Product Study of the Reaction of CH_3 with OH Radicals at Low Pressures and Temperatures of 300 and 612 K[†]

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The product distribution for the title reaction was studied using our time-of-flight mass spectrometer (TOFMS) connected to a tubular flow reactor. The methyl and hydroxyl radicals were produced by an excimer laser pulse ($\lambda = 193$ nm) photolyzing acetone and nitrous oxide in the presence of excess water or hydrogen. Helium was used as the bath gas; the total density was held constant at 1.2×10^{17} cm⁻³. At 300 K the observations were consistent with singlet methylene ($^{1}CH_{2}$) and water as the main product channel with a small contribution of methanol. In contrast, at about 610 K three channels—formaldehyde isomers and methanol in addition to $^{1}CH_{2} + H_{2}O$ —are formed with similar yields. When acetone- d_{6} was used, the production of both CHDO and CD₂O was observed, indicating that two different formaldehyde-producing channels are operating simultaneously. These experimental results are compared with RRKM and master equation calculations on the basis of the properties of the methanol potential energy surface from a recent ab initio study.

1. Introduction

The reaction of hydroxyl radicals with methyl radicals is an important process in the combustion of methane and larger hydrocarbons.^{1,2} The overall rate constant for this reaction has been measured over wide temperature and pressure ranges by a number of investigators.^{3–10} The reaction involves direct addition to form a vibrationally excited methanol molecule, which can then either be stabilized by collision, dissociate back to reactants, or form one of several possible products, shown here as reactions R1–R7. Enthalpies of formation at 298 K from

	ΔH° (298 K,	
	kcal/mol	
$CH_3OH \rightarrow CH_3 + OH$	89.43	(R1)
\rightarrow ¹ CH ₂ + H ₂ O	90.13	(R2)
\rightarrow cis-HCOH + H ₂	77.10	(R3)
\rightarrow trans-HCOH + H ₂	72.92	(R4)
\rightarrow H ₂ CO + H ₂	21.16	(R5)
\rightarrow CH ₂ OH + H	107.57	(R6)
\rightarrow CH ₃ O + H	99.51	(R7)

two different databases^{11,12} (Table 1) can be used to calculate enthalpies of reaction for the reactions shown above. (Although a slightly lower enthalpy of formation for hydroxyl, 8.83 kcal/ mol at 298 K, has been proposed,¹³ for the sake of consistency of relative values we have used the values in Table 1 labeled "Sandia".) The 0 K values obtained by Yu and Muckerman¹⁴ have been extended to 298 K by including the translational, rotational, and vibrational contributions to ΔH° . These are the values shown in R1–R7. They are compared with the experimental values in Table 2.

Hochanadel et al. studied this reaction by following the concentration of methyl radicals with time-resolved absorption spectroscopy at 216.4 nm.⁵ Hydroxyl was generated by the photolysis of water vapor, and methyl was produced by the

 TABLE 1: Enthalpies of Formation at 298 K (kcal/mol)

	Sandia ¹¹	NIST ¹²
CH ₃ OH	-49.0 ± 1.0	-48.0
CH ₃	34.9 ± 1.2	34.82
OH	9.2 ± 1.0	9.32
$^{1}CH_{2}$	102.7 ± 1.8	101.34
Н	52.1 ± 1.0	52.10
H_2O	-57.8 ± 1.0	-57.80
H ₂ CO	-25.9 ± 1.0	-27.7
cis-HCOH	27.8 ± 1.8	
trans-HCOH	23.3 ± 1.7	
CH ₃ O		4.1
H ₂ COH	-4.9 ± 1.1	-2.0

TABLE 2: Enthalpies of Reaction (kcal/mol)

		Sandia ¹¹	NIST ¹²	Yu Mucke	and erman ¹⁴
reaction		(298 K)	(298 K)	(0 K) ^a	(298 K)
CH ₃ OH →	$CH_3 + OH$	93.1	92.14	87.57	89.43
	$^{1}CH_{2} + H_{2}O$	93.9	91.54	88.07	90.13
	cis-HCOH + H ₂	76.8		75.32	77.10
	<i>trans</i> -HCOH $+$ H ₂	72.3		71.14	72.92
	$H_2CO + H_2$	23.1	20.3	19.39	21.16
	$CH_3O + H$		104.2	103.20	107.57
	$H_2COH + H$	106.0		95.09	99.51

^{*a*} Values at 0 K from ref 14 were converted to 298 K by correcting for rotational and vibrational contributions using data from this source.

reaction of OH with methane. Anastasi et al. again used absorption at 216.4 nm to follow the course of the reaction.⁴ Pulse radiolysis of SF₆ produced F atoms, which reacted with CH₄ and H₂O to produce the required radicals. Fagerstrøm et al. used the same method to determine the pressure dependence of the rate constant.³

Laszlo et al. used flash photolysis of acetone to produce methyl radicals and to produce $O(^{1}D)$ from nitrous oxide.⁶ The

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oxygen atoms reacted with H_2 to form the required hydroxyl radical. No pressure dependence was found over a range of 34–350 Torr.

Bott and Cohen measured rate constants at high temperatures in a shock tube.⁷ Hydroxyl radicals were produced by the dissociation of *tert*-butylhydroperoxide, and *tert*-butylperoxide provided methyl radicals. UV absorption at 309 nm was used to follow the decay of OH. These researchers suggested that stabilization of methanol accounted for about 75% of the reaction at a pressure of 1 atm.

Grotheer and co-workers have carried out a number of flowtube experiments on this reaction system.^{8,9} When a microwave discharge was used to generate H and F atoms, the required radicals were produced by the reactions

$$F + CH_4 \rightarrow CH_3 + HF$$
$$H + NO_2 \rightarrow OH + NO_3$$

Mass spectrometry was used to follow the decay of methyl and also to look at products. These authors concluded that stabilization was the major channel (70–90%) at ambient temperature and pressures of 0.22–6.82 Torr. At 300 K, they did not detect the H₂O product of reaction R2, and from their detection limit they concluded that this channel can contribute at most about 5%. Later work by this group extended the temperature range to 600 and 700 K.

The reverse of reaction R2 has been studied by Hack et al.¹⁵ and by Carstensen et al., who produced the methylene radical by laser photolysis of ketene.¹⁶ Laser-induced fluorescence was used to follow the disappearance of ¹CH₂. With the rate constant they determined, together with an equilibrium constant calculated from thermodynamic and spectroscopic data, it is possible to obtain a rate constant for reaction R2.

De Avillez Pereira et al. carried out an extensive investigation of the temperature and pressure dependence of the $CH_3 + OH$ reaction.¹⁰ In a He bath gas at pressures of 7.6–678 Torr and temperatures of 290, 473, and 700 K, the rate of OH decay was followed by laser-induced fluorescence, and CH_3 was monitored by absorption at 216.4 nm. Both radicals were produced simultaneously by the 193 nm photolysis of acetone containing traces of water. Master equation calculations combined experimental rate constants for the removal of OH with RRKM calculations of rate constants for channels with a barrier, and with literature values for the rate constants of channels R1, R2, R6, and R7. These calculations gave pressure-dependent rate constants for the various channels as a function of temperature.

Lin and co-workers have used ab initio molecular orbital theory calculations at the G2M level¹⁷ to characterize the potential energy surface for the CH₃···OH system.¹⁸ Rate constants and branching ratios were obtained from variational transition-state theory and RRKM calculations.

Most recently, Yu and Muckerman have carried out CASSCF calculations to determine geometries and vibrational frequencies of stationary points on the potential energy surface (PES) for this system.¹⁴ The energies were refined by extrapolating multireference CI (MRCI) calculations employing two large basis sets to the complete basis set (CBS) limit.¹⁹ A schematic energy diagram is shown in Figure 1. In this paper their results are used as a starting point in the calculation of rate constants for the reactions of the CH₃···OH system for comparison with experimental findings.



Figure 1. Schematic energy diagram of the $OH + CH_3$ reaction at the MRCI+Q/CBS level of theory with the zero-point energy correction obtained from the CAS(10,10)/cc-pVDZ results. Data from ref 14.

2. Experimental Section

The experiments were performed in our flow reactor/repetitive sampled time-of-flight mass spectrometer apparatus. A detailed description of the apparatus can be found elsewhere, and only an overview will be given here.²⁰ The tubular quartz reactor (1 cm diameter) was coated with boric acid on the inside to reduce surface reactions and with a thin layer of platinum on the outside acting as a conductor used to heat the tube electrically. The temperature was measured with thin-wire thermocouples placed at several positions inside the tube. The temperature variation along the tube was within 7% at 610 K. Precursors, reactants, and products are sampled continuously through a pinhole in the wall of the tube. A portion of the sampled gas is photoionized by the VUV radiation emitted from a hollow cathode lamp (McPherson, model 630) operated with hydrogen as discharge gas. The emitted light is passed through a differentially pumped glass tube, allowing the lamp to be operated without windows, so that the whole spectrum of the H₂ emission can be used for ionization. By switching voltages on the collection grid assembly at a high rate, "snapshots" of the composition of the reaction mixture can be taken, here in intervals of 48 µs.

The radical precursors were photolyzed by the radiation of an ArF excimer laser (Lambda Physik, COMPEX 205), creating a homogeneous distribution of radicals along the tube. Only a fraction (<5%) of the laser light was actually absorbed by the precursors in the reactor tube. The rectangular cross section of the emitted laser radiation was reduced to a square shape by a Galilean telescope made of cylindrical quartz lenses before it entered the reactor tube. Typical energies were 120–250 mJ/ pulse exiting the laser. The laser intensity was monitored separately with two thermoelectric energy meters (Molectron J50), collecting laser radiation reflected off the quartz entrance window or exiting the reactor through the rear window. This intensity was used to calculate shot-by-shot concentrations of OH radicals (see below). Mass spectra were typically summed for 20 000–100 000 laser shots per experiment.

Mass-flow controllers (Tylan General, FC 260) were used to prepare the gas mixtures introduced into the reactor tube. Acetone-1,3- ^{13}C (Cambridge Isotopes Laboratories, 99 atom % ¹³C) and acetone- d_6 (Aldrich, 99.5 atom % D) diluted in helium were prepared in advance and stored in 20-L glass vessels. He (Welco CGI Gas Technologies, UHP grade), H₂ (Matheson, purity 2.1), and the N₂O premix (2% in He, Praxair; purity: N₂O 5.5, He 6.0) were used directly from the tank. Water was introduced by passing He first through a bubbler filled with purified and degassed water before it entered the mass-flow controller. The bubbler was placed in a water bath whose temperature was monitored continuously. The pressure in the flow reactor was controlled by throttling the gas flow through a gate valve at the downstream end of the reactor. The flow velocity employed here was 8 m/s to minimize the pressure drop along the tube.

Isotopically labeled acetone was used here to separate the formaldehyde signal (${}^{13}CH_2O$, m/e = 31) from the main two mass channels associated with ethane (${}^{13}C_2H_6$, m/e = 30 and 32) and to distinguish between formaldehyde coming from the DCOH channel (CHDO, m/e = 31) or produced directly (CD₂O, m/e = 32).

Typical concentrations in the reactor were $(0.9-2) \times 10^{15}$ molecules cm⁻³ of H₂O, 1.5×10^{14} molecules cm⁻³ of N₂O, and $(0.4-2) \times 10^{13}$ molecules cm⁻³ of acetone, and in some experiments a quarter of the He was replaced by H₂ ([H₂] = 3 $\times 10^{16}$ molecules cm⁻³). Under the conditions employed, most of the O(¹D) atoms produced in the 193-nm photolysis of N₂O react either with water, generating two OH radicals, or with H₂, giving OH radicals and H atoms. Water is present in all experiments to rapidly quench vibrationally excited OH radicals.²¹ By changing the acetone concentration or the laser intensity, different initial concentrations of methyl or hydroxyl radicals could be chosen.

For reference measurements, mixtures of C_2H_2 (Matheson, with acetone removed by LN2/dry ice distillation), C_2H_4 (Matheson, >99%), C_2H_6 (Linde, >99%), CH₃OH (Mallinckrodt), NO (Matheson, cleaned by LN2/dry ice distillation), O_2 (Liquid Carbonic), and CH₂O (prepared from paraformaldehyde (Aldrich)) with He were prepared in 3-L glass bulbs.

3. Data Analysis

All data sets came in pairs of experiments: one with and one without N_2O . Because the acetone photolysis at 193 nm produces not only methyl radicals but also small amounts of methylene, giving ethylene and ethane as reaction products, measurements without N_2O served as a "baseline" for subsequent simulation calculations of all data sets. In addition, in separate experiments, photolyzing acetone or ketene in He alone gave values for the loss of methylene due to wall reactions.

Species signals were converted into concentration via calibration constants, which were obtained for stable species in separate experiments. Calibration constants for methyl radicals were obtained directly from the drop in the acetone signal, with a yield of about 96% for the channel, giving $2CH_3 + CO$ under the present conditions. A small fraction of the methyl radicals undergo secondary photolysis, giving $CH_2 + H$. At appropriately high CH_3 concentrations, all methylene radicals can be converted into ethylene, so that by determining the ethylene concentration the calibration constant for methylene radicals can be found. Further descriptions of the calibration procedures and the acetone photolysis can be found elsewhere.^{22,23}

Unfortunately, OH radicals could not be observed because of the low sensitivity of the current apparatus toward this species. Moreover, due to the small absorption coefficient, the drop in the N₂O signal after the laser fired could not be measured accurately. Therefore, the production of hydroxyl radicals was checked in two independent ways. First, N₂O was photolyzed in H₂, and the H₂O product was observed using He instead of H₂ as discharge gas in the hollow cathode lamp. Rate constants and H₂O yields were consistent with a wall loss of OH radicals between 50 and 100 s⁻¹. Second, under typical experimental



Figure 2. Left panel: Experimentally observed traces for the SO + OH calibration reaction. Experimental conditions and initial concentrations (in cm⁻³): T = 302 K, P = 4 Torr, $[H_2O] = 1.6 \times 10^{15}$, $[N_2O] = 2 \times 10^{14}$, $[SO_2] = 3 \times 10^{13}$, $[SO] = [O(^{3}P)] = 5.5 \times 10^{12}$. Right panel: Fraction of N₂O photolyzed as a function of laser intensity measured at the exit of the flow reactor. The initial SO/O(³P) concentrations range from $(1.0-5.5) \times 10^{12}$ cm⁻³. The triangles and circles depict two measurements performed during and at the end of this study.

conditions, but with acetone replaced by $S^{18}O_2$ (Stohler, 99.5 atom % ¹⁸O, no longer available), $S^{18}O$ radicals and ¹⁸O atoms produced in the photolysis of $S^{18}O_2$ converted OH radicals quickly into $S^{18}O^{16}O$ and ¹⁸O¹⁶O:

$$S^{18}O_2 + h\nu (193 \text{ nm}) \rightarrow S^{18}O + {}^{18}O({}^{3}P)$$
 (R8)

$$N_2^{16}O + h\nu (193 \text{ nm}) \rightarrow {}^{16}O({}^{1}D) + N_2$$
 (R9)

$$H_2^{16}O + {}^{16}O({}^{1}D) \rightarrow 2{}^{16}OH$$
 (R10)

$$S^{18}O + {}^{16}OH \rightarrow S^{16}O^{18}O + H$$
 (R11)

$${}^{18}O({}^{3}P) + {}^{16}OH \rightarrow {}^{16}O{}^{18}O + H$$
 (R12)

Therefore, by comparing the SO signal in measurements with and without N_2O , the OH concentration could be deduced via

$$[OH] = \Delta[SO_2]_0^{N_2O} \frac{[SO]_{\infty}^{n_0 N_2O} - [SO]_{\infty}^{N_2O}}{[SO]_{\infty}^{n_0 N_2O}} \frac{k_{R11} + k_{R12}}{k_{R11}}$$

The first factor in the right-hand side product is the initial concentration of SO radicals and $O(^{3}P)$ atoms ($[O(^{3}P)]_{0} = [SO]_{0}$) produced in the photolysis of SO₂. The second factor is the fraction of SO radicals lost in the reaction with OH radicals. Values for these two factors were taken from the experiment (see Figure 2, left panel). The last factor corrects for the loss of OH radicals with $O(^{3}P)$ atoms with rate constants taken from the literature.^{24,25} To find an error estimate for the OH concentration associated with the rate constants, we assumed that the relative errors for both rate constants are equal. Then relative errors of 30% in each rate, a value which we chose conservatively, would cause a 20% error in the OH concentration.

TABLE 3: Mechanism for the CH₃ + OH Reaction: Bimolecular Reactions^a

reaction	Α	β	E_{a}	refs and comments
$O(1D) + H_2 \rightarrow OH + H$	6.624×10^{13}	0	0	28
$O(1D) + H_2O \rightarrow 2OH$	1.300×10^{14}	0	0	28
$O(1D) + H_2O \rightarrow O + H_2O$	2.650×10^{12}	0	0	28
$O(1D) + N_2O \rightarrow NO + NO$	4.030×10^{14}	0	0	28
$O(1D) + N_2O \rightarrow N_2 + O_2$	2.950×10^{14}	0	0	28
$O(1D) + He \rightarrow O + He$	1.800×10^{9}	0	0	upper limit, see ref 55
$O + H_2 \rightarrow H + OH$	3.870×10^{4}	2.7	6260	56
$O + OH \rightarrow O_2 + H$	1.391×10^{14}	0	-218	25
$OH + H_2 \rightarrow H_2O + H$	1.024×10^{8}	1.6	3299	57
$CH + H_2O \rightarrow CH_2O + H$	3.064×10^{16}	-1.42	0	rate constant from ref 58
$CH + H_2 \rightarrow CH_2 + H$	1.867×10^{14}	0	3279	59
$CH + N_2O \rightarrow products$	1.861×10^{14}	0	-511.5	rate constant from ref 60
$CH_2(S) + H_2 \rightarrow CH_3 + H$	5.100×10^{14}	0	0	300 K, rate constant from ref 61
$CH_2(S) + H_2 \rightarrow CH_2(V) + H$	9.000×10^{12}	0	0	300 K, yield from ref 62
$CH_2(S) + H_2 \rightarrow CH_3 + H$	6.000×10^{14}	0	0	600K, see above
$CH_2(S) + H_2 \rightarrow CH_2(V) + H$	0.000×10^{12}	0	0	600 K, see above
$CH_2(S) + H_2O \rightarrow CH_2(V) + H_2O$	2.900×10^{14}	-0.7	0	rate constant from ref 63
$CH_2(S) + H_2O \rightarrow CH_3 + OH$	6.240×10^{13}	-0.7	0	20% deactivation
$CH_2(V) + He \rightarrow CH_2(S) + He$	6.000×10^{10}	0	0	assumed
$CH_2(V) + He \rightarrow CH_2 + He$	6.000×10^{13}	0	0	compare to NH_2 in ref 37
$CH_2(V) + H_2O \rightarrow CH_2 + H_2O$ $CH_2(V) + H_2 \rightarrow H_2 + H_2O$	6.000×10^{12}	0	0	assumed
$CH_2(V) + H_2 \rightarrow H_2 + H_2$ $CH_1 + CH_2 \rightarrow CH_1 + H_2$	1.144×10^{14}	0	0	22
$CH_2 + CH_3 \rightarrow C_2H_4 + H$	1.144×10^{14}	0	0	25 have see also references in ref 22
$CH_2 + CH_2 \rightarrow CO + OH + H$	5.000×10^{12}	0	1500	56
$CH_2 + O_2 \rightarrow 2H + CO_2$	5.000×10^{12}	0	1500	56
$CH_2 + O_2 \rightarrow O + CH_2O$	2.400×10^{12}	0	1500	56
$CH_2 + G_2 = O + CH_2O$ $CH_2 + H \rightarrow CH + H_2$	6.022×10^{12}	0	-1788	57
$CH_2 + OH \rightarrow CH_2O + H$	4.000×10^{14}	0	0	assumed compare to $CH_2 + O$ reaction in ref 31
$CH_2 + OH \rightarrow CO + H_2 + H$	4.000×10^{14}	0	0	assumed
$CH_2 + O \rightarrow CO + H_2$	1.200×10^{14}	0	0	57
$CH_2 + O \rightarrow CH_2O + H$	7.080×10^{14}	Ő	Ő	31
$CH_3 + O \rightarrow CO + H_2 + H$	1.350×10^{14}	Ő	Ő	31
$CH_3 + OH \rightarrow CH_3OH$	11000 / 10	Ū.	Ū.	see text
$CH_3 + OH \rightarrow CH_2(S) + H_2O$				see text
$CH_3 + OH \rightarrow HCOH + H_2$				see text
$CH_3 + OH \rightarrow CH_2O + H_2$				see text
$CH_2O + OH \rightarrow HCO + H_2O$	5.811×10^{6}	2.03	-1263.8	64
$CH_2O + H \rightarrow HCO + H_2$	1.265×10^{8}	1.62	2170	57
$HCO + M \rightarrow H + CO + M$	1.566×10^{14}	0	15759	65
$HCO + H \rightarrow H_2 + CO$	9.033×10^{14}	0	0	65
$HCO + OH \rightarrow H_2O + CO$	1.018×10^{14}	0	0	65
$HCO + O \rightarrow OH + CO$	3.000×10^{14}	0	0	65
$HCO + O \rightarrow H + CO_2$	3.000×10^{14}	0	0	65
$HCO + HCO \rightarrow CH_2O + CO$	2.168×10^{14}	0	0	57
$HCO + CH_3 \rightarrow products$	7.527×10^{14}	0	0	66
$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	7.226×10^{6}	2	864.4	57
$CH_3OH + OH \rightarrow CH_2OH + H_2O$	1.441×10^{6}	2	-840	67
$CH_3OH + OH \rightarrow CH_3O + H_2O$	6.279×10^{6}	2.0	1500	67
$CH_2CO + H \rightarrow HCCO + H_2$	5.000×10^{14}	0	8000	56
$CH_2CO + H \rightarrow CH_3 + CO$	1.807×10^{14}	0	3378	65
$CH_2CO + OH \rightarrow CH_2OH + CO$	1.018×10^{14}	0	0	65
$CH_2CO + CH_2(S) \rightarrow C_2H_4 + CO$	7.838×10^{14}	-0.33	0	61
$CH_3COCH_3 + OH \rightarrow H_2O + CH_3COCH_2$	2.403×10^{0}	4.0	-900	68 Channel francha CD - L CUL - C
$CHD_2 + D \rightarrow CD_3 + H$	1.150×10^{14}	U	0	69; used for the CD_3 + OH reaction
$CD_3 + H \rightarrow CHD_2 + D$	0.230×10^{14}	0	0	assumed

^{*a*} Data are given in Chemkin II format: $k = AT^{\beta} \exp(-E_a/RT)$, with *A* in mol cm³/s, *T* in K, and E_a in cal/mol. CH₂(S) stands for singlet methylene; CH₂(V) stands for vibrationally excited triplet methylene. Not listed explicitly are CH₂(V) reactions, which are the same as those for CH₂.

Isotopically labeled S¹⁸O₂ was used here to separate the S¹⁸O¹⁶O produced in the reaction from precursor S¹⁸O₂ so that the absolute radical concentration could be determined cleanly from the drop in the S¹⁸O₂ concentration after photolysis. The dependence of the OH concentration and thereby ultimately the O(¹D) production on the laser intensity was measured by varying the laser power (see Figure 2, right panel). The O(¹D) production as a function of laser intensity as well as the upper limit for the wall loss of OH of 50 s⁻¹ agreed well with the results obtained with the first method. In addition, similar yield—intensity relationships could be determined for SO₂ and acetone as well,

whereby the ratios of the resulting proportionality factors equaled the ratios of the respective absorption coefficients at 193 nm,^{26–28} which is consistent with the notion that the fraction of photolyzed precursors is a product of absorption coefficient, laser intensity, and an empirical common factor (e.g., $\{\Delta[N_2O]\}/\{[N_2O]\} = C\sigma_{N_2O}^{193} Int_{excimer}^{193}$). This relationship was used further on to determine the O(¹D) concentration for all other experiments.

Simulation Calculations. With a new fitting program, concentration profiles calculated using the Chemkin II program

TABLE 4: Mechanism for the CH₃ + OH Reaction: Pressure-Dependent Reactions^a

reaction	Α	β	E_{a}	refs and comments
CH + H ₂ (+ M) ↔ CH ₃ (+ M) LOW/4.820 × $10^{25} - 2.80590.0/$	1.970×10^{12}	0.43	-370	56
TROE/0.578 122.0 2535.0 9365.0/ $CH_3 + H (+ M) \leftrightarrow CH_4 (+ M)$ $L OW/(5528 + 10^{23} - 1.80 + 0.00)$	2.108×10^{14}	0	0	57
$\frac{1000}{1000} = 1.800.007$ $\frac{1000}{1000} = 1.800.007$ $\frac{1000}{1000} = 1.800.007$ $\frac{1000}{1000} = 1.800.007$	2500×10^{15}	-0.60	175	54 100/ hickor 4
$LOW/8.05 \times 10^{31} - 3.75981.6/$	2.300 × 10	-0.09	175	$54,10\%$ linguet A_{∞}
$CH_3 + O_2 (+ M) \leftrightarrow CH_3O_2 (+ M)$ LOW/4.406 × 10 ²⁴ − 3.00 0.00/	1.762×10^{16}	-1.7	0	28
SRI/0.60 1.0 1.0/ C ₂ H ₄ + H (+ M) \rightarrow C ₂ H ₅ (+ M)	3.974×10^9	1 28	1292	57
$LOW/4.714 \times 10^{18} 0.00760.00/$	5.974 × 10	1.20	1292	51
$C_{2}H_{4} + OH (+ M) \rightarrow C_{2}H_{4}OH (+ M)$ LOW/2 477 × 10 ²¹ -0.80 0.00/	5.300×10^{12}	0	0	28
SRI/0.60 0.001 0.001/	2,500 1015	0.60	175	
$LOW/8.05 \times 10^{31} - 3.75 \ 981.62/$	2.500×10^{15}	-0.69	175	same as $CH_3 + CH_3$; used for the $CD_3 + OH$ reaction
TROE/0.00 570.00 1000.00/				

^{*a*} Data are given in Chemkin II format: low- and high-pressure limit rate constants $k = AT^{\beta} \exp(-E_a/RT)$ with A_{∞} in mol cm³/s, A_0 in mol² cm⁶/s, *T* in K, and E_a in cal/mol. Further information on the format can be found at, e.g., http://www.me.berkeley.edu/gri_mech/data/k_form.html.

TABLE 5: Mechanism for the $CH_3 + OH$ Reaction: Unimolecular and Wall Reactions^{*a*}

reaction	Α	β	Ea	refs and comments
$O(1D) \rightarrow O$	3.000×10^{3}	0	0	determined independently
$HCOH \rightarrow CH_2O$	9.000×10^{3}	0	0	see text
OH → wall	8.000×10^{1}	0	0	used here
$CH_2 \rightarrow wall$	5.000×10^{1}	0	0	used here
$CH_2(S) \rightarrow wall$	3.000×10^{3}	0	0	cumulative loss

^{*a*} Data are given in Chemkin II format: $k = AT^{\beta} \exp(-E_a/RT)$ with A in s⁻¹, T in K, and E_a in cal/mol.

package²⁹ were fitted iteratively to selected mass traces from multiple data sets simultaneously. The current version allows rate constants (A, β , and E_a ; see Tables 3–5 for definition), initial concentrations, calibration constants, and signal offsets to be varied. The minimization routine consists of a genetic algorithm followed by a Simplex algorithm. We chose the genetic algorithm for its robustness in a multidimensional parameter space and its capability to explore this space efficiently. The quality of the concentration profiles at each iteration is evaluated according to a merit function, e.g., χ^2 . The overall goal is, as usual, to minimize the value of this merit function.

The reaction mechanism is summarized in Tables 3-5. We wanted to focus our attention on the product distribution of the $CH_3 + OH$ reaction, such as that of methanol and formaldehyde. In earlier measurements we failed to detect methanol at room temperature; this was attributed to the relatively low concentration of hydroxyl radicals used. To clarify this point, higher OH concentrations were employed here, which, however, made it necessary to include many more reactions in the mechanism.

The analysis of the reaction mechanism revealed that the ${}^{3}\text{CH}_{2}$ + OH reaction played a major role with respect to the formaldehyde signal observed at 300 K. In the absence of experimental or theoretical data on the ${}^{3}\text{CH}_{2}$ + OH reaction, one can only speculate about possible product channels. Presuming that an adduct is formed first, it is interesting to note that this $[\text{H}_{2}\text{C}-\text{OH}]^{\ddagger}$ adduct is connected via a low-lying barrier to isomerization to the $[\text{H}_{3}\text{C}-\text{O}]^{\ddagger}$ complex obtained in the CH₃ + O(³P) reaction, which has two major product channels: CH₂O + H (~84\%) and CO + H₂ + H (~15\%).^{30,31} One might assume that the product distributions for the two reactions would be

similar. However, with the overall rate constant for the ${}^{3}CH_{2}$ + OH reaction chosen to be the same as the one for the CH₃ + O({}^{3}P) reaction, a 50% yield for the CH₂O channel is large enough to explain all of the formaldehyde observed. The CO channel was assumed to contribute the remaining 50% of the overall rate constant.

With respect to the $CH_3 + OH$ reaction, the calculated barrier heights¹⁴ leading to HCOH + H₂ products make these channels more likely than the $CH_2O + H_2$ channel. Here we assume that the isomerization of HCOH to CH_2O is almost instantaneous. However, no experimental data that could confirm or refute this assumption are available.

Surprisingly, the simulated concentration profiles (see below) for the methylene radicals predict a higher methylene signal than actually measured in most measurements at 300 K, and this also causes a higher prediction for the ethylene (m/e = 30) concentration (see Figure 3). This discrepancy is more pronounced at lower CH3 concentrations and higher OH concentrations; however, it disappears if hydrogen is used to generate OH radicals or at the higher temperature of 612 K. Significantly, higher loss rates for methylene (e.g., wall rates up to 700 s⁻¹) or hydroxyl radicals on the reactor wall or lower concentrations of OH radicals could be ruled out as reasons for this discrepancy because these would be incompatible with observations made in the control measurements. To test if the OH concentrations as determined via the calibration measurements (see above) were too high, fits were performed on two datasets (one with H₂O and one with H_2/H_2O), where the input concentrations for OH radicals were chosen to be half their original value. Fewer OH radicals lead to smaller methylene concentrations, shifting the simulated profiles into the "right" direction. However, the fit for the H₂O case is still far from being satisfactory. With respect to the product distribution, the methanol yield had to be raised by a factor of 3, which still leaves ${}^{1}CH_{2} + H_{2}O$ as the major product channel with a yield of at least 70%.

In addition, an overall rate constant for the CH₃ + OH reaction of less than 3×10^{-11} cm³/s would be necessary to explain the behavior observed; this would be in contradiction to literature data, which places the rate constant around (5–6) $\times 10^{-11}$ cm³/s at 300 K and 4 Torr of helium.^{32–34} For the fit



Figure 3. Experimentally observed traces and simulated signal profiles for the ¹³CH₃ + OH reaction. The three calculated profiles in the lower panel were obtained by changing the rate constant for the quenching of vibrationally excited triplet methylene by helium from 2×10^{-13} cm³/s (upper line) to 1×10^{-13} cm³/s (middle line) to 0 cm³/s (lower line). T = 302 K, P = 4 Torr. Initial concentrations (in cm⁻³) used in the simulation calculations: $[H_2O] = 9.4 \times 10^{14}$, $[N_2O] = 1.53 \times 10^{14}$, $[O_2] = 2.3 \times 10^{11}$, $[OH] = 5.5 \times 10^{10}$, $[O(^1D)] = 4.0 \times 10^{11}$, $[^{13}CH_2]$ $= 4.4 \times 10^{10}$, $[^{13}CH_3] = 1.76 \times 10^{12}$, $[H] = 1.1 \times 10^{11}$, $[^{13}CH_2CO] =$ 2.3×10^{10} , $[^{13}CH_3CO^{13}CH_3] = 1.12 \times 10^{13}$.

of the data obtained at 300 K, the rate constant was fixed at 4 \times 10⁻¹¹ cm³/s.

Recent measurements from this laboratory³⁵ on the quenching of ¹CH₂ showed that it is possible for vibrationally excited ³CH₂ to be converted back to ¹CH₂. In the absence of vibrational deactivation, a steady-state concentration of a few percent is possible, implying that the reactivity of such an ensemble could be dominated by reactions of singlet methylene. To explore this possibility, vibrationally excited triplet methylene, ${}^{3}CH_{2}(V)$, which could only be produced in deactivation reactions of singlet methylene, was introduced to the reaction mechanism. Rate constants for vibrational deactivation of ³CH₂(V) were assumed to be similar to those measured for NH2.36,37 Instead of listing individual reactions, a cumulative first-order loss for ¹CH₂ was chosen to account for reactions on the reactor wall and with other molecules such as acetone. As can be seen in Figure 3, a reactivation of ¹CH₂ can have measurable effects, in particular on the observed methylene traces. Within the range of reasonable values for steady-state concentration (here 3%) and vibrational deactivation by He atoms, it was not possible to describe the experimental methylene traces satisfactorily. However, all traces acquired with H₂ present and above 600 K showed little effect of this recrossing, as expected, because the deactivation of singlet methylene or its reaction with H₂ outweigh all other reactions.

According to the simulations, all the formaldehyde generated at 300 K can be attributed to the ${}^{3}CH_{2}$ + OH reaction. To establish an upper limit for the formaldehyde production in the CH₃ + OH reaction, the second channel of the ${}^{3}CH_{2}$ + OH reaction, CO + H₂ + H, was set to 100%, giving a value for the HCOH + H₂ channel of at most 10% of the total rate constant at 300 K and 4 Torr of helium. Because methanol doesnot suffer the difficulties associated with multiple sources, a yield of $6 \pm 3\%$ can be given, where the uncertainty was estimated by considering the uncertainty in determining the rate constant for the ${}^{1}CH_{2} + H_{2}O$ channel as described above.

Above 600 K the situation is completely different. Because the CH₂O and CH₃OH channels of the title reaction have higher yields, fewer OH radicals needed to be generated. In combination with higher methyl radical concentrations used, uncertain reactions such as the 3 CH₂ + OH reaction played a lesser role. Again, setting the two product channels alternately to 100% and 0% changed the yield of the formaldehyde channels of the CH₃ + OH reaction only by 5%. At 612 K and 8 Torr of helium, the total rate constant and yields determined for the various channels are

- CH₃ + OH (+ He) → products $(5.8 \pm 1.2) \times 10^{-11} \text{ cm}^3/\text{s}$ → CH₃OH (+ He) $20 \pm 7\%$ → ${}^1\text{CH}_2 + \text{H}_2\text{O}$ $46 \pm 14\%$
 - \rightarrow CH₂O + H₂/HCOH + H₂ 34 ± 8%

The main uncertainties at this temperature reside with determining initial radical concentrations and the associated calibration constants used to convert counts into concentrations. The two are directly connected, and variations in calibration measurements for stable as well as radical species typically lie within 20%. To get an estimate for the error in the rate constant of the $CH_3 + OH$ reaction, the best value was varied by $\pm 50\%$, keeping the product distribution as it is. While this does not have a large influence on the profiles of the main species (methyl radicals and ethane), the 50% profiles for methanol and formaldehyde lie on the outer limits of the signal noise. Therefore, an error of 20% was adopted for the overall rate constant. Furthermore, a 10% change in the yield of formaldehyde and a 20% change in the yield of methanol would place their simulated concentration profiles just within the noise of the data. Together with the uncertainty in the calibration constants, this leads to the error quoted for the yields.

To distinguish between the two formaldehyde-producing channels at 612 K and 8 Torr of helium, perdeuterated acetone was photolyzed, giving two CD3 radicals. For the simulation calculations, the same mechanism was used as in the all-Hatom system with a few new reactions added (see Tables 3 and 4). Experimental data and simulated profiles are shown in Figure 4. If hydroxymethylene is produced in the $CD_3 + OH$ reaction, then in the absence of isotope scrambling the isomerization should yield singly deuterated formaldehyde, CHDO (m/e =31), in contrast to CD₂O (m/e = 32) resulting directly from an HD loss from the $[CD_3OH]^{\ddagger}$ complex. Indeed, both products are found, and interestingly the CD₂O yield is larger than (or at least similar to) the one for DCOH, which is surprising considering that the corresponding barrier height as calculated by Yu and Muckerman¹⁴ for the dissociation of CH₃OH lies above both the $CH_3 + OH$ entrance channel and the barrier leading to HCOH + H₂. In general, the measured product distributions of the CD_3 + OH and the ${}^{13}CH_3$ + OH reactions



Figure 4. Experimentally observed traces and simulated signal profiles for the CD₃ + OH reaction. The dashed lines are simulated signal profiles without the contributions of CD₂O, CD₃OH (top panel), and CHDO (bottom panel). T = 612 K, P = 8 Torr. Initial concentrations (in cm⁻³) used in the simulation calculations: [H₂O] = 2.3×10^{15} , [N₂O] = 1.4×10^{14} , [O₂] = 3×10^{11} , [OH] = 9.2×10^{10} , [O(¹D)] = 2.53×10^{11} , [CD₂] = 9.6×10^{10} , [CHD₂] = 7.0×10^{10} , [CD₃] = 3.35×10^{12} , [H] = 9.2×10^{10} , [D] = 2.0×10^{11} , [CD₂CO] = 4.1×10^{10} , [CD₃COCD₃] = 1.4×10^{13} .

are in good agreement, with somewhat more methanol and a little less singlet methylene generated in the deuterated case.

 $CD_3 + OH (+ He) \rightarrow products$

$$(5.8 \pm 2.4) \times 10^{-11} \text{ cm}^{3}/\text{s}$$

$$\rightarrow \text{CD}_{3}\text{OH} (+ \text{He}) \qquad 32 \pm 8\%$$

$$\rightarrow ^{1}\text{CD}_{2} + \text{HDO} \qquad 35 \pm 8\%$$

$$\rightarrow \text{DCOH} + \text{D}_{2} \qquad 10 \pm 3\%$$

$$\rightarrow \text{CD}_{2}\text{O} + \text{HD} \qquad 23 \pm 16\%$$

Here, the error in the rate constant is twice as high as in the all-hydrogen case; this is a consequence of uncertainties in the calibration constants, which were in general adopted from the hydrogen-containing species. Because C_2D_6 was a major product species in these reactions, its calibration constants were taken from the analysis of the CD_3-CD_3 recombination under low laser fluences, minimizing the production of CD_2 . The error for the CD_2O + HD channel was chosen to be twice its determined value because the CD_2O signal overlapped with the much larger signal from the main fragmentation channel, $C_2D_4^+$, of the C_2D_6 ionization.

4. RRKM and Master Equation Calculations

A. MULTIWELL. Barker has developed a suite of computer programs that combine RRKM unimolecular rate constant

calculations with various models for weak energy-transferring collisions.38,39 The MULTIWELL suite is particularly well adapted to systems such as the one of interest here, where radical recombination leads to an energetic product that can dissociate through more than one reaction channel. The energy-grained master equation resulting from the combination of energytransfer steps and reactions is solved using a stochastic method originally developed by Gillespie.⁴⁰⁻⁴² Barker and Ortiz³⁹ have successfully applied this method to the reactions of vibrationally excited 2-methylhexyl radicals, which can isomerize by multiple pathways to form any of six stable isomers, can fragment by C-C or C-H bond fission, or can be stabilized by collision. These methods have also been developed by Vereecken et al. and applied to the reaction $H + HNCO.^{43}$ The vibrationally excited H2NCO thus formed can dissociate either to reactants or to $H_2N + CO$.

We have applied MULTIWELL to the $CH_3 + OH$ reaction by calculating rate constants for the unimolecular reaction of vibrationally energized CH_3OH , formed with the appropriate bond formation energy, to yield the products of reactions R1-R7. The rate constants for the recombination reactions can be obtained from the equilibrium constants and the unimolecular dissociation rate constants. Our major interest is in branching ratios, which are given directly by the MULTIWELL calculations. At temperatures up to 1000 K, reactions R6 and R7 are found to be essentially negligible because of high energy barriers.

RRKM rate constants for channels R3-R5 can be calculated using the properties of the corresponding transition states (cis-TS3, trans-TS3, and TS2) given by Yu and Muckerman (Table 7).¹⁴ Table 2 indicates that the Yu and Muckerman values for enthalpies of reactions for these processes are in good agreement with experimental values, although the Yu and Muckerman enthalpies for dissociation of methanol to form either CH_3 + OH or ${}^{1}CH_{2} + H_{2}O$ are lower than experimental values by $\sim 1-2$ kcal mol⁻¹. Nevertheless, for the sake of consistency, and because of some disagreement between values from the two experimental databases, the values of Yu and Muckerman were used in most of the present calculations. Also, from the standpoint of determining the major branching ratios at ambient temperatures, the important factor is the relative barrier heights (intrinsic endothermicities) for channels R1 and R2. The Yu and Muckerman calculations predict that the R2 barrier is higher by 0.5 kcal mol⁻¹. The Sandia reference data¹¹ give a difference of 0.8 kcal mol⁻¹, whereas the NIST values¹² indicate a difference of 0.6 kcal mol^{-1} in the opposite direction. The data analysis of de Avillez Pereira et al. indicated that there was very little difference between these barrier heights, and their calculations were made with the barrier for the ${}^{1}CH_{2} + H_{2}O$ channel higher by 0.4 ± 0.5 kcal mol⁻¹. The calculations of Lin and co-workers¹⁸ lead to an energy for the ${}^{1}CH_{2} + H_{2}O$ channel that is lower than that for the $CH_3 + OH$ channel by 1.6 kcal mol⁻¹. This was criticized by Miller,⁴⁴ who pointed out that Ruscic⁴⁵ had deduced a value of 0.39 ± 0.20 kcal mol⁻¹ in the opposite direction, using experimental values for relevant enthalpies of formation. Therefore, the use of the Yu and Muckerman value for this energy difference appears to be valid.

Channels R1 and R2 proceed through "loose" transition states because there is no barrier for the recombination reaction. In such cases of loose transition states, it is customary to carry out variational transition-state theory (VTST) calculations to determine the parameters of the TS that provide the smallest predicted unimolecular dissociation rate constant. Jordan et al. have applied this procedure to reaction R1, using two models

TABLE 6: Parameters for Reactions R1 and R2

	$\begin{array}{c} R1 \\ (CH_3OH \rightarrow CH_3 + OH) \end{array}$	$\begin{array}{c} \text{R2} \\ \text{(CH_3OH} \rightarrow \text{CH}_2 + \text{H}_2\text{O}) \end{array}$	<i>Т</i> , К
$k_{\rm bi}$ (cm ³ molecule ⁻¹ s ⁻¹) ^a	8.0 (-11)	1.6 (-10)	300
	5.3 (-11)	1.6 (-10)	500
	3.1 (-11)	1.6 (-10)	1000
$K_{\rm diss}$ (molecule cm ⁻³)	3.38 (-39)	1.03 (-39)	300
	3.08 (-13)	1.46 (-13)	500
	9.66 (6)	5.66 (6)	1000
$k_{\rm uni}~({\rm s}^{-1})$	2.70 (-49)	1.65 (-49)	300
	1.64 (-23)	2.33 (-23)	500
	2.99 (-4)	9.06 (-4)	1000
A_{∞} (s ⁻¹)	1.77 (15)	2.49 (15)	300
	3.20 (15)	7.52 (15)	500
	4.17 (15)	1.63 (16)	1000

^a Reference 12.

for the CH_3 ···OH interaction,⁴⁶ and their calculated rate constant at 300 K is about twice as large as the experimental value obtained by de Avillez Pereira et al.

An alternative to the VTST method has been suggested and implemented for several recombination reactions by the Pilling group.⁴⁷ It was shown many years ago by Forst⁴⁸ that the Arrhenius form of the rate constant

$$k_{\infty} = A_{\infty} \exp(-E_{\infty}/kT) = \int_{0}^{\infty} k(E)\rho(E) \exp(-E/kT) dE/Q \quad (1)$$

is related by a Laplace transform to the function $f(E) = k(E)\rho(E)$, where $\rho(E)$ is the state density of reacting molecules at a specific energy *E* and k(E) is the corresponding rate constant. In the above expression, *Q* is the partition function. Thus, with s = 1/kT as the inversion parameter,

$$f(E) = k(E)\rho(E) = \mathcal{L}^{-1}\{Q(s)A_{\infty}\exp(-sE_{\infty})\}$$
(2)

With the added fact that $\mathscr{L}^{-1}{Q(s)} = \rho(E)$, the energy-dependent rate constant becomes

$$k(E) = A_{\infty}\rho(E - E_{\infty})/\rho(E) \qquad E \ge E_{\infty}$$
(3)
= 0 E < E_{\infty}

Thus, if the rate constant can be expressed in the Arrhenius form, it is possible to obtain k(E) using only properties of the reacting molecule and without invoking properties of a TS. De Avillez Pereira et al. have applied this method to reactions R1, R2, R6, and R7, using experimental determinations of the recombination rate constants and calculated equilibrium constants. MULTIWELL has a provision for using this method to obtain k(E), which can then be used in further calculations. This procedure is not completely straightforward: Although the recombination rate constant, $k_{\rm bi}(T)$, for both channels is almost temperature independent and can easily be fitted to an Arrhenius expression, the equilibrium constant, $K_{eq}(T)$, does not exactly fit such an expression over a wide temperature range. Hence, the resulting unimolecular rate constant, $k_{uni}(T)$, does not exactly conform to the requirements of the inverse Laplace transform (ILT) method. In the present calculations, A_{∞} was obtained using the value of k_{uni} calculated at each temperature and with the energy barrier as the value of E_{∞} (this choice of the energy has been suggested by Barker³⁸). The equilibrium constants and rate constants for these two channels are shown in Table 6. The collisional data required for the ME calculations are those used by de Avillez Pereira et al. and are as follows: σ [CH₃OH], 3.626 Å; σ [He], 2.551 Å; ϵ [CH₃OH], 481.8 K; ϵ [He], 10.22 K. The

TABLE 7: Properties of Molecules and Transition States^a

CH ₃ OH	300, 1065, 1098, 1179, 1425, 1497, 1536, 1551, 2936, 2982, 3280, 3797, 4 05 (1,1), 21 2 (1,2)
CH ₃	580, 1424 (2), 3071, 3314 (2); 3.62 (3,1), 1.81 (2, 2).
OH	3613; 0.915 (1,2); electronic degeneracy, 4.
$CH_2({}^1A_1)$	1468, 2868, 3129; 0.87 (2,1), 1.91 (1,2).
H_2O	1709, 3734, 3851; 0.67 (2,1), 1.44 (1,2).
TS2	2374i, 924, 927, 1142, 1177, 1204, 1303, 1523, 1652,
	2185, 2893, 3169; 5.08 (1,1), 19.3 (1,2).
	Barrier height, 89.26 kcal/mol.
cis-TS3	1338i, 522, 636, 888, 1112, 1228, 1296, 1454, 1480,
	2415, 2866, 3711; 5.65 (1,1), 21.7 (1,2).
	Barrier height, 86.97 kcal/mol.
trans-TS3	1419i, 516, 602, 951, 1118, 1201, 1318, 1499, 1536,
	2138, 3199, 3746; 5.57 (1,1), 21.77 (1,2).
	Barrier height, 85.36 kcal/mol.
	Barrier neight, 85.36 Kcal/mol.

^{*a*} Data are given as vibrational levels, cm^{-1} (degeneracy, if \neq 1); moments of inertia, amu Å², (symmetry, dimension).

total collision rate was calculated with a Lennard-Jones model, and the probability function for energy loss was a single exponential with $\langle \Delta E_{\rm down} \rangle = 250 \text{ cm}^{-1}$. To test the importance of collisional deactivation, a few calculations were also made using $\langle \Delta E_{\rm down} \rangle$ values of 125 and 500 cm⁻¹. The energy maximum was 40 000 cm⁻¹, with a grain size of 20 up to 5000 cm⁻¹ and a grain size of 160 cm⁻¹ thereafter. Doubling the energy maximum did not change the results calculated for 300 K.

The results of the MULTIWELL calculations in terms of relative product yields at 300 K using the ILT method are shown in Figure 5a. For comparison with experiment, where redissociation of methanol to reactants (Channel 1) is not observed, and with Variflex calculations, which do not include this channel, the relative yields were renormalized with this channel omitted (Figure 5b). It should be noted in passing, however, that R1 was the major product channel in all our calculations except those at high temperature or pressure. By and large, the relative yields are very similar to the relative product yields that can be calculated from the pressure- and temperaturedependent expressions given by de Avillez Pereira et al., but with a sharper dropoff in the CH₃OH channel at low pressures. The present calculations indicate much larger relative yields of the HCOH + H₂ channels, which is a consequence of a barrier height of 85.4 kcal/mol for t-HCOH formation, much lower than the value of 91.0 kcal/mol used by de Avillez Pereira et al. Xia et al. calculated a barrier height of 85.5 kcal/mol,18 almost exactly the same as that used here. The relative yield of formaldehyde is so low that the values given by the MULTI-WELL calculations are probably accurate only to an order of magnitude, given the time limit placed on the integration process, but the de Avillez Pereira et al. expressions predict a



Figure 5. Relative product yields at 300 K in helium for the dissociation of CH₃OH produced by the reaction CH₃ + OH. These were calculated using MULTIWELL and the inverse Laplace transform (ILT) method for channels R1 and R2 discussed in the text: (a) with channel R1 included; (b) with channel R1 excluded and renormalized. The parameters used in the calculation were taken from ref 14 (YM set). In this and subsequent figures, the symbols for a given product channel are fixed: methanol, squares; R1, pentagons; R2, circles; R3, inverted triangles; R4, triangles; and R5, diamonds.

much lower relative yield of $\sim 10^{-8}$. The barrier height they assumed is several kilocalories per mole larger than that used in this work. The temperature dependence was determined using the ILT method at 300, 500, and 1000 K, and at pressures of 1 and 760 Torr. Even at the highest temperature, the relative yield of the HCOH products is probably below the detection limit. The relative yields of channels R6 and R7, given the high barriers for these channels, are found to be negligible even at 1000 K.

In an attempt to obtain better agreement between the present calculations and the experimental results reported here, calculations were also made using a value of 91.2 kcal/mol for the energy of dissociation of methanol to methyl and hydroxyl radials. This value was obtained by extending the 298 K experimental value¹¹ of 93.1 kcal/mol to 0 K. To maintain the balance between the R1 and R2 channels, the dissociation energy for the ¹CH₂ + H₂O channel was set 0.39 kcal/mol above the value of the R1 channel, in accordance with the experimental difference between the two channels suggested by Ruscic. This means that all other transition states are effectively lowered by roughly 1.8 kcal/mol with respect to the R1 channel. This set of energies is hereafter denoted as YMexp (YM refers to Yu and Muckerman). An additional set of energies in which the barrier height for formaldehyde formation was decreased further



Figure 6. Relative product yields calculated with MULTIWELL and the inverse Laplace transform (ILT) method for channels R1 and R2. The experimental values of the dissociation energy for $CH_3OH \rightarrow CH_3 + OH$ (91.2 kcal/mol) and for ${}^{1}CH_2 + H_2O$ (91.6 kcal/mol) were used, and the barrier for TS2 was reduced to 87.26 kcal/mol (YMexp2 set): (a) 300 K; (b) 612 K. The solid square with error bars is the experimental methanol yield obtained in this work.

by 2 kcal/mol is hereafter denoted as YMexp2. The results obtained using the YMexp2 set are shown in Figure 6.

B. VARIFLEX. Klippenstein et al. have developed a suite of programs suitable for various types of RRKM and ME calculations.⁴⁹ One of the examples included in this suite is the CH₃ + OH reaction, which was set up to model reactions R1 and R2 with the parameters used in the calculations of de Avillez Pereira et al. The relative yields at 300 K and at various pressures obtained in the VARIFLEX calculations are in good agreement with the values obtained by de Avillez Pereira et al. We extended these calculations to include reactions R3-R5 using the same input data, based on the Yu and Muckerman PES, that were used in the MULTIWELL calculations. VARI-FLEX includes an option for use of the ILT method, with the recombination rate constant as the input parameter. The values derived by de Avillez Pereira et al. were used: $k_{-1} = 8.0 \times$ $10^{-11} (T/300)^{-0.79}$ and $k_{-2} = 1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The same collision model was used, with a value of 230 cm^{-1} for $\langle \Delta E_{\text{down}} \rangle$. Rates were evaluated at an energy-resolved level, using a Boltzmann distribution for the rotational energies. The energy range was that used in the original example, from -6000to 5000 cm⁻¹ relative to the CH_3 + OH fragments, and the grain size was also that used in the example, 30 cm^{-1} .

The relative product yields calculated with VARIFLEX as a function of pressure at 300 K are found to be very similar to those obtained with the MULTIWELL calculations. Compared



Figure 7. Bimolecular rate constants calculated using MULTIWELL (ILT with YM set), solid line; VARIFLEX (long dashed line; compared with those of de Avillez Pereira et al., short dashed line): (a) $CH_3 + OH \rightarrow CH_3OH$; (b) $CH_3 + OH \rightarrow CH_2$ (¹A₁) + H₂O.

with the MULTIWELL calculations, the pressure drop-off of the CH₃OH channel is not as rapid. The relative yield of the ¹CH₂ + H₂O channel agrees quite closely with the MULTI-WELL calculations. At low pressures, VARIFLEX predicts slightly lower yields of the HCOH products, but the agreement in the extremely small H₂CO yield is very close. Barker³⁸ points out that bimolecular recombination rate constants for each channel as a function of pressure can be obtained from MULTIWELL results by using the expression

$$k_{\text{bi},\alpha} = (k_{\text{uni},\alpha}^{\infty} / K_{\text{eq},\alpha}) f(P,\alpha)$$
(4)

where $f(P,\alpha)$ is the fraction of dissociations leading to channel α at pressure *P*. A comparison of MULTIWELL and VARI-FLEX values for channels R1 and R2 with those calculated from the expressions in Appendix B in the work of de Avillez Pereira et al. is given in Figure 7.

5. Comparison of Experimental and Calculated Results

300 K, 4 Torr. Under these conditions, the major products (apart from redissociation to $CH_3 + OH$) obtained from the calculations are methanol and ${}^{1}CH_2 + H_2O$. Over the pressure range used in the experiments of de Avillez Pereira et al., the rate constant for methanol formation is essentially constant near the high-pressure limit (8.0×10^{-11} cm³ molecule⁻¹ s⁻¹ at 300 K), within experimental error. Deters et al. made similar measurements at pressures of 45–467 Torr of helium, using transient UV absorption spectroscopy to follow radical concen-

trations.⁵⁰ At 298 K, their average value of the rate constant is 7.3×10^{-11} cm³ molecule⁻¹ s⁻¹, in good agreement with the de Avillez Pereira et al. value. The present RRKM calculations are in good agreement with these experimental values, as a result of using the ILT method to obtain rate constants from experimental data.

The experimental results for the $CH_3 + OH$ reaction at 300 K have to be considered carefully because it was not possible to fit the methylene radical profiles satisfactorily. The most probable explanation for the discrepancy between simulations and data is an unidentified loss of OH radicals. Nevertheless, most of the formaldehyde observed could be ascribed to other sources, while a yield of $6 \pm 3\%$ for the methanol channel can be given. This is in agreement with measurements by Deters et al.,³² who measured a ¹CH₂ yield of around 90% at 298 K and 1 Torr of helium. However, it contradicts results by Oser et al.,⁵¹ who stated that methanol is the prevalent channel under the conditions used here. The experimental yield of methanol $(6 \pm 3\%)$ is much lower than the value at 4 Torr calculated with MULTIWELL (54%, renormalized) or given by de Avillez Pereira et al. (65%). MULTIWELL calculations using the experimental value for the methanol dissociation energy decrease the fraction of methanol formation to 30% by favoring other channels. For the ${}^{1}CH_{2} + H_{2}O$ channel, there is good agreement between the MULTIWELL calculations (41%) and those of de Avillez Pereira et al. (35%). The higher dissociation energy (YMexp set) reduces the MULTIWELL results slightly (32%). All of these are much lower than our experimental value of \geq 70%, which is in reasonably good agreement with the value of 89 \pm 9% obtained by Deters et al. It should be noted that the measurements of this relative yield by Deters et al. are based on measurements of the ³CH₂ radical using laser magnetic resonance spectroscopy. This requires the assumptions that the triplet radical is not formed in a direct reaction and that the singlet methylene is rapidly converted to the triplet state by collisions. Wilson and Balint-Kurti have used ab initio methods to obtain a PES for the direct triplet formation,⁵² and they obtain a barrier height of 6 kcal/mol. VTST methods gave a rate constant of 4.0 \times 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ at 298 K, so the neglect of this possible channel is justified.

Our experiments do not distinguish between the two isomers of HCOH, so the total calculated yield for both isomers should be used for comparison. Experimentally, HCOH was not detected under these conditions, in agreement with a MULTI-WELL value of 5%. In contrast, the YMexp energies give barrier heights for the HCOH + H_2 channels that are 4.2 and 5.8 kcal/ mol lower than the energy for dissociation to reactants, leading to a predicted yield of 38%, due to the reduced yield in other channels. The VARIFLEX calculations of Xia et al. use similar threshold differences of 3.8 and 5.6 kcal/mol. Their calculations do not extend to pressures below 1 atm, but at this pressure the yield of HCOH products is predicted to be 14%. Because de Avillez Pereira et al. assumed a higher barrier for these channels in their calculations, they predict essentially no yield of these products. None of the calculations predict a measurable yield of formaldehyde under these conditions, in agreement with experiment.

612 K, 8 Torr. In contrast to the experiments carried out at 300 K, at 612 K the simulated profiles fit the experimental data very well. The total rate constants measured here agree reasonably well with the high-pressure value of 4.6×10^{-11} cm³/s given for this temperature by de Avillez Pereira et al.,¹⁰ keeping in mind that their measured rate constants showed little pressure dependence above 10 Torr. However, as mentioned

above, the conditions used here were not very sensitive to absolute rate constants. With regard to the product distribution, it could be shown that the methanol, singlet methylene, and formaldehyde channels are all important. For methanol, the experimental value of $20 \pm 7\%$ is in good agreement with the de Avillez Pereira et al. calculated value (31%), and MULTI-WELL gives a value of 18%, which is reduced by a factor of 2 with the (higher) experimental dissociation energies (YMexp set). Humpfer et al.⁹ obtained a value of 8% for this channel at 700 K and 0.5 Torr. For the ${}^{1}CH_{2} + H_{2}O$ channel, there is again good agreement between MULTIWELL (77%) and de Avillez Pereira et al. (69%); the MULTIWELL calculation with higher dissociation energies (YMexp set) decreases this value to 56%. The experimental value obtained in this work ($46 \pm 14\%$) is somewhat lower. Humpfer et al. obtain a value of 38%, in good agreement with the value found in this experimental work. For HCOH, the experimental value of $10 \pm 3\%$ (DCOH) is in reasonable agreement with the value obtained with MULTI-WELL (5%), but the higher dissociation energy calculations give a value of 32%. Humpfer et al. obtained a value of 46% in their experiments with OD in place of OH. Calculations still predict very low yields of formaldehyde; even the higher dissociation energy MULTIWELL model predicts only $\sim 1\%$. This is in distinct contrast to the experimental yield of 23 \pm 16% (CD₂O), which is about 3 times the yield observed by Humpfer et al. (7%). MULTIWELL calculations with the YMexp2 parameters, which decrease the barrier for TS2 by 2 kcal/mol in the higher dissociation energy model, resulted in an increased yield that was still only about 5% (Figure 6b).

As suggested above, the experimental result that the methanol yield increases with temperature in the pressure range between 1 and 10 Torr is in apparent disagreement with the calculations. This may arise from the choice of parameters in the energytransfer model employed in the ME calculations. Here we have employed a temperature-independent $\langle \Delta E_{\text{down}} \rangle$, but Figure 8 shows the calculated methanol yield at 300 and 612 K for three different $\langle \Delta E_{\text{down}} \rangle$ values (125, 250, and 500 cm⁻¹). There is considerable precedent for invoking a model in which $\langle \Delta E_{\rm down} \rangle$ increases with temperature, especially for recombination reactions (see, e.g., the methyl-methyl recombination reaction).53,54 As seen in Figure 8, the present experimental yield of methanol is in excellent agreement with the choice of $\langle \Delta E_{\text{down}} \rangle = 150$ cm⁻¹ at 300 K and 500 cm⁻¹ at 612 K. This is qualitatively in accord with the predictions of a biased random walk (BRW) model that predicted values of 220 and 360 cm^{-1} , respectively.

6. Conclusions

The CH₃ + OH reaction has been investigated both experimentally and theoretically. Isotopic substitution (${}^{12}C \rightarrow {}^{13}C$ and $H \rightarrow D$) facilitated a clean distinction between the main product species in the experimental system: formaldehyde isomers, methanol, and ethane. While the analysis of the experimental data at 300 K and 4 Torr remains inconclusive, the observations indicate that ${}^{1}CH_{2} + H_{2}O$ is the main product channel and stabilization to methanol is of minor importance. At 612 K and 8 Torr, the data show that three channels (${}^{1}CH_{2} + H_{2}O$, CH₂O/HCOH + H₂, CH₃OH) are operating with similar yields, with the direct formation of formaldehyde being more efficient than the production of HCOH.

Two different types of RRKM methods (VARIFLEX and MULTIWELL) have been applied to calculate the product distribution of this reaction using different sets of theoretically and experimentally obtained energies of the potential energy surface. In the pressure range of interest (1-10 Torr), the yield



Figure 8. Methanol yield calculated with MULTIWELL and the inverse Laplace transform (ILT) method for channels R1 and R2 for three values of the $\langle \Delta E_{down} \rangle$ parameter: 125, 250, and 500 cm⁻¹. The experimental values of the dissociation energy for channels R1 and R2 were used, and the barrier for TS2 was reduced to 87.26 kcal/mol (YMexp2 set): (a) 300 K; (b) 612 K. The solid square with error bars is the experimental value obtained in this work.

of the methanol channel is rapidly varying and, as shown by comparison of the MULTIWELL and VARIFLEX results, is sensitive to the parameters of the RRKM calculation and the implementation of the ME solution. In addition, the product yields show a high sensitivity toward the relative position of the transition states in each set.

Despite these sensitivities to unknown parameters, general trends of pressure and temperature dependence of the product distribution can be captured theoretically. At 300 K, qualitative agreement between the present calculations and experimental results was obtained with the Yu and Muckerman energy values leading to ${}^{1}CH_{2} + H_{2}O$ as the dominant products, with methanol being of lesser importance. At 612 K, isomers of formaldehyde, ${}^{1}CH_{2} + H_{2}O$, and methanol are all important channels in the calculated results when the experimental dissociation energies for R1 and R2 were chosen. While the yield of isomers of formaldehyde calculated with the experimental dissociation energies for R1 and R2 at 612 K (identified as mass 30 isomers in Figure 9) is in excellent agreement with experiment, the calculated yield of formaldehyde per se falls well below that observed. It appears that the energy of the transition state to CH₂O would have to be significantly lower than the energy of the entrance channel, $CH_3 + OH$, or the ${}^{1}CH_2 + H_2O$ product channel, and it is unlikely that errors in the ab initio calculations of Yu and Muckerman could be large enough to justify such an assertion.



Figure 9. Relative product yields of ${}^{1}CH_{2}$, CH₃OH, and isomers of CH₂O (mass 30 isomers) at 612 K calculated with MULTIWELL and the inverse Laplace transform (ILT) method for channels R1 and R2. The experimental values of the dissociation energy for channels R1 and R2 were used, but the Yu and Muckerman value for the TS2 barrier was employed (YMexp set). The solid square is the experimental value of the methanol yield, and the solid triangle is the total yield of formaldehyde isomers.

Choosing a constant value for $\langle \Delta E_{\text{down}} \rangle$ could not explain the curious observation that the methanol yield at pressures below 10 Torr increases with temperature. This strongly suggests that a temperature-dependent energy-transfer parameter has to be considered for this reaction.

From an experimental point of view, further experiments, especially on the branching ratios of the HCOH and CH_2O channels at higher temperatures, would be highly desirable to establish their relevance for practical combustion situations as well as to pin down their barrier heights for future calculations. In addition, experimental and theoretical investigations on the fate of HCOH radicals, which we assumed to isomerize rapidly to CH_2O , would be extremely useful for the analysis of future experiments.

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References and Notes

- Olson, D. B.; Gardiner, W. C. J. J. Phys. Chem. 1977, 81, 2514.
 Westbrook, C. K.; Creighton, J.; Lund, C.; Dryer, F. L. J. Phys. Chem. 1977, 81, 2542.
- (3) Fagerström, K.; Lund, A.; Mahmoud, G.; Jadlowski, J. T.; Ratajczak, E. Chem. Phys. Lett. 1993, 204, 226.
- (4) Anastasi, C.; Ellerman, P.; Pagsberg, P.; Polak, S. J. Chem. Soc., Faraday Trans. 1993, 87, 2991.
- (5) Hochanadel, C. J.; Sworski, T. J.; Orgen, P. J. J. Phys. Chem. 1980, 84, 129.
- (6) Laszlo, B.; Dóbé, S.; Bérces, T.; Maria, F. Int. Symp. Gas Kinet., 12th 1992.
 - (7) Bott, J. F.; Cohen, N. Int. J. Chem. Kinet. 1991, 23, 1017.
- (8) Humpfer, R.; Oser, H.; Grotheer, H.-H. Int. J. Chem. Kinet. 1995, 27, 577.
- (9) Oser, H.; Stothard, N. D.; Humpfer, R.; Grotheer, H. H. J. Phys. Chem. 1992, 96, 5359.
- (10) De Avillez Pereira, R.; Baulch, D. L.; Pilling, M. J.; Robertson, S. H.; Zeng, G. J. Phys. Chem. A **1997**, 101, 9681.
 - (11) Allendorf, M. D., www.ca.sandia.gov/HiTempThermo, 2004.
 - (12) NIST Chemistry WebBook, http://webbook.nist.gov/chemistry, 1997.

- (13) Ruscic, B.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Harding, L. B.; Asher, R. L.; Wagner, A. F. J. Phys. Chem. A **2001**, 105, 1.
- (14) Yu, H.-G.; Muckerman, J. T. J. Phys. Chem. A 2004, 108, 8615.
 (15) Hack, W.; Wagner, H. G.; Wilms, A. Ber. Bunsen-Ges. Phys. Chem.
 1988, 92, 620.
- (16) Carstensen, H.-H.; Wagner, H. G. Ber. Bunsen-Ges. Phys. Chem. 1995, 99, 1539.
- (17) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. J. Chem. Phys. **1991**, *94*, 7221.
- (18) Xia, W. S.; Zhu, R. S.; Lin, M. C.; Mebel, A. M. Faraday Discuss. 2001, 119, 191.
- (19) Halkier, A.; Helgaker, T.; Jorgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. Chem. Phys. Lett. **1998**, 286, 243.
- (20) Fockenberg, C.; Bernstein, H. J.; Hall, G. E.; Muckerman, J. T.; Preses, J. M.; Sears, T. J.; Weston, R. E., Jr. *Rev. Sci. Instrum.* **1999**, *70*, 3259.
- (21) Silvente, E.; Richter, R. C.; Hynes, A. J. J. Chem. Soc., Faraday Trans. 1997, 93, 2821.
- (22) Fockenberg, C.; Hall, G. E.; Preses, J. M.; Sears, T. J.; Muckerman, J. T. J. Phys. Chem. A **1999**, 103, 5722.
 - (23) Wang, B.; Fockenberg, C. J. Phys. Chem. A 2001, 105, 8449.
- (24) Blitz, M. A.; McKee, K. W.; Pilling, M. J. Proc. Combust. Inst. 2000, 28, 2491.
- (25) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. J. Phys. Chem. Ref. Data, Suppl. VI 1997, 26, 1329.
- (26) Manatt, S. L.; Lane, A. L. J. Quant. Spectrosc. Radiat. Trans. 1993, 50, 267.
- (27) Ito, H.; Nogata, Y.; Matsuzaki, S.; Kuboyama, A. Bull. Chem. Soc. Jpn. 1969, 42, 2453.
- (28) Sander, S. P.; Kurylo, M. J.; Orkin, V. L.; Golden, D. M.; Huie, R. E.; Finlayson-Pitts, B. J.; Kolb, C. E.; Molina, M. J.; Friedl, R. R.; Ravishankara, A. R.; Moortgat, G. K. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*; Jet Propulsion Laboratory, California Institute of Technology: Pasadena, CA, 2003.
- (29) Kee, R. J.; Rupley, F. M.; Miller, J. A. Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics; Sandia National Laboratories: Albuquerque, NM, 1996.
- (30) Marcy, T. P.; Díaz, R. R.; Heard, D.; Leone, S. R.; Harding, L. B.; Klippenstein, S. J. J. Phys. Chem. A **2001**, 105, 8361.
 - (31) Fockenberg, C.; Preses, J. M. J. Phys. Chem. A 2002, 106, 2924.
- (32) Deters, R.; Otting, M.; Wagner, H. G.; Temps, F.; László, B.; Dóbé, S.; Bérces, T. Ber. Bunsen-Ges. Phys. Chem. **1998**, 102, 58.
- (33) Humpfer, R.; Oser, H.; Grotheer, H.-H.; Just, T. The Reaction System CH3 + OH at Intermediate Temperatures. Appearance of a New Product Channel. *Twenty-Fifth Symposium (International) on Combustion*; The Combustion Institute: Orleans, France, 1994; p 721.
- (34) De Avillez Pereira, R.; Baulch, D. L.; Pilling, M. J.; Robertson, S. H.; Zeng, G. J. Phys. Chem. A **1997**, 101, 9681.
- (35) Hall, G. E., personal communication.
- (36) Xiang, T.-X.; Gericke, K.-H.; Torres, L. M.; Guillory, W. A. Chem. Phys. **1986**, 101, 157.
- (37) Yamasaki, K.; Watanabe, A.; Kakuda, T.; Itakura, A.; Fukushima, H.; Endo, M.; Maruyama, C.; Tokue, I. J. Chem. Phys. A **2002**, *106*, 7728.
- (38) Barker, J. R. Int. J. Chem. Kinet. 2001, 33, 232.
- (39) Barker, J. R.; Ortiz, N. F. Int. J. Chem. Kinet. 2001, 33, 246.
- (40) Gillespie, D. T. J. Comput. Phys. 1976, 22, 403.
- (41) Gillespie, D. T. J. Phys. Chem. 1977, 81, 2340.
- (42) Gillespie, D. T. J. Comput. Phys. 1978, 28, 395
- (43) Vereecken, L.; Huyberechts, G.; Peeters, J. J. Chem. Phys. 1997, 106, 6564.
 - (44) Miller, J. A. Faraday Discuss. 2001, 119, 263.
- (45) Ruscic, B. Photoionization studies of transient and metastable species. Presented at the 22nd Annual Combustion Research Conference,
- 2001, Tahoe City, CA; p 624.
 (46) Jordan, M. J. T.; Smith, S. C.; Gilbert, R. G. J. Phys. Chem. 1991,
- (17) Douting, I. W.: Groop, N. L. P.: Dilling, M. L. Cham, Phys. Lett.
- (47) Davies, J. W.; Green, N. J. B.; Pilling, M. J. Chem. Phys. Lett. 1986, 126, 373.
 - (48) Forst, W. J. Phys. Chem. 1972, 76, 342.
- (49) Klippenstein, S. J.; Wagner, A. F.; Dunbar, R. C.; Wardlaw, D. M.; Robertson, S. H. *VARIFLEX*, Version 1.00, 1.0 ed.; Argonne National Laboratory: Argonne, IL, 1999.
- (50) Deters, R.; Otting, M.; Wagner, H. G.; Temps, F.; László, B.; Dóbé, S.; Bérces, T. Ber. Bunsen-Ges. Phys. Chem. **1998**, 102, 58.
- (51) Oser, H.; Stothard, N. D.; Humpfer, R.; Grotheer, H. H.; Just, T. Direct Measurements of the Reaction CH3 + OH and its Pathways between 300 and 480 K. In *Twenty-Fourth Symposium (International) on Combustion*; The Combustion Institute: Orleans, France, 1992; p 597.
- (52) Wilson, C.; Balint-Kurti, G. G. J. Phys. Chem. A 1998, 102, 1625.
 (53) Klippenstein, S. J.; Harding, L. B. J. Phys. Chem. A 1999, 103, 9388.

(54) Wang, B.; Hou, H.; Yoder, L. M.; Muckerman, J. T.; Fockenberg, C. J. Chem. Phys. A **2003**, 107, 11414.

(55) Shi, J.; Barker, J. R. Int. J. Chem. Kinet. 1990, 22, 1283.

(56) Smith, G. P.; Golden, D. M.; Frenklach, M.; Moriarty, N. W.;

Eiteneer, B.; Goldenberg, M.; Bowman, C. T.; Hanson, R. K.; Song, S.; William C. Gardiner, J.; Lissianski, V. V.; Qin, Z. GRI-MECH 3.0, http://www.me.berkeley.edu/gri_mech/, 1999.

(57) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Frank, P.; Hayman, G.; Just, T.; Kerr, J. A.; Murrels, T.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1994**, *23*, 847.

(58) Blitz, M. A.; Pesa, M.; Pilling, M. J.; Seakins, P. W. J. Chem.
 Phys. A 1999, 103, 5699.

(59) Brownsword, R. A.; Canosa, A.; Rowe, B. R.; Sims, I. R.; Smith, I. W. M.; Stewart, D. W. A.; Symonds, A. C.; Travers, D. J. Chem. Phys. **1997**, *106*, 7662.

(60) Becker, K. H.; Engelhardt, B.; Geiger, H.; Kurtenbach, R.; Wiesen, P. Chem. Phys. Lett. **1993**, 210, 135.

(61) Hancock, G.; Heal, M. R. J. Phys. Chem. 1992, 96, 10316.

(62) Blitz, M. A.; Choi, N.; Kovács, T.; Seakins, P. W.; Pilling, M. J. The Effect of Temperature on Collision Induced Intersystem Crossing in the Reaction of ${}^{1}CH_{2}$ with H_{2} . Presented at the Thirtieth Symposium (International) on Combustion, 2004, Chicago, IL; to be published.

(63) Carstensen, H. H.; Wagner, H. G. Ber. Bunsen-Ges. Phys. Chem. 1995, 99, 1539.

(64) Sivakumaran, V.; Hölscher, D.; Dillon, T. J.; Crowley, J. N. Phys. Chem. Chem. Phys. 2003, 5, 4821.

(65) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, T.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. J. Phys. Chem. Ref. Data **1992**, 21, 411.

(66) Baggott, J. E.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. J. Phys. Chem. 1987, 91, 3386.

(67) Li, S. C.; Williams, F. A. Experimental and numerical studies of two-stage methanol flames. Presented at the Twenty-sixth Symposium (International) on Combustion, 1996, University of Naples, Italy.

(68) Yamada, T.; Taylor, P. H.; Goumri, A.; Marshall, P. J. Chem. Phys. 2003, 119, 10600.

(69) Seakins, P. W.; Robertson, S. H.; Pilling, M. J.; Wardlaw, D. M.; Nesbitt, F. L.; Thorn, R. P.; Payne, W. A.; Stief, L. J. J. Phys. Chem. **1997**, 101, 9974.