Formation of HCOH + H₂ through the Reaction CH₃ + OH. Experimental Evidence for a Hitherto Undetected Product Channel

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Abstract

In an extension of our earlier studies at lower temperatures [4,5] the title reaction was measured directly in a flow reactor at temperatures of 600 and 700 K. The pressure of 0.65 mb was chosen that low in order to reduce the contribution of the stabilization channel. OH was used in an excess over CH_3 . Both reactants along with the reaction products were monitored by mass spectrometry. CH_3 profiles served as the major observable quantity for the extraction of rate data. This had to be done by using computer simulation since it was impossible to work under pseudo-first-order conditions.

The obtained total rate coefficients were divided into channel rate coefficients by means of branching ratios as determined by the mass spectrometric measurement of the reaction products. For $CH_3 + OH$, this led to a rate coefficient, k_{1a} into the stabilization channel, and another one, k_{1e+f} referring to the sum of two H₂-eliminating channels yielding the biradical HCOH and to a minor extent H₂CO. These latter channels have not been measured before.

In order to distinguish between them we switched over from OH to OD to get

$$(1'e) \qquad \qquad CH_3 + OD \longrightarrow HCOD + H_2$$

$$(1'f) \longrightarrow H_2CO + HD$$

so that the biradical and/or aldehyde channels could be determined by their by-products H_2 and HD, respectively. The use of OD makes it also possible to measure the channel

$$(1'd) \qquad \qquad CH_3 + OD \longrightarrow {}^1CH_2 + HDO$$

through its by-product, HDO.

A comparison of the rate coefficients of both systems, i.e., $CH_3 + OH$ and $CH_3 + OD$, indicates that within our error limits no significant isotope effect takes place.

For the rate coefficient into the HCOH channel, we arrive at a preliminary Arrhenius expression in units of cm, molec, and s:

$$k_{1e} = 9.1 \times 10^{-11} \exp(-1500/T).$$

The H_2CO channel could not be detected at our lower temperature rendering us with a rate coefficient at 700 K:

$$k_{1f}(700 \text{ K}) = 1.7 \times 10^{-12}.$$

Since simulation is needed for the deduction of the total rate coefficients as well as of the branching ratios, an uncertainty factor of 1.5 has to be attributed to these numbers. © 1995 John Wiley & Sons, Inc.

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Introduction

According to its significance for virtually all hydrocarbon flames, the title reaction has attracted a lot of attention during the last years, both from an experimental [1-7] as well as from a theoretical point of view [8-12]. Its fascination arises from its occurrence via a bound intermediate, chemically excited methanol, which can react into a variety of product channels. The channels currently under consideration are:

(1a)
$$CH_3 + OH + (M) \longrightarrow CH_3OH + (M) - 92.21 \text{ kcal mol}^{-1}$$

(1b)
$$CH_3 + OH \longrightarrow CH_2OH + H + 3.90 \text{ kcal mol}^{-1}$$

(1c)
$$\longrightarrow CH_3O + H + 11.84 \text{ kcal mol}^{-1}$$

(1d)
$$\longrightarrow {}^{1}CH_{2} + H_{2}O - 0.45 \text{ kcal mol}^{-1}$$

The quoted reaction enthalpies refer to 300 K, and are derived from the Sandia compilation [13] because of its widespread use in modelling databases. According to our own measurements [5], channel 1d may be endothermic as supported by other workers (see, e.g., Refs. [30,36,37]).

Modern chemical kinetic data compilations [14-16] mostly quote these four product channels, yet a supplement is needed through the appearance of H₂-eliminating channels at higher temperatures:

(1e)
$$CH_3 + OH \longrightarrow HCOH + H_2 - 21.0 \text{ kcal mol}^{-1}$$

(1f)
$$\longrightarrow$$
 H₂CO + H₂ - 71.85 kcal mol⁻¹

For the reaction enthalpy of the HCOH channel we quote a value of Melius [17] obtained by BAC-MP4 calculations.

As pointed out by Wagner [18] calculations on the CH₃OH surface [19] predict an exit channel into HCOH + H₂ with a barrier below CH₃ + OH. If this was true, it was to be expected that this channel may be a product route of the reaction CH₃ + OH even at ambient temperature. In fact we failed to detect any signals of H₂ and/or HCOH/H₂CO in our low temperature studies [4,5] between 300 and 500 K nor found anything else in these channels experimentally.

At 700 K, however, we clearly observed a primary formation of molecular hydrogen along with 30 amu signals from HCOH and/or H_2CO . By the use of OD instead of OH we could show that the detected hydrocarbon species is predominantly the carbene like species HCOH (HCOD in this case) rather than formaldehyde. Further measurements on $CH_3 + OD$ at 600 K revealed a relatively strong temperature dependence of the biradical channel and this makes it plausible that it escaped our detection at temperatures below 500 K. At the same time, by extrapolation, it underscores the potential importance of this channel around 1000 K.

It is the aim of this article to provide a description of the experiment (particularly so of the CH_3 source) and to present the data leading to the Arrhenius parameters for this new channel.

Experimental

Flow Reactor Technique

The fast flow reactor technique and its application to the study of radical + atom reactions as well as its use over an extended pressure range have already been described in earlier studies [20,21]. Thus only a brief outline will be given here.

The reactor assembly was exactly as in the diagram shown in [20]. A resistance heated copper block surrounded by a radiation shield was suspended from the reactor top flange so that upon thermal expansion the furnace shifted towards this flange leaving the open distance between the lower reactor end and the sampling nozzle virtually unchanged. The heat conductivity of the copper along with a proper thermal insulation of the reactor unit ensured a sufficiently flat temperature profile. Unavoidably, deviations from the flat profile occurred towards both ends of the reactor, vet in the zone covered by the movable injector, i.e., from x = 5 cm to x = 40 cm the temperature was 700 \pm 5 K (or 600 \pm 4 K) as measured with a thermocouple inserted through the movable injector, before radicals were added to the flow.

The reactor was a quartz tube of 55 cm length and 25.5 mm i.d. which was grinded so as to closely fit the surrounding copper block. For the reduction of heterogeneous effects the inner reactor walls and those of the movable injector were coated with B_2O_3 . Following a procedure used in Gutman's lab [22] we covered the surfaces with a layer of H_3BO_3 solved in water. After a first drying of the prepared reactor with a laboratory drier we annealed it under vacuum for about 1 h at 950 K. The latter step is needed to quantitatively transform the various forms of boric acid into glassy B_2O_3 . This treatment yielded wall coefficients of $6-8 \text{ s}^{-1}$ for CH₃ and about 6 s^{-1} for OH.

Pressures and gas flows were determined as described in an earlier study [23]. The experimental conditions of this study are displayed in Table I. The viscous pressure drop along the reactor axis turned out to be almost negligible.

The reactor was coupled via a conventional nozzle and skimmer system to a quadrupole mass spec which was operated at sufficiently low electron energies (between 11 and 20 eV; 12.1 eV for our main observable, CH_3) so as to minimize undesired fragmentation.

Generation and Calibration of Radicals

In the case of radical-radical reactions it is almost impossible, due to the interference of self-reactions and other side reactions, to use one component in sufficiently large

TABLE I.	Summary of experimental conditions and results. Concentration units: 10 ¹¹	cm^{-3} . k in 10	⁻¹¹ cm ³
$molec^{-1}$ s	$^{-1}$. $p = 0.65$ mbar.		

$CH_3 + O$	H measuremen	ts				
Т	v m/s	t_{\max} ms	$[H_2O]$	[F] ₀	$[CH_3]_0$	k_{1tot}
$\begin{array}{c} 700 \\ \mathrm{CH}_3 +\mathrm{O} \end{array}$	15.4 D measuremen	23.4 ts	650	24-176	2.2	1.47
T	v m/s	$t_{\rm max}$ ms	[D ₂ O]	$[\mathbf{F}]_0$	[CH ₃] ₀	$k_{ m 1tot}'$
700	16.4	23.2	650	22 - 168	2.2	2.35
600	13.0	27.7	920	17.5-160	2.2	1.9

concentrations to ensure pseudo-first-order kinetics. Thus computer modelling is required for the evaluation of the rate coefficients, with the prerequisite that the concentration of the minor component must also be known absolutely. In addition, the profile of the excess component in the absence of the other reactant may also be timedependent due to self-reaction or wall loss. The need to calibrate both reactants and to measure both types of profiles contrasts to the more commonly studied radical/atom + inert molecule systems.

OH source: As described in our earlier articles [4,5] we used OH as excess component and prepared it at the upstream end of the reactor in a fixed source by applying the well-known reaction $H_2O + F \rightarrow OH + HF$, the F atoms being generated in a microwave discharge of F_2 diluted in He. The OH concentration was determined using a scavenger gas which was added to the flow through the movable injector and thus enabled us to measure the OH profiles in the absence of CH₃. Contrary to our earlier studies [4,5], acetaldehyde could not serve as scavenger since it partly decomposed at the hot walls. Instead, we used *n*-butane in an up to 20-fold excess over OH and determined the local OH concentrations from the consumption of C_4H_{10} at this position. In the vicinity the OH source, the concentrations so obtained approached the ones as determined from the F_2 flow assuming a complete dissociation in the microwave discharge.

 CH_3 source: Our earlier CH₃ source, i.e., the fast reaction $CH_4 + F \rightarrow CH_3 + HF$ could not be taken here since at 700 K an untolerably large amount of OH would have been lost through its reaction with CH_4 . Following the literature [24], we used the pyrolysis of azomethane:

$$CH_3NNCH_3 \longrightarrow 2CH_3 + N_2$$
.

For this purpose a small tungsten coil (20 mm length, 5 mm diam., copper leads) was placed into the movable injector in a distance of about 3 cm from the exit holes (see Fig. 1). A heating power of about 40 W was needed to obtain temperatures around 1200 K. The performance of this pyrolytic source is shown in Figure 1: Between 1150 and 1170 K a typical dissociation yield of 80% was achieved. This yield could be slightly increased above 1170 K to 82% and under these conditions, due to the reaction (see [24])

$$CH_3NNCH_3 + CH_3 \longrightarrow CH_3NNCH_2 + CH_4$$

small amounts of CH₄ were formed. At even higher temperatures this latter reaction took over resulting in a severe decrease of the CH₃ yields.

We chose the temperature and the gas flow in the injector (azomethane highly diluted in He, flow velocity of about 80 m/s) such that only 2% CH₄, as measured with the mass spec, was formed rendering us with a negligible amount of CH₃NNCH₂ radicals. Under these circumstances, the 20% of CH₃NNCH₃ surviving the pyrolytic zone resulted in a concentration of only $3*10^{10}$ molec.cm⁻³. A potential source of error could arise from its reaction with OH. To check for this we recorded CH₃NNCH₃ and OH signals while the pyrolytic heater was turned off. The result is, that at 700 K this reaction is considerably slower than the one of CH₃ + OH. Due to the much larger abundances of CH₃, it can therefore be assumed that the reaction CH₃NNCH₃ + OH practically does not interfere under our conditions, neither in terms of additional OH depletion nor in terms of reaction products.



Figure 1. Performance of the pyrolytic CH₃ source.

Another potential source of error caused by our CH_3 source is its influence on the temperature profile. For its assessment the injector was equipped with a tail into which a movable thermocouple could be inserted for the measurement of axial temperatures in the vicinity of the heating coil (see Fig. 1). It dropped very rapidly from 1170 K within the coil and its difference to the unperturbed reactor temperature for 700 K was only 20 K after 3 cm. We therefore allowed the reactants to mix only after this distance. To ensure proper mixing, the kinetic measurements were always started another 4 cm downstream and here the temperature rise due to the pyrolytic device is below 5 K so that it could be neglected in the kinetic calculations.

For the calibration of CH₃, two methods were used: The azomethane flow was measured by a Tylan flow controller (1 sccm full scale) which was calibrated through the pressure drop method. From the known initial azomethane concentrations of typically $1.4*10^{11}$ molec.cm⁻³ or less and the dissociation yields as measured with the mass spec, initial CH₃ concentrations could be derived. The other method involved again a scavenger gas. NO₂ (cf. [4,5]) could not serve this purpose due to its partial decomposition at the hot walls. As an alternative, we used the titration reaction [15]

$$F_2 + CH_3 \longrightarrow CH_3F + F$$

in an excess of F_2 and we made sure that at 700 K F_2 is sufficiently stable. From the measured consumption of F_2 , CH_3 concentrations were derived in favorable agreement with those of the first method and this provides further confidence in our pyrolytic source.

Under our conditions of low initial CH_3 concentrations, its loss by self reaction played only a minor role, i.e., below 10%.

Purity of gases and preparation of precursors: Gas purity grades were as follows: Helium 99.999%, F_2 99% (4.96% mixture in Helium 99.996%). H_2O bidistilled.

Following the literature [25], azomethane was prepared from a complex containing CuCl. After distillation it was cooled and stored as a liquid from which gaseous samples were drawn periodically. The purity was determined by GCMS to be better than 99%.

Results

Measurement of the Excess Component OH

In this study the usual scheme for the evaluation of pseudo-first-order reactions was renounced. Instead of this, rate coefficients were deduced by systematically refining the simulations of the measured decay curves. The usual kinetic procedure could only be taken to provide raw values for the simulations. The reason is seen in Figure 2. Here, an OH profile is shown as determined by the scavenger butane. Obviously, our excess component is far from being constant along the reactor. Rather, a fairly strong decay is observed resulting from the fast reaction sequence

$$(6) \qquad \qquad OH + OH \longrightarrow H_2O + O$$

(7)
$$O + OH \longrightarrow O_2 + H.$$

It is noteworthy, that on the basis of the CEC value [16] for k_6 , i.e., $k_6(700) = 4.1*10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ no good match between experiment and simulation could be achieved. The curve shown in Figure 2 was obtained for $k_6(700) = 3.0*10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and this is the extrapolation value of another recent recommendation [26]. For the wall loss, the simulation yielded $k_9 = 6 \text{ s}^{-1}$.

For $CH_3 + OH$ measurements we used a larger flow velocity and therefore the OH loss was less pronounced than in Figure 2. Nevertheless, the increased OH concentration towards the source region results in an apparently increased reaction rate of $CH_3 + OH$ for higher positions of the movable injector which are translated into larger reaction times. This is seen in the insert of Figure 3 showing log[CH₃] curves with slopes increasing with reaction time. The effect of the OH profile and how it enters the simulation are discussed in [4,5].



Figure 2. OH profile as determined by scavenging with butane. Conditions: $[OH]_0 = 4.7 \text{ E}12 \text{ molec.cm}^{-3}$, p = 3.0 mb, and v = 10 m/s.



Figure 3. Some measured and simulated CH_3 decay curves for $CH_3 + OH$. The number at each curve denotes the respective $[OH]_0$ concentration in units of 10^{12} molec.cm⁻³ at the top end of the reactor as obtained from $[F]_0$. The OH concentration at the start of the reaction is lower. For further conditions see Table I. The insert shows CH_3 profiles in the more familiar log form which is not used here.

To reduce the initial OH concentrations in order to escape its quadratic loss does not really solve our problem because in this case its excess over CH_3 would be insufficient resulting in just a different kinetic problem. Thus careful modelling is the only solution.

Measurements and Simulations of CH_3 Decay Curves and of Reaction Products for $CH_3 + OH$ at 700 K

It is the aim of this article to show the existence of the channels eliminating H_2 and here in particular the one yielding HCOH + H_2 . Therefore, we present here only measurements that were carried out at low pressure (0.65 mbar) because this reduced the role of the stabilization channel, reaction (1a), thus giving more weight to the other channels. These include reactions (1d), (1e), and (1f). We neglected again reactions (1b) and (1c) since we failed to detect any CH₃O/CH₂OH signals. H atoms could be detected, we attribute them, however, mostly to reactions (7) and (12). The nonfinding of CH₂OH signals is also reasonable in the light of new measurements by Seetula and Gutman [29] of the heat of formation for this radical indicating that its value is considerably larger than assumed in [13]. These findings have been confirmed in recent studies by Dobé and co-workers [30,31]. Further measurements and more general aspects of the system CH₃ + OH at elevated temperatures are described in an accompany article [32].

Under the conditions summarized in Table I we measured CH_3 decay curves for a series of F_2 flow into the discharge that directly translate into initial OH concentrations. Some of these curves are shown in Figure 3. One clearly sees their converging behavior for large F_2 flows and this is caused by the sequence (6) + (7) leading to a nonlinear relationship between F_2 flow and the OH concentration within the measurement zone.

As pointed out in our earlier studies [4,5], due to the presence of a large excess of H_2O needed for the OH source, reaction (16), i.e.,

$$^{1}CH_{2} + H_{2}O \longrightarrow CH_{3} + OH$$

which is the reverse of (1d) drives this latter reaction in an early steady state (for other products of rc. 16 see below). In this case, CH_3 radicals consumed by (1d) are mostly replaced by (16) so that our CH_3 decay curves reflect a total rate coefficient approximately given by

$$k_{1\text{tot}} = k_{1\text{a}} + k_{1\text{e}} + k_{1\text{f}}$$
.

The simulated curves shown in Figure 3 were obtained with the mechanism of Table II. To select the rate coefficients, we tried to avoid a mixture of various literature sources and therefore followed mostly the recommendations of the CEC compilation [16]. The best fit was achieved for (700 K, 0.65 mbar)

$$k_{1 ext{tot}} = 1.47 imes 10^{-11} ext{ cm}^3 ext{ molec}^{-1} ext{ s}^{-1}.$$

The individual product channels were assessed by an absolute determination of the reaction products. For channel (1a) this is CH_3OH . For a 90% consumption of CH_3 we got

$$CH_3OH/\Delta CH_3 = 0.13^1$$

leading to

$$k_{1a}(700 \text{ K}, 0.65 \text{ mbar}) = 2.0 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

As products of the channels (1e) and (1f) we recorded 30 amu signals, i.e., H_2CO and HCOH. Further H_2CO sources are provided by reaction (12) and to a minor extent by reaction (17). In principle, these contributions can be simulated, yet our 30 amu signals cannot be used for an absolute product determination due to the unknown mass spectrometric sensitivity of HCOH. H_2 , on the other hand, is a common reaction product of channels (1e) and (1f) and it can be easily measured absolutely. We got $H_2/\Delta CH_3 = 0.87$. This number is already corrected for the contribution of other H_2 sources like heterogeneous H_2 formation at the walls which could be shown to amount to 20%. This leads to

$$k_{1e+f}(700 \text{ K}) = 1.27 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.$$

This number reflects the fact that under our conditions, channels into H_2 that up to now have not been measured, are dominant.

Measurements and Simulations of CH_3 Decay Curves and of Reaction Products for $CH_3 + OD$ at 700 K

In order to separate (1e) and (1f) we had to find a means for distinguishing molecular hydrogen yields formed in these individual channels. Following our earlier study [5],

 1 In this notation, ΔCH_{3} is the methyl consumption through reaction 1. Other methyl sinks include in particular its reaction with O atoms.

1a 1b	$CH_3 + OH + (M) \rightarrow CH_3OH + (M)$ $CH_2 + OH \rightarrow CH_2OH + H$	2.0	E-12	this work
1¢	\rightarrow CH ₂ O + H	neglig	rihlo	
1d	\rightarrow ¹ CH ₂ + H ₂ O	9	E-12	this work
1e	\rightarrow HCOH + H ₂	1.1	E-11	this work
1f	\rightarrow H ₂ CO + H ₂	1.7	E-12	this work
5	$H_2O + F \rightarrow OH + HF$	2.5	E-11	[27]
6	$\tilde{OH} + OH \rightarrow H_2O + O$	3.0	E-12	[26]
7	$O + OH \rightarrow O_2 + H$	2.4	E-11	[16]
8	$OH + F \rightarrow O + HF$	5.8	E-11	[27]
9	$OH (wall) \rightarrow products$	6		this work
10	$O(\text{wall}) \rightarrow 1/2 O_2$	6	estima	ted, this work
11	H (wall) $\rightarrow 1/2$ H ₂	10		this work
12	$CH_3 + O \rightarrow H_2CO + H$	1.4	E-10	[16]
13	$CH_3 + H + (M) \rightarrow CH_4 + (M)$	5	E-13	[16]
14	$CH_3 + CH_3 + (M) \rightarrow C_2H_6 + (M)$	1	E-12	[16]
15	$CH_3 \text{ (wall)} \rightarrow \text{ products}$	6 - 8		this work
16	$^{1}\mathrm{CH}_{2}$ + H ₂ O \rightarrow CH ₃ + OH	8	E-11	[28]
17	$^{1}\mathrm{CH}_{2}$ + OH \rightarrow H ₂ CO + H	3	E-11	[14]
18	$OH + H_2 \rightarrow H_2O + H$	6	E-13	[16]
19	$OH + CH_3OH \rightarrow H_2O + CH_2OH$	3.4	E-12	[16]
20	$OH + H_2CO \rightarrow H_2O + CHO$	1.8	E-11	[16]
21	$OH + HCOH \rightarrow CO_2 + H_2 + H$	1.8	E-11	Guess. This work

TABLE II. Reaction scheme and rate coefficients. (Rate coefficients refer to 700 K and 0.65 mbar. Units of k are molec, cm^3 , and s).

this may be accomplished by using OD instead of OH:

$$(1'e)^2$$
 $CH_3 + OD \longrightarrow HCOD + H_2$

 $(1'f) \longrightarrow H_2CO + HD$

In this case the direct products are: HCOD at 31 amu, accompanied by H_2^3 and H_2CO at 30 amu from reactions (1f) and (12), accompanied by HD.

From reaction (1'a) one gets CH₃OD at 33 amu.

Eventually, the reaction pair (1d) and (16) reads differently:

$$(1'd) \qquad \qquad CH_3 + OD \longrightarrow {}^{1}CH_2 + HDO$$

(16')
$${}^{1}CH_{2} + D_{2}O \longrightarrow CH_{2}D + OD$$

Under the assumption that reaction 16' is unbranched⁴, this means that the D₂O excess required for OD production does not render (1'd) to an early steady state because in this case the reformed methyl radicals are CH₂D rather than CH₃. As a consequence, reaction (1'd) fully contributes to k'_{1tot} , yet this contribution can be

²For the notation, see footnote in Table III.

 $^{^{3}}$ The contribution from heterogeneous H₂ generation is in this case very small since the main source for hydrogen atoms is the reaction of hydroxyl radicals with O atoms upstream of the injector. In the OD case it yields D atoms.

⁴Among the potential other routes the generation of HCOD/DCOD biradicals should be favored for energetic reasons. Since DCOD is only formed through ${}^{1}CH_{2} + D_{2}O \rightarrow DCOD + H_{2}$, its nondetection is a strong hint that rc. 16' is indeed essentially unbranched and this has been shown by Carstensen and Wagner [28] between 255 and 475 K. The role of the stabilization channel should be minor at our low pressures.

assessed by measuring HDO which is separated from the D_2O signals arising from the OD source as well as from OD recombination.

The measured CH_3 curves are thus determined by

$$k'_{1\text{tot}} = k'_{1\text{a}} + k'_{1\text{d}} + k'_{1\text{e}} + k'_{1\text{f}}$$

The experimental conditions are included in Table I, and some of the decay curves are shown in Figure 4. For the simulation we used a modified mechanism according to Table III. The simulated fit shown in Figure 4 was obtained for

$$k'_{1
m tot}(700~{
m K}, 0.65~{
m mb}) = 2.35 imes 10^{-11}~{
m cm}^3~{
m molec}^{-1}~{
m s}^{-1}$$

In Table III, due to lack of literature data, for the OD reactions the same rate coefficients were used as for the OH reactions.

For the important reaction OD + OD we could verify this approximation by measuring OD decay curves to match those of OH within less than 10%.

In order to provide more insight into the channels eliminating molecular hydrogen we measured their product profiles (Fig. 5). From the HD/H₂ profiles (Fig. 5a(a)) it is seen that both product pairs are primarily formed and that HCOD + H₂ is at this temperature strongly favored over H₂CO + HD. This is not reflected by the H₂CO/HCOD profiles as shown by Figure 5(b). By contrast, the H₂CO yields exceed those of HCOD particularly for short reaction times since H₂CO at 30 amu is not only caused by channel (1'f), rather, the reaction CH₃ + O yields a much larger contribution. By the same token our 31 amu signals include a minor contribution from

 $(12'H) \qquad \qquad CH_2D + O \longrightarrow HDCO + H$

in addition to the main contribution from

 $CH_3 + OD \longrightarrow HCOD + H_2.^5$

⁵ The contribution from $CH_2D + OD \rightarrow CHDO + HD(1''f)$ is very small and therefore omitted in Table III.



Figure 4. Some measured and simulated $\rm CH_3$ decay curves for $\rm CH_3$ + OD. For conditions see Table I, 700 K.

1'a	$CH_3 + OD + (M) \rightarrow CH_3OD + (M)$	2.0	E-12	this work
1′d	$CH_3 + OD \rightarrow {}^1CH_2 + HDO$	9	E-12	this work
$1^{\prime\prime} d_{\rm H}$	$CH_2D + OD \rightarrow {}^1CHD + HDO$	6	E-12	this work
1'e	$CH_3 + OD \rightarrow HCOD + H_2$	1.1	E-11	this work
$1^{\prime\prime}e_{ m H}$	$CH_2D + OD \rightarrow DCOD + H_2$	4.4	E-12	this work
$1^{\prime\prime} e_{ m D}$	$CH_2D + OD \rightarrow HCOD + HD$	6.6	E-12	this work
1'f	$CH_3 + OD \rightarrow H_2CO + HD$	1.7	E-12	this work
5'	$D_2O + F \rightarrow OD + DF$	2.5	E-11	estimated
6′	$OD + OD \rightarrow D_2O + O$	3.0	E-12	estimated
7′	$O + OD \rightarrow O_2 + D$	2.4	E-11	estimated
8′	$OD + F \rightarrow O + DF$	5.8	E-11	estimated
9′	$OD (wall) \rightarrow products$	6		this work
10	$O \text{ (wall)} \rightarrow 1/2 \text{ O}_2$	6	estimat	ted, this work
11	H (wall) $\rightarrow 1/2$ H ₂	10	estimat	ted, this work
11'	$D \text{ (wall)} \rightarrow 1/2 D_2$	10	estimat	ted, this wrok
12	$CH_3 + O \rightarrow H_2CO + H$	1.4	E-10	estimated
$12'_{ m H}$	$CH_2D + O \rightarrow HDCO + H$	1.1	E-10	estimated
$12'_{ m D}$	$CH_2D + O \rightarrow H_2CO + D$	3	E-11	estimated
14	$CH_3 + CH_3 + (M) \rightarrow C_2H_6 + (M)$	1	E-12	estimated
15	CH_3 (wall) \rightarrow products	6 - 8		this work
15'	CH_2D (wall) \rightarrow products	6 - 8		this work
16'	$^{1}CH_{2} + D_{2}O \rightarrow CH_{2}D + OD$	3.4	E-11	[25]
17'	$^{1}CH_{2} + OD \rightarrow H_{2}CO + D$	3	E-11	estimated
18′	$OD + H_2 \rightarrow HDO + CHO$	6	E-13	estimated
20'	$OD + H_2CO \rightarrow HDO + CHO$	1.8	E-11	estimated
$21^{\prime\prime}$	$OD + HCOD \rightarrow products$	1.8	E-11	estimated

TABLE III. Modified reaction mechanism for the $CH_3 + OD$ system. (Rate coefficients refer to 700 K and 0.65 mbar. Units of k are molec, cm³, and s).

In order to facilitate the comparison to Table II, the same numbering is maintained. Reactions where in one of the reactants an H atom is replaced by D, are denoted by a prime. Double-prime means that in both reactants H is substituted. In the case of CH_2D reactions, a subscript H or D denotes whether H or D is affected by the reaction.

Many more reactions are possible yet are not included since they play only minor roles. For this same reason reactions (13) and (19) from Table II are omitted which is certainly justified under our conditions of low initial methyl concentrations.

The relative contributions of side reactions to our product yields are shown in Table IV. Its first line displays the product signals as measured at 90% CH₃ consumption and referring to CH₃OD, HCOD, H₂CO, HDO, HD, and H₂. Contributions of reactions other than channels (1'e) and (1'f) were calculated and are shown in the second line. Subtraction leads to the product yields that are to be assigned to reaction 1. For the determination of the channel rate coefficients into (1'e) and (1'f) the calibrated H₂/HD signals were used since they are interfered by only very few other reactions as to be discussed below. From k'_{1tot} along with the product yields of Table IV we get (for 700 K and 0.65 mb):

$$\begin{aligned} k'_{1a} &= 2.0 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \\ k'_{1d} &= 9.0 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \\ k'_{1e} &= 1.1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \\ k'_{1f} &= 1.7 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}. \end{aligned}$$

The $HCOD/H_2CO$ data in Table IV are in brackets since both species were not calibrated. Their mass spectrometric sensitivities were arrived at by comparison of



Figure 5. (a) Product profiles for H_2/HD at 700 K. Simulated curves are based on rate coefficients of Table III. $k_{1'e}$ and $k_{1'f}$ are adjusted to absolute product yields at the end of the reaction. (b) Product profiles for $H_2CO/HCOD$ at 700 K. The simulated curves are scaled to the experimental profiles. This yields the mass spectrometric sensitivity for these species (see text). For clarity, the simulated yields for H_2CO production from $CH_3 + OD$ are also shown.

the experimental profiles with the simulated ones, which are based on our absolute H_2/HD measurement. It turned out that the mass spectrometric sensitivity for H_2CO is roughly 2 times that of CHOD. This result is needed for the simulation of the mixed CHOD/HDCO profiles. Here, in terms of concentration, the HDCO contribution (same sensitivity assumed as for H_2CO) amounts at 700 K only about 10% of the CHOD yield. At 600 K, however, it is much more important.

	H_2	HD	(H ₂ CO)	(HCOH)	HDO	CH ₃ OD
measured yield	7	1	6	6.0	8	1.5
yield of side rxns.	0.5	0	5	0.5	3	0.0
primary yield	6.5	1	1	5.5	5	1.5

TABLE IV. Stable reaction products of $CH_3 + OD$. Concentrations are in units of 10^{10} cm⁻³ and refer to 90% consumption of $[CH_3]_0 = 2.2*10^{11}$ cm⁻³. 700 K and 0.65 mbar.

Due to fragmentation, our HDO measurement is only accurate as to 30% and this uncertainty enters k'_{1d} . Nevertheless, it is worthwhile to note that the difference

$$k'_{1\text{tot}} - k'_{1\text{d}} = k'_{1\text{a}} + k'_{1\text{e}} + k'_{1\text{f}}$$

= 1.45 × 10⁻¹¹ cm³ molec⁻¹ s⁻¹ at 0.65 mb

is in full accord with our result for

$$k_{1\text{tot}} = k_{1a} + k_{1e} + k_{1f}$$

suggesting that the reaction into the individual channels takes place without strong isotopic effects. Therefore, the primes in our notation may be omitted to obtain the channels eliminating molecular hydrogen:

$$k_{1e}(700 \text{ K}) = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

 $k_{1f}(700 \text{ K}) = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.$

Further Measurements for $CH_3 + OD$ at 600 K

In order to obtain the temperature dependence of the new HCOD channel we carried out further measurements at 600 K. The experimental conditions are included in Table I. The decay curves are not shown for the sake of brevity. $k'_{1tot}(600 \text{ K})$ is deduced by the same procedure as outlined above resulting in

$$k'_{1 \text{tot}}(600 \text{ K}) = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.$$

The H₂/HD product yields as needed for the determination of the channel rate coefficients, k'_{1e} and k'_{1f} are shown in Figure 6(a). Both yields are lower and HD disappears in the noise which corresponds to an HD concentration of $5*10^9$ molec/cm³ rendering us with an upper limit for k'_{1f} :

$$k'_{1f}(600 \text{ K}) \le 1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

The H_2 signals, on the other hand, are clearly detectable although with an apparent noise caused by an automatic background subtraction. Other sources to these signals include in particular heterogeneous H_2 generation. These contributions are examined in more detail in the sensitivity analysis (see below). We thus arrive at a corrected product yield referring to the contribution of reaction 1e.

$$H_{2, \rm corr.} / \Delta CH_3 = 0.4 \pm 0.1$$

and this leads to

$$k'_{1\mathrm{e}}(600\ \mathrm{K}) = 7.5 imes 10^{-12}\ \mathrm{cm}^3\ \mathrm{molec}^{-1}\ \mathrm{s}^{-1}$$



Figure 6. (a,b) Product profiles for H₂/HD and HCOD/H₂CO at 600 K.

By combining this result with the $k'_{1e}(700)$ value and assuming an Arrhenius form to describe the temperature dependence, one gets for the apparent activation energy

$$E_a(1e) = 3.0 \pm 1.0 \text{ kcal/mol}$$

The $H_2CO/HCOD$ product profiles as shown in Figure 6(b), on the other hand, are not very different from the 700 K results shown in Figure 5(b). The reason is the overwhelming influence of the reaction of methyl radicals with O atoms yielding either H_2CO or HDCO through

$$(12'H) \qquad \qquad CH_2D + O \longrightarrow HDCO + H$$

Since these reactions are temperature independent their relative importance over our primary reactions, (1'e) and (1'f), is much more pronounced at the lower temperature.

Discussion

Sensitivity Analysis and Error Bar for k'_{1e}

A systematic variation of all rate coefficients in the model (Table III) by a factor of 2 or 0.5, respectively, showed that

$$k_{1\mathrm{e}}' = (H_{2,\,\mathrm{corr.}}/\Delta\mathrm{CH}_3) imes k_{1\mathrm{tot}}'$$

is considerably less prone to model uncertainties than k'_{1tot} . This can be understood by starting with an individual sensitivity analysis for $(H_{2, corr.}/\Delta CH_3)$ and k'_{1tot} in the expression for k'_{1e} .

Figure 7 shows the normalized relative change of the simulated H_2 production, i.e., $(\Delta H_2/H_2)/(\Delta k_i/k_i)$ as a function of reaction time, obtained by decreasing each rate coefficient by a factor of 2. Clearly, rc.1'e is the most sensitive reaction throughout our time interval, the sequence

$$\mathrm{CH}_3 + \mathrm{O} \longrightarrow \mathrm{H}_2\mathrm{CO} + \mathrm{H},$$

 $\mathrm{H} \text{ (wall)} \longrightarrow 1/2 \mathrm{H}_2$

playing a much smaller role. In the CH₃—OH system the other major H source would consist of the reaction

$$O + OH \longrightarrow O_2 + H$$
,

whereas in our case, using OD, this latter reaction produces D atoms rendering the walls less significant for the formation of H_2 .

Other reactions that affect the simulated H_2 yields do so indirectly, for instance through the influence on the OD profiles as in the case of OD + OD or of the source reaction D_2O + F. For the sake of clarity and since our product measurements were



Figure 7. Sensitivity analysis for the production of H_2 .

mostly carried out at larger reaction times, the sensitivity for H_2 is replotted in Figure 8, light bars.

The sensitivity analysis for $k_{1\text{tot}}$ is already discussed in our accompanying article [32] and is displayed there as a function of the reaction time. It was recalculated for the OD case and plotted in Figure 8, hatched bars. The new numbers differ slightly from [32] for a variety of reasons: (i) A different stoichiometry renders the OH generation reaction more sensitive; (ii) due to the active role of the ¹CH₂ channel, $k'_{1\text{tot}}$ is larger than $k_{1\text{tot}}$ leaving less weight to competing reactions like CH₃ + O; and (iii) a different display is used, i.e., $\Delta \ln\{\text{CH}_3(t)/\text{CH}_3(0)\}$ rather than $\Delta \text{CH}_3(t)/\text{CH}_3(0)$.

From Figure 8 one notes that a number of important reactions enter with a different sign so that their combined influence should be smaller. For instance, if the "true" rate coefficient of $CH_3 + O$ were larger, an enhanced apparent CH_3 reaction rate would be measured combined with, due to competition, a decreased H_2 formation. Similar argumentations may be found for other reactions. It is therefore not surprising that k'_{1e} is significantly less sensitive to side and subsequent reactions and this is also shown in Figure 8, solid bars, with the sensitivity bar for this channel approaching unity. Conversely, the sensitivities of only three other reactions, i.e., OD + OD, O + OD, and $CH_3 + O$, respectively, exceed 10%. Based on our OH/OD profile measurements we do not expect a strong isotope effect for the first two reactions and hence estimate in the absence of literature data an uncertainty factor of 1.5 for each of them. This leads to an estimated error of about 25% for the deduced value of k'_{1e} .

Due to uncertainties of the measurement the total error bar may increase to about 40%.

Comparison of Other Studies

As far as we know there exists no other experimental study reporting HCOH as a product of the reaction $CH_3 + OH$. Since this reaction proceeds via excited methanol,



Figure 8. Sensitivity in bargraph display at t = 23 ms. Plotted are the normalized relative changes of: (i) the H₂ production (cf. Fig. 8), light bars; (ii) $k'_{1\text{tot}}$, hatched bars; and (iii) the product term $k'_{1\text{e}} = (\text{H}_{2,\text{corr.}}/\Delta \text{CH}_3)^* k'_{1\text{tot}}$, solid bars.

one may ask whether HCOH is formed if this bound intermediate is approached through a different entrance channel, say via ${}^{1}CH_{2} + H_{2}O$ or via H + CH₃O/CH₂OH. In a very recent study of Carstensen and Wagner [28] the reactions ${}^{1}CH_{2} + H_{2}O/D_{2}O$ were investigated in a photolysis reactor between 255 and 475 K. These authors found that (50 ± 20)% of the consumed ${}^{1}CH_{2}$ resulted in OH formation, another 25% are believed to be quenched into ${}^{3}CH_{2}$ and the remaining 25% to yield stable methanol.

In their early study on $H + CH_3O/CH_2OH$ Hoyermann and co-workers [33] found a formation of HCOH and this was shown by the HCOH ionization curves that were clearly different from the ones of H_2CO . From the use of various differently deuterated radicals, evidence was derived that the HCOH formation occurred via direct abstraction from CH_2OH rather than complex formation. No HCOH was found as product of the reaction $CH_3O + H$. The latter result was confirmed by the recent study of Dobé et al. [34]. Thus from $CH_3 + OH$ there exists a path via excited methanol into $HCOH + H_2$, but not so from ${}^1CH_2 + H_2O$ or from $H + CH_3O/CH_2OH$.

In comparison to the available theoretical studies [12,19] it is interesting that we measured a strong temperature dependence for the HCOH channel which is also reflected by its nondetection in the low temperature range between 300 to 500 K, whereas at 700 K this channel is even the dominant one. For the H₂CO channel this behavior is even more pronounced rendering this route undetectable at 600 K.

At present, there is no explanation for the disagreement to the recent theoretical study carried out by Walch [12].

Potential Role of Isomerization

In this study it is assumed that in the chemically excited adduct, $(CH_3OD)^*$, no H/D exchange takes place. If we were prone to such an exchange the relationship between mass abundance (i.e., 30 vs. 31 amu or 3 vs. 2 amu) and a particular reaction channel would get lost. By contrast, the temperature dependence of these signals and particularly the disappearance of the HD signals at 600 K show that an assignment of the formaldehyde channel to this mass number is possible, so that an H/D exchange is negligible.

As isomerization of HCOH or HCOD into formaldehyde should at our temperatures be prevented by isomerization barrier of about 32 kcal/mol according to Melius [17].

Meaning of the HCOH Channel for Flame Models

At flame temperatures, the exit channel into $H + H_2COH$ is probably the leading one [35,36,38]. This would render the meaning of the HCOH channel to the intermediate temperature regime where it might have an effect on ignition or quenching phenomena. An extrapolation of our results into the regime between 1000 to 1200 K remains very tentative due to the uncertainty of the temperature dependence of this channel. Also, the construction of an energy diagram as attempted in Figure 9 is only preliminary since entropic as well as stabilization effects have to be considered by a master equation calculation [39].

A very recent analysis of the C_1/C_2 chemistry in fuel-rich post flame gases by Woods and Haynes [40] showed the high sensitivities of the $CH_3 + OH$ rate coefficients for C_2H_2 and particularly for CH_4 prediction. The proposed mechanism did not include the new H_2 producing channels and a match to the measured CH_4 profiles could only be achieved by strongly increasing the rate coefficient into $CH_2OH + H$.



Figure 9. Tentative energy diagram for the reaction $CH_3 + OH$.

Here, the use of the new HCOH channel might have been helpful. However, the urgent question arises which subsequent reactions the HCOH biradical might undergo. At present, virtually nothing seem to be known with regard to its gas phase kinetics. A study on its reactivity towards O_2 and OH is underway.

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