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Behavior of Methanol and Formaldehyde in Burned

Gas from Methanol Combustion*

(Effects of Nitric Oxide on Oxidation Reaction)

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Calculations using a chemical kinetic model for the oxidation process of unburned methanol were carried out on exhaust gases from a methanol fueled S.I. engine at air-fuel equivalence ratios of 0.8, 1.0, 1.2, and 1.4.

Good correlation between the calculated and experimental results were obtained for methanol reaction behavior as well as formaldehyde concentration profile.

The conversion reaction of nitric oxide to nitrogen dioxide plays a significant role in the oxidation of unburned methanol and the formation of formaldehyde. The presence of molecular oxygen in exhaust gases has a favorable effect on this conversion. However rich the oxygen may be, methanol oxidation is extremely slow in the absence of nitric oxide. With rich oxygen, methanol oxidation is rapid due to an increasing nitric oxide. It is explained by considering those effects how the methanol reaction rate attains a maximum value in exhaust gases between air-fuel equivalence ratios of 1.0 and 1.2.

Key Words: Internal Combustion Engine, Spark Ignition Engine, Methanol, Formaldehyde, Emission, Chemical Kinetic, Oxidation, Nitric Oxide, Nitrogen Dioxide.

1. Introduction

It has become well known that unburned fuels and their intermediate products from a spark ignition engine are considerably reduced due to the oxidation in exhaust system such as exhaust manifold and exhaust pipe⁽¹⁾. Several investigations on the oxidation of unburned emissions in exhaust system have been theoretically and experimentally done. Nakagawa et al.⁽²⁾ have experimentally studied the oxidation of hydrocarbons and carbon monoxide from a gasoline engine. Brokaw et al.⁽³⁾ have computed the carbon monoxide oxidation rate in various conditions of an automobile exhaust manifold reactor. Takagi et al.⁽⁴⁾ have analysed the oxidations of methane and carbon monoxide by using a chemical kinetic model. In these papers, it was indicated that nitric oxide in exhaust gases had a favorable effects on the oxidations of unburned hydrocarbons and carbon monoxide. However, the quantitative effects of nitric oxide and the importance of the other components in exhaust gases on the oxidations were not reported in these papers. Moreover, a detailed comparison of the experimental results with the calculated results has not been made in any report.

In methanol fueled S.I. engine, unburned fuel, or methanol was oxidized in exhaust system and formaldehyde was formed through the oxidation. From our previous experiments in which the concentrations of exhaust components were measured along the exhaust tube⁽⁵⁾ and by using the reactor tube⁽⁶⁾, it was shown that the reaction behaviors of unburned methanol and formaldehyde in exhaust system depended remarkably on the engine variables such as air-fuel equivalence ratio and ignition timing. The difference of reaction behavior could be explained by the influences of nitric oxide in exhaust gases. Very few theoretical analyses on unburned methanol oxidation in exhaust gases from a methanol fueled S.I. engine are available and there is no report on the effects of nitric oxide on methanol oxidation.

This paper describes theoretically the effects of nitric oxide in exhaust gases on the oxidation of unburned methanol and the formation and destruction of formaldehyde using the chemical kinetic model proposed in a previous report⁽⁷⁾, and discusses the role of nitric oxide and oxygen in reaction process. Moreover, the calculated results were compared with the experimental results from a reactor tube. Consequently, unburned methanol in exhaust gases was principally consumed by hydroxyl radicals which were generated by the conversion reaction of nitric oxide to nitrogen dioxide. This conversion reaction required hydroperoxyl radicals, and molecular oxygen played a significant role in the formation of hydroperoxyl radicals. It was obvious that molecular oxygen had favorable effects on formaldehyde forma-

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tion and nitric oxide had favorable effects on formaldehyde destruction. From these reaction mechanism, it was possible to predict theoretically the oxidation of methanol and the formation and destruction of formaldehyde in exhaust system with various air-fuel equivalence ratios and ignition timings.

2. Calculation procedures

2.1 Reaction scheme

A reaction scheme on methanol oxidation used in this paper consists of 94 elementary reactions involving 24 chemical species. The rate constants of these reactions, with only one exception, were the same as adopted in the previous work (7). This reaction scheme was used to predict the reaction behaviors in an exhaust system over a wide range of air-fuel equivalence ratios ϕ_{AF} (0.8–1.4) at a relatively low temperature (700–1000 K). In the previous report, the formation reaction rate constant of Reaction (11), (Reaction number is the same one in the previous work.) $CH_2O + OH = CHO + H_2O$, was taken to be $2.9 \times 10^{13} \exp(-3.1/RT)$ (unit: cm, kJ, K, mol, s) proposed by Kuratani (8). However, the use of this value for lean mixture conditions led to a noticeable difference between the calculated results and the experiments. Accordingly, the rate constant of this reaction was modified to $5.0 \times 10^{15} \exp(-54.4/RT)$ as proposed by Westenberg et al. (9) and cited by Wilson et al. (10).

2.2 Calculation model and initial concentrations

The calculation model and the assumptions for calculation were determined by the same method as in the previous work. The calculations were carried out for the initial gas concentrations which were determined by the following two methods.

In the first calculation, the initial concentrations of the measurable components were set for the values measured at engine exhaust port when methanol engine was operated at $\phi_{AF}=0.8, 1.0, 1.2$, and 1.4, a speed of 1500 rpm, an ignition timing of TDC, an wide open throttle. The initial concentrations of the immeasurable components (U_i), which were marked with asterisks in Table 1, were determined by referring to chemical equilibrium concentrations (C_i) at flame temperature in methanol-air mixture. As examined in our previous report, U_i was estimated to be equal to $C_i \times 10^{-4}$. This paper adopted this as it was. A set of initial gas concentrations are listed in Table 1.

In the second calculations, in order to clarify the quantitative effects of nitric oxide and oxygen on the reaction behaviors, the concentrations of nitric oxide and oxygen in the initial gas composition at $\phi_{AF}=0.8$ and 1.0 were changed with the concentrations of other components kept the same as shown in Table 1.

3. Calculated results

3.1 Effects of air-fuel equivalence ratio

3.1.1 Unburned methanol

Fig. 1 shows the calculated results of the concentrations of unburned methanol (CH_3OH) as a function of residence time (τ). The calculations were performed for $\phi_{AF}=0.8, 1.0, 1.2$, and 1.4 at gas temperatures (T) of 900, 950, and 1000 K. The results showed that the oxidation rate of methanol was remarkably dependent on air-fuel equivalence ratio, and it was extremely high at $\phi_{AF}=1.0$ and 1.2, while it was low at $\phi_{AF}=0.8$ and 1.4. For example, at a temperature of 1000 K, only 20 % of methanol was consumed at $\phi_{AF}=0.8$, while above 95 % was consumed at $\phi_{AF}=1.0$ and 1.2 during the residence time of 10 ms.

Table 1 Initial species concentrations for calculated runs.

	$\phi_{AF}=0.8$	$\phi_{AF}=1.0$	$\phi_{AF}=1.2$	$\phi_{AF}=1.4$
species	mol. fraction	mol. fraction	mol. fraction	mol. fraction
CH_3OH	3.200×10^{-3}	2.700×10^{-3}	2.800×10^{-3}	3.000×10^{-3}
* CH_2OH	6.891×10^{-7}	5.611×10^{-7}	2.260×10^{-7}	1.000×10^{-7}
CH_2O	5.200×10^{-5}	1.100×10^{-4}	1.900×10^{-4}	1.050×10^{-4}
* CHO	1.830×10^{-8}	1.570×10^{-8}	9.449×10^{-9}	6.200×10^{-9}
CH_4	6.400×10^{-5}	2.500×10^{-5}	1.500×10^{-5}	8.000×10^{-6}
* CH_3	4.740×10^{-8}	2.610×10^{-8}	1.460×10^{-8}	1.300×10^{-8}
* CH_2	4.740×10^{-9}	2.610×10^{-9}	1.460×10^{-9}	1.300×10^{-9}
* CH	4.740×10^{-10}	2.610×10^{-10}	1.460×10^{-10}	1.300×10^{-10}
CO	4.150×10^{-2}	1.650×10^{-2}	1.200×10^{-3}	6.600×10^{-4}
CO_2	7.000×10^{-2}	9.500×10^{-2}	9.930×10^{-2}	8.698×10^{-2}
* OH	5.681×10^{-7}	7.341×10^{-7}	5.880×10^{-7}	4.200×10^{-7}
* H	7.630×10^{-7}	5.730×10^{-7}	2.549×10^{-7}	1.000×10^{-7}
H_2	2.500×10^{-2}	1.310×10^{-2}	5.020×10^{-3}	3.000×10^{-3}
* O	1.510×10^{-7}	2.650×10^{-7}	2.460×10^{-7}	1.800×10^{-7}
O_2	5.000×10^{-3}	9.000×10^{-3}	2.980×10^{-2}	5.219×10^{-2}
* H_2O_2	1.430×10^{-7}	1.230×10^{-7}	9.910×10^{-8}	8.799×10^{-8}
* HO_2	7.021×10^{-8}	5.699×10^{-8}	4.319×10^{-8}	3.600×10^{-8}
H_2O	2.310×10^{-1}	2.110×10^{-1}	1.986×10^{-1}	1.740×10^{-1}
* N	1.000×10^{-10}	1.740×10^{-10}	3.629×10^{-10}	4.371×10^{-10}
N_2	6.240×10^{-1}	6.520×10^{-1}	6.628×10^{-1}	6.799×10^{-1}
NO	1.800×10^{-4}	5.000×10^{-4}	3.200×10^{-4}	2.000×10^{-4}
NO_2	9.000×10^{-6}	1.300×10^{-5}	1.880×10^{-4}	1.300×10^{-5}
* N_2O	1.570×10^{-14}	1.570×10^{-14}	1.570×10^{-14}	1.570×10^{-14}
* HNO	1.259×10^{-14}	1.259×10^{-14}	1.259×10^{-14}	1.259×10^{-14}

However, the amount of methanol consumption was reduced to 23 % in a leaner mixture of $\phi_{AF}=1.4$. A similar trend was observed at temperatures of 950 and 900 K. These calculated results agreed qualitatively with the experimental results of reactor tube in our previous work(6).

The reason for slow oxidation rate at $\phi_{AF}=0.8$ was considered to be due to a low concentration of oxygen in exhaust gases. However, at $\phi_{AF}=1.4$ with rich oxygen, the oxidation rate became less than that at $\phi_{AF}=1.0$ and 1.2. Consequently, the highest oxidation rate was obtained between $\phi_{AF}=1.0$ and 1.2. From these calculated results, it is clear that the oxidation rate of unburned methanol is not dependent on only oxygen in exhaust gases. The characteristics of the oxidation is very similar to that of nitric oxide emission which shows a maximum level around $\phi_{AF}=1.0$ or 1.2.

3.1.2 Formaldehyde

Formaldehyde (CH_2O) formed with methanol oxidation was also affected by air-fuel equivalence ratio. Fig. 2 shows the calculated results of formaldehyde concentrations under the same conditions of Fig.

1. Formaldehyde concentration profiles as a function of residence time were remarkably dependent on both air-fuel equivalence ratio and reaction temperature. At a temperature of 900 K, formaldehyde increased monotonously with the residence time in either case of air-fuel equivalence ratio. The increasing rates of formaldehyde concentrations with time were dependent on air-fuel equivalence ratio. It attained minimum at $\phi_{AF}=0.8$ and maximum at $\phi_{AF}=1.4$.

At a temperature of 950 K, formaldehyde at $\phi_{AF}=1.0$ and 1.2 attained maximum value near $\tau=10$ ms and decreased at more than $\tau=10$ ms. The trends of rise and fall were remarkable in the case of $T=1000$ K. Formaldehyde concentrations at $\phi_{AF}=1.0$ and 1.2 increased to maximum values approximately at $\tau=3$ and 5 ms respectively, and rapidly decreased beyond them. Accordingly, formaldehyde concentrations at $\tau=10$ ms became remarkably low under these air-fuel equivalence ratios. On the other hand, formaldehyde went on increasing with the residence time at $\phi_{AF}=0.8$ and 1.4.

Fig. 1 Effects of air-fuel equivalence ratio on methanol oxidation

Fig. 2 Effects of air-fuel equivalence ratio on the formation and destruction of formaldehyde.

From these formaldehyde concentration profiles, it seems that the formation rate and destruction rate of formaldehyde are high at $\phi_{AF}=1.0$ and 1.2, while the formation rate is higher than the destruction rate at $\phi_{AF}=1.4$. However, it is not clear from only these results which of the gas components in exhaust gases is a decisive factor for formaldehyde concentrations, because they were dependent on both formation rate and destruction rate.

The calculated results of formaldehyde concentration agreed qualitatively well with the experimental results from reactor tube which showed that the increasing rate of formaldehyde concentrations attained maximum value at $\phi_{AF}=1.4$ and minimum value at $\phi_{AF}=0.8$.

3.2 Effects of nitric oxide

3.2.1 In case of low oxygen concentration

Fig. 3 shows the calculated results obtained by changing nitric oxide concentration alone in exhaust gases at $\phi_{AF}=0.8$. The measured nitric oxide concentration was 180 ppm at $\phi_{AF}=0.8$. Methanol was scarcely oxidized under these conditions. However, even if nitric oxide concentration was raised to 500 ppm corresponding to $\phi_{AF}=1.0$, methanol consumption amount was far less than that of $\phi_{AF}=1.0$ shown in Fig. 1 (b). At these air-fuel equivalence ratio, it is obvious that an increase in nitric oxide has little effect on methanol oxidation and formaldehyde concentrations.

Fig. 3 Effects of nitric oxide on the reaction behaviors of methanol and formaldehyde in case of lean oxygen ($\phi_{AF}=0.8$)

3.2.2 In case of $\phi_{AF}=1.0$

Fig. 4 shows the calculated results obtained by changing nitric oxide at $\phi_{AF}=1.0$. Nitric oxide had stronger effects on methanol and formaldehyde reactions than in case of $\phi_{AF}=0.8$. Methanol oxi-

dation rate increased with an increase in nitric oxide. Formaldehyde formation rate increased with an increase in methanol oxidation rate. The difference of concentration in exhaust gases is able to explain the reason why the difference of nitric oxide effect on methanol and formaldehyde reactions depends on air-fuel equivalence ratio.

Fig. 4 Effects of nitric oxide on the reaction behaviors of methanol and formaldehyde in case of $\phi_{AF}=1.0$.

3.2.3 Effects of oxygen

Fig. 5 shows the calculated results of methanol and formaldehyde in case of $O_2=2, 3$, and 4 %. Methanol oxidation rate became higher with an increase in oxygen. In order to clarify the relation between the concentrations of nitric oxide and oxygen and the oxidation of methanol, the maximum methanol oxidation rates $(\Delta CH_3OH/\Delta \tau)_{max}$ obtained from these calculations are shown in Fig. 6. It is obvious from this figure that methanol oxidation is dependent on oxygen as well as nitric oxide.

Formaldehyde was also affected by both species. The increasing rate and decreasing rate in formaldehyde concentrations became higher with an increase in nitric oxide and oxygen. Consequently, the residence time τ_{max} which gave the highest value of formaldehyde concentration was gradually shorter as the concentrations of nitric oxide and oxygen became higher. Fig. 7 shows the relationship of τ_{max} to oxygen concentrations at $T=950$ K. τ_{max} is capable of representing some degree of reaction for formaldehyde formation. Namely, a small τ_{max} implies that formation rate and the destruction rate of formaldehyde are high, while a large τ_{max} implies that both rates are low or the destruction rate is less than the formation rate. Fig. 7 shows that τ_{max} suffers a stronger effect of oxygen than that of nitric oxide and rapidly decreases as oxygen concentration increases from 0.9 to 2.0 %.

Fig. 5 Effects of oxygen on the reaction behaviors of methanol and formaldehyde.

Fig. 6 Effects of oxygen and nitric oxide on maximum methanol oxidation rate.

Fig. 7 Effects of oxygen and nitric oxide on τ_{max} .

From the results of Figs. 6 and 7, it is obvious that oxygen in exhaust gases has extremely strong effects on methanol and formaldehyde reaction behaviors. As is evident from the calculated results of $\text{O}_2 = 4 \%$ and $\text{NO} = 50 \text{ ppm}$ shown in Fig. 5 (c), methanol oxidation, however rich oxygen may be, is extremely slow in a low nitric oxide. On the other hand, formaldehyde concentrations are gradually increasing with the residence time under these conditions. These calculated results correspond to the case of $\phi_{\text{AF}} = 1.4$ shown in Fig. 1 (d) and Fig. 2 (d).

4. Discussions

4.1 Methanol

It became evident from the calculated results that methanol oxidation in exhaust gases was dependent on air-fuel equivalence ratio and it attained maximum value near the stoichiometric ratio and decreased as the mixture became progressively richer or leaner. This phenomenon was caused by the differences of the concentrations of nitric oxide and oxygen in exhaust gases.

This section describes the factors that have effects on the reaction behavior from the view point of chemical kinetics. As proposed in the previous paper (7), eight elementary reactions shown in Table 2 are possible for methanol oxidation.

Table 2 Elementary reactions for methanol consumption.

No.	Elementary reactions
(1)	$\text{CH}_3\text{OH} + \text{M} = \text{CH}_3 + \text{OH} + \text{M}$
(2)	$\text{CH}_3\text{OH} + \text{O}_2 = \text{CH}_2\text{OH} + \text{HO}_2$
(3)	$\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_2\text{OH} + \text{CH}_4$
(4)	$\text{CH}_3\text{OH} + \text{O} = \text{CH}_2\text{OH} + \text{OH}$
(5)	$\text{CH}_3\text{OH} + \text{H} = \text{CH}_3 + \text{H}_2\text{O}$
(6)	$\text{CH}_3\text{OH} + \text{H} = \text{CH}_2\text{OH} + \text{H}_2$
(7)	$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$
(8)	$\text{CH}_3\text{OH} + \text{HO}_2 = \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$

To ascertain the relative importance of the eight elementary reactions, the net reaction rates of each reaction at $T=950\text{ K}$ and $\tau=10\text{ ms}$ are shown in Fig. 8. The net reaction rate considerations suggest that Reactions (5), (6), and (7) are the dominant reactions for methanol oxidation in either case of ϕ_{AF} . Therefore, the main attack on methanol comes from H atoms and OH radicals. Approximately 98 % of methanol were consumed by these reactions irrespective of air-fuel equivalence ratio. Thus, OH radicals and H atoms play an important role in methanol oxidation under the conditions of the present study.

Fig. 8 Net reaction rates of methanol consumption reactions at $\tau=10\text{ ms}$.

In our previous reaction scheme, 26 elementary reactions were proposed as the source of OH radicals. Among these 26 elementary reactions, the following Reactions (79) and (81) are found especially important as a main source of OH radicals.

Above 90 % of OH radicals were produced by these two reactions. One more important species of H atoms for methanol oxidation was principally produced through the following two reactions.

The formation reaction of H atoms includes eight elementary reactions besides these two reactions in the previous model. However, H atoms formed by those eight reactions were so small in quantity that 74 % of H atoms was produced by Reaction (52) and 12 % by Reaction (71). The formation of H atoms required OH radicals which had been produced by reactions (79) and (81).

Since nitrogen dioxide is generally much less than nitric oxide in high temperature exhaust gases, NO_2 involved in Reaction (81) is considered to be one which has been converted from NO through Reaction (79). Accordingly, it is evident that the conversion reaction of NO to NO_2 plays a significant role in methanol oxidation in exhaust gases.

On the other hand, similar behaviors were observed in the reactor experiments. Fig. 9 shows the concentrations of exhaust gas components measured at reactor tube end. The experiments were performed on the exhaust gases at $\phi_{AF}=1.2$ and $IT=-20^\circ\text{CA}$. The experimental results showed that a decrease of methanol started from the temperature for the conversion of NO to NO_2 began. An increase of formaldehyde was observed at the beginning of this conversion reaction. The amount of methanol consumption increased with an increase in the amount of the conversion of NO to NO_2 . The conversion reaction of NO to NO_2 required HO_2 radicals which had been produced by a set of six elementary reactions listed in Table 3. Since these reactions except Reaction (66) were caused by reaction with oxygen, HO_2 radicals increased with an increase in the concentrations of oxygen in exhaust gases. An increase in HO_2 radicals activated the conversion reaction of NO to NO_2 and consequently increased the concentrations of OH radicals in a reaction system. According to those reaction mechanism, NO and O_2 are found to be strong factors in methanol oxidation in exhaust gases.

Fig. 9 Concentrations of exhaust gas components measured at reactor tube end.

Table 3 Elementary reactions for HO_2 radicals formation.

No.	Elementary reactions
(2)	$\text{CH}_3\text{OH} + \text{O}_2 = \text{CH}_2\text{OH} + \text{HO}_2$
(9)	$\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$
(17)	$\text{CH}_2\text{O} + \text{O}_2 = \text{CHO} + \text{HO}_2$
(23)	$\text{CHO} + \text{O}_2 = \text{CO} + \text{HO}_2$
(66)	$\text{O} + \text{H}_2\text{O}_2 = \text{OH} + \text{HO}_2$
(68)	$\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$

Fig. 10 shows the experimental results in cases of varying the concentrations of nitric oxide in reactor tube at $\phi_{AF}=1.0, 1.2, \text{ and } 1.4$. The abscissa shows the oxygen concentrations due to a change in air-fuel equivalence ratio. The ordinate denotes the amount of methanol consumption (ΔCH_3OH) in the reactor tube. The amount of methanol consumption increased with an increase in oxygen and became higher as nitric oxide increased. From these experimental results, it can be experimentally confirmed that oxygen as well as nitric oxide in exhaust gases has a favorable effect on methanol oxidation.

Judging from methanol oxidation behavior in exhaust gases obtained from the chemical kinetic and experimental data, it can be stated that methanol oxidation does not occur by a direct reaction with oxygen but by reaction with OH radicals and H atoms. Accordingly, it is necessary for these radical species to be continuously supplied to the reaction system for continuing the methanol oxidation. The supply source of radical species is the conversion reaction of NO to NO₂. It is obvious from the chemical kinetic considerations that this conversion reaction requires HO₂ radicals, and oxygen in exhaust gases plays a significant role in the formation of HO₂ radicals.

Fig. 10 Effects of oxygen and nitric oxide on the amount of methanol consumption. (experimental results).

Table 4 Elementary reactions for formaldehyde formation.

No.	Elementary reactions
(9)	$CH_2OH + O_2 = CH_2O + HO_2$
(10)	$CH_2OH + M = CH_2O + H + M$
(32)	$CH_3 + O = CH_2O + H$
(33)	$CH_3 + O_2 = CH_2O + OH$
(37)	$CH_3 + OH = CH_2O + H_2$

4.2 Formaldehyde

As shown in Table 4, there are two paths to the formation of formaldehyde, one through hydroxymethyl radicals (CH_2OH) and the other through methyl radicals (CH_3). To examine the contribution of these reactions to formaldehyde formation, the net reaction rates at $T=950\text{ K}$

and $\tau=10\text{ ms}$ are shown in Fig. 11. As is obvious from this figure, formaldehyde is principally formed by the reaction between CH_2OH and O_2 in all cases of air-fuel equivalence ratio. Accordingly, oxygen in exhaust gases has a favorable effect on formaldehyde formation.

On the other hand, nine elementary reactions are possible for formaldehyde destruction. Above 90 % of CH_2O was destroyed by the following two reactions;

The chemical kinetic mechanism for formation and destruction of formaldehyde shows that an increase in oxygen in exhaust gases makes the formation rate fast and an increase in nitric oxide makes the destruction rate fast. Thus, formaldehyde concentrations are determined by the difference in rate between the formation and the destruction. These reaction mechanisms can explain why formaldehyde concentrations attained maximum value at $\phi_{AF}=1.4$ in the previous experiments⁽⁵⁾.

Fig. 11 Net reaction rates of formaldehyde formation reactions at $\tau = 10\text{ ms}$.

4.3 A characteristic of methanol oxidation

The authors indicated that the conversion reaction of NO to NO₂ played an important role in methanol oxidation and required HO₂ radicals. HO₂ radicals were produced by means of six elementary reactions previously shown in Table 3. As a result of examining the relative importance of HO₂ formation reactions, Reactions (9), (17), and (68) were found to be principal reactions. Above 54 % of total HO₂ radicals resulted in Reaction (9), 25% from Reaction (17), and 20 % from Reaction (68) under the conditions of $\phi_{AF}=1.0$ and $T=950\text{ K}$. Since CH_2OH and CH_2O in Reac-

tion (9) and (17) are peculiar intermediate products of methanol oxidation, the amount of H_2O_2 formation became higher in methanol oxidation than in hydrocarbon oxidation. Consequently, the magnitude of the conversion reaction of NO to NO_2 , of course, is expected to be greater than that in hydrocarbon oxidation.

Fig. 12 Differences between methanol and methane in oxidation rate.

Fig. 12 shows the calculated results of methane oxidation together with those of methanol oxidation. The calculations were performed by applying the present reaction scheme to the initial values of 2700 ppm for CH_4 , 0 ppm for CH_3OH , 0 ppm for CH_2OH , and 11 ppm for CH_2O . The net reaction rates of Reaction (79) in both cases are also shown in this figure. As is evident from comparison of the two cases, the net reaction rate of Reaction (79) is much greater in methanol than in methane. These calculated results suggest that methanol, unlike hydrocarbon fuels, can be easily oxidized in exhaust gases. This is one of the features of the oxidation in methanol combustion.

5. Conclusions

This paper examines kinetically the methanol oxidation process in exhaust gases from a methanol fueled S.I. engine operated at air-fuel equivalence ratios between 0.8 and 1.4, and clarifies the effects of nitric oxide and oxygen in exhaust gases on the oxidation of methanol and the formation and destruction of formaldehyde. The calculated results agreed relatively well with the experimental results.

The results obtained are summarized as follows;

(1) The oxidation of unburned methanol in exhaust gases occurred by the reaction with OH radicals and H atoms. The conversion reaction of nitric oxide to nitrogen dioxide was the main source of these radical species. The reaction required HO_2 radicals which had been pro-

duced by the reaction between molecular oxygen and the intermediate products of methanol oxidation.

(2) In these reaction processes, the oxidation of unburned methanol was extremely affected by nitric oxide and oxygen in exhaust gases. Namely, methanol oxidation became faster with an increase in nitric oxide and oxygen. However rich oxygen might be, methanol oxidation was extremely slow in the absence of nitric oxide and however rich nitric oxide might be, it was equally slow in the absence of oxygen. Consequently, the methanol oxidation rate attained maximum value near air-fuel equivalence ratios of 1.0 and 1.2.

(3) The concentration of formaldehyde in exhaust gases depended on the difference between the formation rate and the destruction rate. An increase in oxygen increases the formation rate and an increase in nitric oxide increases the destruction rate. On account of this mechanism, formaldehyde concentrations became high under the conditions of air-fuel equivalence ratio of 1.4 with rich oxygen and lean nitric oxide.

(4) The conversion reaction of nitric oxide to nitrogen dioxide in methanol oxidation compared favorably with that in methane oxidation, because the amount of HO_2 radicals formation was higher in methanol oxidation than in methane oxidation. For these reasons, methanol, unlike hydrocarbon fuels, is expected to be easily oxidized in exhaust gases.

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