# Direct Measurement of the Reaction $CH_3$ + OH at Ambient Temperature in the Pressure Range 0.3–6.2 mbar

## H. Oser, N. D. Stothard, R. Humpfer, and H. H. Grotheer\*

Institute for Physical Chemistry of Combustion, DLR, Pfaffenwaldring 38, 7000 Stuttgart 80, FRG (Received: July 22, 1991; In Final Form: February 28, 1992)

The falloff behavior of the CH<sub>3</sub> + OH recombination reaction CH<sub>3</sub> + OH  $\rightarrow$  CH<sub>3</sub>OH (1a) has been quantitatively investigated for the first time. Methyl decay profiles were measured in a flow reactor at 300 K and in a pressure range between 0.3 and 6.2 mbar. The experimental conditions were such that a possible channel to <sup>1</sup>CH<sub>2</sub> + H<sub>2</sub>O did not contribute strongly to the CH<sub>3</sub> profiles. Rate coefficients were extracted from the data by comparison of the experimental profiles with computer simulations. The results are in accord with the limiting rate coefficient suggested by Hochanadel et al.,  $k^{\circ}_{1a}(298 \text{ K}) = 9.3 \times 10^{-11} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1.1</sup> The experimental falloff curve is described by use of this value for  $k^{\circ}$ , together with an interpolation formula given by Troe,<sup>2</sup> from which an approximate value for the low-pressure limit  $k^0_{1a} = (2.5 \bullet 1.0) \times 10^{-27} \text{ cm}^6$  molecule<sup>-2</sup> s<sup>-1</sup> has been derived (bath gas helium). For a quantitative assessment of the possible channel to <sup>1</sup>CH<sub>2</sub> + H<sub>2</sub>O, reaction 1d, measurements of H<sub>2</sub>O were carried out, yielding an estimated upper limit for the rate coefficient of  $k_{1d}(300 \text{ K}) \leq 5 \times 10^{-12} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>.

#### Introduction

According to a recent compilation of kinetic data<sup>3</sup> for the title reaction, the following routes, besides (1a), may be of some importance:

$$CH_3 + OH (+M) \rightarrow CH_3OH$$
 (1a)

$$CH_3 + OH \rightarrow H + CH_2OH$$
 (1b)

$$CH_3 + OH \rightarrow H + CH_3O$$
 (1c)

$$CH_1 + OH \rightarrow {}^1CH_2 + H_2O$$
 (1d)

The energy diagram for these reactions along with a potential  $CH_2O$  channel is shown in Figure 1. (The heats of formation are taken from ref 4 due to their widespread use in chemical-kinetic computer programs. See also Discussion section). The  ${}^{1}CH_{2}$ channel is slightly exothermic by -0.43 kcal mol<sup>-1</sup> according to ref 4 and, on the basis of these data, should be accessible at room temperature if no energy barrier is assumed. Four experimental papers are quoted in ref 3, none of them being a direct study of the elementary reactions in question. At room temperature, Hochanadel et al.<sup>1</sup> modeled the CH<sub>3</sub> decay curves obtained from photolysis of a mixture of H<sub>2</sub>O, CH<sub>4</sub>, and N<sub>2</sub> at 1 atm, to yield  $k_{1}^{\infty} = 9.3 \times 10^{-11} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}$ . This number was recently confirmed by the room temperature study of Anastasi and coworkers,<sup>5</sup> in which reaction 1a was initiated by pulse radiolysis of an Ar, SF<sub>6</sub>,  $H_2O$ , CH<sub>4</sub> mixture and the resulting CH<sub>3</sub> decay curves were monitored by transient absorption spectroscopy. The rate coefficient  $k^{\infty}_{1}$  so obtained, however, has to be taken with care, since the effect of O atoms on both CH<sub>3</sub> and OH was not accounted for. In other studies, Hack et al.<sup>6</sup> measured the reverse of channel 1d and derived  $k_{1d}(298 \text{ K}) = 3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ s<sup>-1</sup>.

By modeling the results from shock-tube studies above 1700 K on the  $C_2H_6 + O_2^7$  and later on the  $CH_4 + O_2^8$  systems, Just and co-workers obtained best fits of the measured H atom profiles when  $k_{1c}$  or  $k_{1b} = 1.5 \times 10^{-10} \exp(-7800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

In addition, calculations using unimolecular rate theory have been performed for reaction  $1.9^{-11}$  There is qualitative agreement between the earlier studies of Tsang and Hampson<sup>9</sup> and Dean and Westmoreland.<sup>10</sup> At temperatures near ambient, and at any pressure of practical importance, the CH<sub>3</sub>OH channel is close to its high-pressure limit and is supposed to be the only one of importance. At flame relevant temperatures under normal pressures, channel 1b is assumed to take over. In ref 10, a channel to <sup>1</sup>CH<sub>2</sub> is allowed for; however, according to this model it is of minor importance.

A rather different behavior is displayed by a model recently proposed by Pilling and co-workers.<sup>11</sup> Here, following the study in ref 6, channel 1d is fast at all temperatures. It may be exceeded by the CH<sub>3</sub>OH channel, but at normal pressures only at ambient temperature. At elevated temperatures, this latter reaction to CH<sub>3</sub>OH is far into the falloff region, and although included in the system, its contribution is unimportant in comparison with (1d).

The implication for flame modeling is that, according to the data of refs 9 and 10, the reaction of  $CH_3 + OH$  would mostly act as a chain-terminating step through the dominance of channel 1a at low temperatures and would exhibit chain-propagating behavior at high temperatures.<sup>10</sup> Contrary to this, due to the subsequent reactions of <sup>1</sup>CH<sub>2</sub>, the Pilling model would yield chain propagation even at low temperatures.

To illustrate this effect, the laminar flame velocities of premixed, free,  $CH_4$ -air flames (stoichiometric mixture) were calculated by inserting rate coefficients corresponding to either ref 10 or 11 (Warnatz code). This produced an effect on the laminar flame velocity, which, despite being a gross feature, changed from 36 cm s<sup>-1</sup> for Dean and Westmoreland coefficients to as much as 48 cm s<sup>-1</sup> when the coefficients suggested by Pilling were used. In view of the obvious importance of the title reaction for flame models, accurate experimental data are needed in a sufficiently broad temperature and pressure regime. As a first step to this end, the falloff behavior of the association channel 1a has been measured in a fast-flow reactor at ambient temperature. For channel 1d, an upper limit was derived, whereas channels 1b and 1c should play no role at this temperature on thermochemical grounds.

#### **Experimental Section**

The fast-flow reactor and its application to the study of radical + atom reactions have already been described in an earlier study,<sup>12</sup> as has its use over an extended pressure range.<sup>13</sup> Thus, only a very brief outline will be given here. Two Teflon reactors have been used, each of length 50 cm, with internal diameters of 29 and 39 mm for the higher and lower pressures, respectively. The flow velocities ranged from ca. 1200 to 3800 cm s<sup>-1</sup>, corresponding to maximum reaction times of 30 to 8 ms, respectively, as summarized in Table I. Helium was used as carrier gas. Corrections allowing for the pressure drop, for axial diffusion, and for deviation from plug flow were applied in the customary manner.<sup>12-14</sup> Species detection was accomplished by a time-of-flight mass spectrometer (at low ionization energies), which was coupled to the flow reactor by the usual nozzle–skimmer arrangement.

Radicals were produced at two sources, a fixed one for OH, positioned upstream of the reactor, and a movable one for  $CH_3$ , essentially comprising of a movable quartz rod with a thin inner

| P/mbar | <i>v</i> /cm s <sup>-1</sup> | t/ms | $[CH_3]_0 \times 10^{-11}/mole-$<br>cules cm <sup>-3</sup> | $[CH_4] \times 10^{-13} / molecules cm^{-3}$ | $[H_2] \times 10^{-14} / \text{mole-}$<br>cules cm <sup>-3</sup> | $[NO_2] \times 10^{-12} / mole-cules cm^{-3}$ | $k_{1a}^{a}/cm^{3}$<br>molecule <sup>-1</sup> s <sup>-1</sup> |
|--------|------------------------------|------|--|--|--|---|---|
| 0.3    | 1253                         | 26.1 | 1.8  | 3.1  | 2.4  | 2.9-9.4                                       | $8.0 \times 10^{-12}$   |
| 0.5    | 1871                         | 30.0 | 3.0  | 3.0  | 2.9  | 2.1-9.7                                       | $1.4 \times 10^{-11}$   |
| 0.7    | 1753                         | 17.1 | 1.6  | 3.0  | 1.7  | 4.0-13.5                                      | $1.8 \times 10^{-11}$   |
| 1.1    | 2415                         | 10.9 | 3.0  | 1.9  | 0.7  | 2.9-9.9                                       | $2.2 \times 10^{-11}$   |
| 2.2    | 3326                         | 8.5  | 1.8  | 1.2  | 1.8  | 2.9-11.5                                      | $3.5 \times 10^{-11}$   |
| 3.3    | 4049                         | 8.6  | 2.0  | 1.1  | 1.5  | 2.5-11.4                                      | $5.0 \times 10^{-11}$   |
| 6.2    | 3787                         | 7.9  | 2.5  | 9.9  | 1.5  | 2.4-9.1                                       | $6.0 \times 10^{-11}$   |

<sup>a</sup> Total estimated error in  $k_{1a} \pm 30\%$ .



Figure 1. Energy diagram for the  $CH_3 + OH$  system. Data from ref 4.

capillary tube ending in a mixing head.

For CH<sub>3</sub> generation, the reaction

$$CH_4 + F \rightarrow CH_3 + HF$$

was used. F atoms were prepared by microwave discharge of a diluted  $F_2$ -He mixture in an alumina-coated side arm at the upstream end of the movable rod. CH<sub>4</sub>, in a 20-fold excess, was added to the F atom flow through the inner capillary in such a way that the reaction distance between mixing head and end of movable injector was sufficient to ensure total consumption of the F atoms. Proper mixing turned out to be crucial for the suppression of the undesired subsequent reaction

 $CH_3 + F \rightarrow products$ 

which is likely to occur in regions of local  $CH_4$  depletion.  $CH_3$ was used as the minor component in order to minimize its relatively fast self-reaction (see Table II). Since it was not possible to work under pseudo-first-order conditions, due to the influence of secondary reactions and to consumption of the excess component OH (mainly by side reactions), a proper evaluation of the measured  $CH_3$  decay profiles was only possible by means of computer simulation, and this required a knowledge of the initial  $CH_3$ concentration. Its calibration was performed via the fast titration reaction

$$CH_3 + NO_2 \rightarrow CH_3O + NO$$

in a sufficient excess of NO<sub>2</sub>.<sup>15</sup>

The concentrations of  $CH_3$  so obtained were very close to the experimentally measured consumption of  $CH_4$  upon reaction with F atoms. Under the conditions of a moving radical source, the  $CH_3$  wall loss fully enters the  $CH_3$  decays. However, the loss on Teflon is fortunately very small (typically 2 s<sup>-1</sup> for a 3-cm-diameter reactor<sup>16</sup>).

For the generation of OH radicals, two commonly used methods exist:

$$H + NO_2 \rightarrow NO + OH$$
  
F + H<sub>2</sub>O  $\rightarrow$  HF + OH

In this study, the first reaction was used, with a large excess of H atoms, produced in a  $H_2$  discharge, over NO<sub>2</sub> (concentrations

TABLE II: Reaction Scheme and Corresponding Rate Constants

| no. | reaction                                      | $k(300 \text{ K})/\text{cm}^3$<br>molecule <sup>-1</sup> s <sup>-1</sup> | ref        |
|-----|---|--|------------|
| la  | $CH_3 + OH(+M) \rightarrow CH_3OH$            | a  |            |
| 16  | $CH_3 + OH \rightarrow H + CH_2OH$            | <i>b</i>   |            |
| lc  | $CH_3 + OH \rightarrow H + CH_3O$             | <i>b</i>   |            |
| ld  | $CH_3 + OH \rightarrow H_2O + {}^1CH_2$       | $\leq 5 \times 10^{-12}$   | this study |
|     | source reactions                              |  |            |
| 2   | $NO_2 + H \rightarrow OH + NO$                | $1.3 \times 10^{-10}$  | 19         |
| 3   | $CH_1 + F \rightarrow CH_2 + HF$              | $7.8 \times 10^{-11}$  | 2          |
| Ĵ   |   |  | -          |
|     | subsequent reactions of OH                    |  |            |
| 4   | $OH + OH \rightarrow H_2O + O$                | $1.9 \times 10^{-12}$  | 2          |
| 5   | $OH + O \rightarrow H + O_2$                  | $2.6 \times 10^{-11} c$  | 2          |
| 6   | $OH + wall \rightarrow products$              | 5 s <sup>-1</sup>  | 20         |
|     | subsequent reactions of CH.                   |  |            |
| 7   | $CH_1 + CH_2 (+M) \rightarrow C_2H_2$         | $(1.1-5.0) \times 10^{-11}$  | 15 16      |
| é   | $CH + O \rightarrow HCHO + H$                 | $1.3 \times 10^{-10}$  | 13, 10     |
| 0   | $CH + H (+M) \rightarrow CH$                  | $(0.2 - 4.0) \times 10^{-12}$  | 21         |
| 10  | $CH_3 + H(+M) \rightarrow CH_4$               | $(0.2-4.0) \land 10$   | 13         |
| 10  | $CH_3 + wall \rightarrow products$            | 28   | 15         |
|     | reactions of ${}^{1}CH_{2}$                   |  |            |
| 11  | $^{1}CH_{2} + H_{2} \rightarrow CH_{3} + H$   | $1.2 \times 10^{-10}$  | 9          |
| 12  | $^{1}CH_{2} + CH_{4} \rightarrow 2CH_{3}$     | $7.1 \times 10^{-11}$  | 9          |
| 13  | $^{1}CH_{2} + H_{2}O \rightarrow CH_{3} + OH$ | $1.6 \times 10^{-10}$  | 6          |
|     | additional reactions                          |  |            |
| 1.4 |   | 2 -14  |            |
| 14  | U + wall - products                           | 4 5  |            |
| 1.5 | $\neg$ + wall $\rightarrow$ products          | 38'"   |            |

<sup>a</sup>See Table I and Figure 5. <sup>b</sup>Unimportant at 300 K. <sup>c</sup>Lowest value taken within quoted error limits,  $k_5 = (3.3 \pm 0.7) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>d</sup>Data taken from earlier flow tube work: model insensitive to variation of these parameters.

are given in Table I), in order to prevent any interference from the possible subsequent reaction

$$CH_3 + NO_2 \rightarrow CH_3O + NO$$

The H atom concentration was estimated from a measured efficiency of the  $H_2$  discharge of typically 10%, and in all cases it was greater than  $2 \times 10^{13}$  molecules cm<sup>-3</sup>. This choice of reaction for OH production has the obvious disadvantage that recombination of CH<sub>3</sub> radicals with the residual H atoms can occur, although this will only play a minor role, since the reaction is fortunately far in the falloff regime. Another important feature is the presence of H<sub>2</sub>, which scavenges any <sup>1</sup>CH<sub>2</sub> from channel 1d to re-form CH<sub>3</sub>, so that the CH<sub>3</sub> profiles remain effectively free from interference from reactions of <sup>1</sup>CH<sub>2</sub>. Use of the alternative F/H<sub>2</sub>O system to generate OH is not so favorable, since the excess H<sub>2</sub>O required to ensure total conversion of the F into OH would interfere with the detection of small quantities of H<sub>2</sub>O stemming from reaction 1d.

The OH radicals were calibrated by using an excess of  $CH_3$ -CHO as scavenger. Unlike HCHO,  $CH_3CHO$  is easy to handle, and its reaction with OH is sufficiently fast<sup>17</sup> so that the consumption upon reaction with OH can be used as a convenient mode of calibration. Addition of  $CH_3CHO$  through the movable injector enables the OH concentration profile along the flow tube to be traced out (see Figure 2). The OH gradient, even in the presence of  $CH_3$ , is mostly governed by the gas-phase reactions (4) and (5) and the wall loss (6). For injector positions far upstream, the OH concentrations so obtained approach the initial  $NO_2$  con-



Figure 2. Experimental and simulated OH profiles, along with simulated O and H atom profiles along reactor  $(CH_3 \text{ absent})$ .



Figure 3. Experimental and simulated CH<sub>3</sub> decay profiles. Open symbols are experimental data. Broken lines represent the corresponding simulated CH<sub>3</sub> decay for the same conditions and a given  $k_{1a}$ . Solid lines indicate the change in the simulated CH<sub>3</sub> decay profiles for a 20% change in  $k_{1a}$ . Error bar shows the accuracy of a measured profile (ca. ±20%).

centration. The quadratic behavior of the OH recombination reaction (4) prevents the use of OH in a great excess over  $CH_3$ , so that pseudo-first-order conditions can be achieved only approximately.

#### **Results of Experimental and Simulated Decay Curves**

For each of the seven pressures studied between 0.3 and 6.2 mbar (see Table I), the NO<sub>2</sub> concentration was varied in the range  $(3-10) \times 10^{12}$  molecules cm<sup>-3</sup>, in order to obtain a series of  $[CH_3]-(t)$  decay profiles as a function of  $[NO_2]$ . After subtraction of a small constant background contribution to the CH<sub>3</sub> signal from CH<sub>4</sub> fragmentation, these profiles were sufficiently exponential in nature (see Figure 3), to allow treatment with the usual pseudo-first-order evaluation procedure to obtain the overall rate coefficients for the consumption of CH<sub>3</sub>. The error bars of ca. 20% in the measurements represent the estimated uncertainties in an experimental profile (15%) and also include a contribution (ca. 5%) to the CH<sub>3</sub> signal arising from the fragmentation of CH<sub>4</sub>. The larger overall error in the  $k_{1a}$  values of Table I arises from fitting of the data over a range of NO<sub>2</sub> concentrations.

A refined treatment, to extract the coefficients of interest, requires a consideration of the complete kinetic system (see Table II), using computer modeling, in which the rate coefficients are fine-tuned so as to match experimental and simulated  $CH_3$  decay curves. Three different effects may be discerned, leading to a significant deviation from normal pseudo-first-order kinetics:





**Figure 4.** Sensitivity analysis. Effect of a 30% increase in a particular rate coefficient on the standard simulated methyl decay profile 2.2 mbar, 300 K. (Note  $k_{1d}$  increased by a factor of 10.)

(i) OH Profiles. A simulated OH decay curve in the absence of  $CH_3$  is shown in Figure 2 along with measured points. The profile is determined in particular by the reaction sequence

$$OH + OH \rightarrow H_2O + O$$

$$OH + O \rightarrow H + O_2$$

Other possible side reactions such as  $OH + CH_4$  and  $OH + H_2$ play an insignificant role at room temperature and may therefore be neglected. The effect is that for injection of  $CH_3$  at "low" positions, i.e., short reaction times of  $CH_3$  with OH, a considerable OH loss occurs upstream of the injector between generation zone and point of addition of the  $CH_3$ . Consequently, a proper simulation program has to calculate the effect of the OH reactions upstream of the injector, in order to yield the effective initial concentrations for a second integration, which now refers to the downstream regime and includes the reactions of  $CH_3$ . Time resolution is achieved by moving the injector in a stepwise fashion from its lowest to highest position, enabling the final radical concentrations at the detector to be simulated as a function of reaction time.

(ii) Methyl Recombination. This provides a time-dependent contribution to the measured  $CH_3$  decay curves simply for concentration reasons: at low residence times, larger  $CH_3$  concentrations are prevalent, which consequently increase the amount of decay by reaction 7.

(*iii*) Effect of O Atoms. Due to their generation and consumption via reactions 4 and 5, respectively, O concentrations tend to peak approximately in the middle zone of the reactor, as shown in Figure 2. Although the concentrations are relatively low (ca.  $10^{11}$  molecules cm<sup>-3</sup>), O atoms yield a nonnegligible contribution to the observed decay curves, due the fast reaction with CH<sub>3</sub> radicals.

The relative contributions of these effects to the decay curves shown in Figure 3 may be summarized as follows (numbers in parentheses refer to the lower curve, i.e., the larger initial OH concentration). (i) For short reaction times ("low" injector positions) the initial OH concentration is typically 16% (30%) lower than for longer reaction times ("high" injector positions) due to OH loss, yielding a corresponding reduction in the rate of the primary reaction (1). (ii) The maximum contribution of the methyl recombination reaction to the total rate of CH<sub>3</sub> removal occurs at short reaction times, where little CH<sub>3</sub> has been removed, and is ca. 13% (6%) decreasing to ca. 3% (<1%) with increasing reaction time. (iii) The rate of reaction of methyl with O atoms provides, under the chosen experimental conditions, a relatively time-constant contribution to the total CH<sub>3</sub> removal rate of ca. 9% (17%).

The net effect of these processes happens to yield decay curves looking like exponentials, despite the complexity of the system. The influence of side and subsequent reactions on the  $CH_3$  profiles,



Figure 5. Falloff curve for the reaction  $CH_3 + OH (+M) \rightarrow CH_3OH$  at 300 K.

including the effect of the traveling injector (i.e., partial consumption of the excess component OH prior to addition of CH<sub>3</sub>), was treated by a sensitivity analysis (Figure 4). Here, starting with the standard rate coefficients giving a best fit between experiment and simulation, ([CH<sub>3</sub>]<sub>std</sub>, dashed line in Figure 4), the percentage change in the methyl decay profile  $(\Delta[CH_3]/[CH_3]_{std})$ was calculated for a 30% increase in a particular rate coefficient (exception:  $k_{1d}$ , where, due to the uncertainty in this value, the effect of a 10-fold increase on the  $CH_3$  decay is illustrated). Clearly, the most sensitive parameter is  $k_{1a}$ , that for the primary reaction  $CH_3 + OH \rightarrow CH_3OH$ , validating the approach used to evaluate the system. Of the side reactions, the most sensitive is reaction 9, the recombination of CH<sub>3</sub> with H atoms. This channel is far in its falloff and will not affect the behavior of the system, since the H atoms are present in an almost undisturbed excess (Figure 2). Rather, this leads to an almost time- and [OH]-independent contribution to the CH<sub>3</sub> decays  $(k_9[H] \approx$ constant), which, like a wall loss, can be easily separated through the variation of [OH]<sub>0</sub>. For the decays of Figure 3, reaction 9 contributes ca. <25% (13%) to the total CH<sub>3</sub> removal rate.

 ${}^{1}CH_{2}$  reactions have no influence on the decay profiles for reasons discussed below.

Table I provides a summary of the experimental conditions and results. The rate data for  $k_{1a}$  are obtained by matching first-order rate constants from experimental CH<sub>3</sub> decays with simulations from a computer model consisting of 15 elementary reactions and 16 species (see Table II). Two typical measured and simulated profiles are displayed in Figure 3. The resulting falloff curve is shown in Figure 5.

## Results of Product Analysis: Role of the <sup>1</sup>CH<sub>2</sub> Channel

In an attempt to obtain further evidence for the mechanism of Table II, a quantitative product analysis for CH<sub>3</sub>OH and H<sub>2</sub>O was also undertaken. The result is in brief that, depending on the particular conditions, between 70% and 90% of the consumed CH<sub>3</sub> radicals react to produce CH<sub>3</sub>OH. This confirms that, under the present conditions, reaction 1a is the major route. The products of reactions 7 and 8, C<sub>2</sub>H<sub>6</sub> and HCHO, respectively, were also detected but not quantitatively measured. CH<sub>4</sub> produced from reaction 9 could not be monitored due to the presence of excess CH<sub>4</sub> required for CH<sub>3</sub> production.

 ${}^{1}CH_{2}$  radicals formed in (1d) could not be detected, since they would quickly react through reactions 11-13, so that  ${}^{1}CH_{2}$  mole fractions would remain low. Indeed, the simulations show that  ${}^{1}CH_{2}$  reaches a maximum concentration of ca.  $10^{8}-10^{9}$  molecules  $cm^{-3}$  within less than 0.4 ms, well within the mixing zone.

Fortunately, the <sup>1</sup>CH<sub>2</sub> reactions have very little effect on the CH<sub>3</sub> profiles, since under the conditions used ([H<sub>2</sub>]:[CH<sub>4</sub>]:[H<sub>2</sub>O] ca. 100:10:1) any CH<sub>3</sub> radicals entering channel 1d and producing <sup>1</sup>CH<sub>2</sub> would be effectively reformed via the rapid reaction 11. The



**Figure 6.** Comparison of measured and simulated water profiles along the reactor for  $k_{1d} = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (2.2 \text{ mbar, } [\text{NO}_2] = 6 \times 10^{12} \text{ molecules cm}^{-3}).$ 

excess H<sub>2</sub> and fast rate coefficient of (11) renders the other  ${}^{1}CH_{2}$ -consuming reactions (12) and (13) of little importance. This is so far very important since, firstly, the reaction scheme then becomes insensitive to  $k_{13} \equiv k_{-1d}$  even if a value as large as the one suggested by Hack et al. is taken and, secondly, reaction 12 would regenerate two CH<sub>3</sub> radicals. The small sensitivity of our simulated CH<sub>3</sub> profiles to  $k_{1d}$  is also shown in Figure 4, in which the displayed effect is produced by a 10-fold increase in this coefficient. Hence at these low temperatures, where routes 1b and 1c are unimportant, the CH<sub>3</sub> decays are mostly sensitive to channel 1a.

However, the existence of channel 1d could be investigated through the formation of water. The accuracy is limited, since the product water has to be detected in a background of water arising from OH recombination, although it was possible to reduce this by lowering the concentration of the OH excess component. The analytical problem is displayed in Figure 6. The full curve depicts a simulated H<sub>2</sub>O profile stemming from OH recombination only, along with measurements that were obtained by passing NO<sub>2</sub> through the movable injector into a flow of H atoms to enable time resolution of the water signal. Under the conditions of a static detector, in which measurements are performed at the end of the reactor, the water signals did not change significantly upon addition of CH<sub>3</sub> or when the CH<sub>3</sub> source was driven from lowest to highest position. This means that the additional water ascribed to reaction 1d has to be below our sensitivity for  $H_2O$  of about  $2 \times 10^{10}$  molecules cm<sup>-3</sup>, as represented by the error bars. For the simulation in the presence of CH<sub>3</sub> to yield a water concentration within the error limits of the water measurements, an upper limit of  $k_{1d} = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  has to be taken (dashed curves in Figure 6): a value of  $k_{1d} = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ s<sup>-1</sup> would produce water in excess of the observed levels (dotted curve in Figure 6).

### Discussion

The resulting rate constants obtained for the reaction 1a over the pressure range 0.3-6.2 mbar are shown in the falloff curve of Figure 5. At the high-pressure side, the coefficients determined in this study approach those obtained by Hochanadel et al.<sup>1</sup> and more recently by Anastasi and co-workers<sup>5</sup> ( $k^{\infty}_{1a} = 9.3 \times 10^{-11}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). By taking this value in conjunction with a simple fitting formula (see e.g. ref 2)

$$k = \frac{k^{0}[\mathbf{M}]}{1 + k^{0}[\mathbf{M}]/k^{\infty}} [0.6^{(1+lg^{2}(k^{0}[\mathbf{M}]/k^{\infty}))^{-1}}]$$

a value for  $k_{1a}^0 = (2.5 \pm 1.0) \times 10^{-27}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> has been obtained for M = He. Clearly, the value of  $k_{1a}^0$  deduced is only a preliminary one, and a more exact value requires fitting of experimental data over a temperature range. For this reason, a further investigation is currently under way to extend the range of measurement to higher temperatures. Figure 5 also displays

TABLE III: Measured and Simulated Water Concentrations<sup>a</sup>

| P, mbar | $[NO_2] \times 10^{-12}$ | $[H_2O]_{exp} \times 10^{-12}$ | $[H_2O]_{sim} \times 10^{-12}$ |
|---------|--------------------------|--------------------------------|--------------------------------|
| 0.31    | 9.20                     | 1.98                           | 2.03                           |
| 0.52    | 9.70                     | 2.30                           | 2.26                           |
| 0.72    | 7.86                     | 1.50                           | 1.48                           |
| 1.1     | 4.28                     | 0.59                           | 0.60                           |
| 2.2     | 3.50                     | 0.29                           | 0.28                           |
| 3.3     | 3.81                     | 0.32                           | 0.31                           |
| 6.2     | 4.29                     | 0.36                           | 0.37                           |

<sup>a</sup>All concentrations in units of molecules cm<sup>-3</sup>.

the disagreement between the falloff curve determined in this study and the one deduced from the Pilling model. This actually reflects an inconsistency between the current results for channel 1d and the data of Hack et al.,<sup>6</sup> on which the model of Pilling is based.

Hack measured for the reaction

 $^{1}CH_{2} + H_{2}O \rightarrow products$ 

 $k = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  by following the total  ${}^{1}\text{CH}_2$ loss from reaction with  $H_2O$  and quenching to  ${}^{3}CH_2$ , using LIF. From OH product measurements, it was deduced<sup>6</sup> that the relative weight of the channel to  $CH_3 + OH$  (-1d) is greater than 50%, leading to  $k_{-1d} = 1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . For the calculation of the equilibrium constant,  $\Delta H_f^{\circ}_{298}({}^{3}\text{CH}_2) = 93.0 \pm 1.0$ kcal mol<sup>-118</sup> was used, along with  $\Delta H^{\circ}_{298} = 9.1$  kcal mol<sup>-1</sup> for the energy separation  ${}^{3}CH_{2} \rightarrow {}^{1}CH_{2}$  (see ref 6 and references therein). The resulting  $K_{p(-1d)}(300 \text{ K}) = 4.6$  leads to  $k_{1d} = 3.5 \times 10^{-11} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>, in conflict with the upper limit of 5  $\times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> determined from our water measurements. This disagreement is even larger if current values for the heats of formation are used. The Sandia data<sup>4</sup> used in Figure 1 yield  $K_{p(-1d)} = 0.5$ , leading to a rate coefficient for  $k_{1d} = 3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Since the current evaluation of  $k_{-1d}$  is based solely on the water measurements, the calibrated water signals were compared with the simulations of the water arising from the OH recombination (CH<sub>3</sub> absent). As can be seen in Table III and Figure 6, the agreement between experimental and simulated concentrations is satisfactory and gives confidence to the analysis.

Furthermore, use of a value of  $k_{1d}$  of the order of  $3 \times 10^{-10}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> in the simulations would lead to a pronounced increase in water production, raising the original signal (from OH recombination) by more than a factor of 7 upon addition of CH<sub>3</sub> (highest injector position, 2.2 mbar,  $[NO_2] = 3.5 \times 10^{12}$  molecules cm<sup>-3</sup>)—certainly well within the experimental detection limit for water.

This leaves uncertainties inherent in the thermodynamic data, especially those referring to the heat of formation of  ${}^{1}CH_{2}$ , as a source of the remaining discrepancy. This aspect seems to be supported by the experiments of Hack et al. in which it was possible to measure the rotationally excited OH produced from the  ${}^{1}CH_{2} + H_{2}O$  reaction and to determine a rotational temperature of  $470 \pm 60$  K. Such an observation may be explained if in the direction  ${}^{1}CH_{2} + H_{2}O \rightarrow CH_{3} + OH$  the reaction is

exothermic rather than endothermic, as suggested by the Sandia (1991) data. Unfortunately, this is not the only explanation for excited OH, since it could have been generated at least in part by vibrationally hot <sup>1</sup>CH<sub>2</sub>. Presently, at least part of the discrepancy can be ascribed to the uncertainties in the heats of formation of the radicals involved, in particular <sup>1</sup>CH<sub>2</sub>. Hack and co-workers<sup>6</sup> have pointed out that the cumulative uncertainties may lead to a reaction enthalpy of  $\Delta H^{\circ}_{-1d} \approx -2$  kcal mol<sup>-1</sup> so that the equilibrium constant  $K_{-1d}(300 \text{ K})$  would be raised to about 30, bridging the gap between the measurements of Hack et al. and those currently reported. Further work is required to clarify this point. By going to higher temperatures it may be possible to monitor the  ${}^{1}CH_{2}$  channel and derive an activation energy.

Acknowledgment. Thanks are extended to Dr. C. Anastasi for providing a copy of his  $CH_3 + OH$  study prior to publication and to Drs. Hack and Temps for helpful discussions. We also gratefully acknowledge the many valuable suggestions of Prof. Th. Just and the financial support of the Bundesministerium für Forschung und Technologie within the research association TECFLAM.

Registry No. H<sub>2</sub>, 1333-74-0; CH<sub>3</sub>, 2229-07-4; OH, 3352-57-6.

#### **References and Notes**

(1) Hochanadel, C. J.; Ogren, P. J.; Sworski, T. J. J. Phys. Chem. 1980, 84, 129.

(2) Chemical Kinetics and Photochemical Data for use in Stratospheric Modelling; Evaluation Number 9, JPL Publication 90-1, 1990.

(3) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Frank, P.; Just, Th.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. J. Phys. Chem. Ref. Data, in press.

(4) Kee, R. J.; Rupley, F. M.; Miller, J. A. Sandia Report 1987, and update 1991.

(5) Anastasi, C.; Beverton, S.; Ellermann, T.; Pagsberg, P. J. Chem. Soc., Faraday Trans. 1991, 87, 2325.

(6) Hack, W.; Wagner, H. Gg.; Wilms, A. Ber. Bunsen-Ges. Phys. Chem. 1988, 92, 620.

(7) Bhaskaran, K. A.; Frank, P.; Just, Th. High Temperature Methyl Reactions with Atomic and Molecular Oxygen. In Proceedings of the 12th Symposium on Shock Tubes and Waves; The Magnes Press: Jerusalem, 1979; p 503.

(8) Just, Th.; Roth, P. Proc. Symp. (Int.) Combust., 20th 1984, 807.

(9) Tsang, W.; Hampson, R. F. J. Phys. Chem. Ref. Data 1986, 15, 1087.

(10) Dean, A. M.; Westmoreland, P. R. Int. J. Chem. Kinet. 1987, 19, 207.

(11) Green, N. J.; Pereira, A. R.; Pilling, M. J.; Robertson, S. H. Presented

at the 23rd Symposium (International) on Combustion, 1990; poster. (12) Grotheer, H. H.; Just, Th.; Riekert, G.; Walter, D. Chem. Phys. Lett. 1988, 148, 530.

(13) Oser, H.; Walter, D.; Stothard, N. D.; Grotheer, O.; Grotheer, H. H.

Chem. Phys. Lett. 1991, 181, 521. (14) Kaufmann, F. J. Phys. Chem. 1984, 88, 4909. (15) Walter, D.; Grotheer, H. H.; Davies, J. W.; Pilling, M. J.; Wagner,

A. Proc. Symp. (Int.) Combust. 23rd 1990, 107-114.
(16) Grotheer, H. H.; Walter, D. To be published.
(17) Michael, J. V.; Keil, D. G.; Klemm, R. B. J. Chem. Phys. 1985, 83, 1630.

(18) Böhland, T.; Temps, F.; Wagner, H. Gg. J. Chem. Phys. 1987, 91, 1205.

(19) Wagner, H. Gg.; Welzbacher, U.; Zellner, R. Ber. Bunsen-Ges. Phys. Chem. 1976, 80, 1023

(20) Grotheer, H. H.; Riekert, G.; Meier, U.; Just, Th. Ber. Bunsen-Ges. Phys. Chem. 1985, 89, 325.

(21) Brouard, M.; MacPherson, M. T.; Pilling, M. J. J. Phys. Chem. 1989, 93, 4047.