$CH_3 + O_2 \rightarrow H_2CO + OH$ Revisited

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New reflected shock tube kinetics experiments have been performed on the reaction $CH_3 + O_2 \rightarrow H_2CO + OH$ over the temperature range 1244−1502 K. This study was carried out using a White cell multipass (path length = 7 m) optical system observing OH-radical absorption at 308 nm. Within experimental error, the new results are in excellent agreement with an earlier study from this laboratory and have therefore been combined with the earlier data, yielding an updated Arrhenius description for the rate constant, $k = (1.06 \pm 0.32) \times 10^{-12} \exp(-6801 \pm 439K/T)$ cm^3 molecule^{-1} s^{-1}. This result is compared to earlier determinations, evaluations, and theory.

Introduction

The reaction of CH_3-radicals with O_2

$$CH_3 + O_2 \rightarrow H_2CO + OH \quad (1)$$

is an important propagation reaction in the combustion chemistry of almost all saturated hydrocarbons from CH_4 to constituents in gasoline. As discussed in a recent paper from this laboratory,[1] other reactive processes are possible, but only one additional reaction

$$CH_3 + O_2 \rightarrow CH_3O + O \quad (2)$$

is important at high temperature and low pressure.

In the aforementioned work,[1] rate constants for reaction 2 were evaluated using data from four investigations,[1−4] and the rate constant expressions describing these studies were within ±30% of the evaluation,

$$k_2 = 1.253 \times 10^{-11} \exp(-14\,241K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (3)$$

giving confidence in eq 3 over the experimental temperature range of the studies, 1250−2430 K, used in the evaluation. However, a similar evaluation for reaction 1 using five previous studies[1,3−6] over the temperature range 1237−2430 K gave

$$k_1 = 3.11 \times 10^{-13} \exp(-4953K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (4)$$

The eq 4 evaluation from this laboratory[1] was less satisfactory, being within only ±46% (over respective T-ranges of the studies) of three of the studies used in the evaluation,[1,3,6] with two[4,5] being either higher or lower than eq 4 by about a factor of 3. Furthermore, extrapolating the modified Arrhenius expression determined by Herbon et al.[6] (1590−2430 K) down to 1250 K gives a value that is only 27% of that calculated from eq 4 for the same temperature. However, the Hessler et al.[6] expression is within ∼10−30% of eq 4 over their temperature range, 1237−1520 K. Because of these inconsistencies in k_1, there is a continuing interest in the title reaction, and this has prompted the present work.

Experimental Section

We earlier described a long absorption path White cell multipass optical system for OH-radical detection in the reflected shock regime[7] and used it to measure high-temperature rate constants.[1,8,9] In this work, we have increased the path length for absorption from 32 passes (2.798 m) to 80 passes, giving a total path length of 6.996 m, thereby increasing the sensitivity for detection by 2.5. In addition, we have improved the optical beam control, resulting in an increased signal-to-noise level. These two improvements combine to minimize the effects of secondary reaction perturbations.

Gases. High-purity He (99.995%), used as the driver gas, was from AGA Gases. Scientific grade Kr (99.999%), the diluent gas in reactant mixtures, was from Spectra Gases, Inc. The ∼10 ppm impurities (N_2 2 ppm, O_2 0.5 ppm, Ar 2 ppm, CO_2 0.5 ppm, H_2 0.5 ppm, CH_4 0.5 ppm, H_2O 0.5 ppm, Xe 5 ppm, and CF_4 0.5 ppm) are all either inert or in sufficiently low concentration so as to not perturb OH-radical profiles. The diluent gas also contained ∼10% Electronic Grade He (99.9999% from AGA Gases) to vibrationally relax O_2. Distilled water, evaporated at one atmosphere into ultrahigh-purity grade Ar (99.999%) from AGA Gases, was used at ∼25 Torr pressure in the resonance lamp. Scientific grade O_2 (99.999%), for reaction mixtures, was obtained from MG Industries and was used without additional purification. Analytical grade CH_3I (99%) from Aldrich Chemical Co. Inc. was further purified by bulb-to-bulb distillation with the middle third being retained. Test gas mixtures were accurately prepared from pressure measurements using a Baratron capacitance manometer and were stored in an all-glass vacuum line.

Results and Discussion

Figure 1 shows a typical concentration profile for OH-radical buildup in an experiment at 1389 K and a simulation using the mechanism given previously[1,10] with one additional updated rate constant for the reaction, $H_2CO + OH \rightarrow H_2O + HCO$.[11] In the simulation, eq 3 was used for reaction 2, and the rate constant

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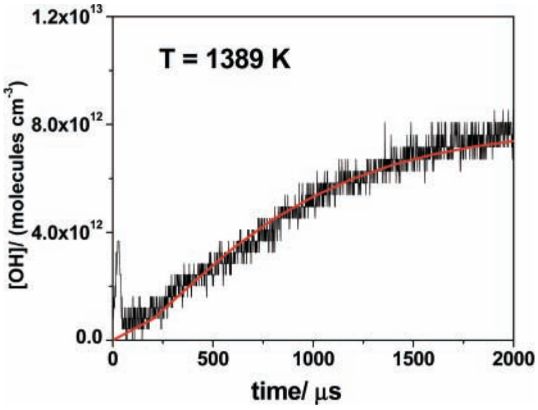

Figure 1. A typical [OH] profile. The solid line is a fit using a full reaction mechanism with only k_1 varied. The conditions for the experiment are $P_1 = 10.89$ Torr and $M_s = 2.407$, $T_5 = 1389$ K, $\rho_5 = 2.125 \times 10^{18}$ molecules cm^{-3}, $[CH_3I]_0 = 9.055 \times 10^{12}$ molecules cm^{-3}, and $[O_2]_0 = 1.457 \times 10^{17}$ molecules cm^{-3}.

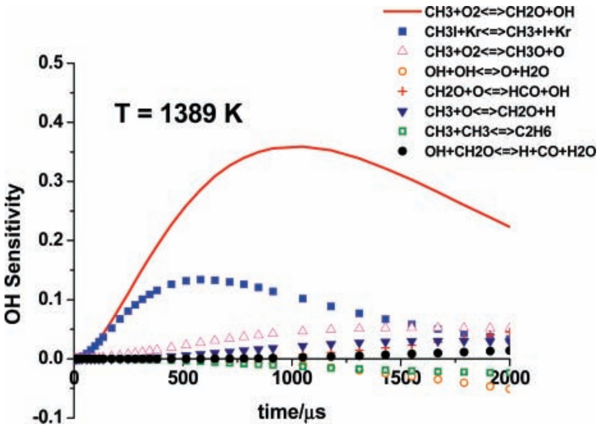

Figure 2. OH-radical sensitivity analysis for the profile shown in Figure 1 using the full reaction mechanism scheme and the final fitted value for k_1 listed in Table 1. The eight most sensitive reactions are shown in the inset.

TABLE 1: High-Temperature Rate Data for $CH_3 + O_2 \rightarrow CH_2O + OH$

$X_{CH_3I} = 4.261 \times 10^{-6}$		$X_{O_2} = 6.857 \times 10^{-2}$	$X_{He} = 1.105 \times 10^{-1}$	
P_1/Torr	M_s[a]	$\rho_5/(10^{18}$ cm$^{-3})$[b]	T_5/K[b]	k_{1c}
10.87	2.435	2.141	1423	7.15(−15)[c]
10.89	2.407	2.125	1389	7.00(−15)
10.87	2.411	2.125	1394	7.00(−15)
10.87	2.509	2.211	1501	1.10(−14)
10.89	2.510	2.216	1502	1.90(−14)
15.92	2.256	2.877	1244	2.50(−15)
15.84	2.383	3.042	1369	4.10(−15)
15.82	2.331	2.967	1317	4.60(−15)

[a] The error in measuring the Mach number, M_s, is typically 0.5−1.0% at the one standard deviation level. [b] Quantities with the subscript 5 refer to the thermodynamic state of the gas in the reflected shock region. [c] Parentheses denote the power of 10.

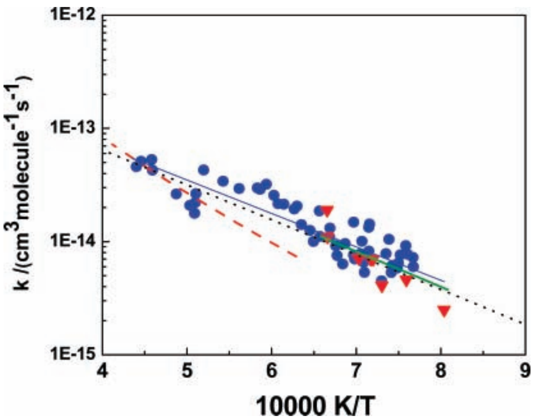

Figure 3. Arrhenius plot of the data for k_1 from ref 1 (●) and Table 1 (▼) over the T-range 1244−2272 K. Solid blue line, fit to the present and earlier data (eq 6 in text); red dashed line, ref 3; green solid line, ref 6; dotted line, ref 12 (eq 7 in text).

for only reaction 1 was varied to fit the initial profile. Figure 2 shows the OH sensitivity analysis corresponding to the Figure 1 experiment. It is clear that the profile is most sensitive to reaction 1, and the resulting k_1 for this experiment is given in Table 1 along with similar values for seven other experiments performed in the lower-T regime (i.e., ≤1502 K). As in the earlier work,[1] the long-time [OH] predictions fell below the measurements; however, better predictions resulted if we considered the HCO radicals formed from $H_2CO + OH \rightarrow H_2O + HCO$ to be vibrationally hot, giving H + CO products instantaneously. This postulated process does not affect the values for k_1 because initial slope analysis was used for the k_1 determinations.

The earlier 54 data points for k_1 from this laboratory[1] are plotted in Arrhenius form in Figure 3 along with the new data from Table 1. The previous 54 data points gave

$$k_1 = (8.36 \pm 2.47) \times 10^{-13} \exp(-6395 \pm 446 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

However, if the 54 values from the previous work[1] and the 8 new values from Table 1 are combined, the linear-least-squares Arrhenius expression derived from the 62 experiments is

$$k_1 = (1.06 \pm 0.32) \times 10^{-12} \exp(-6801 \pm 439 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

Within the experimental scatter, there is little difference between eqs 5 and 6 (i.e., only ±7%).

After considering all of the previous data on reaction 1, the recent 2005 Baulch et al. evaluation[12] recommends

$$k_1 = 1.10 \times 10^{-12} \exp(-7094 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (7)$$

over the T-range 1000−2500 K. Equations 6 and 7 are also shown in Figure 3 along with the Herbon et al.[3] and Hessler et al.[6] results. Equation 6 agrees even better with the data of Hessler et al. than our earlier evaluation, eq 4. It also agrees with the Baulch et al. evaluation,[12] eq 7, within experimental error, and is somewhat closer to the Herbon et al. study.

The $CH_3 + O_2$ reactions have been theoretically addressed by Zhu et al.,[13] and reactions 1 and 2 occur on $^2A'$ and $^2A''$ states, respectively. Ground-state reactants on the $^2A''$ state can directly react over a substantial barrier to give reaction 2 products or, at lower-T, cross over to the $^2A'$ state giving reaction 1 products. According to Zhu et al.,[13] this latter process has a barrier of 15.0 kcal mol^{-1} above separated ground-state reactants. We earlier suggested[1] that better agreement with experiment resulted if this barrier were lowered by 1.6 kcal mol^{-1}. If the energetics of the transition state is the only property considered (i.e., structures and force fields are not modified), to obtain convergence between theory and experiment, the barrier height would now have to be lowered to between 7.6 and 8.1 kcal mol^{-1}. This adjustment then gives values that are within ±30% of eqs 6 or 7 for most of the *T*-range, only becoming higher by ~40% at $T = 2270$ K.

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