture of $O_2$ and $N_2$ acting as the secondary air. Some excited radicals were also detected in the flame by using optical-emission spectrophotometry.

## Experimental

A burner with three concentric quartz tubes, one outside the other, was constructed. In the innermost tube (4 mm$\phi$) the premixed combustible gas was allowed to flow. The flame was anchored on top of this tube. The second tube (18 mm$\phi$) was the combustion room, and the secondary air was let flow through it. The outermost tube (22 mm$\phi$) was for the flowing of the coolant air. All gas-flow rates were regulated by flow meters with precision needle valves. The premixed combustible gas consisted of a mixture of methane (99.0% purity), 90 cm$^3$/min, and air, 500 cm$^3$/min. The secondary air was a mixture of $O_2$ and $N_2$. Its composition and flow rate were varied by keeping the rate of one component in the mixture constant while varying the other. Thus, for an $O_2$ flow of 65 cm$^3$/min, $N_2$ was varied between 50 and 260 cm$^3$/min, and for a $N_2$ flow of 170 cm$^3$/min, $O_2$ was varied from 58 to 95 cm$^3$/min. These constant flows were chosen because an $O_2/N_2$ mixture with these flow rates maximized the ESR signal of the H atoms.

The flame height was estimated from close-up color photographs taken of the flame under different burning conditions. The scale of the pictures was determined by comparing the diameter of the innermost tube as measured on the photographs with its real size.

The H atoms present in the flame were detected by means of ESR (a Varian E-109 spectrometer, X-band with 100 kHz modulation) using the flame-in-cavity method, which has been described elsewhere.[3] A recent improvement of the experimental method was the use of a cylindrical $TE_{011}$ large-access cavity (Varian, Model E-235), which accepts a large burner. A large burner was needed for the flame to be stabilized under a variety of burning conditions.

The excited radicals in the flame were studied from their optical emission spectra. These were recorded by inserting the burner into the detection chember of a conventional fluorescence spectrophotometer (Hitachi, Model, MPF-2A).

## Results and Discussion

*Apparent Burning Velocity.* The flame showed a bright blue inner-cone flame and a faint bluish outer flame. The height of the inner flame decreased with an increase in the $O_2$ content in the secondary air, as is shown in Fig. 1A. At an $O_2$ flow rate of less than 55 cm$^3$/min, the flame was not stably anchored at the top of the burner, but started to lift off. Under the present experimental conditions, the apparent burning velocity in the inner flame can be roughly approximated as inversely proportional to the inner-flame height.[6] The apparent burning velocity thus increases with an increase in the $O_2$ flow rate in the secondary air. At an increasing $N_2$ flow, the tip of

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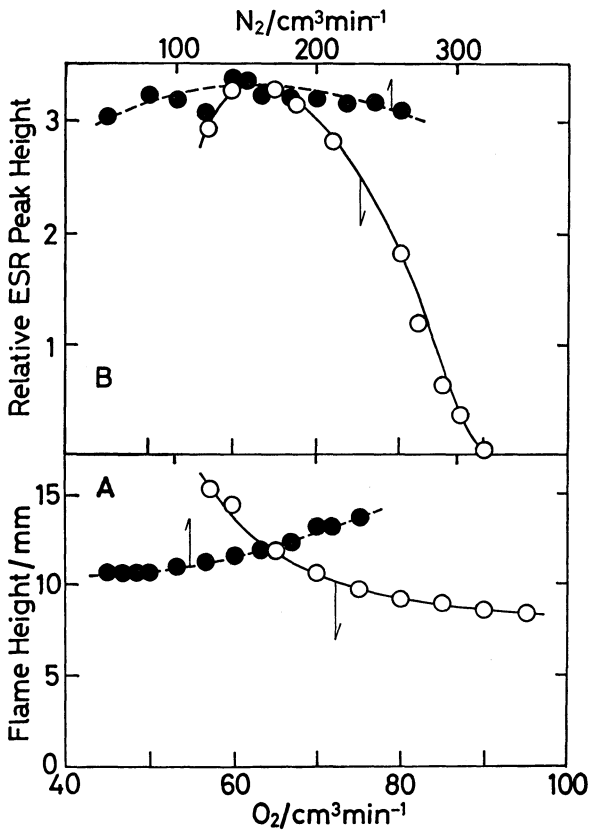


Fig. 1. Dependence of (A) the height of the inner cone flame and (B) the ESR intensity of the H atoms in a Bunsen-type methane-air flame on the composition of the secondary air. Data shown by open circles were obtained for a constant $N_2$ flow of 170 $cm^3$/min. Data shown by closed circles were for a constant $O_2$ flow of 65 $cm^3$/min.

the inner flame became less and less luminous, and the outer flame disappeared. The inner cone height increased, as is shown in Fig. 1A, indicating a decrease in the apparent burning velocity.

These observations agree well with Kimura and Ukawa's results obtained from a propane/air flame where an increased $O_2/(O_2+N_2)$ ratio raised the burning velocity.[7] Apparently the secondary air affects the combustion characteristics in the inner flame.

*H Atoms in the Flame.* The ESR spectrum observed from the flame consisted of two sharp lines with a hyperfine separation of 51.0 mT centered at 330 mT. It is assigned to H atoms. The sensitivity of the ESR measurements depends on the position in the resonant cavity. As a matter of fact, the spectral intensity varied depending on the location of the burner in the cavity along the cavity axis. This dependece was more pronounced in the present study than in the previous study.[3] The difference is attributed to the fact that, in the present study, the H atoms are confined in a more limited region of the flame burning in a wider combustion room. This is consistent with our previous result, obtained by the point-to-point probe-sampling method,[4] that the H atoms are mostly located within 1 cm downstream from the flat inner flame of a free-burning methane-air Bunsen flame.

The spectral intensity of the H atoms in the flame under different burning conditions was examined by locating the burner so as to maximize the intensity. It was found to depend drastically on the flow of $O_2$ in the secondary air, as can be seen in Fig. 1B. The $O_2$ content in the secondary air apparently affects the chemical reaction in the inner cone. The $N_2$ flow, however, can be changed over a wide interval, thereby changing the total flow of the secondary air, without having much effect on the H-atom signal. As an increase in the $N_2$ flow is accompanied by a decrease in the apparent burning velocity, it seems that even though the reaction zone is broadened (diluent effect), the chemical reactions are essentially unaffected.

Neither the concentration profile in the flame nor the absolute concentration was determined in the present study. However, the observed ESR intensity can be regarded as a measure of the H-atom steady-state concentration averaged over the whole flame. The confinement of the H atoms in a narrow region excludes the possibility that the change in the ESR intensity with the varying $O_2$ flow may be primarily due to the change in the flame shape. Actually, the intensity changed little, though the reaction zone was apparently broadened with the increase in the $N_2$ flow. The temperature in the flame monitored with a fine Pt–Rh thermocouple was the highest in or close to the inner-cone flame and changed from 1620 to 1760 K, depending on the burning conditions. The ESR intensity shown in Fig. 1B has not been corrected with the flame temperature, because the temperature effect is of no significance.

It has previously been demonstrated by probe-sampling a Bunsen flame and ESR detection that H atoms are abundant in the fuel-rich inner flame and that they are consumed by reacting with $O_2$, probably coming from the secondary air:[4]

$$H + O_2 \rightarrow O + OH. \quad (1)$$

Here we have found that the apparent burning velocity in the inner flame increases at higher $O_2$ flow rates, while the H-atom steady-state concentration is tremendously reduced(see Fig. 1). This results from Reaction 1, effectuated by the involvement of $O_2$ from the secodary air even in the inner flame. The overall combustion reactions are accelerated, the lifetime of the H atoms being reduced. The chain-carrying intermediates which support the flame at a low $O_2$ content in the atmosphere surrounding the flame are H atoms, while at a high $O_2$ content O atoms and OH radicals are chain carriers. These observations are consistent with Pickering and Linnett's analysis of the relations among the $O_2$%, the burning velocity, and the calculated equilibrium concentrations of H, O, and OH for a premixed ethylene/air flame.[8]

*Excited Free Radicals in the Flame.* An example of the optical emission spectra recorded from the flame is shown in Fig. 2. According to the literature data,[9] the observed spectrum is composed of emission lines due to OH, CH, and $C_2$ radicals and a broad continuum due to $CO_2$. Weak emission lines due to CHO radicals are also discernible. It is known that

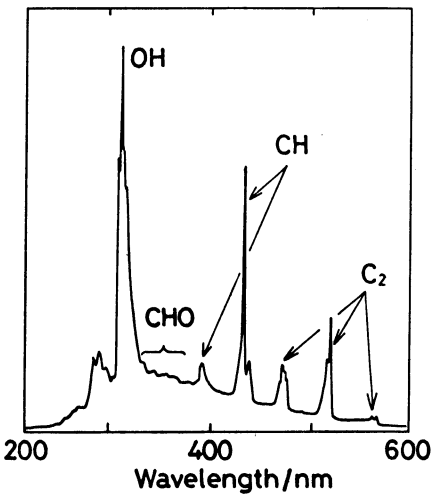


Fig. 2. An example of optical emission spectra recorded from the luminous inner cone flame of a Bunsen-type methane-air flame. No correction of the photometer sensitivity was made.

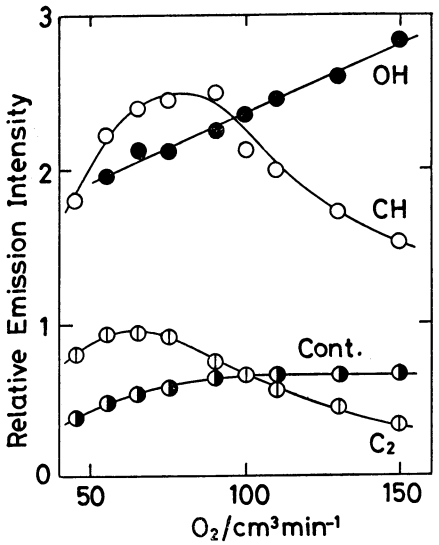


Fig. 3. Dependence of the optical emission from excited free radicals (and continuum spectrum due to $CO_2$) on the flow rate of $O_2$ in the secondary air. The $N_2$ flow rate was kept constant at 170 $cm^3$/min. The emission comes mostly from the luminous inner cone.

the emissions of Bunsen flames almost exclusively originate from the inner premixed flame and that they are chemiluminescence in nature.[9] The exception is the OH emission, which comes from the outer flame as well.

The effects of the composition of the secondary air on those chemiluminescences are pictured in Fig. 3. The emission intensities are sensitively dependent on the $O_2$ flow rate in the secondary air. The OH emission intensity increases steadily with an increase in the $O_2$ flow rate. The CH and $C_2$ emissions have maximum intensities at the $O_2$ flow rates of 90 and 60 $cm^3$/min respectively. These emissions come from the corresponding electronically excited radicals, which are generated through side-reactions in the overall process of combustion.[9] However, the dependence of these intensities on the $O_2$ flow rate indicates the far-reaching involvement of $O_2$ from the secondary air in the chemical reactions in the inner flame. Similar intensity variations have been reported for the CH and $C_2$ emissions in low-pressure premixed hydrocarbon flames with a varied fuel-to-air ratio.[9]

*Conclusions.* Bunsen-type burners are now incorporated in many gas appliances, yet the combustion chemistry of these burners has been but little elucidated because of their complexity as chemical reaction systems. The present investigation has been focussed on one of the principal reaction intermediates of combustion, the H atoms, in the methane-air Bunsen-type flame. It has been found that the H-atom ESR spectrum is significantly affected by the $O_2$ content in the secondary air. These results, combined with those of the optical-emission study of the excited free radicals, indicate that the inner cone of the Bunsen-type flame is not a wholly premixed flame, but that it is affected by the entrainment and diffusion of the secondary air. This provides a convenient experimental method to study the chemical reactions in combustion by simply mixing an additive in the secondary air.

The present authors are grateful of the Toyota Foundation for the financial support (1977—1979) needed to initiate the present investigation. One of the authors (O. C.) also acknowledges the support of the Yamada Foundation and the Swedish Natural Science Research Council for his stay at Hokkaido University.

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