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Kinetics of the Reaction between Methyl Radicals and Oxygen Atoms between 294 and 900 K

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The kinetics of the reaction of methyl radicals with oxygen atoms has been investigated in a heatable tubular reactor coupled to a photoionization mass spectrometer. The reactants (CH_3 and $O(^3P)$) were generated homogeneously in the reactor by the simultaneous in situ photolysis of acetone and SO_2. Initial conditions were always chosen to yield $[O]/[CH_3]_0 > 20$. The decay of CH_3 was monitored as a function of [O] to yield rate constants for the reaction $O + CH_3 \rightarrow H_2CO + H$ at five temperatures between 294 and 900 K. The rate constant was found to be independent of temperature, having a value 1.4×10^{-10} cm^3 molecule^{-1} s^{-1}, and also independent of density in the range used in this study, $(3–24) \times 10^{16}$ molecule cm^{-3}. The mechanism was verified by direct observations of H_2CO production. The new experimental method, which can be used to investigate many reactions of oxygen atoms with free radicals, is described in detail.

Introduction

The chemistry of methyl radicals in high-temperature combustion processes is unique. Unlike other alkyl radicals, CH_3 is almost impervious to thermal decomposition.[1] Reaction of CH_3 with molecular oxygen involves a significant activation energy and is therefore slow.[2-5] More complex alkyl radicals react rather rapidly with molecular oxygen at elevated temperatures because exothermic production of olefins is possible,[6,7] a process which occurs with little or no activation energy. The only fast reactions involving CH_3 under typical combustion conditions are those with atoms and small inorganic free radicals (such as H, O, and OH) or with other small, relatively stable hydrocarbon radicals (e.g., CH_3, C_3H_3, C_3H_5).[8] For example, modeling studies have shown that the reaction

$$CH_3 + O \rightarrow H_2CO + H \qquad (1)$$

is the most important reaction consuming CH_3 in stoichiometric methane–air flames.[9] Under fuel-rich conditions, recombination, which leads to C_2 chemistry, becomes an additional important reaction of the methyl radical,[10]

$$CH_3 + CH_3 \rightarrow C_2H_6 \quad (\text{or } H + C_2H_5) \qquad (2)$$

The kinetics of reaction 1 has been the subject of numerous investigations because of its important role in high-temperature combustion processes.[8] However, with the exception of one study conducted between 1700 and 2300 K,[3] reaction 1 has not been isolated for direct study except at or very near ambient temperature.[11-14] Most investigations at elevated temperatures which have gained some knowledge of the kinetics of this reaction combined observations of species concentration profiles in premixed flames (or in shock-heated mixtures of fuel and oxygen) with simulations of the chemistry of the systems studied by using mechanisms which included reaction 1.[15-17]

The room temperature studies have obtained values of k_1 in the range $(1.0–1.8) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[11-14] The reaction appears to proceed exclusively by the mechanism indicated.[18] Because k_1 is essentially the CH_3–O collision number, the reaction is presumed to proceed without an energy barrier. This presumption is borne out by the results of the high-temperature investigation by Bhaskaran, Frank, and Just who determined that $k_1 = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} throughout the temperature range covered, 1700–2300 K.[3] So, in spite of the dearth of studies of reaction 1 at elevated temperatures, the kinetics of this important combustion reaction appears to be relatively well understood over a significant range of conditions.

We have now investigated the kinetics of reaction 1 from 294 to 900 K. The study was conducted in part to gain additional quantitative knowledge of the kinetics of this reaction at elevated temperatures but also to test and to use a new, versatile procedure for studying the kinetics of reactions of oxygen atoms with free radicals. Reaction 1 was studied in a heatable tubular reactor coupled to a photoionization mass spectrometer. The procedure used involves the simultaneous generation of both labile reactants in the reactor using UV laser photolysis under conditions which are suitable for studying the kinetics of the reaction between them. The results of this investigation and a description of the new experimental procedure are presented here.

Experimental Section

Overview of Experimental Procedure. The experimental apparatus used and most of the procedures employed to reduce the data have been described previously.[19-21] Pulsed unfocused 193-nm radiation (5 Hz) from a Lambda Physik EMG 101E excimer laser was directed along the axis of a heatable 1.05 cm i.d., uncoated quartz tubular reactor. Gas flowed through the tube at 4 m s^{-1} and was completely replaced between laser pulses. The flowing gas contained SO_2 (the O-atom source; <0.3%), acetone (the CH_3 source; typically 0.01%), and the carrier gas (He) which was always in great excess (>99%). Gas was sampled

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through a 0.043 or 0.020 cm diameter hole (located at the end of a nozzle in the wall of the reactor) and formed into a beam by a conical skimmer before it entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion was photoionized and then mass selected. Temporal ion signal profiles were recorded from a short time before each laser pulse to as long as 25 ms following the pulse by using a multichannel scalar. Data from 3000 to 30 000 repetitions of the experiment were accumulated before the data were analyzed.

The two reactants (CH_3 and O) were produced simultaneously by laser photolysis:

$$SO_2 \xrightarrow{193\ \text{nm}} SO + O(^3P) \qquad (3)$$

$$CH_3COCH_3 \xrightarrow{193\ \text{nm}} 2\ CH_3 + CO \qquad (4)$$

The initial concentrations of O and CH_3 were determined from the measured extents of photodecomposition of SO_2 and acetone whose concentrations were chosen to yield an O-atom concentration which was at least a factor of 20 greater than the initial CH_3 concentration in each experiment. Under these conditions oxygen atoms were not significantly depleted by reaction 1. The decay of CH_3 was measured as a function of [O] to obtain the rate constant of reaction 1.

The photodecomposition of acetone at 193 nm produces CH_3 which is vibrationally excited.[22] However, since the vibrational relaxation time of CH_3 under our experimental conditions[22] is short (<0.1 ms) compared to the reaction time (10–25 ms), it is the thermal reaction between CH_3 and O that is being observed in these experiments.

SO_2 Photolysis as a Source of Oxygen Atoms. SO_2 is an excellent photolytic source of $O(^3P)$ for kinetic studies. There has been some prior use of SO_2 for this purpose,[23-28] but it has not heretofore been used in investigations of the kinetics of reactions between oxygen atoms and hydrocarbon free radicals. The photolysis of SO_2 at 193 nm has four important properties which make a useful O-atom source.

1. Photolysis at 193 nm yields essentially only SO and $O(^3P)$. This study, and ones which will follow, involve the reactions of ground-state oxygen atoms with polyatomic free radicals. The photolysis process should therefore not simultaneously yield oxygen atoms in any excited states. Although 193-nm photolysis can produce SO in the $^1\Delta$ state in addition to the $^3\Sigma^-$ ground state, there is not enough energy available to produce excited oxygen atoms in a single-photon process.[29,30] $SO(^1\Delta)$ appears not to be produced to a significant degree during this photolysis. An attempt was made to detect it by monitoring the SO ion signal using a photoionization energy (9.5 eV) which is energetic enough to ionize $SO(^1\Delta)$ but not $SO(^3\Sigma^-)$. (Ground-state SO has an ionization potential of 10.3 eV.[31]) No ion signal from $SO(^1\Delta)$ was detected.

Additional searches were conducted for products of multi- or multiple-photon processes, $O(^1D)$ and sulfur atoms. In the experiments conducted to determined the extent of $O(^1D)$ production, CH_4 was added to the system, and the yield of CH_3 (produced by the rapid reaction, $O(^1D) + CH_4 \rightarrow OH + CH_3$) measured. No detectable amount of CH_3 was produced when SO_2 was photodecomposed in the presence of CH_4. It could be concluded that the yield of $O(^1D)$ was less than 0.01% that of $O(^3P)$. Sulfur atoms were produced by the photolysis process in detectable concentrations. The S-atom yield depended on the laser fluence to the 1.5 power, which suggests it is produced by both one- and two-photon processes. The sulfur atom yield was measured by using a titration procedure. Molecular oxygen was added to the system and the SO yields with oxygen present and absent were compared. There was no detectable difference in SO yields. It was concluded that the S-atom concentration produced by photolysis was less than 1% that of $O(^3P)$.

2. SO_2 is chemically inert. The free-radical reactants (O and CH_3 in this study) should not react to a significant degree with the O-atom source. The O-atom concentration must remain as nearly constant as possible in these experiments, and the decay of CH_3 should be due principally to the reaction with oxygen atoms. Both CH_3 and oxygen atoms do not react with SO_2 to a measurable extent. The reaction

$$O + SO_2 \rightarrow SO + O_2 \qquad (5)$$

is endothermic by 53.5 kJ/mol and hence does not have a significant rate in these experiments. The spin-forbidden recombination

$$O + SO_2\ (+\ M) \rightarrow SO_3\ (+\ M) \qquad (6)$$

is likewise too slow at the gas densities used in these studies to consume noticeable amounts of oxygen atoms.[32] Any possible reaction between CH_3 and SO_2 was too slow to detect and hence had an insignificant rate compared to that of reaction 1. The reactions of polyatomic free radicals with SO_2 have not been extensively studied. An addition reaction is possible:[33]

$$CH_3 + SO_2\ (+\ M) \rightarrow CH_3SO_2\ (+\ M) \qquad (7)$$

We have tried to measured the rate of this reaction by generating CH_3 at 248 nm (from CH_3I) in the presence and absence of SO_2. At this longer wavelength SO_2 is not photodecomposed. In these experiments, the CH_3 decay rates (which were very slow and due only to heterogeneous processes) were identical in the presence and in the absence of SO_2.

3. SO, the second photoproduct produced by the photolysis of SO_2, is significantly less reactive with hydrocarbon free radicals than is the oxygen atom. Its presence does not provide an additional sink for CH_3 which would obscure direct observation of reaction 1. This fact was established for CH_3 by tests in which the decay of SO produced by the photolysis of SO_2 was monitored under very different conditions, in the presence of an excess of CH_3 ($[CH_3]/[SO]_0 = 20$). There was no decay of the SO whether CH_3 was present or absent over the full temperature range of this study, indicating that there was no measurable reaction occurring between SO and CH_3 under these conditions. Similar tests will be performed in future experiments involving other free radicals to determine whether or not this same important property persists.

Recombination reactions involving SO (e.g., $CH_3 + SO + M \rightarrow CH_3SO + M$) may occur, but their rates are too low to measure at the gas densities used in these studies.

4. SO_2 photodecomposes to a significant extent with unfocused 193-nm laser radiation. The oxygen-atom concentration must be determined in these experiments. Values are obtained from the measured extents of SO_2 photolysis. Photodecomposition above 1–2%/pulse can be measured with the desired accuracy (±5%). The high absorption cross section of SO_2 at 193 nm ($\sigma = 6 \times 10^{-18}$ cm^2)[34] and high O-atom quantum yield[35,36] assure that a significant fraction of SO_2 photodecomposes when unfocused laser radiation is used (which is required to obtain uniform photolysis along the

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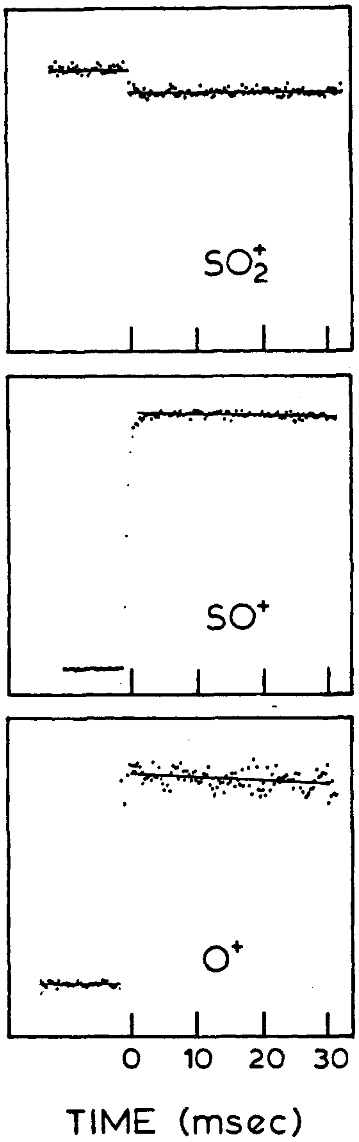

Figure 1. Plot of ion-signal profiles of SO_2 and its photolysis products recorded in experiments conducted at 360 K. $[SO_2]_0 = 4.0 \times 10^{13}$ molecule cm^{-3}. $[M] = 6.1 \times 10^{16}$ molecule cm^{-3}. Percent SO_2 decomposition = 6.2 (base line of SO_2 ion signal is not shown).

tubular reactor). In a typical experiment, the SO_2 decomposition was 2.5–3.0%/pulse (but always above 1.5%).

Sample ion signal profiles of SO_2 and its photolysis products are shown in Figure 1. The small decay of oxygen atoms is due to heterogeneous loss. Below 400 K this decay was so slow that the measured initial O-atom concentration was used uncorrected in the data analysis discussed below. Above 400 K, the O-atom decay (due to these same processes) was greater and had to be taken into account. The O-atom concentration following photolysis was determined from the observed depletion of SO_2 caused by photodecomposition (see Figure 1) and from the known concentration of SO_2 in the reactor.

Acetone Photolysis as the CH_3 Source. Acetone was chosen as the CH_3 source because of its high absorption coefficient (which permitted measurement of initial CH_3 concentrations) and relatively low reactivity. The reaction of acetone with oxygen atoms is slow[37] and consumed less than 1% of the atoms, even at the highest temperature of this study. The CH_3 + acetone reaction is too slow to be detected even at 900 K.[38] Finally, the O + acetone reaction does not regenerate CH_3,[37] a process which, if it did occur, would seriously complicate interpretation of the experimental observations.

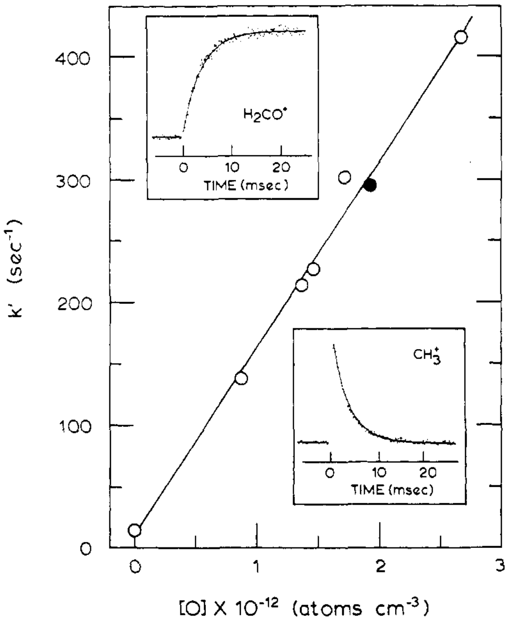

Figure 2. Plot of $[CH_3]$, first-order decay constants vs. [O] for series of experiments conducted at 294 K. $[M] = 6.1 \times 10^{16}$ molecule cm^{-3}. Inserts are ion-signal profiles recorded during experiments conducted at $[O] = 1.93 \times 10^{12}$ molecule cm^{-3} (closed circle on figure). Lines through data are exponential functions from nonlinear least-squares fits. Fitted exponential constants (k') are 295 s^{-1} (for CH_3 decay) and 265 s^{-1} (for H_2CO growth).

Data Analysis. Under the experimental conditions of this study, the significant reactions of CH_3 and O were reaction 1 and two heterogeneous loss processes:

$$CH_3 + O \rightarrow H_2CO + H \quad (1)$$

$$CH_3 \rightarrow \text{heterogeneous loss} \quad (8)$$

$$O \rightarrow \text{heterogeneous loss} \quad (9)$$

Initial CH_3 concentrations were kept low (below 1×10^{11} molecule cm^{-3}) not only to maintain [O] in large excess but also to assure that radical–radical reactions (such as reaction 2) had negligible rates in these experiments. In each group of experiments conducted to measure k_1, the CH_3 decay constant was measured at least once with a lower acetone concentration than was used in the remaining experiments in order to observe the effect of changing $[CH_3]_0$ (as well as $[CH_3COCH_3]$ itself). Lowering the acetone concentration by a factor of 2 did not alter the CH_3 decay rate at all, which verified that reaction 2, as well as the CH_3 + CH_3COCH_3 reaction, did not consume measurable amounts of CH_3.

The initial O-atom concentration was usually changed by varying the SO_2 concentration in the system. However, in each set of experiments, the O-atom concentration was also reduced once by lowering the laser fluence by a factor of 2 instead of reducing the SO_2 concentration. This gave an opportunity to compare the results of two experiments in which the extent of SO_2 photolysis was different by a factor of 2 (typically 1.5 and 3.0%) but where $[O]_0$ was the same. The CH_3 decay constant was always the same in two such experiments. This behavior was expected. Nevertheless this test was repeatedly performed to increase confidence that the O-atom concentration can be quantitatively determined from the measured extent of SO_2 photolysis under the experimental conditions used in this study.

In the experiments conducted between 295 and 400 K, the O-atom concentration remained essentially constant during the time the CH_3 decay was monitored (25 ms). The decay of $[CH_3]$ was exponential in shape due to the pseudo-first-order conditions. The CH_3^+ ion signal profiles were fit to an exponential function ($[CH_3^+]_t = [CH_3^+]_0 \exp(-k't)$) by using a nonlinear least-squares

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TABLE I: Conditions and Results of Experiments To Measure Rate Constants of the Reaction between Oxygen Atoms and Methyl Radicals

T,[a] K	10^{-16}[M], molecule cm^{-3}	$10^{-10}[CH_3]_0$,[b] molecule cm^{-3}	typical SO_2 decomp, %	10^{-12}[O], molecule cm^{-3}	k_s, s^{-1}	k_9, s^{-1}	$10^{10}k_1$, cm^3 molecule^{-1} s^{-1}
295	3.0	5.4	4.5	0.69–2.72	9.3	3.2	1.58
294	6.1	3.0	8.5	0.88–2.67	15.2	0.0	1.52
295	11.8	5.0	2.5	1.11–3.06	12.3	0.5	1.32
296	24.2	5.1	2.5	0.54–2.70	17.4	1.5	1.34
360	6.1	4.4	6.0	0.33–2.25	3.8	1.6	1.40
360	12.1	9.5	3.0	1.04–2.42	7.7	0.0	1.59
450	6.2	4.6	5.0	0.85–2.15	3.4	9.8	1.64
450	12.1	12.2	3.0	1.25–2.74	2.7	2.5	1.22
600	3.1	4.3	3.0	1.02–2.12	7.1	34.6	1.51
600	6.2	11.	3.0	1.94–4.66	5.2	35.7	1.20
600	18.1	5.8	3.0	1.26–2.52	5.5	10.2	1.12
900	6.0	12.8	3.5	1.04–3.11	2.0	10.6	1.58

[a] Temperature uncertainty ±3 K (295 and 360 K), ±4 K (450 and 600 K), ±6 K (900 K). [b] These are maximum values of $[CH_3]_0$ used. The percent decomposition of acetone ranged from 0.5 at room temperature to 5 at 900 K. In experiments conducted using the lower oxygen-atom concentrations, $[CH_3]_0$ was also lowered (usually by reducing the acetone concentration) to maintain $[O]/[CH_3]_0 > 20$.

procedure. The rate constant for reaction 1 was obtained from slopes of plots of k' vs. [O] since, for the above mechanism, $k' = k_1[O] + k_8$. A sample CH_3^+ decay profile with the fitted exponential function and a plot of k' vs. [O] are shown in Figure 2.

Above 400 K (in the experiments conducted at 450, 600, and 900 K) the heterogeneous loss of O atoms was not a negligible process and had to be taken into account. In these higher temperature experiments the O-atom concentration was still always in large excess ($[O]/[CH_3]_0 > 20$). The observed O-atom decay was a kinetically first-order process with a rate constant, k_9, between 3 and 40 s^{-1}. In these higher temperature experiments, the decay of CH_3 is not exponential but rather obeys the equation[39]

$$[CH_3]_t = [CH_3]_0 \exp(-k_8 t) \exp[k''\{\exp(-k_9 t) - 1\}/k_9] \qquad (I)$$

$$k'' = k_1[O]_0$$

In these higher temperature experiments, the CH_3^+ ion signal decay profile was fit to eq I to obtain $[CH_3]_0$ and k''. The O-atom decay rate constant, k_9, was not an adjusted parameter in eq I but was measured at the temperature and density of the study. The value of k_1 was obtained, in an analogous manner to that used in the lower temperature experiments, from the slope of a plot of k'' vs. $[O]_0$.

Reaction Products. The H_2CO produced by reaction 1 was monitored in each set of experiments conducted below 600 K at one of the O-atom concentrations used (see the upper insert in Figure 2). These ion-signal profiles were fit to an exponential growth function $[H_2CO] = [H_2CO]_\infty (1 - \exp\{-k't\})$. In each case the growth constants obtained from this fit agreed with the CH_3 decay constants measured under the same experimental conditions within 10%. Neither HCO nor CH_2, products of alternative reaction routes, were detected in experiments at 298 and 600 K.

These observations confirm that reaction 1 is the mechanism of the O + CH_3 reaction,[18] and more importantly, show that products of the reactions of oxygen atoms with free radicals can be quantitatively monitored in experiments of this type. The mechanisms of the reactions of oxygen atoms with larger alkyl radicals proceed by more than one route.[40,41] None is extensively characterized, particularly at elevated temperatures. This ability to monitor products in real-time experiments will make it possible in future studies to identify reactive routes of these more complex reactions and to determine chemical branching behavior as a function of temperature.

Assessment of Accuracy of k_1. The most probable uncertainty of the values of k_1 determined in this study is ±20%. This takes into account the accuracies of the measured gas flow rates and total pressure, the determination of [O], and the accuracy of k' (or k'') obtained from the measured CH_3^+ ion signals.

A potential systematic error arises from the use of signal averaging in these experiments. The measured SO_2 depletion and CH_3 decay profiles are averages over many experiments in which the initial O-atom concentration fluctuates about the measured mean value. Pilling and co-workers have analyzed this problem in detail for several mechanisms and reaction conditions, including a first-order reaction under pseudo-first-order conditions (one reactant in excess whose concentration fluctuates). Even under extremely unfavorable conditions (25% standard deviation in the concentration of the reactant in excess, e.g., [O]) there would be only a 0.3% systematic error in the value of k_1 derived from exponential fits through the average decay signals of the second reactant and the average value of $[O]_0$.[42] The laser fluctuations in the current investigation had a standard deviation below 15%. Hence this potential source of error was not significant in these experiments.

Gas Sources and Purification Procedures. The gases used were obtained from Matheson (SO_2, 99.98% min) and Linde (Helium, 99.995% min). Acetone was obtained from Mallinckrodt (99.5% min) and CH_3I from Aldrich (99% min). Helium was used as provided while all other materials used were degassed by freeze–pump–thaw cycles and used without further purification.

Photoionization Energies Used To Detect Reactants and Products. Three photoionization energies were used in the mass spectrometer during this investigation. A neon resonance lamp (16.67, 16.85 eV) was used to detect oxygen atoms and SO_2, an argon lamp (11.62, 11.83 eV) to detect H_2CO and CH_2, and a hydrogen lamp (10.2 eV) to photoionize SO, CH_3, HCO, and acetone.

Discussion

Comparison of Results with Those of Prior Studies. There is good agreement between the values of k_1 obtained at ambient temperature and those reported in earlier studies. The average of our four values of k_1 at 295 K (1.4×10^{-10} cm^3 molecule^{-1} s^{-1}) is in the middle of the range of the prior determinations of k_1, (1.0–$1.8) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[11-14] Three of the four prior studies performed essentially the same experiment.[11-13] The approach to steady state of methyl radicals (produced by the $O + C_2H_4 \rightarrow CH_3 + HCO$ reaction and subsequently consumed by reaction 1) was monitored under conditions of small depletion of the reactants, O and C_2H_4. Under these conditions, the rate constant for reaction 1 could be obtained directly from the observed growth of $[CH_3]$ since $[CH_3]_t = [CH_3]_\infty [1 - \exp(-k_1[O]t)]$. In the fourth study, CH_3 radicals (produced by the F + CH_4 reaction) were mixed with oxygen atoms in a fast-flow reactor.[14] The exponential decay of the CH_3 radicals in the presence of an excess

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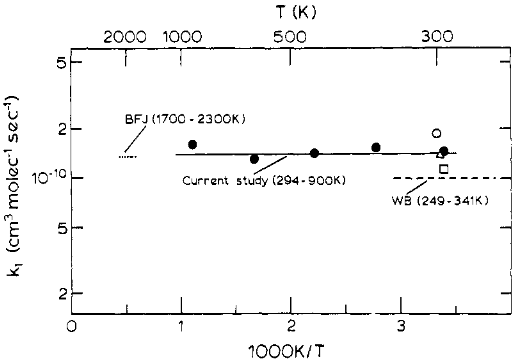

Figure 3. Arrhenius plot of measured values of $CH_3 + O \rightarrow H_2CO + H$ rate constant (k_1) obtained in the current study (closed circles and solid line) and in prior investigations: open circle, Slagle, Pruss, and Gutman, ref 12; open triangle, Washida, ref 13; open square, Plumb and Ryan, ref 14; dotted line, Bhaskaran, Frank, and Just, ref 3; dashed line; Washida and Bayes, ref 11.

of oxygen atoms was recorded, and the data were used to obtain k_1.

Over the range of temperatures covered (294-900 K), k_1 was found to be independent of temperature (see Table I). A similar temperature independence of k_1 was observed in two other studies. An extrapolation of the constant value of k_1 obtained in the current study (1.4 x 10^{-10} cm^3 molecule^{-1} s^{-1}) to the 1700-2300 K temperature range covered by Bhaskaran, Frank, and Just yields a value virtually identical with the one they obtained throughout this temperature range, 1.3 × 10^{-10} cm^3 molecule^{-1} s^{-1}.[3] Their high-temperature study of the kinetics of reaction 1 was essentially the thermal equivalent of the photochemical experiment used in the current investigation. CH_3 and O were produced suddenly at low concentrations by shock-heating precursor molecules (N_2O and C_2H_6) highly diluted in an inert gas. In these experiments, concentrations of H and O were monitored by using atomic absorption. Conditions were chosen to yield a high degree of sensitivity of these measurements to the rate constant of reaction 1. In the only other investigation of the temperature dependence of k_1, Washida and Bayes also found none in their study conducted near ambient temperature, 259-341 K.[11]

The rate constants for reaction 1 obtained in the current study and in the prior direct investigations of this reaction are plotted in Figure 3. The close agreement among the results of these investigations increases confidence that the kinetics of this reaction is established quantitatively for most conditions encountered in combustion processes.

In a data evaluation of prior investigations of reaction 1, Warnatz had suggested a consensus value of k_1 = 1.2 × 10^{-10} cm^3 molecule^{-1} s^{-1} which is independent of temperature (300-2500 K) for use in combustion modeling.[8] This average value of earlier direct and indirect determinations of k_1 is only slightly below our measured values.

SO_2 as a Source of Oxygen Atoms for Kinetic Studies. The 193-nm photolysis of SO_2 has proven to be an excellent source of ground-state oxygen atoms for kinetic studies. Decomposition using unfocused excimer laser photolysis is extensive enough (2-5%) to be accurately measured, thus providing the means to determine oxygen atom concentrations quantitatively. The procedures described in this paper for studying the kinetics of the CH_3 + O reaction can be used to investigate the kinetics and mechanisms of many additional reactions of oxygen atoms with free radicals.

The low reactivity of SO_2 with free radicals simplifies data analysis. No reactions of O or CH_3 with SO_2 could be detected. For this reason the range of conditions which could be used in these kinetic studies was not limited by the presence of SO_2 in the system but was determined essentially completely by the conditions which can be produced and maintained in the tubular reactor.

The increasing importance of the heterogeneous loss of oxygen atoms above 600 K can be taken into account with confidence by the data analysis described in this study even if the loss is significant (up to 30% during the testing time). Since the O-atom decay rate can be measured (in the absence of the second reactant) and is not altered by the reaction under study (because the oxygen atom concentration is always maintained in large excess), the data obtained in these high-temperature experiments can be analyzed in a straightforward manner to obtain the desired quantitative information on the kinetics of the reaction under study.

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Isomerization Kinetics of Partly Delocalized Radicals Observed by Muon Spin Rotation

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Barriers to isomerization by rotation about a partial double bond in α-carbonyl-, α-carboxyl-, and α-carbamide-substituted alkyl radicals have been determined by means of the technique of muon spin rotation. They agree with those observed previously by electron spin resonance but are higher than the thermochemically determined stabilization energies of similar species.

1. Introduction

Resonance stabilization of organic radicals has been a topic of interest in recent years. Well-known examples are allyl and benzyl radicals including substituted derivatives,[1-6] and furthermore, α-carbonyl- and α-alkoxycarbonylalkyl radicals.[7-12] Usually, resonance energies are derived from thermochemical

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(1) Benson, S. W. In *Thermochemical Kinetics*; Wiley: New York, 1976.