ESR and Mass-Spectrometric Studies of Methanol Combustion. I. The Correlation between Labile and Stable Chemical Entities in Free-Burning Methanol-Air Flames under Atmospheric Pressure

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The concentration profiles of labile (H, O, and OH) and stable chemical entities (CH_3OH, O_2, CH_2O, H_2, H_2O, and CO_2) in premixed methanol-air flames under atmospheric pressure have been studied by the probe-sampling-ESR method combined with mass-spectrometric detection. The concentrations of the labile intermediates have been determined by correcting their destruction in the sampling probe caused by gas-phase reactions, wall reactions, and reactions at the pinhole of the probe. The observed profiles are in good agreement with the numerical model developed previously by Westbrook and Dryer, except that the concentration changes in all the entities are quicker than expected. The dependence of the maximum concentrations of the labile intermediates on the composition of the premixed gas is essentially the same as that observed for the methanol-air flames at low pressure.

The combustion of common fuels consists of chain reactions, with atomic H and O, and the OH radical as principal chain carriers. As these labile intermediates are paramagnetic, the electron spin resonance (ESR) is possibly a useful method for combustion-chemical studies. Actually, since the pioneering work by Westenberg and Fristrom,[1)] a combination of the ESR method and the probe-sampling technique has been used for examining the concentration profiles of H and O atoms in combustion flames.[2–4)] In 1980, Noda et al.[5)] succeeded, as a result of the continual progress in ESR technique, to detect simultaneously all the labile intermediates, H, O, and OH, in a methane-air flame; they thus showed the wide applicability of the ESR method to this research field. Since then, there have appeared extensive studies of the concentration profiles of the unstable intermediates in combustion flames by means of the ESR method.[6–8)]

The present investigation concerns the chemical reactions in methanol-air flames under atmospheric pressure. This is an extension of our previous ESR investigation,[7)] where only the profiles of the labile intermediates were determined. The purpose of the present investigation was to determine comprehensively both the labile intermediates and the stable entities, including reactants and final products, by combining the mass spectrometric method with the probe-sampling-ESR method.

The combustion chemistry of methanol is attracting interest, because methanol is expected to be one of the future alternatives to petroleum resources. It is one of the simplest model fuels other than hydrocarbons for combustion-chemical studies, and so it has been extensively studied both theoretically and experimentally. Westbrook and Dryer have developed a numerical model for laminar flames of methanol-air mixtures.[9)] This model has been substantiated by the agreement between the concentration profiles of the stable entities calculated based on the model and those observed experimentally from low-pressure methanol-air flames by Akrich et al. using the gas-chromatographic method.[10)] More recently, Pauwels et al. have determined the concentration profiles of labile intermediates in the low-pressure methanol-air flames by using the ESR method, and have claimed that the observed dependence of the maximum concentration of H, O, and OH on the composition of the premixed gas agrees well with that predicted on the basis of the model.[6)] Very recently, Andersson et al.[11)] have studied the concentration profiles of both labile intermediates and stable entities in the flame by means of the mass-spectrometric method. They[11,12)] have also examined the numerical model on the basis of their experimental data and the rate constants recently proposed for some elementary reactions,[13)] and have argued that the diffusion constants of the chemical entities used in the previous model[9)] were too large, while the rate constant for the CHO decomposition were too low. In order fully to elucidate the chemical reactions in the methanol combustion, experimental data are still needed on the concentration profiles of both labile intermediates and stable entities simultaneously observed in the methanol-air flame under various conditions. The present investigation was aimed at supplementing the previous experiments on the low-pressure methanol-air flames.[6,10,11)]

Experimental

The burner used was made of brass and had a mouth (8 mm in diameter) shaped in such a way that the distribution of the gas-flow velocity in the cross-section area of the mouth was approximately uniform.[7)] The secondary air was not allowed to flow through in order to keep the mixing of the surrounding air into the flame as low as possible.[14)] A fine stainless steel grid made of 0.3 mm meshes was put on the burner mouth to prevent flash-back. The flow rate of air from a cylinder was controlled with a precision needle valve. Liquid methanol was continuously injected into the air stream, which had been preheated to 403 K.

The reacting gas was continuously sampled from the flame through a pinhole (about 0.1 mm in diameter) of a

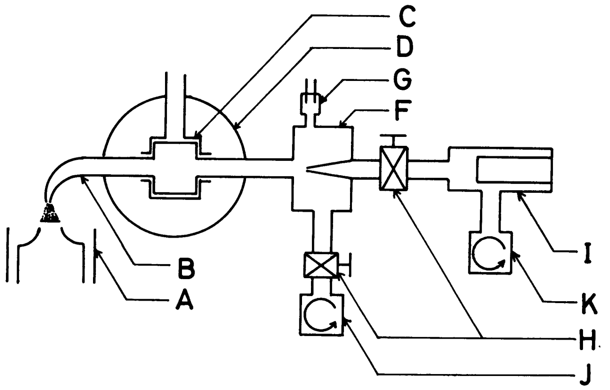

Fig. 1. Schematic view of the experimental set-up. A; burner, B; sampling probe, C; ESR cavity, D; magnet, F; condenser, G; vacuum gauge, H; vacuum valve, I; quadrupole mass spectrometer, J; primary pumping system (mechanical booster and rotary pumps), K; secondary pumping system (diffusion and rotary pumps).

quartz sampling probe, led to an ESR cavity, and subjected to ESR measurements with an X-band spectrometer (Varian, Model E-109) equipped with a large access cavity (TE_{011} mode, Model E-235) at a low pressure (24—80 Pa) in order to examine the concentrations of H, O, OH, and O_2. The calibration of the ESR signal intensities to determine the absolute concentrations within the cavity was made with reference to the intensity of O_2 (for H and O) or NO (for OH) of known concentrations.[15,16] A part of the sampled gas was further led to a quadrupole mass spectrometer (Nihon Shinku, Model MSQ-150A), and the concentrations of stable entity in it were measured at a total pressure of 10^{-3} Pa in the ionization chamber. The whole experimental set-up is shown schematically in Fig. 1. Washing the sampling probe with HF, with NaOH, and then with HNO_3 was found to be the best treatment to prevent the destruction of labile intermediates on the wall during sampling, as has been reported previously.[6]

The gas was sampled at several positions on the center axis of the flame by moving the flame with respect to the sampling probe. The flame temperature was measured with a SiO_2-coated Pt/Pt-Rh thermocouple (0.1 mm in diameter) at the same positions. No correction was made for radiation loss.

Results and Discussion

Flame and Observed Spectra. The flame obtained consisted of a flat, bright, bluish region and a faint, outer, conical region. The former lay 1—2 mm above the burner mouth and was essentially of the premixed-flame nature. The latter had the diffusion-flame nature, and the visible boundary of its top lay 10—18 mm above the burner mouth, depending on the composition of the premixed gas. The flame was found to be axially symmetric both in appearance and in the concentrations of the chemical species. No visual change was observed on inserting the sampling probe. The flow rate of the gas with a different composition was kept constant at 1.0 l min^{-1}. The sampled gas was cooled by adiabatic expansion and showed nearly the ambient temperature.

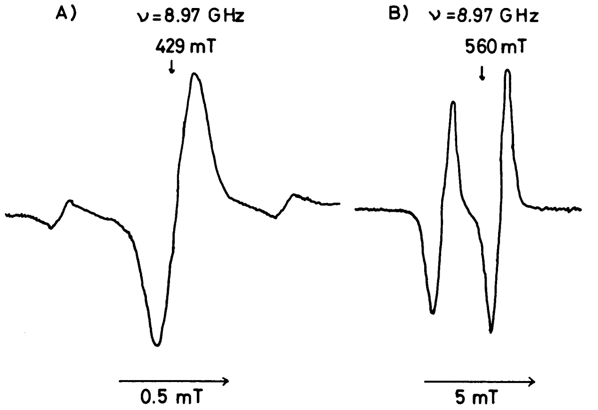

Fig. 2. Typical examples of ESR spectra due to (A) O atoms and (B) OH radicals recorded at 24 Pa.

The ESR spectra due to $H(^2S)$, $O(^3P_2, ^3P_1)$, $OH(^2\Pi_{3/2}, ^2\Pi_{5/2})$, and $O_2(^3\Sigma_g^-)$ were observed from the sampled gas, as in the previous studies of methane-air[5] and methanol-air flames.[6,7] A part of the observed ESR spectra, where the spectral intensity was monitored, attributable to O and OH is shown in Fig. 2. The concentrations of these labile intermediates in the sampled gas within the ESR cavity were determined from the double integration of the observed differential spectral curves after the calibration mentioned in the Experimental section.

Intense mass spectra were detected at m/z=2, 14, 16, 17, 18, 28, 31, 32, and 44 from the sampled gas. The concentration of H_2, H_2O, CH_3OH, and CO_2 were determined directly from the spectral intensities at the mass number of 2, 18, 31, and 44 respectively. Because the peak at m/z=32 due to parent CH_3OH ions overlapped with the peak of the O_2 ions, the CH_3OH concentration was determined from the fragment peak at m/z=31. The concentration of CH_2O was determined by subtracting the contribution of CH_3OH from the spectral intensity at m/z=30. Each spectral intensity was calibrated with reference to the intensity of the corresponding gas of a known concentration. The uncertainty of the concentrations thus determined was less than 10%. The concentration of CO could not be determined because of the overlapping of the N_2 spectrum.

Reactions in the Sampling Probe and Their Correction. A serious problem involved in the probe-sampling procedure is the destruction of labile intermediates in the probe before they can be measured. There are two possible types of processes responsible for the destruction; one is bimolecular gas-phase reactions in the probe such as

$$O + OH \longrightarrow O_2 + H, \tag{1}$$

$$OH + OH \longrightarrow H_2O + O, \tag{2}$$

with a low activation energy, while the other is first-order reactions on the wall.

It was found that the logarithm of the mole fractions of the labile intermediates decreased linearly with the increase in the sampling pressure in the pressure range of 40—80 Pa, and that the gradient of the linear decrease was almost unchanged when the sampling probe was about doubled in length. If the above linear dependence on the sampling pressure is due to the first-order destruction on the wall, the gradient could be expected to be proportional to the length of the probe (residence time in the probe).[6] Therefore, the actual destruction of the labile intermediates in the probe cannot be described simply by the first order wall reaction.

Figure 3 shows the observed concentrations of the labile intermediates in the ESR cavity as a function of their residence time in the probe before reaching the ESR cavity. The residence time was changed by using extension tubes of different lengths. The pressure in the probe was kept constant at 40 Pa. All the H and O atoms and OH radicals appear to follow the first-order decay with different rate constants. However, the extrapolation of the observed straight lines to t=0 will not give the actual concentration of the labile intermediates in the flame, for the bimolecular gas-phase reactions become important in the early period.

Using the rate constants, $k_1=1.0\times 10^7$ and $k_2=1.5\times 10^3 T^{1.14}$ $m^3\,mol^{-1}\,s^{-1}$, reported by Warnatz,[17] and also the observed concentrations of all the chemical species involved in Reactions 1 and 2, and assuming a constant temperature, 300 K, of the sampled gas in the probe, the rate constants for the wall reactions were determined by computer simulations to be 1.71×10^2, 1.53×10^2, and 1.07×10^3 s^{-1} for H, O, and OH respectively for the present sampling conditions. The solid curves in Fig. 3 are the best-fitting simulation curves. The destruction caused by the bimolecular gas-phase reactions is significant for O atoms when the OH concentration is high.

Pauwels et al.[6] first reported that the wall reactions are primarily important in the destruction of the labile intermediates at low sampling pressures (5.3—13.3 Pa) and at low temperatures, but they have very recently suggested that the gas-phase reactions should not be ignored.[8] The correction for the destruction of the labile intermediates in the sampling probe made in their recent study is essentially the same as that developed independently in the present study.

Another difficult problem inherent in the probe-sampling is the destruction of labile intermediates caused by reactions at the pinhole and/or at the very end of the probe tip. The temperature and pressure of the sampled gas are necessarily much higher there than in the main body of the sampling probe, where the sampling gas has already been cooled by adiabatic expansion. Biordi et al.[18] have studied the concentration of chemical species in low-pressure CH_4-O_2-Ar flames by using molecular-beam mass spectrometry, and examined the change in the concentration profiles with sampling probes of different cone angles. Their results indicate that the destruction of OH is much more remarkable with small angled cones (smaller than 40°) than with large angled cones. We confirmed the same effect of the cone angle by using two probes, 40°-angled and 15°-angled cones: the observed OH concentrations were higher for the former probe. It should be noted, however, that the observed concentrations of H and O showed almost no difference between these two probes.

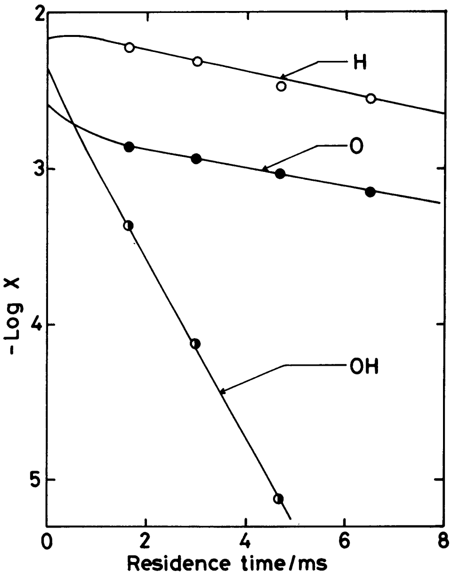

Fig. 3. The dependence of the observed concentrations (X, in mole fraction unit) of the labile intermediates in sampled gas on the residence time of the gas in the sampling probe before reaching at the ESR cavity for the methanol-air flame of stoichiometric composition under the atmospheric pressure. The curves are determined by simulating the destruction of the labile entities due to the gas phase reactions and the wall reactions in the probe (see text for detail).

The effect of the surface treatment of the probe is also significant for the destruction at the pinhole. The observed OH concentrations were found to be three times higher for the 40° cone angle and ten times higher for the 15° cone angle after the HF treatment than before, though the normal wall destruction was not affected by the HF treatment. There is no way at the moment to determine the correction factor for the OH destruction at the pinhole, and so we assumed there to be no destruction at the pinhole for the HF-treated 40°-angled probe. As a whole, the ambiguity in the ESR determination of concentrations is the largest for OH, but it is thought to be within the factor of 2.

Concentration Profiles. The chemical reactions in the outer flame region are strongly dependent on the physical conditions, such as the diffusion of the surrounding air into the flame. The concentration profiles of only the labile intermediates, mostly in the down-stream region, have been observed and discussed in previous studies of methane-air[5] and methanol-air[7] flames. In the present study, therefore, we focussed our attention on the concentration profiles in the inner flame region, where the behavior of the profiles shows more inherently the chemical nature of the combustion process. The concentration profiles of both labile intermediates and stable entities in the flame were determined for three different equivalence ratios, defined as $\phi=([\text{fuel}]/[O_2])_{\text{actual}}/([\text{fuel}]/[O_2])_{\text{stoichiometric}}$, of the premixed gas. The results are shown in Figs. 4—6, where all the concentration are expressed in mole fraction units. The concentrations of the labile intermediates are presented after correction for the partial destruction during sampling attributable to the gas-phase and wall reactions. The equivalence ratios examined were in the range of 0.82—1.53, because it was difficult to stabilize the flame in the low-ϕ (fuel-lean) region.

The results obtained from the stoichiometric flame (Fig. 4) show that methanol is totally consumed within the region 1 mm from the burner mouth. Correspondingly, the O_2 concentration also decreases in this region, sharply at first and then slowly. The generation of the final combustion products, CO_2 and H_2O, start at or close to the burner mouth, and their concentrations reach the plateau value when the methanol is completely consumed. The H_2O generation is observed to occur in an earlier region than the CO_2 generation. This observation is consistent with their formation routes: for H_2O, the reaction

$$CH_3OH + OH \longrightarrow CH_2OH + H_2O, \tag{3}$$

occurring in early stage of the combustion is one of the main routes, while CO_2 comes mainly from this reaction;

$$CO + OH \longrightarrow CO_2 + H, \tag{4}$$

which occurs at a later stage of the combustion.

Among the stable intermediate entities, CH_2O appears only in a narrow region and shows a concentration maximum. In contrast, H_2 is distributed over a wide region and shows two concentration maxima. The first H_2 maximum coincides in location in the flame with the CH_2O maximum. The high local concentration of CH_2O is in accord with Bowman's proposal,[19] based on a shock-wave study, that the main oxidation path of methanol at high temperatures is: $CH_3OH \rightarrow CH_2OH \rightarrow CH_2O \rightarrow CHO \rightarrow CO \rightarrow CO_2$.

The concentrations of all the labile intermediates increase sharply, simultaneously with the rapid consumption of CH_3OH and O_2. According to the model of Westbrook and Dryer,[9] the most important reactions for the methanol consumption are:

$$CH_3OH + OH \longrightarrow CH_2OH + H_2O, \tag{3}$$

$$CH_3OH + H \longrightarrow CH_2OH + H_2, \tag{5}$$

$$CH_3OH + H \longrightarrow CH_3 + H_2O, \tag{6}$$

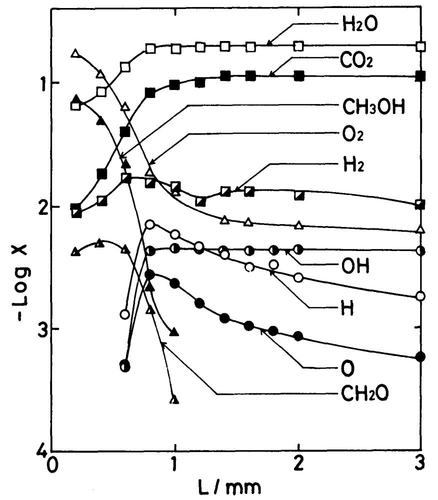

Fig. 4. Concentration profiles of both labile intermediates and stable entities in the methanol-air flame of stoichiometric composition (ϕ=1.0). The concentrations are presented in mole fraction unit (X) in the logarithmic scale. The distance (L) is between the burner mouth and the sampling point on the center axis of the flame.

$$CH_3OH + O \longrightarrow CH_2OH + OH, \tag{7}$$

and the H thus generated reacts with O_2 thus:

$$H + O_2 \longrightarrow O + OH. \tag{8}$$

The observed results agree qualitatively with the model of methanol-air combustion. The concentrations of H and O decrease slowly after passing their maxima, while that of OH remains constant. A closer examination of Fig. 4 may reveal that the sharp increase in the labile intermediates appears to be somewhat later than the rapid drop in the concentrations of CH_3OH and O_2 and the rapid increase in the concentrations of H_2O and CO_2. This apparent delay can be attributed to the effect of the diffusion of the chemical species in the flame; it will be discussed in detail in the following paper of this series.[20]

The peak of the CH_2O concentration appears to be well in advance of the accumulation of the labile intermediates. This may be attributed to its formation by the efficient reaction:

$$CH_2OH + O_2 \longrightarrow CH_2O + HO_2, \tag{9}$$

suggested by Westbrook and Dryer.[9]

Figures 5 and 6 show the effect of the increase in the equivalence ratio. Although the general features of the concentration profiles are the same for all the equivalence ratios examined, the maximum concentrations of the labile and stable intermediates depend on the ϕ value. It may be noted that the OH concentration shows slow decrease after passing through its maximum under fuel-rich conditions.

As the effect of the equivalence ratio was found to be the most noticeable for the maximum concentration of the labile intermediates, it was studied in detail over a

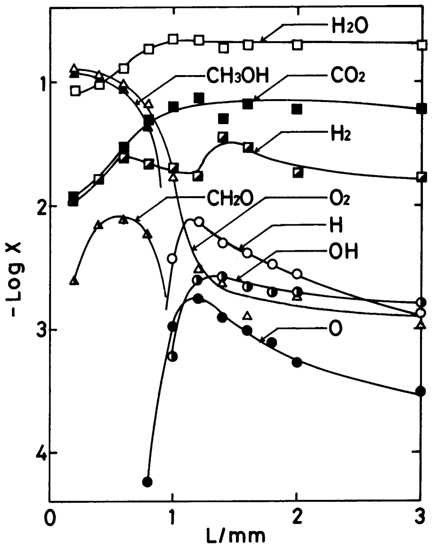

Fig. 5. Concentration profiles for the methanol-air flame of equivalence ratio ϕ=1.2.

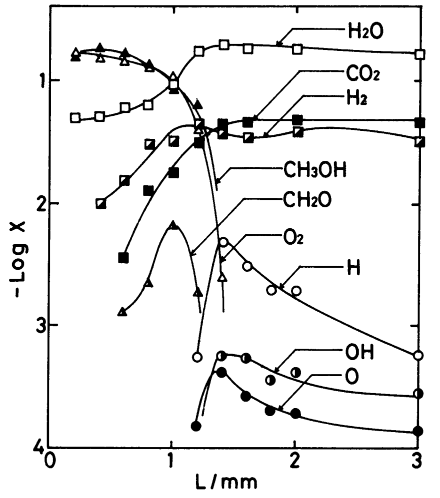

Fig. 6. Concentration profiles for the methanol-air flame of equivalence ratio ϕ=1.5.

wider range of ϕ, 0.82—1.53, as shown in Fig. 7. H shows a broad maximum around ϕ=1.1. The maxima for O and OH lay at smaller ϕ values. These results, essentially the same as those reported by Pauwels et al.[6] for the low-pressure methanol-air flames, indicate that the dependence of the maximum concentration on the equivalence ratio is little dependent on the pressure.

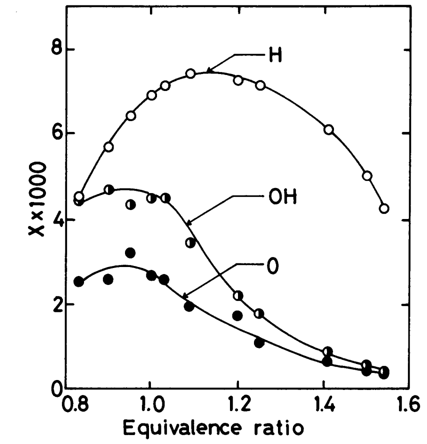

Fig. 7. Dependence of the maximum concentrations of the labile intermediates in the methanol-air flame on the equivalence ratio.

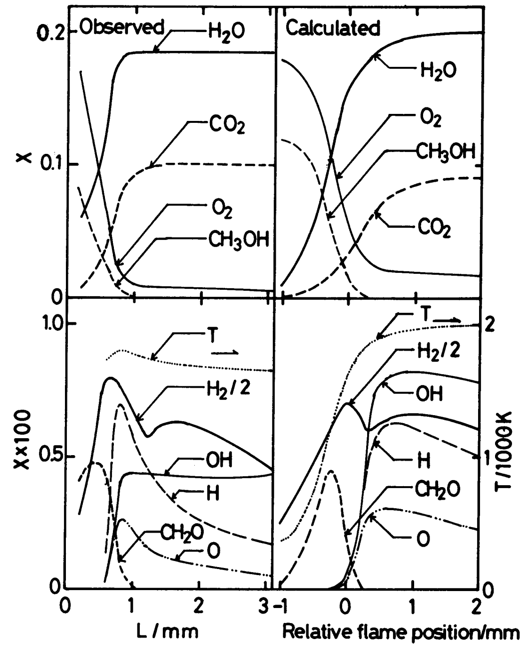

Fig. 8. Comparison of the labile intermediates and stable entities observed by the ESR and mass spectrometric methods and those calculated by Westbrook and Dryer based on the numerical model for the methanol-air flame under atmospheric pressure.

Comparison with the Numerical Model. Westbrook and Dryer[9] have constructed a comprehensive numerical model of methanol combustion, which includes 26 chemical species and 84 elementary reactions. Based on this model, they have then calculated the concentration profiles by computer-simulation for one-dimensional methanol-air premixed flames under different pressures. Model calculations for methanol combustions have recently been made also by other research group,[11-13] but they have not shown the concentration profiles under atmospheric pressure.

The observed concentration profiles are compared with the calculated ones in Fig. 8 for the flame of ϕ=1.0. One can see suite a good coincidence between the observed and calculated profiles for both stable entities and labile intermediates, though the calculations have made for an ideal adiabatic flame isolated from its surroundings. The observed maximum concentrations of O and H are in good agreement with the calculated values. The decrease in the observed H and O concentrations after the maximum is faster than that expected from the calculations. This may be attributed to the heat loss to the surroundings, which has not been taken into account in the model calculations. Among the labile intermediates, the concentration of OH shows the poorest agreement in absolute value, but the difference between the observed and the calculated values is within a factor of 2. This difference may be due partly to the actual temperature being lower than the calculated one and partly to the destruction of OH at the pinhole of the probe during sampling.

The calculations[9] have predicted a double-peaked concentration profile for H_2; the first peak is predominantly attributable to Reaction 5, and the second peak, to Reaction 10:

$$CH_3OH + H \longrightarrow CH_2OH + H_2, \qquad (5)$$

$$H_2O + H \longrightarrow H_2 + OH. \qquad (10)$$

This prediction was satisfactorily proven by the present observation of the two peaks. The observed concentration change in CH_3OH, H, H_2O, and OH is consistent with the predominance of Reactions 5 and 10, leading to the H-generation around the peak positions.

Perhaps the most significant difference between the observation and the calculation is that the transient change in all the observed concentration profiles is quicker than that of the calculated profiles. We examined the perturbation of the flame attributable to the sampling probe in a separate experiment for the methane-air flame and found that the insertion of the sampling probe into the flame caused no serious change in the concentration profiles. The effect of the spatial resolution of the sampling procedure is, if any, to flatten the transient change in the concentration profiles. It can, therefore, be suggested that the calculated concentration change is somewhat too slow. The same difference between calculation and observation has been found for low-pressure methanol-air flames; it has been suggested that it is attributable to too big diffusion coefficients and too small a rate constant for the CHO decomposition used in the calculations.[11,12]

Conclusions

In order to elucidate the chemical reactions involved in the complex combustion process, it is indispensable to determine experimentally the distribution of as many chemical species as possible, both stable and labile, in the combustion system. In the present investigation, the concentration profiles in the methanol-air flame under atmospheric pressure were comprehensively determined by means of ESR measurements combined with mass-spectrometric measurements. The results obtained are totally consistent with the reaction scheme widely accepted, and are in fairly good agreement with the prediction based on the numerical model.[9]

There is no essential difference between the present observations at atmospheric pressure and the previous observations for the stable entities[10,11] and for the labile entities,[6,11] all at low pressures. The experimental conditions of combustion-chemical studies are generally difficult to control; therefore, the results obtained here are not precise enough to check the numerical model in detail. However, it can safely be concluded that the present results give, from the experimental point of view, general support for the previous numerical model and prove that the model can predict the pressure effect properly.

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