

KINETICS OF THE HIGH TEMPERATURE, LOW CONCENTRATION CH₄ OXIDATION VERIFIED BY H AND O ATOM MEASUREMENTS

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In the kinetics of methane oxidation at high temperatures H and O atoms are very important reactants. In this study concentrations of both these atoms were directly measured behind reflected shock waves in relatively low concentration CH₄-O₂ mixtures diluted in Ar. The temperatures ranged $1850\text{ K} \leq T \leq 2500\text{ K}$, the pressures were about 1.8 bar, and the concentrations varied between 5 and 50 ppm for CH₄, and 10 and 2000 ppm for O₂. Atomic resonance absorption spectroscopy (ARAS) was used to measure H and O atom concentrations in nearly 90 individual experiments. Computer simulation based on a reaction model allowing for 25 elementary reactions and selected rate coefficients, was in good agreement with the experimental results. The influence of the elementary reaction $\text{CH}_3 + \text{OH} \rightarrow \text{CH}_3\text{O}/\text{CH}_2\text{OH} + \text{H} \rightarrow \text{CH}_2\text{O} + 2\text{H}$, proposed earlier, was confirmed by these experiments.

Introduction

The oxidation of methane is one of the most-studied hydrocarbon combustion systems. Many experimental works have contributed to the understanding of combustion kinetics, beginning with the early ignition delay measurements of Skinner et al.¹ and Kistiakowski et al.² up to measurements of radical and neutral species concentrations in the reaction zone, for example.³⁻⁹ Kinetic models show the important role of H and O atoms, but no measurement of their concentrations have been reported. At low reactant concentrations of the CD₄-O₂ system, Chiang and Skinner¹⁰ measured D atoms only and gave a simple kinetic interpretation.

The review article of Gardiner et al.¹¹ summarizes the overall picture and the uncertainties in methane oxidation kinetics. The discussion on the nature of the primary high temperature oxidation step of CH₄ seems to be settled. The H atom abstraction from CH₄ is accepted as initiating the complex chemistry. The rate coefficient is well established¹² and our own ARAS (atomic resonance absorption spectroscopy) measurements have contributed to solving that problem.¹³ Secondary reactions in the methane oxidation system are still

debated. Many CH₄-O₂ oxidation mechanisms of varying complexity and completeness have been published.^{14,15,16}

The rate coefficients of secondary reactions, important in the CH₄-O₂ reaction system, have been refined in recent works. Our own results for individual CH₄, CH₃ and CH₂O reactions, measured at high temperatures under extremely low concentration conditions, helped to understand the details of the reaction chemistry.¹⁷⁻²⁰ The ARAS method used in conjunction with shock tube techniques could be confirmed as a successful approach to kinetic data acquisition.

In the present study, H and O atoms were measured behind reflected shock waves in CH₄/O₂ mixtures using the ARAS detection technique. The reactants are very highly diluted in argon so that the chemistry can be assumed to be independent of transport processes. In addition, interdependence of the elementary reactions is relatively weak. The influence of C₂ hydrocarbon reactions in stoichiometric and lean mixtures is small. For data interpretation, a kinetic model is synthesized from earlier ARAS results and other recent rate coefficients. The aim of the computer simulations is to confirm or to modify rate coefficient data.

Experimental

Shock Tube and Gases

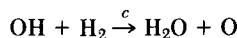
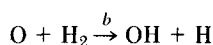
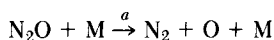
The H- and O-atom concentrations produced in the highly diluted CH₄-O₂ mixtures were measured behind reflected shock waves in a stainless steel tube of 79 mm diameter. The internal surface is specially prepared for high vacuum purposes. The tube can be heated and is evacuated via a special end plate valve by a forepump, turbomolecular pump, and liquid nitrogen-cooled titanium sublimation pump to pressures down to about 10⁻⁸ mbar. As molecular sieves prevent the forepump oil from entering the tube, the residual gas is practically free of hydrocarbons. The leak-plus-outgassing rate is on the order of 8 · 10⁻⁷ mbar/min. A detailed description of the experimental setup is given elsewhere.^{13,17}

Only very pure gases, carefully mixed in a special storage bottle, were used in our experiments. The diluent argon was supplied by Messer-Griesheim and certificated to be 99.9999% pure, with N₂ being the main impurity. The initial mol fraction of CH₄ (99.9995% with N₂ and H₂O as main impurities) in argon varied between 5 and 50 ppm. The relative concentration of O₂ (99.998% with Ar and N₂ specified as main impurities) in the mixtures was between 10 and 2000 ppm.

Resonance Absorption Technique and Calibration

The measurement technique applied in this investigation is atomic resonance absorption spectroscopy of H-atoms at the Lyman-α doublet at 121.6 nm and of O-atoms at the OI triplet at 130.5 nm. It is a line emission-line absorption method with the spectral shape of the emitter line not being known in detail and assumed to be mainly influenced by self-reversal. Hence, calibration experiments have to be made to find the correlations between measured absorption and atom concentrations. For O atom calibrations, the partial equilibrium behind shock waves in Ar/N₂O mixtures was used. Results of the calibration characteristics, i.e., variation of fractional light absorption as a function of O atom concentration are given for example in.²¹

The calibration procedure for H atoms can only be performed on the basis of kinetic properties. The rate of H₂ dissociation, based upon the results of Myerson,²² was used for temperatures higher than 2200 K. For lower temperatures, mixtures of 2 ppm N₂O and 200 ppm H₂ were shock heated. The following set of rate coefficients was found to give the best agreement with H-dissociation at high temperatures:



$$k_a = 2.40 \cdot 10^{-9} \exp(-30\,800 \text{ K/T}) \text{ cm}^3 \text{ s}^{-1}$$

$$k_b = 3.80 \cdot 10^{-10} \exp(-6\,920 \text{ K/T}) \text{ cm}^3 \text{ s}^{-1}$$

$$1900 \leq T \leq 2800 \text{ K}$$

$$k_c = 3.67 \cdot 10^{-11} \exp(-2\,590 \text{ K/T}) \text{ cm}^3 \text{ s}^{-1}$$

The consistency of this set was further checked by varying the N₂O-H₂-mixtures: 20 ppm N₂O/100 ppm H₂, 10 ppm N₂O/50 ppm H₂, and measuring the O-atom-profiles. Agreement between the calibration results from H₂ dissociation measurements and from H and O atom measurements in the N₂O-H₂ reaction system could only be obtained using the *k_b* value of Pamidimukkala and Skinner.²⁴ Recent measurements of Frank and Just²⁵ with a high sensitivity on *k_b* gave identical results, which can best be described by the given expression. The influence of reaction *c* was negligible in these experiments. Variation of *k_c*, given by Baulch, by factors 1.25 or 0.8, respectively, gave practically no changes in the calculated O atom profiles. The same is true for the standard mixture of 2 ppm N₂O/200 ppm H₂, used for H atom calibration.

For orientation purposes, only one point on each of the H and O atom calibration curves is given here. At temperatures of about 2000 K and pressures of 1.8 bar a concentration of [H]_{0.5} = 2.8 · 10¹² molecules cm⁻³ leads to an absorption of A = 0.5. Under the same conditions, an O atom concentration of [O]_{0.5} = 1.2 · 10¹³ molecules cm⁻³ is needed. Examples of calibration curves are given in.^{21,13} The values [H]_{0.5} and [O]_{0.5} depend on the experimental conditions under which the light sources are operated, see for example.³⁶

The absorption of the atomic resonance line intensities by the initial reactants CH₄ and O₂ and by molecules generated during the reaction kinetic process must be carefully considered. The highest concentration in the reaction system is O₂, followed by CH₄. Their absorption cross sections were measured at both wavelengths under different temperature conditions. Results given in^{21,26} are:

$$\sigma_{\text{O}_2}(\text{H}_\alpha) = 5.1 \cdot 10^{-18} \exp(-3140 \text{ K/T}) \text{ cm}^2$$

$$\sigma_{\text{O}_2}(\text{OI}) = 1.0 \cdot 10^{-18} \exp(-1560 \text{ K/T}) \text{ cm}^2$$

$$\sigma_{\text{CH}_4}(\text{H}_\alpha) = 1.9 \cdot 10^{-17} \text{ cm}^2$$

$$\sigma_{\text{CH}_4}(\text{OI}) = 1.5 \cdot 10^{-17} \text{ cm}^2$$

Because of the relatively low initial concentrations the additional absorption by O₂ and CH₄ is very weak in the present experiments. In the case of the

TABLE I
Experimental data of measured H atom concentrations in CH₄/O₂/Ar mixtures

T K	[Ar] 10 ⁻¹⁵ cm ⁻³	[CH ₄]/[O ₂] ppm/ppm	[H] 10 ⁻¹² cm ⁻³				
			100 μs	200 μs	400 μs	600 μs	800 μs
1848	7.70	40/80	1.2	1.75	2.3	2.5	2.75
1924	7.32		3.0	4.3	5.2	6.2	7.5
2030	7.12		8.0	12.2	15.3	—	—
1910	7.66	20/40	1.6	2.7	3.8	4.4	4.8
1960	6.98		2.1	4.0	5.5	6.5	7.8
2050	6.78		6.9	10.0	15.0	—	—
2170	6.50		18	—	—	—	—
1800	7.50	10/20	—	0.4	0.65	0.9	1.0
1840	7.63		—	0.5	0.9	1.3	1.6
2052	7.19		3.5	7.2	10.8	14.0	—
2110	5.45		4.6	7.8	12.0	15.0	19.0
1928	7.39	5/10	0.5	0.9	1.7	2.25	2.7
1992	7.04		1.1	2.1	3.6	4.7	5.5
2060	5.75		1.6	2.9	4.9	6.5	7.5
2140	6.48		4.8	7.9	11.5	14.5	—
2175	5.64		4.1	7.3	12.2	14.7	16.0
1903	7.70	50/500	1.6	2.5	3.5	4.8	6.8
1940	7.42		2.1	2.9	5.5	8.5	15
1970	7.20		3.0	4.6	9.2	16.9	—
1975	7.09		4.0	5.2	10.0	—	—
1830	7.62	20/200	0.4	0.6	0.75	0.8	0.9
1963	7.45		2.0	3.2	4.7	6.2	8.2
2030	7.16		4.1	6.2	10.3	17.0	—
1895	7.72	10/100	0.7	1.15	1.6	1.9	2.2
1988	7.05		1.4	2.6	4.0	5.8	7.5
2180	6.60		10.0	15.0	—	—	—
1928	7.73	50/2000	1.0	1.2	3.1	7.2	>15
1948	7.40		1.2	1.7	4.1	10.8	>18
1970	7.23		1.6	2.3	5.1	18.0	—
1995	6.0		1.8	2.2	4.0	10.0	—
2015	7.26		2.4	4.6	18.5	—	—
1848	7.55	20/800	0.35	0.4	0.45	0.55	0.7
1962	7.02		1.0	1.5	2.0	3.7	6.2
1978	7.27		1.25	1.65	2.7	4.25	7.0
2005	7.19		1.70	1.9	3.75	7.0	10.6
2127	6.50		7.0	10.0	18.0	>25	>20
1869	7.68	10/400	0.3	0.4	0.55	0.60	0.75
2024	7.13		1.5	2.0	3.3	5.0	7.0
2048	6.77		1.7	2.6	4.0	6.3	8.6
2170	6.44		5.4	7.9	12.5	15.0	17.0

TABLE I (continued)
Experimental data of measured H atom concentrations in CH₄/O₂/Ar mixtures

T K	[Ar] 10 ⁻¹⁸ cm ⁻³	[CH ₄]/[O ₂] ppm/ppm	[H] 10 ⁻¹² cm ⁻³				
			100 μs	200 μs	400 μs	600 μs	800 μs
2020	7.02	5/200	1.1	1.7	2.2	2.6	3.25
2041	6.62		1.4	2.1	3.2	4.0	4.8
2053	7.22		1.6	2.4	3.0	4.2	6.3
2300	5.33		8.0	10.5	12.5	12.5	10.5
2370	5.23		11.5	13.5	14.0	11.5	9.0
2135	5.60	10/1000	1.6	2.0	3.5	5.2	6.0

short-lived reaction intermediates, it was assumed that they never reach concentrations sufficient to cause interference absorption. This assumption seems to be plausible because of the very high absorption cross sections of H and O atoms in relation to typical cross sections for molecules.²⁶

Temperature Behind the Reflected Shock

The mean temperature behind the reflected shock wave was computed from the incident shock speed using one-dimensional gasdynamic theory. The optical windows were located 15 mm from the end plate of the shock tube. Under these conditions cooling of the reaction volume by heat transfer in the temperature boundary layer can be assumed to be small. It is known that shock boundary layer effects can cause a small time-dependent temperature increase or decrease, depending on the shock tube dimension and the experimental conditions. This was ignored in the computer simulations.

Results

The reaction behaviour of CH₄ with O₂ was studied behind shock waves, in a temperature range of 1850 K ≤ T ≤ 2500 K, at pressures between 1.6 and 2.1 bar. Different gas mixtures, highly diluted in argon, with initial [O₂]/[CH₄] concentration ratios of 2, 10, 40 and 100 were used. In each experiment, the measured incident shock speed served to calculate temperature and pressure behind the reflected shock, and a H_α or an OI absorption curve was recorded. Because of the different sensitivities of the two resonance absorption methods, the initial conditions had to be chosen differently for the two atomic species. The usable temperature range for mixture investigated was limited on the low temperature side by the detection limit and at the high temperature end, in particular at high con-

centrations, by absorptions which had to be less than 85%. As the optical arrangement had a time constant of about 25 μs, the experimental conditions chosen were such that in cases of 85% absorption, this had to occur at times greater than 150 to 200 μs.

Nearly 90 individual experiments were made under a broad range of experimental conditions. These data are difficult to present in a concise form. We have attempted to summarize all results in Table I and Table II by giving the temperature and initial concentrations for each experiment, together with up to 5 points of measured H or O atoms. The experimental uncertainties of the H and O atom concentrations are of the order of ±20%.

Three different types of H atom concentration profiles were obtained. Under stoichiometric conditions, [H] increased linearly, with a tendency to level off at longer times (see black points in Fig. 1). An example of the second type of measured H atom concentration profiles is shown in Fig. 2. After a fast increase, a quasi-steady state level is reached where a more or less accelerated H atom production is observed. An example of the third type of measured H atom concentration is shown in Fig. 3. After a fast increase, a maximum concentration is reached followed by a slight decrease. This type of an H profile was obtained at temperatures T > 2130 K, low initial concentrations of CH₄ and high O₂ excess.

In nearly all cases, the measured O atom concentrations start after a short induction period with a more or less linear increase. In most experiments, this is followed by an accelerated O atom production (see Fig. 4). In some cases a tendency to level off was observed before the measured concentration increased exponentially with time (see Fig. 5). At very low initial concentrations of CH₄, a long period of linear increase of O atoms was measured with a weak deceleration at the end of the measuring time (see Fig. 6).

TABLE II
Experimental data of measured O atom concentrations in CH₄/O₂/Ar mixtures

T K	[Ar] 10 ⁻¹⁸ cm ⁻³	[CH ₄]/[O ₂] ppm/ppm	[O] 10 ⁻¹³ cm ⁻³				
			100 μs	200 μs	400 μs	600 μs	800 μs
2064	7.15	40/80	0.15	0.37	0.58	0.74	1.05
2085	7.18		0.2	0.45	0.69	0.9	1.25
2145	6.50		0.35	0.7	1.30	2.2	3.5
2190	6.58	20/40	0.20	0.40	0.80	1.1	1.75
2364	5.91		0.6	1.30	2.75	4.0	5.5
2394	5.61		0.7	1.60	3.40	4.9	6.1
2180	6.54	10/20	—	0.15	0.30	0.45	0.61
2327	5.86		0.2	0.45	1.0	1.4	1.8
2437	5.10	5/10	0.2	0.5	1.1	1.6	2.0
1891	7.70	50/500	0.12	0.25	0.4	0.47	0.65
1925	7.40		0.15	0.30	0.5	0.7	1.0
1980	7.20		0.35	0.60	1.0	2.0	3.0
2006	7.15		0.5	1.1	2.1	4.5	>7.0
1952	7.45	20/200	—	0.2	0.4	0.6	0.78
2042	7.17		0.2	0.55	1.2	1.75	2.8
2133	6.80		0.65	1.35	3.3	7.2	—
2242	6.66		1.4	2.6	>6	—	—
2082	6.86	10/100	0.10	0.30	0.70	1.05	1.4
2157	6.55		0.2	0.55	1.25	2.0	3.2
2227	6.29		0.3	0.9	1.8	3.4	4.8
1844	7.65	50/2000	—	0.25	0.4	0.6	0.8
1923	7.60		0.2	0.6	1.2	2.3	5.4
1950	7.30		0.5	0.9	1.7	3.8	>7.0
1965	7.50		0.6	1.3	3.7	7	—
1985	7.30		0.6	1.4	3.6	~11.5	—
1985	6.00		0.5	1.0	2.0	4.5	>7.0
2009	7.25		0.9	2.1	7.0	—	—
2004	7.19	20/800	0.25	0.55	1.25	2.2	3.7
2088	6.91		0.7	1.7	4.5	>7	—
2066	7.26	10/400	0.25	0.65	1.3	2.2	3.65
2080	6.92		0.28	0.62	1.3	2.35	3.50
2188	6.62		0.6	1.5	4.0	6.65	—
2344	5.94		2.0	5.0	7.2	—	—
2144	6.53	5/200	—	0.4	0.9	1.4	1.85
2378	5.94		0.75	1.9	4.0	5.3	6.3
2435	5.57		0.85	2.1	3.75	5.0	6.0
2100	5.54	10/1000	0.3	0.65	1.3	2.45	3.5

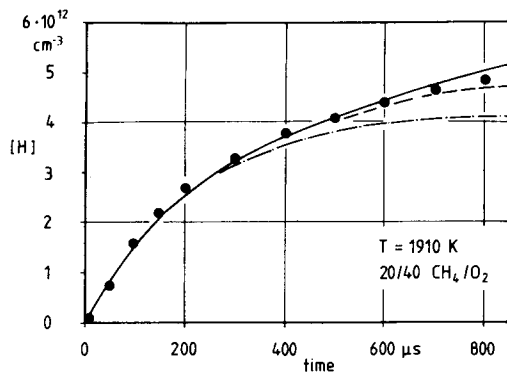


FIG. 1. Measured (black points) and calculated H atom concentrations.

$T = 1910 \text{ K}$ $[\text{Ar}] = 7.66 \cdot 10^{18} \text{ cm}^{-3}$

$[\text{CH}_4]/[\text{O}_2] = 20 \text{ ppm}/40 \text{ ppm}$

— · — · — calculated with reactions R1 to R5

— · — — calculated without reaction R7

———— calculated with full reaction mechanism

Discussion

The overall reaction scheme for computer simulations of the experimental results is presented in Table III. It is a simplified $\text{CH}_4\text{-O}_2$ mechanism consisting of 27 elementary reaction steps. Rate coefficient data from earlier experiments were used as far as possible. Because of the low concentrations in the ppm range, only 5 to 10 reactions of the scheme are actually important in describing the

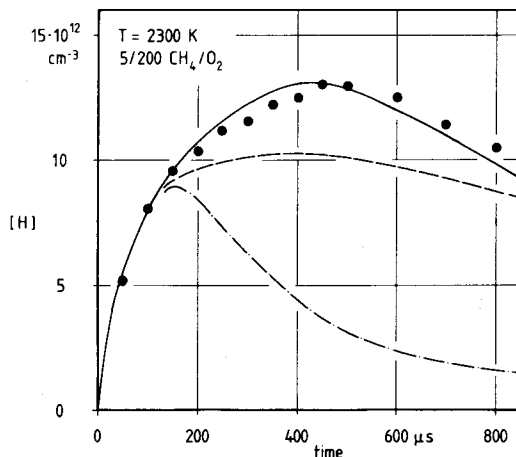


FIG. 3. Measured (black points) and calculated H atom concentrations.

$T = 2300 \text{ K}$ $[\text{Ar}] = 5.33 \cdot 10^{18} \text{ cm}^{-3}$

$[\text{CH}_4]/[\text{O}_2] = 5 \text{ ppm}/200 \text{ ppm}$

— · — · — calculated with reactions R1 to R5

— · — — calculated without reaction R7

———— calculated with full reaction mechanism

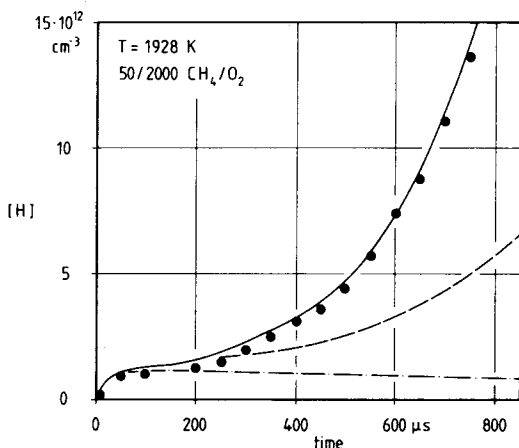


FIG. 2. Measured (black points) and calculated H atom concentrations.

$T = 1928 \text{ K}$ $[\text{Ar}] = 7.73 \cdot 10^{18} \text{ cm}^{-3}$

$[\text{CH}_4]/[\text{O}_2] = 50 \text{ ppm}/2000 \text{ ppm}$

— · — · — calculated with reactions R1 to R5

— · — — calculated without reaction R7

———— calculated with full reaction mechanism

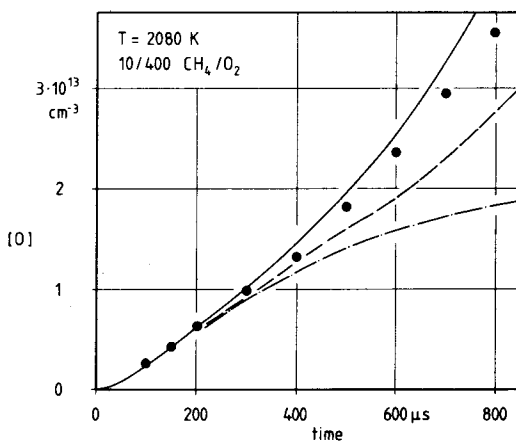


FIG. 4. Measured (black points) and calculated O atom concentrations.

$T = 2080 \text{ K}$ $[\text{Ar}] = 6.92 \cdot 10^{18} \text{ cm}^{-3}$

$[\text{CH}_4]/[\text{O}_2] = 10 \text{ ppm}/400 \text{ ppm}$

— · — · — calculated with reactions R1 to R5

— · — — calculated without reaction R7

———— calculated with full reaction mechanism

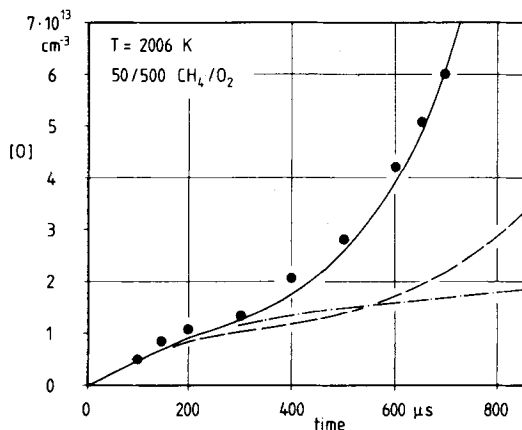


FIG. 5. Measured (black points) and calculated O atom concentrations.

$T = 2026 \text{ K}$ $[\text{Ar}] = 7.15 \cdot 10^{18} \text{ cm}^{-3}$

$[\text{CH}_4]/[\text{O}_2] = 50 \text{ ppm}/500 \text{ ppm}$

— · — · — calculated with reactions R1 to R5

— — — calculated without reaction R7

———— calculated with full reaction mechanism

decrease with increasing reaction number. This classification was also used within the groups of CH₄, CH₃ and CH₂O reactions.

The first 5 reactions of Table III are sufficient to describe the beginning of CH₄ combustion under the chosen conditions. They are analogous to these used by Chiang and Skinner¹⁰ in their CD₄/O₂ reaction system. The primary thermal decomposition of CH₄ is followed by the very important H + O₂ chain branching reaction and by additional CH₄ reactions, which produce CH₃ radicals. The rate coefficients k_1 to k_5 seem to be well established. Unfortunately the modeling depends fairly strongly on R2. Small differences between the values for k_2 given by Baulch et al.,²³ Schott²⁷ and Pamidimukkala and Skinner²⁴ may have relatively large effects upon the computed H and O profiles. Therefore some H and O atom measurements were performed in N₂O/H₂/O₂ mixtures, diluted in argon to reexamine the rate coefficient k_2 . The results²⁵ can be presented as

$$k_2 = k_{2,\text{Baulch}} \cdot (0.9 \pm 0.1) \quad 1800 \text{ K} \leq T \leq 2600 \text{ K}$$

and are about 25% higher than the Arrhenius expression obtained by Pamidimukkala and Skinner²⁴ at lower temperatures.

Reactions of CH₃ become important at about $[\text{CH}_3]/[\text{CH}_4]_0 \geq 0.1$ to 0.2. The rate of CH₃ + O is very fast and the rate coefficient is known from low and high temperature measurements.^{28,29,19} The rate coefficient, as well as the products of CH₃ + OH, is less well known in the literature and we prefer to use the value of^{19,30} for the H₂ channel and a slightly modified value of¹⁹ for the CH₃O +

H channel, followed by the fast decomposition of CH₃O/(CH₂OH). The other important CH₃ reaction with O₂ continues to be a matter of debate. Chiang and Skinner¹⁰ in their D atom measurements used reaction 10 as the only relevant CD₃ reaction followed by the thermal decomposition of CD₂O. They used the high rate coefficient value k_{10} of Olson and Gardiner.¹⁴ In the more direct measurements of,¹⁹ the rate coefficients k_9 and k_{10} were found to be of very little significance and we prefer to use the values given there. The rate coefficient k_{10} of Table III is consistent with the extrapolated upper limit value obtained by Baldwin and Golden.³⁹ Reaction channel 9 must be seen together with the fast thermal decomposition of the CH₃O/(CH₂OH) complex. The coefficients k_9 and k_{10} of¹⁹ were recently supported by an experimental and theoretical study of Hsu et al.³⁷ CH₃ reactions 13 and 14 are of minor importance under the present conditions. The recombination reactions of CH₃ (11 and 12) do not occur to any significant extent, consequently C₂H₅, C₂H₄ and other C₂ molecules appear only in small fractions. Of course this would be different, when considering a fuel-rich system. For these conditions, we plan to present measurements supported by model calculations in the near future.

The formaldehyde chemistry of Table III is summarized by 5 elementary reactions. Under the present conditions, the H atom and the H₂ channels of the thermal dissociation of CH₂O have been taken into consideration, using the rate coefficient of Rimpel and Just.^{20,19} The other CH₂O reactions were taken from Dean et al.³¹ Of the possible CH₂

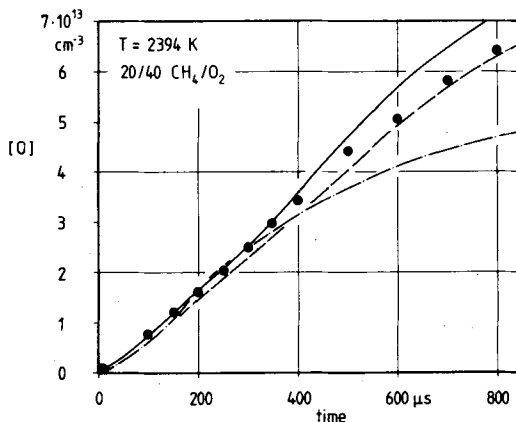


FIG. 6. Measured (black points) and calculated O atom concentrations.

$T = 2394 \text{ K}$ $[\text{Ar}] = 5.61 \cdot 10^{18} \text{ cm}^{-3}$

$[\text{CH}_4]/[\text{O}_2] = 20 \text{ ppm}/40 \text{ ppm}$

— · — · — calculated with reactions R1 to R5

— — — calculated without reaction R7

———— calculated with full reaction mechanism

TABLE III
Simplified reaction mechanism of the $\text{CH}_4\text{-O}_2$ system highly diluted in argon

Reaction		Rate coefficient $\text{cm}^3 \text{ s}^{-1}$	Ref.
1	$\text{CH}_4 + \text{Ar} \rightleftharpoons \text{CH}_3 + \text{H} + \text{Ar}$	$7.85 \cdot 10^{-7} \exp(-46\,900/T)$	13
2	$\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$	$0.9 \cdot 3.67 \cdot 10^{-10} \exp(-8\,450/T)$	23/25 ^{a)}
3	$\text{CH}_4 + \text{H} \rightleftharpoons \text{CH}_3 + \text{H}_2$	$1.20 \cdot 10^{-9} \exp(-7\,530/T)$	13
4	$\text{CH}_4 + \text{O} \rightleftharpoons \text{CH}_3 + \text{OH}$	$6.80 \cdot 10^{-10} \exp(-7\,030/T)$	17
5	$\text{CH}_4 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}$	$4.70 \cdot 10^{-11} \exp(-2\,500/T)$	17/34
6	$\text{CH}_3 + \text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{H}$	$1.33 \cdot 10^{-10}$	19
7	$\text{CH}_3 + \text{OH} \rightleftharpoons \text{CH}_3\text{O} + \text{H}$	$1.50 \cdot 10^{-9} \exp(-7\,800/T)$	19 ^{a)}
8	$\rightleftharpoons \text{CH}_2\text{O} + \text{H}_2$	$1.33 \cdot 10^{-11}$	19
9	$\text{CH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{O}$	$1.17 \cdot 10^{-11} \exp(-12\,900/T)$	19
10	$\rightleftharpoons \text{CH}_2\text{O} + \text{OH}$	$8.87 \cdot 10^{-11} \exp(-17\,400/T)$	19/39
11	$\text{CH}_3 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_5 + \text{H}$	$1.33 \cdot 10^{-9} \exp(-13\,400/T)$	18/26
12	$\rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$	$3.50 \cdot 10^{-10} \exp(-9\,690/T)$	26
13	$\text{CH}_3 + \text{H} \rightleftharpoons \text{CH}_2 + \text{H}_2$	$1.20 \cdot 10^{-10} \exp(-7\,600/T)$	33/26
14	$\text{CH}_3 + \text{Ar} \rightleftharpoons \text{CH}_2 + \text{H} + \text{Ar}$	$3.23 \cdot 10^{-8} \exp(-46\,100/T)$	33/26
15	$\text{CH}_2\text{O} + \text{Ar} \rightleftharpoons \text{CO} + \text{H}_2 + \text{Ar}$	$1.37 \cdot 10^{-8} \exp(-35\,000/T)$	20
16	$\rightleftharpoons \text{HCO} + \text{H} + \text{Ar}$	$3.00 \cdot 10^{-8} \exp(-40\,400/T)$	20
17	$\text{CH}_2\text{O} + \text{OH} \rightleftharpoons \text{HCO} + \text{H}_2\text{O}$	$1.25 \cdot 10^{-11} \exp(-84/T)$	31
18	$\text{CH}_2\text{O} + \text{O} \rightleftharpoons \text{HCO} + \text{OH}$	$3.00 \cdot 10^{-11} \exp(-1\,550/T)$	31
19	$\text{CH}_2\text{O} + \text{H} \rightleftharpoons \text{HCO} + \text{H}_2$	$5.50 \cdot 10^{-10} \exp(-5\,280/T)$	31
20	$\text{CH}_2 + \text{O}_2 \rightleftharpoons \text{CO}_2 + \text{H} + \text{H}$	$2.20 \cdot 10^{-11} \exp(-760/T)$	40/41/16 ^{b)}
21	$\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$	$\exp(-29.82 + 9.07 \cdot 10^{-4} T)$	35
22	$\text{O} + \text{H}_2 \rightleftharpoons \text{OH} + \text{H}$	$3.80 \cdot 10^{-10} \exp(-6\,920/T)$	24
23	$\text{OH} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H}$	$3.67 \cdot 10^{-11} \exp(-2\,590/T)$	23
24	$\text{OH} + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{O}$	$2.50 \cdot 10^{-15} \cdot T^{1.14}$	23
25	$\text{HCO} + \text{Ar} \rightleftharpoons \text{CO} + \text{H} + \text{Ar}$	$2.67 \cdot 10^{-10} \exp(-7\,400/T)$	32
26	$\text{CH}_3\text{O} + \text{Ar} \rightleftharpoons \text{CH}_2\text{O} + \text{H} + \text{Ar}$	$3.30 \cdot 10^{-10} \exp(-10\,000/T)$	c)
27	$\text{C}_2\text{H}_5 + \text{Ar} \rightleftharpoons \text{C}_2\text{H}_4 + \text{H} + \text{Ar}$	$7.80 \cdot 10^{-10} \exp(-13\,390/T)$	6

a) See text.

b) This is probably not an elementary reaction.

c) rate coefficient assumed, results not sensitive to the value chosen.

reactions known to be fast, only the reaction with O_2 is included in the mechanism. O_2 is one of the initial reactants and its concentration is high, in most cases, as compared to the other possible reactants. Nevertheless, the contribution of the somewhat arbitrarily proposed reaction 20 is very small. Reactions 20 to 24 are well known but of minor importance to simulate the measured H and O atom concentrations under the present low concentration conditions. The last three reactions of Table III are thermal decomposition reactions. The radicals HCO and C_2H_5 are known to decompose very fast at high temperatures. Under the present low concentration conditions, HCO and C_2H_5 reactions with O_2 , H, OH and O are unimportant. The rate coefficient of

the CH_3O (CH_2OH) decomposition is assumed. The results are not sensitive to the value chosen. All the rate coefficients of the reverse reactions of Table III were computed from JANAF table equilibrium values.

The effects of the various elementary reactions on the time-dependent production of H and O atoms were examined by several computer calculations with the full or reduced reaction mechanism of Table III. Results obtained with a reduced reaction scheme R1 to R5 are shown as dashed-dotted curves in Figures 1–6. In all cases, the first part of the modeled H and O atom concentrations are in agreement with the measurements. The differences between these simple model calculations

and the experimental results increase with increasing reaction time, depending on the CH₄/O₂ mixtures and the reaction temperature. For stoichiometric conditions and low reaction temperatures (Figure 1), the agreement is relatively good even for larger reaction times, whereas large divergences are obtained in mixtures with high O₂ excess, for example Figure 2. It is clear that under these conditions, where CH₄ has reacted to a larger extent, the influence of CH₃ reactions together with R2 will become more and more dominant.

The solid lines in Figures 1 to 6 represent computer calculations obtained with the full reaction mechanism of Table III. In these examples as well as in most of the results of Tables I and II, the computer model fits the experimental concentration profiles quite well. Besides R2, CH₃ reactions R6 and R7 cause a distinct acceleration of the H and O atom production at mean reaction times and lead to a decisive approach to the experiments. In the present simplified reaction model, reaction R7, appears important and necessary as proposed by Bhaskaran, Frank and Just.¹⁹ All attempts to reproduce the measured H and O atom concentrations through computer simulation without R7 proved unsuccessful, in particular at higher O₂ concentrations. The dashed lines in Figures 1 to 6 represent computed H and O concentrations without reaction R7. The present experimental results, compared to kinetic modeling appear to confirm the necessity of reaction R7. The same conclusions were recently reached by Levy and Sarofim³⁸ in their attempt to model C₂H₄-air flames. The present modeling cannot be considered to give very exact val-

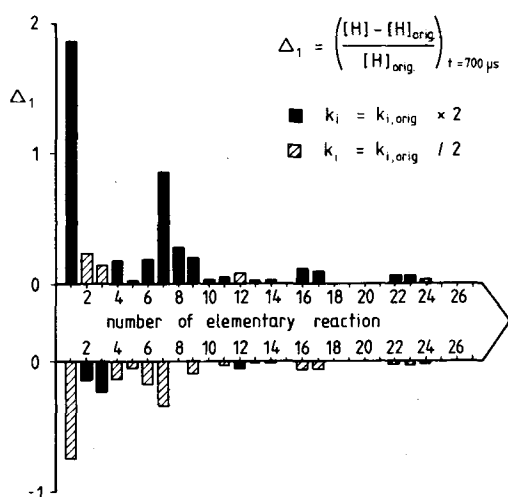


FIG. 7. Sensitivity analysis of the reaction mechanism of Table III based on H atom concentrations computed under the experimental conditions of Figure 2.

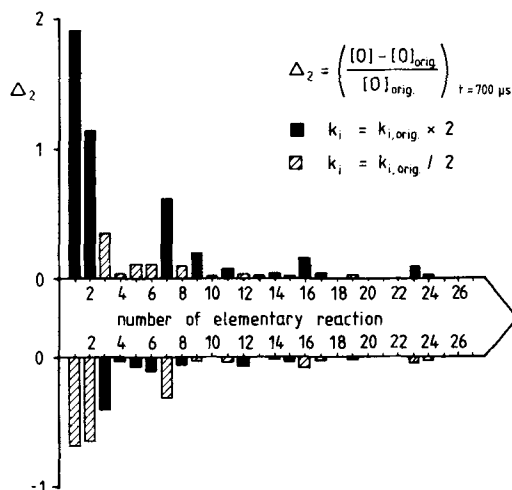


FIG. 8. Sensitivity analysis of the reaction mechanism of Table III based on O atom concentrations computed under the experimental conditions of Figure 5.

ues for the rate coefficient k_7 , since the parameters for k_7 depend upon the ones chosen for k_2 . The same was true for the experiments reported in.¹⁹ As it was pointed out in²⁶, determination of a reliable rate coefficient for this reaction calls for experimental conditions specifically designed for this purpose. The relatively high activation energies of reactions 7 and 11 seem not to be compatible with a simple recombination-dissociation model.^{42,43,44} In this model a chemical activated complex is assumed, which usually belongs to an electronic singlet potential curve. At high temperatures, however, it seems to be necessary to take transition states into account, which in our case belong to triplet potential curves. For reactions 7 and 11, one must assume a potential barrier on the order of 5 to 6 kcal/mol, if the reactions are considered in the exothermal direction. It is possible to find reasonable TST configurations and pertinent frequencies by which our experimental results in the high temperature regime, $T > 1500$ K, can be predicted. At lower temperatures the reactions are governed more and more by the process along the singlet potential curves.

To show the relative importance of the different elementary reactions a sensitivity analysis based on two individual results was conducted. All rate coefficients of the reaction scheme of Table III were successively varied by factors of 2 or 0.5. The relative change in the computed atom concentrations at $t = 700$ μ s are shown in Figure 7 for H atoms under the conditions of Figure 2. In this special example, the dominant influence of the initial CH₄ decomposition reaction on the generated H atoms

is noticeable up to 700 μ s. The important influence of reaction R7 is evident. The contribution of the other reactions up to R9 is about 20%. In this particular case, the influence of all other reactions is of minor importance.

The second example of a sensitivity analysis, shown in Figure 8, was carried out for O atoms under the conditions of Figure 5. Again the important contribution of the initial CH_4 reaction on the O atom concentration, even at time $t = 700$ μ s, is obvious. In this case, the sensitivity on the chain branching reaction $\text{H} + \text{O}_2$ is very important, as well as the influence of R7. Apart from reaction R3 the contribution of all other reactions is less than 20%.

Conclusion

This work presents for the first time H and O atom concentration profiles, measured for a broad range of experimental conditions at low concentrations of CH_4 and O_2 in Ar. The computer modeling led to a satisfactory agreement with the experimental results without larger variations in the rate parameters. The rate coefficients used were preferentially chosen from earlier ARAS or, if not available, from other high temperature measurements and are confirmed by the present results. Nevertheless, it can not be excluded that modified kinetic models with modified rate coefficients may be able to reproduce the present experimental data as well.

Very recently we also incorporated $\text{CH}_3 + \text{OH} \rightarrow \text{CH}_2 + \text{H}_2\text{O}$ in our system. For the fast subsequent reactions of $\text{CH}_2 + (\text{O}_2, \text{O}, \text{OH}, \text{H})$ we used the recent high temperature results obtained by Bhaskaran, Frank and Just.⁴⁵ As we have stated earlier, in the case of CH_3/O_2 ,¹⁹ it was again impossible to model the CH_4/O_2 and the CH_3/O_2 systems using this $\text{CH}_3 + \text{OH} \rightarrow \text{CH}_2 + \text{H}_2\text{O}$ reaction channel alone. The necessity of the relatively fast reaction $\text{CH}_3 + \text{OH} \rightarrow \text{CH}_3\text{O}(\text{H}_2\text{COH}) + \text{H}$ at temperatures greater than 1800 K is thus reiterated.

Acknowledgments

The authors wish to thank K. Thielen for his assistance. The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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COMMENTS

J. A. Miller, *Sandia National Laboratories, USA*.
I am very surprised at the result you presented for the reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$. A few years ago I did classical trajectory calculations¹ on this reaction using the Melius-Blint *ab initio* potential. My results fell exactly on Shott's² experimental result ($1250 \text{ K} < T < 2500$). These results are very interesting because the "local" activation energy is about 4 kcal/mole below the endothermicity. It would be a very strange circumstance if both the theoretical and experimental results were wrong in *exactly* the same unusual way.

Nevertheless, there are some known problems with the Melius-Blint potential. The H—O₂ bond energy is too small, there is a small (nonphysical) energy barrier in the H—O₂ entrance channel, and the potential is too attractive at large O—OH separations. The only one of these deficiencies that obviously should affect the rate coefficient in question, however, is the last one, and it should lead to rate coefficients that are too large, not too small (probably with minimal effect at high temperature). The handling of quantum effects in the trajectory calculations also introduces a systematic error toward high, not low, rate coefficients. These effects are consistent with the recent discussion/evaluation of Dixon-Lewis³ and explain why the trajectory results are about a factor of two higher than Howard and Smith's⁴ result (obtained from the reverse rate coefficient using the equilibrium constant) at room

temperature. There is only about a 30% discrepancy at 500 K, however.

Nevertheless, your result makes life interesting. We plan to make improvements in the potential in the not-to-distant future and to compute rate coefficients from trajectories in both directions and from variational transition state theory. Hopefully, we will all learn something from this exercise.

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W. C. Gardiner, *University of Texas, USA*. In comparing new to old values for the rate constants of $\text{O} + \text{H}_2$ and $\text{OH} + \text{H}_2$ one should remember that the literature values considered most reliable over 1000 K were originally obtained as ratios. Direct comparisons therefore become inconsistent if adjustments are made, as in this paper, to the rate constant of $\text{H} + \text{O}_2$.

Authors' Reply. We simply compared the absolute (extrapolated) rate coefficients regardless of how they were derived. I should mention, however, that in the temperature range 1600 to 1200 K the Schott-expression does not deviate considerably from either Baulch's recommendation or from recent experimental evaluations published by Dixon-Lewis.¹ The ratios which you have mentioned, lead in this temperature range, when based on Schott's expression to "correct" values for $O + H_2$ and $OH + H_2$.

Larger discrepancies appear for $k(H + O_2)$ at temperatures greater than 1600 K. We found for example at 2500 K a rate coefficient which is about a factor of 2.2 larger than Schott's value.

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D. M. Golden, SRI International, USA. I have difficulty understanding how a reaction even on a

triplet surface can have such a high pre-exponential factor as well as a high intrinsic barrier. I refer to the process: $CH_3 + OH \rightarrow CH_2OH + H$.

Authors' Reply. The precision of our evaluation of the Arrhenius parameters for $CH_3 + OH \rightarrow H_2COH + H$ is presently not very high. Our modeling of CH_3/O_2 and CH_4/O_2 systems in the temperature range 1800 to 2300 K yielded for this reaction rate coefficients of $8 \cdot 10^{12}$ to $1.1 \cdot 10^{13}$ at 1800 K and $2.5 \cdot 10^{13}$ to $3.5 \cdot 10^{13}$ cm³/mol·s at 2300 K respectively. The modeling of CH_4/O_2 can be satisfactorily performed with $k \approx 9 \cdot 10^{14} \exp(-7800/T)$ as given in this paper. A slightly better modeling is possible with $k \approx 2 \cdot 10^{15} \cdot \exp(-9580/T)$. With these parameters for k we were able to model two systems: CH_3/O_2 and CH_4/O_2 . We also found that the assumption of an alternative channel: $CH_3 + OH \rightarrow CH_2 + H_2O$ even with the fast subsequent $CH_2-(O_2, O, H)$ reactions cannot explain the experimental results of the two systems.

Whether my explanation, based on the assumption of a triplet-triplet interaction and a pertinent TST-state with a not too tight structure is correct, or not, cannot be answered yet.

I regard this as a challenge for the theorists.