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ESR and Mass-Spectrometric Studies of Methanol Combustion. III. The Effect of CS_2 and CH_3NH_2 Additions on the Concentration Profiles of Chemical Species in a Methanol–Air Flame

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The concentration profiles of chemical species (labile and stable) in methanol–air free-burning flames with and without the addition of CS_2 and CH_3NH_2 have been examined by means of the probe-sampling-ESR method, combined with mass-spectrometric measurements. In addition to the principal labile intermediates (H, O, and OH) and stable species (CH_3OH, O_2, H_2, CH_2O, CO_2, and H_2O), SO_2 and NO have been detected from the flame when it has been doped with CS_2 or CH_3NH_2 respectively. The observed results indicate that the addition of these dopants depresses the concentration of OH and raises the concentration of H_2 in the primary reaction zone, where SO_2 and NO are efficiently generated. The observed concentration profiles have been discussed in terms of the reaction mechanism of the oxidation of sulfur and nitrogen compounds.

In the previous works of this series,[1,2] we studied the concentration profiles of labile intermediates (H, O, and OH) and stable species (CH_3OH, O_2, CH_2O, CO, H_2, H_2O, and CO_2) in methanol–air premixed flames at atmospheric and low pressures by means of the probe-sampling-ESR method, combined with mass-spectrometric measurements. The chemical reactions during methanol combustion have been examined on the basis of the experimental results. The study will be extended here to the methanol–air flame doped with CS_2 and CH_3NH_2 in order to elucidate the chemical effects of these compounds on methanol combustion. CS_2 and CH_3NH_2 are examples of sulfur and nitrogen compounds which have simple chemical structures.

The chemical reactions of combustion involving sulfur and nitrogen compounds are interesting to study because their oxidation products, such as SO_x and NO_x, are the main sources of air pollution. In addition, sulfur compounds are believed to modify chemically the combustion processes in these flames. For example, it is known that SO_2 catalyzes the recombination of labile free radical intermediates in hydrogen,[3,4] hydrocarbon,[5] and carbon monoxide flames.[6] It is also known that the formation of NO from combustion is much affected by the presence of a sulfur compound in the flames.[4,7] However, there has been little investigation thus far reported on the chemical aspects of doping the flames with sulfur and nitrogen compounds.

As has been shown in the previous studies of our group[8,9] and others,[10] the concentration profiles of the labile intermediates in combustion flames can be examined comparatively easily by the ESR method. These previous studies have indicated that both the formation and the decay of the labile intermediates are sensitively dependent on the combustion conditions. Therefore, the chemical modification of combustion processes may be expected to be proven by observing the concentration profiles of the labile intermediates. With this expectation, the present study was planned. During the course of the preparation of this paper, Pauwels et al.[11] have reported the effect of H_2S addition on the concentration profiles of the labile intermediates in low-pressure methanol–air flames studied by the ESR method. In the present study, CS_2 and CH_3NH_2 are used as dopants. These studies as a whole will shed light on the chemical effects of doping the combustion of methanol under various combustion conditions.

Experimental

The burner used was made of brass and had a mouth 8 mm in diameter, as has been described previously.[1,9] Reagent-grade methanol was used as a fuel without further purification. Methanol with and without dissolved carbon disulfide, CS_2, and methylamine, CH_3NH_2, of reagent grade was continuously injected into the air stream supplied from a cylinder, regulated with a rotermeter, and preheated to 403 K. The composition of the premixed gas may be expressed by the equivalence ratio, ϕ, defined as: $\phi=([\text{fuel}]/[O_2])_{\text{actual}}/([\text{fuel}]/[O_2])_{\text{stoichiometric}}$. The flow rate of the premixed gas was kept constant at $1.0\ \text{l min}^{-1}$. The flame thus obtained was found to be axially symmetric. It consisted of a flat, bluish inner flame 1—2 mm above the burner mouth and a cone-shaped, faint-bluish outer flame 10 mm in height. The flame temperature was estimated by using a fine SiO_2-coated Pt/Pt-Rh thermocouple (0.1 mm in diameter) without correction for the radiative heat loss.

The concentration profiles of such labile intermediates as H, O, OH, and NO, together with O_2, in the flames were determined by means of the probe-sampling-ESR technique with an X-band ESR spectrometer previously described in detail.[1] About one-fifth of the reacting gas was continuously sampled through a pin hole (about 0.1 mm in diameter), and subjected to ESR measurements at 24 Pa. The residence time of the sampled gas in the sampling probe before reaching the ESR cavity was about 1.5 ms. A fraction of the sampled gas was then led to a quadrupole mass spectrometer to determine the concentration profiles of

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stable species (CH_3OH, CO_2, H_2O, H_2, CS_2, and SO_2). The mass spectrometric measurements were made at a total pressure of 10^{-3} Pa. The concentration profiles (all in mole fraction unit) were obtained on the center axis of the flame.

Results and Discussion

Observed ESR and Mass Spectra. ESR spectra due to H, O, OH, and O_2 were detected from both the doped and undoped flames. The features of the spectra were the same as has been reported previously.[1,8,9] When the fuel methanol was doped with a small amount of CH_3NH_2, an ESR spectrum with nine hyperfine lines centered at 830 mT (at 8.97 GHz) due to NO was additionally detected. The hyperfine splitting was found to be 2.7 mT, in agreement with that of NO($^2\Pi_{3/2}$) studied previously.[12] When the methanol was doped with CS_2, no additional spectrum was detected. Pauwels et al.[11] have recently observed the ESR spectrum due to SO and SH from low-pressure methanol flames doped with H_2S. The concentrations of SO and SH in the present atmospheric pressure flame are probably too low for ESR detection.

The intensity of the ESR spectra was calibrated with reference to the spectrum of O_2 (for H and O) and NO (for OH and NO) of known concentrations in the ESR cavity. The correction for the destruction of H, O, and OH in the sampling probe was made in the way described previously.[1]

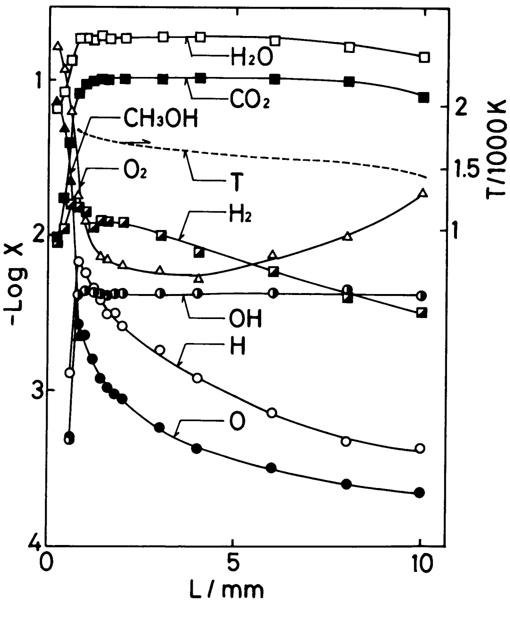

Fig. 1. The profiles of concentrations of stable and labile chemical species and temperature in a free-burning methanol–air flame of stoichiometric composition. The concentrations are presented in mole fraction units (X) on a logarithmic scale. The distance (L) is between the burner mouth and the sampling point on the center axis of the flame.

CH_3OH, H_2, CH_2O, CO_2, and H_2O were detected from both the doped and undoped flames by using the mass spectrometric method. When a small amount of CS_2 was added to the fuel methanol, additional intense spectra at $m/z=64$ and 76 were also detected. They are attributable to SO_2 and CS_2. The concentrations of these stable species were determined from the observed spectral intensities with reference to those of mixtures of known concentrations.

Concentration Profiles in the Undoped Flame. Figure 1 shows the concentration profiles of the labile intermediates and stable species in the flame of methanol–air premixed gas with the stoichiometric equivalence ratio: $\phi=1.0$ (CH_3OH: 12.3%, O_2: 18.4%, and N_2: 69.3%). The concentration profile of CH_2O is not shown in Fig. 1 in order to avoid complexity of illustration, because the distribution of CH_2O was found to be limited to a restricted region in the inner flame. The concentration profiles in the inner flame region of the undoped methanol–air flame at atmospheric pressure were studied and reported in detail previously.[1]

The observed results in Fig. 1 show that O_2 and CH_3OH are consumed, while CO_2, H_2O, and H_2 are generated rapidly, in the inner-flame region. After the rapid generation, H_2O and CO_2 remain unchanged in concentration in the outer flame region. In contrast, H_2 decreases in concentration monotonously. The O_2 concentration shows a minimum value at about 4 mm above the burner mouth, and then it gradually increases. This increase is due to the diffusion of O_2 from the surrounding air into the flame.

The flame temperature reaches a maximum in the inner-flame region, after which it decreases monotonously downstream.

The concentrations of H, O, and OH increase rapidly and reach the maximum value in the inner flame region. The concentration of H and O then decrease continuously in the outer flame region, whereas the concentration of OH remains unchanged. Comparing the present results with those for the fuel-rich ($\phi=1.25$) methane–air and fuel-lean ($\phi=0.75$) methanol–air flames reported previously,[8,9] the overall features of the concentration profiles of the labile intermediates can be said to be little dependent on the equivalence ratio around $\phi=1.0$, in both the inner- and outer-flame regions.

Effect of CS_2 Addition. Figure 2 shows the concentration profiles of CS_2 and SO_2 in the CS_2-doped flame. The premixed gas had a composition of CH_3OH: 11.6%, O_2: 18.5%, N_2: 69.4%, and CS_2: 0.46%. This composition gives almost a stoichiometric equivalence ratio, $\phi=1.02$, if the combustion of CS_2 is expressed as $CS_2+3O_2 \rightarrow CO_2+2SO_2$. The concentration profiles of CH_3OH, H_2O, and CO_2 are also shown in Fig. 2 for the sake of comparison. CS_2 is rapidly consumed and SO_2 is concomitantly generated in the

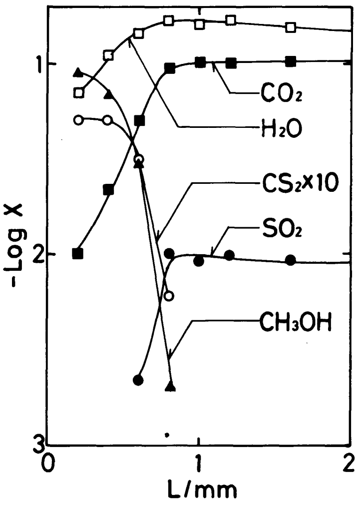

Fig. 2. Concentration profiles of CS_2, SO_2, CH_3OH, CO_2, and H_2O in a free-burning methanol-air flame doped with CS_2.

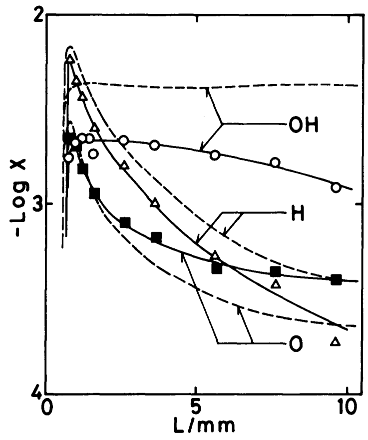

Fig. 3. Effects of CS_2 addition on the concentration profiles of labile intermediates in a free-burning methanol-air flame. The dashed lines and the solid lines denote the flame without and with addition of 0.46% CS_2.

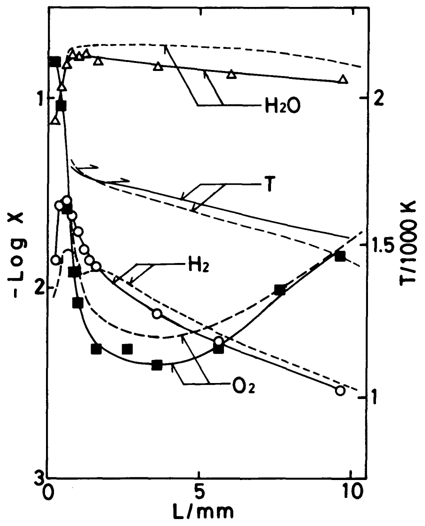

Fig. 4. Effects of CS_2 addition on the profiles of concentrations of stable species and temperature in a free-burning methanol-air flame. The dashed lines and the solid lines denote the flame without and with addition of 0.46% CS_2.

inner-flame region, where CH_3OH is converted effectively and rapidly into H_2O and CO_2. The SO_2 thus-formed keeps a constant concentration throughout the downstream region of the flame, where almost all the S atoms exist in the form of SO_2.

The effect of the CS_2 addition on the concentration profiles of the labile intermediates is shown in Fig. 3. The maximum concentration of OH in the inner flame region is reduced by as much as 50%. In contrast, the maximum concentrations of H and O are not very much affected.

The dependence of the maximum concentration of the labile intermediates on the concentration of the added CS_2 was also studied. Qualitatively, the depression of the concentration of the labile intermediates becomes more remarkable with an increase in the CS_2 concentration. The effect of $(CH_3)_2SO$ as a dopant was also studied for comparison. The results were found to be qualitatively the same as those for CS_2.

The effect of CS_2 addition on the concentration profiles of the stable species is shown in Fig. 4. The concentration profiles of CH_3OH, CH_2O, and CO_2 are not affected significantly; therefore, they are not shown in Fig. 4. The flame temperature is lowered in the inner flame region and raised in the outer flame region by CS_2 addition.

One of the most remarkable effects of CS_2 addition is an increase in the H_2 concentration in the inner-flame region. According to the reaction model proposed by Westbrook and Dryer,[13] the main source of H_2 in the upstream region of the undoped methanol-air flame is the following reaction:

$$CH_3OH + H \longrightarrow H_2 + CH_2OH. \qquad (1)$$

However, the rate of Reaction 1 in the inner-flame region is not promoted by the addition of CS_2, because the concentration of H is decreased, and the concentration of CH_3OH is not affected by the addition of CS_2.

Pauwels et al.[11] have recently studied the effect of the addition of H_2S to low-pressure methanol-air flames. They found an increase in the H_2 concentration as in the present case of the CS_2 addition. They have interpreted the increase as being due to the additional path of H_2 formation in the presence of H_2S:

$$H_2S + H \longrightarrow H_2 + SH. \qquad (2)$$

However, the present results for CS_2 addition cannot be interpreted in the same way as those for H_2S addition; CS_2 cannot act as a primary source of H_2 because it has no H atoms. No hydrogen source, such as H_2S, originating from the added CS_2 could be observed in a concentration high enough to be responsible for the significant additional H_2 formation.

Another possible mechanism is that the increase in the H_2 concentration is attributable to the scavenging of OH by the added CS_2. The decrease in the OH concentration depresses the reaction;

$$H_2 + OH \longrightarrow H_2O + H, \qquad (3)$$

which is otherwise an effective loss process of the H_2 generated by Reaction 1. Actually, the significant decrease in the OH concentration was observed in the inner-flame region on adding CS_2 to the flame.

The concentrations of H, O, and OH can be calculated by assuming a partial equilibrium in the flame based on the following rapid reactions:

$$H_2 + OH \rightleftharpoons H_2O + H \qquad (3)$$

$$H_2 + O \rightleftharpoons OH + H \qquad (4)$$

$$O_2 + H \rightleftharpoons O + OH \qquad (5)$$

The partial equilibrium concentrations are given as:

$$X_e(OH) = [K_4K_5X(H_2)X(O_2)]^{1/2} \qquad (6)$$

$$X_e(H) = K_3X(H_2)^{3/2}[K_4K_5X(O_2)]^{1/2}/X(H_2O) \qquad (7)$$

$$X_e(O) = K_3K_5X(H_2)X(O_2)/X(H_2O) \qquad (8)$$

By using the equilibrium constants in the literature[14]: K_3=0.21 exp(7640/T), K_4=2.27 exp(−938/T), and K_5= 300·$T^{-0.372}$ exp(−8565/T), the observed concentrations of the corresponding stable species, and the observed flame temperatures, the equilibrium concentrations have been calculated to be $X_e(OH)=5.8\times10^{-3}$, $X_e(H)=7.0\times10^{-3}$, and $X_e(O)=2.2\times10^{-3}$ for the undoped flame and $X_e(OH)=5.5\times10^{-3}$, $X_e(H)=1.1\times10^{-2}$, and $X_e(O)=2.3\times10^{-3}$ for the CS_2-doped flame, both at a position 1.0 mm above the burner mouth. Considering the uncertainty in the observed flame temperatures caused by the radiative heat loss, the uncertainty of the calculated equilibrium concentrations is estimated to be within a factor of 1.5. The observed X values agree with the calculated X_e values in the undoped flame. In contrast, the observed X(H) and X(OH) values are significantly lower than the equilibrium concentrations for the CS_2-doped flame. These disagreements indicate that a decrease in the concentrations of labile intermediates upon the addition of CS_2 is not to be interpreted as being due to a decrease in the flame temperature. The decrease in the labile intermediates is probably caused by rapid reactions between the labile intermediates and sulfur species, such as CS_2, S, SO, and SO_2.

The comparison between calculated X_e and observed X values was originally made by Pauwels et al.[11] for undoped and H_2S-doped methanol flames: the observed X values of the labile intermediates were found to be generally lower than the calculated X_e values when the flame was doped with H_2S. This effect of H_2S addition is especially significant for H and OH. The present results are in general accordance with those reported by Pauwels et al.

As is shown in Fig. 3, the concentrations of H and OH are depressed by the addition of CS_2 in the outer flame region, where the added CS_2 has almost entirely been converted to SO_2. This effect can be interpreted in terms of the well-known function of SO_2 in catalyzing the recombination of the labile intermediates:[15]

$$X + SO_2 + M \longrightarrow XSO_2 + M \qquad (9)$$

$$Y + XSO_2 \longrightarrow XY + SO_2 \qquad (10)$$

where X and Y represent H, O, or OH. According to Reactions 9 and 10, the concentration of O can also be expected to be depressed by the existence of SO_2 in the outer-flame region. Actually, an enhancement of the O concentration was observed, as is shown in Fig. 3. Necessarily, an additional reaction path (or paths) of generating O can be expected in the outer-flame region when the flame is doped with CS_2, but it or they are not yet known. The diffusion of O_2 from the surrounding air into the present flame under the ambient conditions may play an important role in this.

Effect of CH_3NH_2 Addition. Figure 5 shows the effects of the addition of CH_3NH_2 on the concentration profiles of the labile intermediates. The composition of the premixed gas for this doped flame was CH_3OH: 11.6%, O_2: 18.4%, N_2: 69.4%, and CH_3NH_2: 0.58%. The equivalence ratio was 1.02, based on the presumed combustion reaction: $CH_3NH_2+(9/4)O_2\rightarrow$

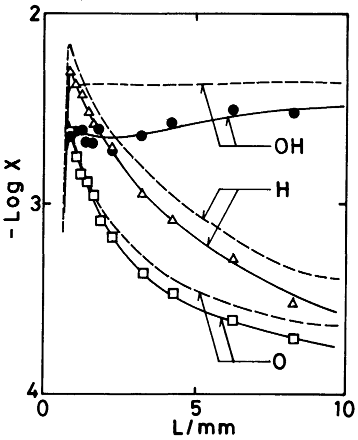

Fig. 5. Effects of CH_3NH_2 addition on the concentration profiles of labile intermediates in a free-burning methanol–air flame. The dashed lines and the solid lines denote the flame without and with addition of 0.58% CH_3NH_2.

CO_2+(5/2)H_2O+(1/2)N_2. The concentrations of the labile intermediates are qenerally lowered by the CH_3NH_2 addition. The effect is most significant for OH in the inner-flame region. It was also found that the depression of the concentrations of H and OH was more and more significant with an increase in the concentration of CH_3NH_2 added within the examined concentration range up to 1.2%, while the change in the concentration of O was rather insensitive in the higher CH_3NH_2-concentration range.

Dzotsenidze et al.[16] have studied the effect of the addition of CH_3NH_2 and NO on the H concentration in a rarefied H_2–O_2 flame at 700 K by using the ESR method: They have found a decrease in the H concentration upon the addition of CH_3NH_2 and NO. They have also found that the effect of added NO on the H concentration is significant. We examined also, in a separate experiment, the effect of adding NO to a methanol–air flame at atmospheric pressure. In this high-temperature flame, NO addition shows little effect on the concentrations of H, O, and OH. Thus, the effect of doping with CH_3NH_2 on the concentration of the labile intermediates seems to be the same for both high- and low-temperature flames, whereas the effect of doping with NO is not.

The effects of added CH_3NH_2 on the concentration profiles of stable species are shown in Fig 6. NO is rapidly formed from the added CH_3NH_2 in the inner-flame region, and it keeps a constant concentration downstream. About 50% of the N atoms of the added CH_3NH_2 exist in the form of NO in the flame after such a rapid NO formation. The concentration profiles of CH_3OH, H_2O, and CO_2 were found to be unchanged by the addition of CH_3NH_2 to the flame. The concentrations of CH_2O and CH_3NH_2 in the CH_3NH_2-doped flame could not be determined because of the overlap of their mass-spectral lines with those of NO (m/z=30) and CH_3OH (m/z=32) respectively.

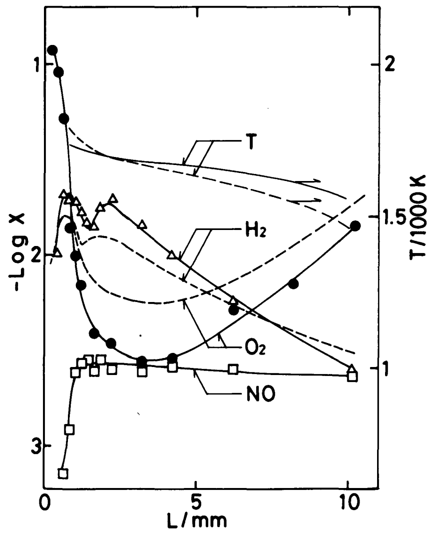

Fig. 6. Effects of CH_3NH_2 addition on the profiles of concentrations of H_2 and O_2, and temperature in a free-buring methanol–air flame. The dashed lines and the solid lines denote the flame without and with addition of 0.58% CH_3NH_2.

Two of the most significant effects of CH_3NH_2 addition are the enhancement of H_2 formation and the depression of the OH concentration occurring concomitantly in the inner-flame region. Such changes in the concentration of H_2 can be interpreted in the same way as for CS_2 addition: The decrease in OH caused by CH_3NH_2 addition depresses the oxidation of H_2 through Reaction 3.

Another possible mechanism is the formation of H_2 through the following reaction:

$$CH_3NH_2 + H \longrightarrow CH_3NH(\text{or } CH_2NH_2) + H_2. \quad (11)$$

According to the rate constant, $k_{11}=1.8\times10^7\exp(-2670/T)\ \mathrm{m^3\,mol^{-1}\,s^{-1}}$, reported by Blumberg and Wagner,[17] this reaction can have a rate constant of the same order of magnitude as that of the main H_2-forming reaction in the inner flame region (Reaction 1),[18] $k_1=4.0\times10^7\exp(-3070/T)\ \mathrm{m^3\,mol^{-1}\,s^{-1}}$, at the observed flame temperature. However, the enhancement of H_2 formation can not be attributed solely to Reaction 11, because the added concentration of CH_3NH_2 is not high enough for Reaction 11 to proceed at a significant rate.

The observed concentrations of H, O, and OH at the position 1 mm above the burner mouth were compared with the concentrations calculated by assuming a partial equilibrium based on Equations 6—8. It was found that the observed concentration is lower than the equilibrium concentration for H and OH in the CH_3NH_2-doped flame. This is the same trend as that observed in the CS_2-doped flame. The only different effect of doping between CH_3NH_2 and CS_2 is that the O concentration in the outer-flame region is lowered by CH_3NH_2 addition, whereas it is increased by the CS_2 addition. This may be due to the reaction of the NO oxidation, NO+O→NO_2, in the CH_3NH_2-doped flame.

Conclusion

The concentration profiles of the labile intermediates and the stable species in a methanol–air flame at atmospheric pressure with and without added carbon disulfide and methylamine were examined by means of a probe-sampling ESR method combined with mass-spectrometric measurements. The two dopants were found to be oxidized quickly into SO_2 and NO respectively. These products were comparatively stable, even in a high-temperature methanol–air flame. These dopants affect the chemical reactions in the inner-flame region by depressing the concentration of labile OH and by effectively enhancing the formation of H_2 from the principal fuel, CH_3OH. The effect of the H_2S-doping of the low-pressure methanol–air flame has very recently been studied by Pauwels et al.[11] The present results for the CS_2-doping are essentially the same as for H_2S-doping. These two studies by means of the ESR method show some of the general aspects of the chemical effects of sulfur compounds on the combustion reactions of methanol. They also show the usefulness of utilizing the ESR method for studies of the chemical modification of combustion. It should be stressed that the concentration profiles of labile intermediates are more sensitively dependent on the doping than are the concentration profiles of the stable intermediates.

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