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A Flash Photolysis Study of CH_4-O_2 Mixtures behind Shock Waves: Examination of Reaction of CH_3+O_2

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ArF laser photolysis in the mixtures of CH_4 and O_2 highly diluted in Ar has been conducted behind reflected shock waves, where O and H atoms have been monitored using the ARAS technique. The rate constant for the reaction $CH_4+O \rightarrow CH_3+OH$ (1) has been directly determined to be $10^{-8.95\pm0.27}\exp[-(15.4\pm2.0)\text{kcal mol}^{-1}/RT]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range of 1365—1840 K. Also the consecutive reactions; $CH_3+O_2 \rightarrow CH_3O+O$ (3a) and $CH_3+O_2 \rightarrow CH_2O+OH$ (3b) have been examined more directly than in previous thermally initiated experiments, and the combinations of k_{3a} and k_{3b} have been evaluated at the temperature range from 1622 to 1840 K.

The reaction of methyl radical with molecular oxygen at wide temperature ranges has been extensively investigated so far because it is one of the key reactions in combustion of alkane. However, there still remain conflicting conclusions on the rate constant and the mechanism[1-9].

In previous studies, slow initiation reactions often masked the consecutive fast reactions, and so most kinetic information on the chain (branching) reactions had to be derived by indirect estimation using numerical simulations or approximate analyses with a steady-state assumption.

In contrast, laser photolysis combined with highly sensitive detection system can in principle eliminate speculative analyses for side reactions. Thus, the rate constants for reactions of selectively prepared radicals or atoms of concern have been directly measured by the flash photolysis of shock heated gas with the ARAS system.[10,11] Recently, direct flash photolysis experiments on the reactions $H+NH_3 \rightarrow H_2+NH_2$[12] and $H+H_2S \rightarrow H_2+HS$[13] have revealed the rate constants which are about an order of magnitude larger than those obtained by indirect measurements. Thus, reexamination of the titled reaction using such a technique will be important and attactive.

Experimental

In this study, mixtures of CH_4 and excess amount of O_2, highly diluted in Ar, were irradiated by an ArF excimer laser beam (193 nm) behind reflected shock waves. O atoms were produced via the photolysis of vibrationally excited O_2 (mainly $v''=2$)[14] and the time dependencies of the concentrations of O and H atoms were monitored with the atomic resonance absorption spectroscopy (ARAS). All the experiments were performed with Ar as a buffer gas and the total pressure ranged from 1.3 to 2.6 atm.

A shock tube of a diaphragmless type with a low pressure section of 4 m long and 5 cm i.d. was used; an ArF laser with output energy of 10—30 mJ cm^{-2} was used to photolyze O_2 through a quartz window of 1×4 cm attached at the end plate. The ArF laser was fired at 50—100 μs after the reflected shock waves passed through the observation section. The ARAS system was composed of a microwave discharge lamp in which 1% O_2 or H_2 diluted in He was flowed, a VUV monochromator (Ritsu VUV-2000), and a solar blind photomultiplier (Hamamatsu Photonics R-976).

The ARAS signals were recorded in a digital oscilloscope and stored and analyzed with a microcomputer. Time dependencies of the absolute concentrations of H and O atoms were determined by using calibration curves obtained by conducting thermal decomposition experiments in H_2-O_2-Ar, N_2O-Ar, and N_2O-H_2-Ar mixtures.

As the reproducibility of the shock wave conditions with the present shock tube was good, improvements of the S/N ratio of the signals were also tried in some cases by averaging up to 5 shots. The averaging procedure was effective also on cancelling the shot-to-shot fluctuation of the absorption profiles.

Results

The present study was performed with sample mixtures of 20—217 ppm CH_4 and 2470 ppm—2.0% O_2 diluted in Ar. The initial concentration of atomic oxygen was kept less than 16% of that of methane by adjusting the power of ArF excimer laser beam, and the initial conditions for the relative concentrations, $[O] \ll [CH_4] \ll [O_2]$, were always satisfied.

Examples of the profiles of absorption intensity at 130.6 and 121.6 nm are shown in Fig. 1(a) and (b), respectively. As the back ground signals due to vibrationally excited O_2 were observed at both the wavelengths, corrections of the baselines were made by contrasting the absorption signals with and without laser photolysis under similar experimental conditions.

As shown in Fig. 1(a), the absorption signal due to atomic oxygen increased immediately after the ArF laser was fired, and then decayed gradually with time. The initial decay of O atom concentration is caused by reaction (1)

$$O + CH_4 \rightarrow OH + CH_3, \qquad (1)$$

which is followed by

$$CH_4 + OH \rightarrow CH_3 + H_2O. \qquad (2)$$

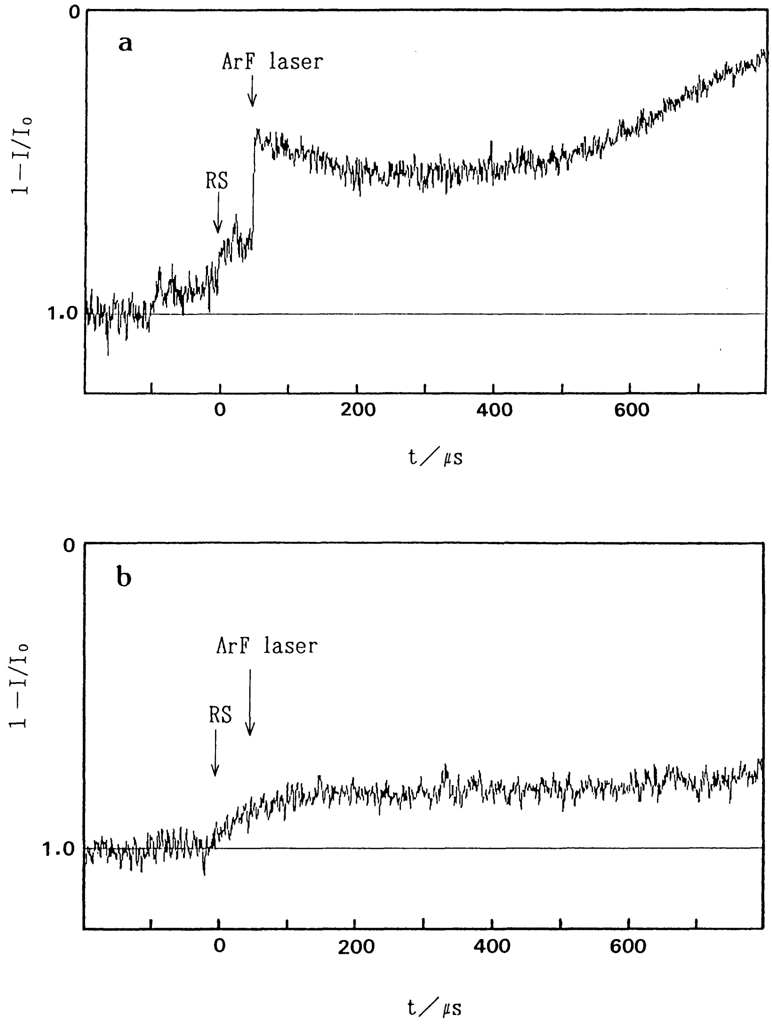

Fig. 1. Examples of ARAS signal at 130.6 and 121.6 nm with ArF laser photolysis behind reflected shock waves in CH_4-O_2-Ar mixtures. $t=0$ denotes the arrival of the reflected shock wave at the observation station of ARAS indicated by RS, and ArF was fired at $t=50$ μs. (a): absorption at 130.6 nm in 67 ppm CH_4+2.0% O_2+Ar, $T=1670$ K, $P=1.36$ atm. The initial concentration of O atoms was 3 ppm. (b): absorption at 121.6 nm in 58 ppm CH_4+2470 ppm O_2+Ar, $T=1654$ K, $P=2.2$ atm.

As the experiments were performed with excess amount of O_2 in this study, the methyl radicals formed in reactions (1) and (2) were mostly consumed by (3a) and/or (3b)

$$CH_3 + O_2 \rightarrow CH_3O + O \quad (3a)$$

$$\rightarrow CH_2O + OH. \quad (3b)$$

CH_3O produced in (3a) decomposed rapidly by the process[15]

$$CH_3O + M \rightarrow CH_2O + H + M. \quad (4)$$

In this experiment, H atoms were produced mainly via reaction (4) as well as via the thermal decomposition of CH_4

$$CH_4 + M \rightarrow CH_3 + H + M, \quad (5)$$

at higher temperatures range (T>1800 K). However, they were rapidly consumed by

$$H + O_2 \rightarrow OH + O \quad (6)$$

because the concentration of O_2 was relatively high.

The time dependence of O atom concentration observed in the experiment was compared with that calculated by the numerical simulations based on the rate constants proposed by Warnatz,[16] where the other elementary reactions to which the concentration profile of atomic oxygen was less sensitive were also taken into considerations (up to 80 elementary reactions based on the mechanism of Westbrook[17]).

The numerical analyses indicated that the initial decay profile of O atom concentration was mostly governed by the rate constant for reaction (1) without being affected very much by other side reactions specially at the lower temperature range below 1500 K, and that the concentration profile of O atoms after the initial decay part was sufficiently sensitive to the rate of the consecutive reaction (3). It was also indicated by the numerical simulations that the concentations of atomic oxygen without flash photolysis were lower by at least an order of magnitude than those with flash photolysis under the same experimental conditions. Thus, much higher initial concentrations of CH_4 and O_2 are needed to detect atomic oxygen in the case of no flash photolysis; the time history of the concentration of atomic oxygen is affected very much by a lot of side reactions other than reaction (3a) when the initial concentration of CH_4 or O_2 is increased.

Below 1500 K, observed concentration profiles of atomic oxygen showed single exponential decay without showing appreciable regeneration of atomic oxygen by the subsequent reactions, as was predicted by the numerical calculations. The rate constant for reaction (1) could be directly evaluated from the pseudo-first-order analysis of this decay curve, because the concentration profile of atomic oxygen was found to be insensitive to the rate of reaction (3) at this low temperature under the present experimental conditions.

The reproduction of O atoms by the consecutive reactions becomes evident above 1600 K and does not show a single exponential decay profile of O atom concentration, as shown in Fig. 1(a). In this case, the initial decay part of O atom concentration between 0—50 μs is analyzed to evaluate the rate constant for reaction (1). Also, an observed reproduction behaviour of atomic oxygen is compared with simulated ones to evaluate k_{3a} and k_{3b}.

Examples of the fittings are shown in Fig. 2. Curve a shows the best fit for $k_{3b}=0$, which gives $k_{3a}=5.93\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}, whereas curve b is for $k_{3a}=0$ giving $k_{3b}=4.14\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. Although k_{3b} was required to be larger than k_{3a} by about an order of magnitude to achieve the consistency of the calculated concentration profiles of atomic oxygen with the observed profile, calculated concentration profiles could be fitted to the experimental result in both cases. Possible combinations of k_{3a} and k_{3b} have been determined as follows. With a given value for k_{3a}, numerical calculations were performed to obtain values for k_{3b} which gave the observed concentrations of atomic oxygen at 300, 400, and 500 μs. Then these three values were averaged. Varying a value for k_{3a}, a straight line such as shown in Fig. 3 was obtained at each temperature. Thus, it was impossible to determine the branching fractions for (3a) and (3b) from the observed profile of O atom concentration.

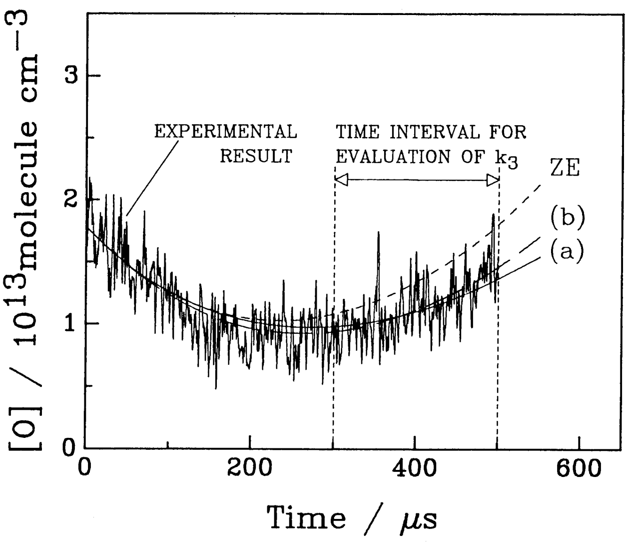

Fig. 2. Comparison of the experimental and calculated profiles of O atoms. Initial condition: 67 ppm CH_4+ 2.0% O_2+3 ppm O+Ar, T=1647 K, P=1.36 atm. (a): numerical simulation with $k_{3a}=5.93\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} and $k_{3b}=0$, (b): numerical simulation with $k_{3a}=0$ and $k_{3b}=4.14\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, ZE: numerical simulation with the rate constants for reaction (3) proposed by Zellner and Ewig.[5]

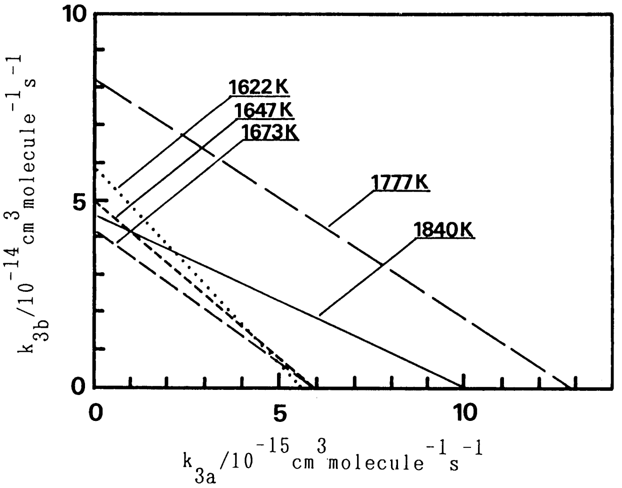

Fig. 3. Possible combinations of k_{3a} and k_{3b}. Each line represents combinations of k_{3a} and k_{3b} which are consistent with observed O atom concentrations at t=300–500 μs at each temperature.

The concentration profiles of H atoms, in contrast, were not so useful for discussing the mechanism of CH_3+O_2 reaction. An example of the profile of 121.6 nm absorption is shown in Fig. 1(b). It gradually increased when reflected shock wave passed through the observation station, and then reached a steady state at relatively low temperature range below 1700 K: no distinguishable difference between the profiles with and without ArF laser photolysis was observed. As similar profiles were observed when O_2–Ar mixtures were shock heated, it was concluded that the observed absorption was due to vibrationally excited O_2 and not to H atoms. At higher temperature range, the absorption intensity increased due to generation of H atoms with substantial induction time. However, such delayed production processes of H atoms were not useful for evaluating the rate constants for reaction (3) independently. Numerical simulations based on the evaluated rate constants for reaction (3) also indicated that the concentration of H atoms should be well below the detection limit for H atoms of this experimental system (about 10^{-11} mol cm^{-3}) before 400 μs in the present experimental conditions.

The present results on the rate constant k_1 agree very well with those of previous work[18-25] as shown in Fig. 4. A least-square analysis of the rate constants measured in this study gives

$$k_1 = 10^{-8.95\pm0.27}\exp(-15.4 \pm 2.0\ \text{kcal mol}^{-1}/RT)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$
$$(T = 1365\text{—}1840\ \text{K}),$$

where the limits of error represent one standard deviations.

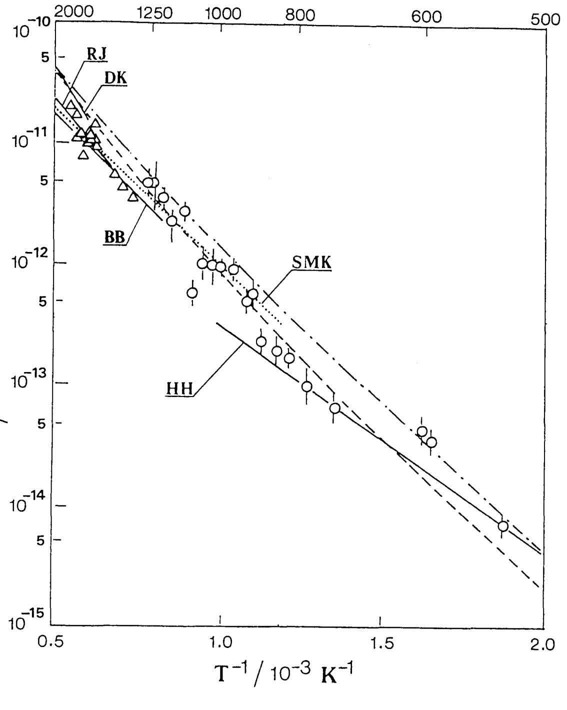

Fig. 4. Comparison of the rate constant for the reaction $O+CH_4 \rightarrow OH+CH_3$ (1). Experimental result; triangle: Present study, circle: Felder and Fontijn (Ref. 25), BB: Brabbs and Brokaw (Ref. 2), RJ: Roth and Just (Ref. 20), DK: Dean and Kistiakowsky (Ref. 21), HH: Herron and Huie (Ref. 22), SMK: Sutherland et al. (Ref. 26), calculation by transition state theory (Ref. 27); dashed curve: without Wigner's correction, dash-dotted curve: with Wigner's correction for tunneling effect.

Discussion

While the rate constants for the reactions (3a) and (3b) could not be evaluated independently in this study, reaction (3a) has been proposed to be the dominant channel by several groups.[1-3,7] So, it seems meaningful to compare the present result assuming that $k_{3b}=0$ with previous ones. The values for k_{3a} with $k_{3b}=0$, which will now be denoted as k_{3a0}, were reevaluated in a more sophisticated manner than that used in the preceding section. With consideration of standard deviations of observed O atom concentrations, the probability density functions of k_{3a} were obtained at 300, 400, and 500 μs independently. Then these functions were multiplied by weights and summed over to obtain the total probability density function of k_{3a}, where the weight was regarded as proportional to the sensitivity of O atom concentration to k_{3a}. An expectation value obtained from this total probability density function was regarded as the most probable value for k_{3a}. An error limit was also evaluated from the total probability density function, and represents 68% of accuracy. k_{3a0} evaluated in such a manner are summarized in Table 1.

Our k_{3a0} values are compared with previous results of indirect measurements of k_{3a} in Fig. 5. As shown in Fig. 5, k_{3a0} shows an excellent agreement with previous measurements on k_{3a} and also agrees very well with the estimation given by Warnatz.[16] As the sensitivity of a concentration profile of atomic oxygen to k_{3b} is less than to k_{3a} by about an order of magnitude, k_{3a} is reduced only by 10—20% from k_{3a0} even if $k_{3b}=k_{3a}$. An ab-initio calculation of the potential energy surface of the CH_3+O_2 system performed by Kamiya[18] indicates that reaction (3b) proceeds via a transition state ($^2A'$), which lies clearly above the potential energy curve ($^2A''$) leading to the formation of CH_3O+O. According to this result, k_{3b} is not expected to be larger than k_{3a}.

As is shown in Fig. 5, Zellner and Ewig[5] indicated that k_{3b} was much larger than k_{3a} below 2000 K, while the value for k_{3a} proposed by them is consistent with other measurements,[1,2,7] the estimation by Warnatz,[16] and k_{3a0} evaluated in this study. In order to examine the validity of their conclusion, the concentration profiles of atomic oxygen were compred with those calculated by numerical computations using their proposed rate constants for (3a)

Table 1. Summary of the Evaluated Values for k_{3a} with $k_{3b}=0$

Temperature/K	Pressure/atm	k_{3a0}[a]/cm^3 molecule^{-1} s^{-1}
1622	1.3	$(6.8\pm4.2)\times10^{-15}$
1647	1.3	$(6.1\pm2.3)\times10^{-15}$
1673	1.4	$(6.1\pm2.2)\times10^{-15}$
1777	1.5	$(1.4\pm0.8)\times10^{-14}$
1840	1.6	$(9.6\pm3.8)\times10^{-15}$

a) Values obtained with consideration of the experimental uncertainties (see text).

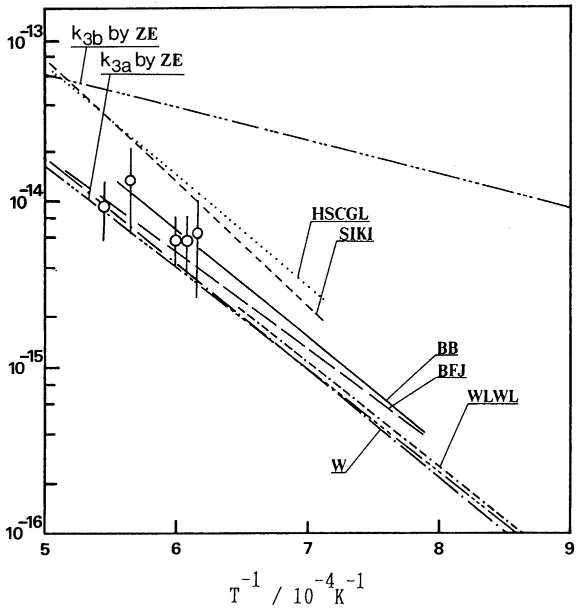

Fig. 5. Summary of the experimental results on the rate constant for the reaction CH_3+O_2 (3). all the date correspond to k_{3a} if unspecified; circle: The present values for k_{3a} with $k_{3b}=0$ which are obtained with consideration of the experimental uncertainties (see text), BFJ: Bhaskaran et al. (Ref. 1), BB: Brabbs and Brokaw (Ref. 2), HSCGL: Hsu et al. (Ref. 3), SIKI: Saito et al. (Ref. 4), ZE: Zellner and Ewig (Ref. 5), WLWL: Wu et al. (Ref. 7), W: estimation by Warnatz (Ref. 16).

and (3b). An example of such simulations is shown in Fig. 2 by dotted curve labeled ZE. It is suggested that the rate constant for (3b) proposed by Zellner and Ewig seems to be too large, because all the concentration profiles of atomic oxygen observed in this study are below the results of the simulations performed with the rate constants for reaction (3a) and (3b) proposed by them.

In this study, the examination of reaction (3) was limited in a very narow temperature range. The sensitivity of a concentration profile of atomic oxygen to the rate constant for reaction (3a) became too low below 1500 K unless the initial concentration of O_2 was much higher than that in the present experiments. But the intense absorption by too much O_2 obscured the ARAS signals in this case. At higher temperature range, decomposition of CH_4 and many other side reactions became significant, and thus the sensitivity of concentration profiles of atomic oxygen to the rate constant for reaction (3a) was no longer high enough relative to other consecutive reactions. Examination of this process at wider temperature range (specially at low temperatures) seems to be still meaningful.

The present experimental result on the rate constant for reaction (1) agrees very well with those of previous indirect studies[19-24] as well as those of the direct measurements in a static cell[25] or shock tube flash photolysis studies.[26] These experimental results agree very well with the theoretical calculation based on the transition state theory(TST).[27]

Including the experimental data at lower temperatures, the pronounced nonlinearity of the Arrhenius plot is indicated, which is mainly caused by the large temperature dependence of the vibrational partition function of the transition state. According to the TST calculation together with theoretical POL-CI calculation of the potential energy surface,[28] the effective activation energy varies from 14.3 kcal mol^{-1} (1000 K) to 18.6 kcal mol^{-1} (2000 K): this is consistent with the present experimental result of 15.4±2.0 kcal mol^{-1} (T=1365—1840 K).

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