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ABSTRACT

STUDY OF ELEMENTARY REACTIONS OF COMBUSTION IMPORTANCE AT ELEVATED TEMPERATURES AND PRESSURES

by Manuvesh Sangwan

The aim of the present study is to study the kinetics of elementary reactions of combustion importance at elevated temperatures and pressures. High pressure is encountered in many systems of practical importance such as internal combustion engines and rocket combustion chambers. Several reactions of OH, CH₃ and HO₂ radicals are studied. The pressure range covered in this study is 1 - 100 bar and the temperature range is 292 - 834 K. The experimental approach used is laser photolysis coupled to UV transient absorption spectroscopy. A unique high pressure heatable flow reactor is employed and a novel approach of direct introduction of liquid precursors using a high pressure syringe pump is developed in this study. Methyl radicals are produced by photolysis of acetone at 193.3 nm. Hydroxyl radicals are generated in the reaction of electronically excited oxygen atoms $O(^{1}D)$, produced in the photolysis of N₂O at 193.3 nm with H₂O. The reaction of $O(^{1}D)$ and hydroxyl with H₂O₂ produce hydroperoxy radicals. Temporal profiles of CH_3 and HO_2 are recorded via absorption at 216.4 and 224 nm, using xenon arc lamp and a spectrograph, OH radicals are monitored via transient absorption of light from a dc discharge H₂O/Ar low pressure OH discharge lamp at ca. 308 nm. The absolute intensity of the photolysis light inside the reactor is determined by an accurate in situ actinometry based on the ozone formation in the presence of molecular oxygen. The reactions studied are OH + OH \rightarrow products (k_{OH+OH}), CH₃ + OH \rightarrow products (k_{CH3+OH}) , $CH_3 + CH_3 \rightarrow products$ $(k_{CH3 + CH3})$, and $CH_3 + HO_2 \rightarrow products$ $(k_{CH3+HO2})$.

The pressure dependent rate constant in the self-reaction of OH radical is parameterized using the Troe expression as $k_{1b,inf,OH+OH} = (2.3 \pm 0.5)x10^{-11}(T/300)^{-0.5}$ cm³molecule⁻¹s⁻¹, $k_{1b,0,OH+OH} = [He] (1.4 \pm 0.5)x10^{-30}(T/300)^{-4.6\pm0.5}$ cm³molecule⁻¹s⁻¹, $F_c = 0.37$. The V-shaped temperature dependence of disproportionation channel ($k_{OH+OH->H2O+O}$) based on combined current and previous studies in the temperature range of 233 - 2380 K is (5.1 exp(-T/190 K) + 0.30(T/300 K)^{1.73})x10^{-12} cm³molecule⁻¹s⁻¹. The rate constant of the reaction of CH₃ and OH is determined as $k_{CH3 + OH} = (1.20 \pm 0.20)x10^{-10}(T/300)^{-0.49}$ cm³molecule⁻¹s⁻¹ pressure independent over the 1 - 100 bar range. The rate constant of self reaction of CH₃+CH₃ is $k_{CH3+CH3} = 5.94x10^{-11}$ (T/300)^{-0.31}cm³molecule⁻¹s⁻¹. The reaction of methyl radicals with hydroperoxy radicals (CH₃+HO₂->products), is studied at 295 K and 1 bar (He). The rate constant is $(3.7 \pm 1.8)x10^{-11}$ cm³molecule⁻¹s⁻¹ (295 K, 1 bar, He).

STUDY OF ELEMENTARY REACTIONS OF COMBUSTION IMPORTANCE AT ELEVATED TEMPERATURES AND PRESSURES

by Manuvesh Sangwan

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemistry

Department of Chemistry and Environmental Science

May 2013

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STUDY OF ELEMENTARY REACTIONS OF COMBUSTION IMPORTANCE AT ELEVATED TEMPERATURES AND PRESSURES

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- Manuvesh Sangwan, Evgeni N. Chesnokov, and <u>Lev N. Krasnoperov</u>, Kinetics of Reactions of Combustion Importance at Elevated Temperatures and Pressures, Podium presentation at the 22nd International Symposium of Gas Kinetics, Boulder, CO, June 18 - 22, 2012
- Manuvesh Sangwan, Evgeni N. Chesnokov and <u>L.N. Krasnoperov</u>, Reactions CH₃ + OH, CH₃ + CH₃, and OH + OH Studied over 1-100bar Pressure and 298
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"What we think, or what we know, or what we believe is, in the end, of little consequence. The only consequence is what we do"

—John Ruskin

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CHAPTER 1

INTRODUCTION

1.1 Objective

Elementary reactions are a central part of models of combustion processes. To better understand the combustion phenomena, it is important to study the kinetics of elementary reactions involved in combustion processes. Advanced models of combustion consist of differential equations that describe the processes of heat transport, combustion chemistry and fluid dynamics. Combustion chemistry incorporates detailed reaction mechanisms. Detailed reaction mechanisms are important for improvement in performance and optimization of the efficiency of combustion processes.

Combustion mechanisms consist of hundreds of elementary reactions of atoms, radicals free and stable molecules. Many of these reactions are of a recombination/dissociation nature or proceed via an intermediate complex, and, therefore, are pressure (buffer gas density) dependent. These predictive models play a crucial role in the design and optimization of combustion systems and devices. Internal engine knock, emission of environmentally noxious substances (such as NOx, soot, unburned hydrocarbons, heavy metals) are the problems which require understanding of comprehensive kinetics mechanisms with well characterized elementary reactions. Despite the substantial progress in measurement of elementary reactions at well controlled conditions, the experimental kinetic data required for advancement of combustion model at elevated pressures and temperatures is insufficient.

1

Reaction conditions with high and variable pressures are encountered in practically important combustion process, e.g in internal combustion engines and rocket combustion chambers. Because of the complexity encountered, laboratory measurements usually provide rate constants at "convenient" pressures (0.001 - 1 bar). Data obtained at low pressures are then extrapolated to combustion conditions. Such extrapolations are based on theoretical foundations and may introduce significant additional uncertainties into the models predictions. Reliable high pressure and high temperature data is required to both validate and improve predictive model performance at pressures greater than one atmosphere, which is usually the case in combustion.

1.2 Background and Motivation

In this research, elementary chemical reactions involving free radicals (OH, CH_3 , and HO_2), important in combustion processes are studied. The underlying theme that relates all these measurements is that they facilitate improved modeling and understanding of combustion and flame chemistry at elevated pressures. The studied reactions are:

(1)	OH +	OH
(2)	CH3 +	OH
(3)	CH3 +	CH_3
(4)	CH3 +	HO_2

1.2.1 OH + OH \rightarrow products

The Hydroxyl radical plays an essential role in atmospheric ¹⁻⁷ and in combustion ⁸⁻¹⁴ chemistry. In atmospheric conditions, OH can be considered as the major initiator of the radical reaction.¹⁻⁷ This is one of the reasons for numerous studies of the kinetics and mechanisms of gas phase reactions of this radical.¹⁵⁻¹⁷ Due to high reactivity of hydroxyl

radical, its concentrations in typical practically important systems are low, and the selfreaction 1 plays only a minor role:

$$OH + OH \rightarrow H_2O + O$$
 (1a)

$$\rightarrow$$
 H₂O₂ (1b)

However, this reaction is very important in the laboratory kinetic studies of hydroxyl radicals, where the concentrations must be sufficiently high to provide accurate monitoring of the radical decay. This reaction not only provides an additional sink for the radical, but also initiates a sequence of secondary, highly undesirable reactions of oxygen and hydrogen atoms, formed in channel 1a and subsequent reactions 2 and 3:

$$O + OH \rightarrow O_2 + H$$
 (2a)

$$\rightarrow$$
 HO₂ (2b)

$$H + OH \rightarrow H_2 + O$$
 (3a)

 \rightarrow H₂O (3b)

In addition, reaction 1 is one of the simplest radical-radical reactions, where both the singlet and triplet states play comparable roles.¹⁸⁻²⁴ It is generally accepted that reaction 1a proceeds via the triplet state, and is buffer gas pressure independent.^{18-19,25} Reaction 1b is assumed to proceed through the singlet state, and is pressure dependent, as other recombination reactions.^{22,24} It should be noted, that the two major interfering reactions, 2 and 3, also have pressure independent and pressure dependent components, which further complicates experimental studies of the kinetics of hydroxyl radical.

Despite the large number of experimental and theoretical studies of reaction 1, there are still remaining issues that require attention. Recently, Troe presented an extended analysis of the dissociation – recombination kinetics of H_2O_2 .²⁶ The analysis of the pressure fall-off is consistent with the accepted value of the rate constant $k_{1a} = (1.4\pm0.2)x10^{-12}$ at 298 K. However, the most recent direct measurements of Bahng and Macdonald ²⁷ are in significant, almost a factor of two, discrepancy with this value (2.7 $\pm 0.9)x10^{-12}$. The experimental high pressure data that are used to create the pressure fall-off curves for k_{1b} at elevated temperatures are sparse.²⁸ In experimental study, rate constant of reaction 1 was measured in single pressure points of ca. 85 - 90 bar at four temperatures.

In addition, the turning point in the temperature dependence of the disproportionation channel 1a, which is expected from the combination of the low temperature and high temperature shock tube studies was never observed in a single experimental study. To study the reaction of methyl radicals with hydroxyl over extended temperature and pressure ranges kinetic data on an extended temperature and pressure grid is required. These reasons are the motivations for the current study.

1.2.2 CH₃ + OH \rightarrow products

Hydroxyl and methyl plays an important role in combustion chemistry. This reaction is a multi-channel reaction which proceeds via an intermediate complex.²⁹⁻³¹ The energetically open reaction channels are:²⁹⁻³⁰

CH ₃	+	OH	\rightarrow	$^{1}CH_{2}$	+	H ₂ O	(4a)
			\rightarrow	CH ₃ OH			(4b)
			\rightarrow	CH ₃ O	+	Н	(4c)
			\rightarrow	CH ₂ OH	+	Н	(4d)
			\rightarrow	cis-HCOH	+	H ₂	(4e)
			\rightarrow	trans-HCOH	+	H ₂	(4f)
			\rightarrow	CH ₂ O	+	H ₂	(4g)

As suggested in previous studies, channels 4a and 4b are the main reaction channels. However, the relative importance of the reaction channels is temperature and pressure dependent.³²⁻³³ Despite the large number of experimental studies on the reaction of CH₃ with OH, there is no experimental data on the pressure dependence of this reaction at elevated pressures and temperatures. All previous experimental studies have been performed at low to moderate pressures (0.0006 – 5 bar). In addition, there is still significant discrepancy in the absolute rate constants and in the temperature dependence at ambient as well as elevated temperatures. These are the motivations for the current study.

1.2.3 CH₃ + CH₃ \rightarrow products

$$CH_3 + CH_3 \rightarrow C_2H_6$$
 (5a)

$$\rightarrow$$
 C₂H₅ + H (5b)

The recombination reaction of methyl radical is of substantial importance for combustion. This reaction acts as a major termination reaction in the oxidation and pyrolysis of hydrocarbons.³² It is frequently used as a reference reaction in kinetic studies of radical - radical reactions.³² While there have been numerous studies of this very important reaction, limited data available at elevated pressures and high temperatures. High pressure measurements allow better understanding of the temperature dependence and the high pressure limit in this reaction.

1.2.4 CH₃ + HO₂ \rightarrow products

The reaction of CH_3 and HO_2 plays an important role in hydrocarbon combustion.³⁴⁻³⁶ The reaction of hydrogen atoms (e.g., produced in dissociation of formyl radical, HCO) with molecular oxygen leads to a relatively unreactive hydroperoxy radical, HO_2 . However, subsequent reaction of HO_2 with CH_3 (e.g., in fuel rich mixtures) might lead to efficient chain propagation via channel 6a. The sensitivity analysis of methane combination ranks reaction 6 among the 5 most important reaction in the mechanism.³⁵⁻³⁶ This reaction is exothermic, there are several product channels.

$$CH_3 + HO_2 \rightarrow CH_3O + OH$$
 (6a)

$$\rightarrow \quad CH_2O + H_2O \tag{6b}$$

$$\rightarrow$$
 CH₃OOH (6c)

$$\rightarrow CH_4 + {}^{3}O_2 \tag{6d}$$

$$\rightarrow CH_4 + {}^{1}O_2 \qquad (6e)$$

Channel 6a is considered to be a major chain propagation reaction in high pressure methane oxidation³⁷, whereas channel 6d is a chain termination step at elevated temperatures. At elevated temperatures methoxy radicals produced in channel 6a easily dissociate to form H-atoms and CH₂O. Therefore, at intermediate temperatures and elevated pressures reaction 6a is crucial in the mechanism of natural gas combustion.³⁷ The channels 6d and 6e are direct abstraction reactions which occur on a triplet and singlet PESs producing molecular oxygen in the ground and excited electronic surface.³⁸⁻³⁹ The relative importance of other channels is assessed in previous theoretical studies.⁴⁰⁻

⁴¹ The branching ratio of channel 1a and 1d is important for modeling ignition in high pressure combustion systems.⁴⁰ Radical HO₂ is perhaps one of the most difficult transient species for direct kinetic studies, especially at elevated temperatures. One of the problems is the lack of a convenient direct photo-generator of HO₂. Despite the importance of reaction 6 in combustion mechanism, very limited experimental studies have been performed.

1.3 Scope and Organization of Thesis

The primary objective of this current work is to study kinetics of elementary chemical reactions that are important in combustion and flames. Several reactions are studied by employing high pressure flow reactor using absorption spectroscopy. Laser photolysis, transient UV absorption, direct introduction of liquid precursors at high pressure are developed to generate, detect and measure the transient radical species (OH, CH_3 , HO_2) at high temperatures and high pressures.

Chapter 2 describes the experimental apparatus, generation and monitoring of free radicals. Chapter 3 summarizes the absorption cross sections measurements important for studying the elementary reactions. Chapter 4 presents the results on the reaction between OH and OH radicals. Chapter 5 presents the results on the reaction of CH₃ and OH radicals. The reactions of CH₃ and CH₃ and CH₃ and HO₂ are discussed in Chapter 6 and 7, respectively. Chapter 8 consists of conclusions. The numbering of reactions described in separate chapters, starts from 1 in each chapter. This arrangement is adopted to simplify the numbering of all relevant reactions involve in reaction mechanism of the title reaction in that chapter.

CHAPTER 2

EXPERIMENTAL APPARATUS

2.1 Introduction

Pulsed laser photolysis is widely used in chemical kinetics to study elementary reactions. The experimental approach used in this study is based on excimer laser photolysis coupled to UV-vis transient absorption spectroscopy and a high-pressure flow system. A sketch of the experimental set up is shown in Figure 2.1. To achieve uniform concentration profiles across the reactor cross-section, the laser beam is formed using a spherical lens (f = +30 cm, the distance from the reactor center 82 cm) and a cylindrical lens (f = +30 cm, the distance from the reactor center 35 cm). Helium is used as the buffer gas in all measurements. The measurements are performed over the 1 - 100 bar pressure and 25 - 561 °C temperature range. A unique heatable high-pressure flow reactor of a novel design is employed (Figure 2.2).

2.2 Heatable High Pressure Flow Reactor

The reactor is made of 12.7 mm O.D. (1/2") stainless steel tubing. The central part of the tube (20 cm) is inserted into an aluminum cylindrical block, which serves as a heat distributor. Two electrical resistance heaters are located within the aluminum block parallel to the reactor. A thermocouple (K-type, Omega) is located in the middle of the block. The reagents are supplied through a 3.175 mm O.D. (1/8") stainless steel tube that is passed seven times (total length 140 cm) through the aluminum block for pre-heating (Figure 2.2). Such an arrangement ensured complete pre-heating of the reactant mixture to the reactor temperature without using additional ovens and temperature controllers.



Figure 2.1 Experimental set up schematics. ArF Excimer laser (EX100 GAM Laser Inc., 193.3 nm, 40 mJ); E - beam expander, consists of a spherical lens f= 30 cm and cylindrical lens f= 30 cm (light homogeneity in the cell: ±14% in vertical direction and ±10% in horizontal direction); M_5 , M_3 – dielectric mirrors with high reflectivity at 193 nm at 45⁰; M_3 –dielectric mirror with high reflectivity at 308 nm and 45⁰; L_1 , L_2 and L_3 – fused silica lenses; D1 and D2 diaphragms forming monitoring beam (1/4" each). Several source of monitoring light are used: Xe arc lamp (75 W, Oriel Instruments), radiofrequency discharge low pressure mercury lamp, and DC discharge OH lamp (see text). M_1 , M_2 – dielectric mirrors with high reflectivity at 193 nm normal incident light. These mirrors are installed at 19⁰ incident angle, which leads to the shift of the high reflectivity range originally centered at 193 nm to 200 – 230 nm. This combination of mirrors work as a bandpass filter for the 200 – 230 nm region, attenuating the visible light from the arc lamp by a factor of ca. 200.

Calculations based on the Graetz formula for gas heating in a Poiseuille's flow ⁴² show guaranteed pre-heating of the gas flow well within 0.001 K for the experimental conditions used in the current work. Two UV-grade quartz windows (12.7 in diameter, 9.5 mm thick) are sealed at the end of the reactor at ambient temperature outside the high-temperature zone using Viton O-rings. The pre-heated reactant mixture entered the

reactor tube in the center and left through two outlets located on two sides 5 cm away from the center but within the uniform temperature zone. Additional buffer gas flows entered the reactor near the windows to flush gas from the windows towards the outlets.

Two additional thick (9.5 mm) quartz windows, separated by a stainless steel insert, are placed without sealing inside the reactor near the reactor outlets. The length of the insert determined the optical path in the zone of reactants of 10.13 cm. The reactant mixture is flowing towards the inside windows, leaving through four small grooves in the insert towards the reaction wall, where it is mixed with the external windows flush flow penetrating through the narrow gap between the inside window and the reaction wall, and leaves the reactor through the exhaust outlets (see insert in Figure 2.2 B). In this way, the two flows (reactant and flush) never meet within the observation zone. This "four windows" configuration prevented penetration of the reactants out of the observation zone, provided precise definition of the observation zone within the uniform temperature region and allowed avoiding of windows sealing at elevated temperatures. The axial temperature profiles are measured in 1 cm steps along the reactor length for each set of the experimental conditions (the temperature set points, total flows and pressures) used in kinetic measurements. One of the windows is replaced by a movable coaxial 1.6 mm O.D. K-type thermocouple $(1/16^{"})$ sealed using a commercial adapter.





Figure 2.2 Sketch of the high-pressure flow reactor (A) and the flow pattern around internal windows (B).

One of the internal windows is replaced with a ceramic cylinder with a hole in the center for the thermocouple. The temperature profiles are uniform within \pm 5 K in the

reactant zone. Average temperature in the reactant zone is taken as the reactor temperature.

The gas flow rates are controlled by high pressure mass flow controllers (Brooks, model 5850). All flow controllers are calibrated and routinely checked for the sensitivities drift (see Appendix 1). The total flow rates of the reactant mixtures with helium are typically in the range 6 - 75 sccs. Additional flush flows to the cold reactor windows are in the range 4.5 - 10 sccs. Liquid H₂O is injected into the high pressure system using a precision syringe pump (Harvard Apparatus, Model PHD 4400). The flow of liquid H₂O in the range 0.4 – 18 μ L/min is flowing from the syringe pump through a capillary tube to an evaporator kept at 90 °C. It is observed that this approach produce steady and stable flow of H₂O over the pressure range 1 – 100 bar.

Concentrations of the precursors used N₂O, H₂O, O₂, and H₂O₂, are calculated and based on the flow rates, temperatures and pressure, small correction for non - ideal gas behavior are introduced. The photolysis laser photon fluence inside the reactor is varied in the range $(2.4 - 9.7)\times10^{15}$ photons cm⁻². The excimer laser used for this study is ArF EX-100 (GAM Laser Inc.). The repetition rate of the laser is set to ensure complete replacement of the gas mixture in the reactor between the pulses (0.1 - 4 Hz depending on pressure).

2.3 Generation of Radicals

2.3.1 OH Radical Generation and Monitoring

Hydroxyl radicals are generated using pulsed photolysis of N_2O in the presence of water at 193.3 nm (ArF excimer laser):

$$N_2O$$
 + $hv (193 \text{ nm}) \rightarrow O(^1D) + N_2$ (1a)

$$\rightarrow N(^4S) + NO(^2\Pi)$$
(1b)

$$O(^{1}D) + H_{2}O \rightarrow 2OH(v=0,1)$$
 (2a)

$$\rightarrow O(^{3}P) + H_{2}O \qquad (2b)$$

$$\rightarrow$$
 H₂ + O₂ (2c)

The quantum yield of the major channel 1a is unity within 1%, the minor channel 1b is less than 0.8%.⁴³ The fraction of vibrationally excited hydroxyl radicals OH(v=1) formed in the reaction of O(¹D) + H₂O (reaction 2a) is 22 - 30%.⁴⁴⁻⁴⁷ According to more recent data the yield is 22-24%.⁴⁴⁻⁴⁶ A Fraction of O(¹D) formed in the photolysis of N₂O reacts with N₂O:

$$O(^{1}D) + N_{2}O \rightarrow NO + NO$$
 (3a)
 $\rightarrow O_{2} + N_{2}$ (3b)

$$\rightarrow$$
 O(³P) + N₂O (3c)

The temporal profiles of the hydroxyl radical decay are monitored by absorption in the UV (multiline at ca. 308 nm).

2.3.2 CH₃ Radical Generation and Monitoring

Photolysis of acetone at 193.3 nm is used to produce CH_3 radicals. There are two other possible channels in the photolysis of acetone at this wavelength:

$(CH_3)_2CO$	+	hv(193 nm)	\rightarrow	2CH ₃	+	CO	(4a)
			\rightarrow	CH ₂ COCH ₃	+	Н	(4b)
			\rightarrow	CH_4	+	CH ₂ O	(4c)
$O(^1D)$ +	CH_4		\rightarrow	CH ₃	+	OH	(5)

In additional experiments (Chapter 7), methane is used to generate CH₃ radicals (reaction 5). Lightfoot et al.⁴⁸ measured the quantum yields of different channels in photolysis of acetone at 193.3 nm. They determined $\phi_{4a} = 0.95$, $\phi_{4b} = 0.03$, and $\phi_{4c} = 0.02$ at 300 K with a negligible temperature dependence (over the 300 - 600 K temperature range). The decay of the methyl radical is monitored by absorption at 216.4 nm (1200 groove/mm grating, 300 mm focal distance, both slits 0.25 mm, triangle slit function, FWHM = 0.64 nm) using a xenon arc lamp combined with an imaging spectrometer (Acton 300i).

2.3.3 HO₂ Radical Generation and Monitoring

Hydroperoxy radicals are generated in the reaction of OH and $O(^{1}D)$ (produced in pulsed photolysis of N₂O (reaction 3)) with H₂O₂.

OH + H_2O_2 \rightarrow H_2O + HO_2 (6a) O(¹D) + H_2O_2 \rightarrow OH + HO_2 (6b) The decay of HO_2 radicals is monitored by absorption at 224 nm (1200 groove/mm grating, 300 mm focal distance, both slits 0.25 mm, triangle slit function, FWHM = 0.64 nm) using a xenon arc lamp combined with an imaging spectrometer (Acton 300i).

2.4 Low Pressure H₂O / Ar DC Lamp

A low pressure resonance hydroxyl lamp is employed in this study. Because the absorption cross-sections of hydroxyl depend upon the lamp parameters, mainly due to the gas temperature in the lamp, a detailed description of the low pressure H₂O/Ar lamp is provided. The lamp is made of glass tubing 4.0 mm ID, 6.0 mm OD, 10.0 cm long, equipped with two fused silica windows. Argon flow is saturated with water vapor at ambient temperature (296 ± 3 K) and 1.28 atm (4.0 psig) pressure. The H₂O/Ar gas mixture enters near the output window and pumped through the discharge tube with the flow rate of 137 sccm at pressure 40 Torr. The lamp is powered from a stabilized high voltage DC power supply (2900 V via a ballast resistor of 66 kOhm). The electrode near the light exit window is the anode (positive). The discharge current is 37 mA, the discharge length 10.0 cm. The discharge tube is vigorously cooled by a strong stream of compressed air. The linear power density dissipated in the discharge is 1.94 W/cm. The output light from the lamp is focused inside the cell using a fused silica lens, and after the cell onto the entrance slit of an imaging spectrograph.

2.5 Imaging Spectrograph

The imaging spectrograph (Acton 300i) is equipped with a PMT (Hamamatsu R106) with a preamplifier (EMI) and a gated intensified CCD (ICCD) camera (ICCD Max, Roper Scientific). The residual light from the excimer laser pulse is removed using a liquid filter $(4.3 \times 10^{-2} \text{ M} \text{ solution of NaCl in water, 1 cm})$. The liquid filter provides virtually complete depression of the 193 nm light. A photomultiplier tube (Hamamatsu R106) mounted on the exit slit operates on a reduced number of dynodes (6) with a high voltage divider current (maximum 2.7 mA), which ensures good linearity and lower noise at high photon fluxes.



Figure 2.3 Rise time of the signal at "C" setting of PMT preamplifier.

The typical anode current is 10 to 20 μ A. The PMT signal is preamplified (EMI preamplifier), digitized and stored using a digital storage oscilloscope (LeCroy 9310A, Dual channel, 400 MHz, 100 Msamples/s, 50 Kpts/ch). The time resolution is determined by the preamplifier setting and can be set to $t_{1/2} = 0.04$, 0.13, 0.5, or 7 μ sec. Typically, the 0.5 μ sec time constant is used (the measured actual rise time $t_{0.1-0.9}$ is 0.46 μ sec). The traces are accumulated (500 to 5000 pulses) and transferred to a PC for processing. The

ICCD camera installed on the second outlet of the spectrograph is used to record transient spectra.

2.6 ArF Excimer Laser

ArF excimer laser from GAM Inc. (model EX100) is used as a photolyzing source. It generates 20 ns pulses with maximum energy of 60 mJ at 193.3 nm. The photolysis laser beam is merged before the cell with, and separated after the cell from the monitoring beam using two 45° multilayer dielectric mirrors (CVI). While the photolysis beam fills homogeneously the whole cross-section of the reactor (see below), the monitoring beam is formed by two ¹/₄" diaphragms before and after the reactor (Figure 2.1).



Figure 2.4 Homogeneity profile of laser beam across the reactor cross section.
Before entering the reactor, the laser beam is formed (to provide uniformity) with a spherical (f = 30 cm, the distance to the reactor 70 cm) and a cylindrical (f = 30 cm, the distance from the reactor 23 cm) lenses. The beam profile is measured by scanning with a small aperture diaphragm (ca. 0.5 mm) combined with an energy meter (Figure 2.4). The beam uniformity across the reactor cross-section is \pm 7.3 % from the mean value (Figure 2.4).

2.7 In Situ Actinometry

There are several difficulties in measuring the rate constants of radical - radical reactions. The most critical one is the necessity of knowing the absolute radical concentrations. In this work, the absolute concentrations of radicals are determined based on the photon flux inside the reactor, the absorption cross-section of N₂O at 193.3 nm, and the efficiency of conversion of $O(^1D)$ atoms produced in the photolysis of N₂O to these radicals. The absorption cross-section of N₂O is accurately known at 298 and 1 bar. At other conditions, the absorption cross-sections of N₂O are measured in this work (Chapter 3).

The major source of errors is in the determination of the laser light intensity inside the reactor. The outside laser energy meters require calibrations; in addition, windows transmittance drift due to film deposition caused by contaminations introduces additional errors. In this work, *in situ* laser light actinometry based on the stable molecule formation with very well characterized cross-section at the monitoring wavelength is used. Specifically, ozone formation, monitored at 253.6 nm, in the photolysis of N₂O/O₂/N₂ mixtures at 1 bar and 298 K is used. An approach based on ozone *depletion* in photolysis at 248 nm is used (Ravishankara et al.⁶¹) to determine *in situ* photon flux from a KrF laser to determine *in situ* photon flux from a KrF laser.

In these measurements, N₂O diluted with 5.0% O₂ in the N₂ mixture is pumped through the reactor at ambient (measured) pressure and photolyzed at 193.3 nm. Formation of O₃ is monitored using low pressure RF discharge mercury lamp at 253.6 nm. After formation in the photolysis, excited oxygen atoms O(¹D) undergo relaxation in collisions with nitrogen ($k_{q,N2} = 2.6 \times 10^{-11}$)¹⁷ and oxygen ($k_{q,O2} = 4.0 \times 10^{-11}$)¹⁷ or react with N₂O ($k = 1.35 \times 10^{-10}$). The concentration of oxygen-nitrogen mixture (2.43x10¹⁹ molecule cm⁻³) is much higher than the concentration of N₂O used in this experiments (7.4x10¹⁶ molecule cm⁻³) which provides almost complete (98.5%) relaxation of O(¹D) to the ground state oxygen atoms O(³P) and subsequent conversion to ozone in fast (ca. 56 µsec) reaction with molecular oxygen, O(³P) + O₂ + M \rightarrow O₃ + M.

The difference in the absorbances is used to calculate the concentration of ozone formed. Sample ozone formation traces are shown in Figure 2.5 (Only the initial parts of the traces are shown to resolve the build-up stage. In the measurements, a longer time domain (ca. 10 ms) is used). Trace A – absorbance profile with the mixture N₂O/O₂/N₂ (N₂O = 2.28 Torr, 5.0% O₂/N₂ mixture, total pressure 1 bar) in the reactor (between the two internal windows). Trace B – "blank" experiment, the flow of N₂O is turned off, only O₂/N₂ mixture is pumped through the reactor.



Figure 2.5 In situ actinometry based on the ozone formation.

The residual absorbance is due to the photolysis of molecular oxygen inside the reactor and between the external and internal windows flushed with the O_2/N_2 mixture, as well as in the air outside the reactor where the photolysis beam and the monitoring beam overlap. The difference in the absorbances, ΔA , is used to calculate the concentration of ozone formed due to the photolysis of N₂O. The photon fluence *F* (photons cm⁻²) is then calculated as:

$$F = \frac{\Delta A}{\sigma_{03} \cdot l \cdot 0.985 \cdot \sigma_{N20} [N_2 O]}$$
(2.1)

where $\sigma_{03} = (1.148\pm0.034)\times10^{-17}$ cm²molecule⁻¹ is the ozone absorption cross section at 253.6 nm;⁶² l = 10.13 cm is the length of the reactor (the distance between the two internal windows), and $\sigma_{N20} = (8.77\pm0.44)\times10^{-20}$ cm²molecule⁻¹ is the N₂O absorption cross section at 193.3 nm⁶² (all at 298 K and 1 bar). All actinometry measurements are performed at pressure 1 bar and ambient temperature, where all required cross-sections are accurately known.The relaxation of O(¹D) to the ground state oxygen atoms O(³P) is almost complete (0.985).

Usually, two such determinations are performed – before and after a series of measurements. Simultaneously, the readout of the pyroelectric detector measuring laser pulse energy after passing the reactor (Figure 2.1) is recorded. The readout of the pyroelectric detector in the kinetic measurements is used then to introduce proper corrections for the drift of the laser energy during the series of experiments.

CHAPTER 3

ABSORPTION CROSS SECTIONS MEASUREMENTS

3.1 N₂O Absorption Cross-Sections at 193.3 nm

The absorption cross-section of N_2O at 193.3 nm is pressure and temperature dependent. The cross-sections at 193.3 nm are measured directly using ArF laser light and an energy meter at 1, 10, 30 and 100 bar (Figure 3.1). The cross-section of N_2O increases with temperature (almost linearly); the slope slightly increases with pressure (Figure 3.1). At each pressure, the temperature dependences of the cross-section are fitted by second order polynomials:

$$\sigma_{\rm N2O}/10^{-20} \,\,{\rm cm}^2 {\rm molecule}^{-1} = a_0 + a_1({\rm T/K} - 298) + a_2({\rm T/K} - 298)^2 \tag{3.1.}$$

The coefficients of the polynomial are listed in Table 3.1. This representation of the absorption cross-sections is used in the data processing in all studies. The dependences on temperature are almost linear, and linear fits with two fitting parameters are almost indistinguishable from linear fits forced through zero at zero temperature. In addition, assuming linear pressure dependence of the slope, the fit results in the following expression:

He pressure / bar	a ₀	a ₁	a ₂
1	8.15	2.74×10^{-2}	0
3	8.27	2.79×10^{-2}	2.15×10^{-6}
10	8.71	2.97×10^{-2}	9.68x10 ⁻⁶
30	8.45	2.83×10^{-2}	0
100	9.54	2.17×10^{-2}	25.9x10 ⁻⁶

Table 3.1 Polynomial Coefficients for the Absorption Cross-Section of N_2O as a Function of Temperature and Pressure (He) (Equation 3.1)

$$\sigma_{193.3}(N_2O)/10^{-22} \text{ cm}^2 \text{molecule}^{-1} = (2.865 + 0.00233 \text{ (p}_{He}/\text{bar})) (T/K)$$
 (3.2)

This formula reproduces the experimental data with the accuracy of \pm 5.4% at all pressures (\pm 1 st. dev.).



Figure 3.1 Absorption cross-section of N_2O at 193.3 nm measured directly using ArF excimer laser light at different temperatures and pressures. Filled circles – 1 bar, open circles – 10 bar, filled squares – 30 bar, and open squares – 100 bar. Buffer gas – He.

3.2 OH Apparent Absorption Cross Sections and the Spectroscopic Model

Determination of the rate constant of a second order reaction requires accurate determination of the absolute concentrations of free radicals. A multi-line light source (a DC powered H_2O/Ar discharge lamp) is used to record the hydroxyl temporal profiles. The apparent cross-sections of hydroxyl radical at different temperatures and pressures

are determined as follows. Mixtures of N₂O/H₂O/He are photolyzed at 193.3 nm using a uniform beam. The transient intensity profiles are recorded and processed according to the reaction mechanism. The initial concentrations of OH radicals are determined via the photon fluence, the absorption cross-sections of N₂O (measured separately), and the fraction of O(¹D) atoms converted to hydroxyl radical. The conversion efficiency $((1/2)[OH]_0/[O(^1D)]_0)$ is calculated based on a small mechanism of reactions involving O(¹D) atoms, and is always close to unity (ca. 84%) which ensures reliable determination of this parameter. The photon fluences are determined in additional *in situ* actinometry (Chapter 2) experiments via ozone yield in the N₂O/N₂/O₂ + 193.3 nm system at 1 bar and 298 K. In all experiments, the relative laser beam intensity is recorded with high accuracy using a pyroelectric sensor, due corrections for the laser power drift are introduced, when needed.

The emission spectrum of the hydroxyl lamp as well as the absorption spectrum of OH radical consists of a large number of narrow rotational lines grouped around 308 nm. The relative intensity as well as the widths of the absorption lines depend on the reactor temperature and pressure. Consequently, the apparent absorption cross-section of hydroxyl is also temperature and pressure dependent.

The relative intensities of the different rotational lines in the hydroxyl lamp as well as their shapes and widths depend upon the conditions inside the lamp discharge (gas temperature, pressure, composition, etc.). Therefore, care is taken to characterize and specify the lamp construction and operational parameters, and to keep them constant. It should be stressed, that for the current results on the apparent cross-section of hydroxyl to be transferrable to other studies, the lamp parameters should be closely followed.



Figure 3.2 Emission spectrum of the low pressure H_2O/Ar lamp. Solid line is the spectrum obtained from the lamp, dotted line is the simulation of the spectrum using LIFBASE program.

The apparent cross-sections of hydroxyl radical are shown in Figure 3.3 at different temperatures and pressures relevant to the current study. The experimental cross-sections are directly used in the data processing and the rate constant determinations. For the purposes of the data interpolation and the evaluation of the "curves of growth", a spectroscopic model is built (contributed by Dr. Evgeny N. Chesnokov). The solid lines in Figure 3.3 represent the model fit to the experimental data.

The spectroscopic model is defined by Dr. E. N. Chesnokov as follows. The emission spectrum of the hydroxyl lamp is a superposition of narrow lines:

$$I_E(\lambda) = \sum_i A_i \cdot f_D(\lambda - \lambda_i)$$
(3.3)

where λ_i and A_i are the line positions and the relative intensities in the OH emission spectrum, and $f_D(\lambda-\lambda_0)$ is the line shape function (assumed to be Gaussian with Doppler broadening only because of the low pressure in the hydroxyl lamp, 40 Torr). In the calculations, the 187 strongest lines are taken into account. The line intensities and the line shape functions are defined to be normalized:

$$\sum_{i} A_{i} = \int f_{D}(\lambda - \lambda_{i}) d\lambda = 1$$
(3.4)

The line positions λ_i and the relative line intensities A_i are calculated using the LIFBASE software.⁴² The calculations require the hydroxyl rotational temperature. To determine the rotational temperature of hydroxyl radicals in the lamp, the lamp emission spectra are recorded (with low resolution of 0.18 nm) and compared with the spectra simulated using LIFBASE. The rotational temperature determined in this way is 1300 K. Furthermore, the translational temperature (which enters the Doppler line width) of hydroxyl radicals in the lamp is assumed to be equal to the rotational, 1300 K.

The absorption spectrum of hydroxyl radicals is constructed in a similar manner:

$$I_A(\lambda) = \sum_i B_i \cdot f_V(\lambda - \lambda_i, T, p)$$
(3.5)

where B_i are the relative intensities of the absorption lines in the OH absorption spectrum, $f_V(\lambda-\lambda_i, T, p)$ is the Voigt line shape function which depends on the temperature and pressure in the reactor. The relative line intensities B_i are calculated for different temperatures using LIFBASE. The collision broadening parameter is assumed to be the same for all lines. The following temperature and pressure of the collision broadening parameter is assumed:

$$\Delta \lambda_{FWHM} = a \cdot p \cdot \left(300K/T\right)^b \tag{3.6}$$

In 3.6, $\Delta \lambda_{\text{FWHM}}$ is the full width at half maximum of the Lorentz shaped line, *a* and *b* are the empirical parameters. The apparent cross section is then calculated as:

$$\sigma_{OH}(T,P) = SF \cdot \int I_E(\lambda) I_A(\lambda) d\lambda$$
(3.7)

where SF is a scaling factor. The spectroscopic model has three fitting parameters: the scaling factor *SF*, the collision broadening constant *a* and the parameter *b* that determines the temperature dependence of the collision broadening according to Equation 3.6. The results of the model fits (with a = 0.0045 Å/bar and b = 0.3) are shown in Figure 3.3. The agreement of the model with the experimental data and the model is quite good, in particular taking into account the simplifying assumptions and the few fitting parameters of the model. The model reproduces perfectly the temperature dependences of the cross-sections. The absolute values deviate at elevated pressures about 7 - 9%, however, not in a systematic manner. Most probably these deviations reflect the experimental accuracy. It should be stressed that the hydroxyl lamp emission spectrum in this model is characterized by only one parameter, the rotational temperature, which is obtained from an independent measurement. The spectroscopic model is used only in the curves of growth calculations, direct experimental data are used in the kinetic data processing.

The empirical fitting parameter a is in good agreement with the average collisional line broadening for the $A^2\Sigma^+(\upsilon=0) \leftarrow X^2\Pi(\upsilon=0)$ transition at 293 K of 0.0047



Figure 3.3 Apparent absorption cross-section of hydroxyl radical as a function of temperature at different pressures. Solid lines represent fits by the spectroscopical model. The model: rotational temperature in the lamp 1300 K, 187 lines, emission lines Doppler broadened with translational temperature equal to the rotational temperature, FWHM/Å =0.01957 (at T=1300K), absorption lines with Voigt profile, collision broadening FWHM/Å=0.0045 (298 K/T)^{0.3}(p_{He}/bar).

3.2.1 The "Curves of Growth" for the Apparent Absorption Cross-Section of Hydroxyl Radical

Due to comparable widths of the absorption and emission lines as well as to the multitude of lines with different oscillator strengths the Beer-Lambert law is, in general, not applicable, and the apparent cross-sections can be used only for small absorptions that do not exceed about 1%. To evaluate the deviations from the Beer-Lambert law at larger absorptions, the spectroscopic model described above is used. The results of the calculations for 300 K and 0.01 – 100 bar pressure (He) are shown in Figure 3.4. In this figure, the ratio of the apparent cross-section, (defined as $\sigma_{app} = \ln(I_0/T)/([OH]I])$ and the apparent cross-section in the limit of very small absorptions, $\sigma_{app,0}$, is plotted vs. the apparent absorbance, $\ln(I_0/T)$. In case of the Lambert-Beer law applicability, these curves would be constant (unity) independent of the apparent absorption. This representation allows simple correction of the observed absorbance profiles. The deviations from Beer-Lambert law are linear with high accuracy when apparent absorbance do not exceed 15%, and can be expressed as:

$$A_{app}/A_{app,0} = \sigma_{app}/\sigma_{app,0} = 1 - S A_{app}$$
(3.8)

In Equation 3.8, S is the slope of the ratio $\sigma_{app}/\sigma_{app,0}$ plotted vs. A_{app} . This slope depends on temperature and pressure; the deviations are larger at low pressures. The values of the slope at 300 K are shown in Figure 3.4. The analysis shows, that for apparent absorbances < 0.5 % the correction does not exceed 1% at any pressure, and is neglected in the data processing. For maximum absorbances encountered in this work (<

6%), linear representation Equation 3.9 is very accurate (and can be used for absorbances up to 15%), and is used to correct the data:

$$A_{app,0} = [OH]\sigma_{app,0}l = A_{app}/(1-S A_{app})$$
(3.9)

It is also apparent from Figure 3.4 that for absorbances 30 - 50%, the deviations from the Beer-Lambert law are large, by a factor of two or higher. Without proper corrections, it leads to apparently longer decay profiles which can lead to gross underestimation of the rate constants (by a factor or two or even higher, especially at low pressures).



Figure 3.4 Reduced "Curves of Growth" for hydroxyl radical for different bath gas pressures at T = 300 K. The ratio of the apparent cross-section and the apparent cross-section in the limit of zero concentrations, $\sigma_{OH,app}/\sigma_{OH,0}$, is plotted vs. the apparent absorbance A_{app} (with the base e, $A_{app} = \ln(I_0/I)$). Linear approximation of the dependences is accurate for $A_{app} < 0.15$ (better than 0.25%).



Figure 3.5 The initial slopes, S, of the dependences of $\sigma_{OH,app}/\sigma_{OH,0}$ vs. the apparent absorbance (A_{app} = ln(I₀/I)) at different pressures at 300 K. The linear correction $\sigma_{OH,app}/\sigma_{OH,0} = 1 - S A_{app}$ is applicable at A_{app} < 0.15. The numerical values of the slopes are listed within the plot.

The slopes S from Equation 3.9 obtained using linear regression over the 0 - 15% range of the apparent absorbances are listed in Table 3.2 for the temperature grid used in this study.

T / K	0.01 bar	0.1 bar	1 bar	3 bar	10 bar	30 bar	100 bar
298	2.01	1.98	1.56	1.29	1.00	0.89	0.76
354	1.64	1.62	1.29	1.07	0.84	0.75	0.65
414	1.29	1.27	1.04	0.86	0.68	0.62	0.55
555	0.87	0.86	0.73	0.61	0.48	0.45	0.40
626	0.73	0.72	0.62	0.52	0.42	0.39	0.36
714	0.60	0.60	0.53	0.44	0.35	0.33	0.31
769	0.55	0.54	0.48	0.41	0.33	0.31	0.29
834	0.49	0.49	0.44	0.38	0.30	0.28	0.26

Table 3.2 The Slopes of the Dependences of $\sigma_{OH,app}/\sigma_{OH,0}$ vs. the Apparent Absorbance $(A_{app} = \ln(I_0/I))$ at Different Pressures and Temperatures The Linear Regression $\sigma_{OH,app}/\sigma_{OH,0} = 1 - S A_{app}$ is used over the Range $0 < A_{app} < 0.15$

3.3 Acetone Absorption Cross-Sections at 193.3 nm

To measure the absorption cross sections of acetone as a function of temperature and pressure, acetone-water solutions with the mole fractions of acetone in the 0.02 - 0.04 ranges are used. The solutions are degassed using freeze – pump - thaw cycles. Acetone - water solution are supplied to the reactor using a precision digital syringe pump (Harvard PHD 4400), the flow rate is varied from 10 μ L/min at 1 bar to 0.2 μ L/min at 100 bar. The flow rate of helium is 900 - 3,600 sccm. Light from an ArF excimer laser (GAM Laser) at 193.3 nm is used to measure the absorbance.

The intensity of the laser light passed through the cell is measured with and without the acetone/water mixture entering the reactor using a pyroelectric sensor. The

reference light intensity is provided by measuring the intensity of blue fluorescence from a quartz plate installed before the entrance of the reactor. The fluorescence light is passed through the spectrograph and measured by a photomultiplier tube (PMT). This allowed significant reduction of the measurement errors associated with the fluctuation of laser pulse energy.

Table 3.3 Absorption Cross-Sections of Acetone $(\sigma_{193.3}(acetone) / 1x10^{-18} \text{ cm}^2\text{molecule}^{-1})$ at 193.3 nm at Different Temperatures and Pressures, Measured using Laser Light at 193.3 nm. Errors are One Standard Deviation

p / bar	1 bar	3 bar	10 bar	30 bar	100 bar
T / K					
291				5.07 ± 0.04	7.93 ± 0.04
296	3.34 ± 0.04	3.68 ± 0.04	4.19 ± 0.04		
414	4.47 ± 0.04	4.81 ± 0.04	5.13 ± 0.04	5.66 ± 0.04	7.75 ± 0.04
555	5.34 ± 0.04	5.71 ± 0.04	6.08 ± 0.04	5.99 ± 0.04	7.64 ± 0.04
626	5.55 ± 0.04	5.95 ± 0.04	6.49 ± 0.04	6.31 ± 0.04	7.06 ± 0.04
714	5.94 ± 0.04	6.38 ± 0.04	6.41 ± 0.04	6.15 ± 0.04	6.76 ± 0.04

The cross-sections measured using laser light are confirmed in the study of the broadening of the acetone absorption using xenon arc lamp and ICCD camera. UV spectra of acetone at different temperatures and pressures are measured.

The ICCD camera couple with spectrograph is employed to measure the change in the UV spectrum in the presence and in the absence of acetone in the reactor at different conditions. The absorption cross sections of acetone are plotted in Figure 3.6 and listed in Table 3.3.



Figure 3.6 Absorption cross-sections of acetone at 193.3 nm as a function of temperature at different pressures. Open circles: 1 bar, filled circles: 3 bar, open triangles filled up: 10 bar, open squares: 30 bar, and stars: 100 bar (He)

CHAPTER 4

 $OH + OH \rightarrow Products$

4.1 Introduction

Hydroxyl radical plays a central role both in atmospheric ¹⁻⁷ and in combustion ⁸⁻⁹ ¹⁰⁻ ¹⁴chemistry. This is the one of the reasons for numerous studies of the kinetics and mechanisms of gas phase reactions of this radical.¹⁵⁻¹⁷ Due to high reactivity of this radical, its concentrations in typical systems are low, and the self-reaction 1 plays only a minor role:

$$OH + OH \rightarrow H_2O + O$$
(1a)
$$\rightarrow H_2O_2$$
(1b)

However, this reaction is very important in the laboratory kinetic studies of hydroxyl radicals, where the concentrations should be sufficiently high to provide accurate monitoring of the radical decay. This reaction not only provides an additional sink for the radical, but also initiates a sequence of secondary, highly undesirable reactions of oxygen and hydrogen atoms, formed in channel 1a and subsequent reactions 2 and 3:

$$O + OH \rightarrow O_2 + H$$
 (2a)

$$\rightarrow$$
 HO₂ (2b)

 $H + OH \rightarrow H_2 + O$ (3a)

$$\rightarrow$$
 H₂O (3b

In addition, reaction 1 is one of the simplest radical-radical reactions, where both the singlet and triplet states play comparable roles.¹⁸⁻²⁴ It is generally accepted that reaction 1a proceeds on the triplet PES, and is buffer gas pressure independent.^{18,19,25,26} Reaction 1b is assumed to proceed on the singlet PES, and is pressure dependent, as other recombination reactions.^{22,24} It should be noted, that the two major interfering reactions, 2 and 3, also have pressure independent and pressure dependent components, which further complicates experimental studies of the kinetics of hydroxyl radical reactions.

There have been numerous experimental studies of reaction 1. Kaufman and Del Greco used fast discharge flow system with OH detection using absorption spectroscopy.⁴⁵⁻⁴⁶ An additional stoichiometric factor of 3/2 is involved in the data interpretation, due to subsequent fast reaction of the reaction product, oxygen atom, with hydroxyl radical (reaction 2). The derived rate constant at 300 K is 1.3×10^{-12} cm³molecule⁻¹s⁻¹ (actually, the reported value is 2.5×10^{-12} cm³molecule⁻¹s⁻¹, the value is recalculated with the correct account of the stoichiometric number⁴⁷). Caldwell and Back⁴⁸ evaluated the relative importance of channels 1a and 1b based on the measured yields of H₂ and O₂ from flash photolysis of H₂O vapor over a range of energy, water vapor pressure, and pressure of added inert gases (He, Ar, Xe, N₂). Dixon-Lewis et al. used quantitative ESR spectroscopy in combination with a fast flow system to study reaction 1 at ca. 1 Torr.⁴⁹ NO was used as a paramagnetic calibration gas.

$$H + NO_2 \rightarrow OH + NO$$
 (4)

As in the previous study,⁴⁵ fast reaction 4 was used to produce OH radicals. The rate constant at 300 K is 2.6×10^{-12} cm³molecule⁻¹s⁻¹. Wilson and O'Donovan used mass-spectrometry in combination with the fast discharge flow tube.⁵⁰ The rate constant obtained, 2.1×10^{-12} cm³molecule⁻¹s⁻¹, is somewhat lower than that obtained in the previous study.³² Breen and Glass reported 0.84×10^{-12} cm³molecule⁻¹s⁻¹ using ESR detection,⁵¹ significantly lower than in all previous measurements. The discrepancy was assigned to the non-inclusion of the hydroxyl wall loss reaction in the reaction mechanism in previous studies, which in this study was too high (124 s⁻¹). Mulcahy and Smith⁵² performed mass-spectrometric study of the products of the primary and secondary reactions of the species generated in reaction 4, and relative determination of the rate constant of reaction 1 at pressures below 1 Torr. The rate constant is 1.83×10^{-12} cm³molecule⁻¹s⁻¹. McKenzie et al. reported 2.2×10^{-12} cm³molecule⁻¹s⁻¹,⁵³ ESR was used as a detection technique.

Another ESR study at room temperature by Westenberg and DeHaas⁵⁴ with careful accounting of the wall loss resulted in 2.3×10^{-12} cm³molecule⁻¹s⁻¹. Clyne and Down used resonance fluorescence for OH detection.⁵⁵ The room temperature rate constant is 1.7×10^{-12} cm³molecule⁻¹s⁻¹. Farquharson and Smith used discharge flow-resonance fluorescence, to yield 1.7×10^{-12} cm³molecule⁻¹s⁻¹.⁵⁶ All fast flow tube studies were performed at low (Torr range) pressures combined with different OH detection techniques, and all relied upon the same source of hydroxyl radicals, reaction 4.

Trainor and Von Rosenberg employed flash photolysis of water vapor to generate OH radical, with time-resolved monitoring by UV absorption.⁵⁷ The reported value is 2.1×10^{-12} cm³molecule⁻¹s⁻¹ at room temperature. All single room temperature low

pressure measurements resulted in the rate constant of reaction 1 (channel 1a) within the range $(0.84 - 2.6) \times 10^{-12} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

Temperature dependence in the low temperature range of reaction 1a is a subject of some controversy. Wagner and Zellner used flash photolysis of H₂O combined with resonance absorption of OH to measure rate constant of reaction 1 in the range 250-580 K.⁵⁸ They found weak positive temperature dependence with the activation energy of ca. 2 kJ mol⁻¹. The room temperature rate constant is 1.42×10^{-12} cm³molecule⁻¹s⁻¹. Subsequently, Zellner et al.⁵⁹ extended the study to measure pressure fall-off in reaction 1 over a sub-atmospheric pressure range (26 - 1100 mbar) at 253, 298, and 353 K.

On the other hand, Bedjanian et al., using discharge flow combined with massspectrometric detection obtained slightly negative temperature dependence in the range 233 to 360 K at 1 Torr of He.⁴⁷ The apparent activation energy obtained is -1.7 kJ mol⁻¹, the room temperature rate constant obtained is 1.44×10^{-12} cm³molecule⁻¹s⁻¹. Both the room temperature value and the negative temperature dependence of Bedjanian et al. are currently accepted in the IUPAC recommendation.¹⁵ Sun and Li, using the discharge flow coupled with mass spectrometry and resonance fluorescence method measured the rate constant of reaction 1 in the temperature range 220 - 320 K at 1 Torr.⁶⁰ The rate constant for the reaction at 298 K is determined to be 1.20×10^{-12} cm³molecule⁻¹s⁻¹, negatively dependent on temperature with the apparent activation energy of - 3.7 kJ mol⁻¹. Most recently Bahng and Macdonald re-measured the rate constant of reaction 1 using laser photolysis – transient IR absorption in the temperature range at low bath gas pressures in the range 293 - 373 K.²⁷ They confirmed the negative temperature dependence of k_{1a}. however, their room temperature rate constant is on the high side of the previous measurements, 2.7×10^{-12} cm³molecule⁻¹s⁻¹.

There have been studies of reaction 1 over extended pressure ranges.^{28,61} Forster et al.⁶¹ used laser photolysis combined with saturated laser induced fluorescence of OH. Experiments were performed between 1 and 150 bar of the bath gas helium allowed for falloff extrapolations to the high pressure limit of the recombination reaction 1b. The high pressure limit rate constant at ambient temperature for reaction 1b is evaluated as $2.2 \times 10^{-11} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. The low pressure extrapolation of the fall-off curve (combined with the previous literature data) resulted in $k_{1a} = 1.9 \times 10^{-12} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. In the subsequent study²⁸ the measurements were extended on the 200 - 700 K temperature range. In their study, at four elevated temperatures the rate constants of reaction 1 were measured in single pressure points of ca. 85 - 90 bar.

Reaction 1a has been studied at high temperatures using shock tubes. Ernst et al.⁶² used thermal decomposition of HNO₃ as a source of OH radicals, and resonance UV absorption to monitor the radical decay over the temperature range 1200 - 1800 K. Wooldridge et al. also used thermal decomposition of HNO₃ as a source of OH, but narrow laser line absorption to monitor OH at 306.7 nm.⁶³ The experiments were conducted over the temperature range 1050 - 2380 K and the pressure range 0.18 - 0.60 atm. Both these studies resulted in positive temperature dependence with the apparent activation energy of 20 - 22 kJ mol⁻¹. Sutherland et al. derived the rate constant of reaction 1 based on the directly measured rate constant of the reverse reaction, $O(^{3}P) + H_{2}O$, and the reaction thermochemistry.⁶⁴ The absolute value of the rate constant

determined in this way is in good agreement with the data of Wooldridge et al., with a less positive temperature dependence (ca. 9 kJ mol⁻¹).

Reaction 1 was extensively studied theoretically.¹⁸⁻²⁵ Harding and Wagner¹⁸ performed calculations using variational transition state theory on ab initio MCSCF electronic potential energy surfaces that correlate reactants with products. After the barrier scaling to match the experiment at room temperature, agreement with the experiment was obtained over the full temperature range, including a sharp upward curvature above 1000 K. The excited state surface was shown to be important in this curvature, contributing over 35% of the rate constant at higher temperatures. For the reverse direction, it was argued that the H₂O + O measured rates are about a factor of two too large, although this difference could be largely accounted for by uncertainty in the equilibrium constant.

The long-range interaction potentials between two OH radicals were characterized using ab initio multireference CI calculations.²⁵ There are four singlet surfaces correlating with ground-state OH radicals. These states strongly interact, which results in a complex reaction path for addition. At very long separations ($r_{0-0} > 0.8$ nm) where the four states are nearly degenerate, the electrostatic dipole-dipole interaction dominates. At intermediate distances (r_{0-0} of 0.3 - 0.6 nm) hydrogen bond provides the major attractive force. At short distances ($r_{0-0} < 0.25$ nm) covalent bonding is important. In this region only one singlet surface remains attractive.

Karkach and Osherov¹⁹ investigated stationary points on the H_2O_2 triplet potential energy surface. The transition states and minimum energy structures on the lowest triplet H_2O_2 potential surface were analyzed. Several energetically possible reaction channels were evaluated using the transition state theory. Kuhn et al.²⁰ performed calculations of the electronic ground state potential energy surface of hydrogen peroxide by two different ab initio techniques. Braunstein et al.²³ calculated global potential energy surfaces for the three lowest triplet states in O+H₂O collisions and performed classical trajectory calculations for the reverse reaction 1a (O(³P)+H₂O(X¹A₁) \rightarrow OH(X²Π)+OH(X²Π)). Computed rate constants are in accord with the measurements in the 1000 - 2400 K temperature range.⁴⁹

Braunstein et al.²³ applied simplified statistical adiabatic channel theory to calculate specific rate constants, product quantum state distributions, and the rate constant for the reaction HOOH \rightarrow 2 OH. Troe and Ushakov²⁴ used statistical adiabatic channel model combined with classical trajectory calculations for the dissociation/recombination dynamics of hydrogen peroxide. Specific rate constants k(E,J), thermal rate constants k in the high pressure limit, as well as the lifetime distributions are determined. The calculated thermal high pressure rate constants for HO recombination is in reasonable agreement with the experimental data⁴⁴ and is represented by $k_{1h inf} = (0.376 (298 \text{ K/T})^{0.47} + 0.013 (\text{T}/298 \text{ K})^{0.74}) 10^{-10} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ over the range 60 - 1500 K.

Sellevåg et al.⁶⁵ investigated the ground-state potential energy hypersurface of the reaction by means of high-level ab initio methods. Variable reactions coordinate transition-state theory, classical trajectory simulations, and a two-transition-state model was used to calculate the rate constant in the high pressure limit. A two-dimensional master equation is used to characterize the pressure falloff of reaction 1 and to calculate

the low-pressure limiting rate coefficient. The results are in good agreement with the study of Troe and Ushakov.²⁴

Despite the large number of experimental and theoretical studies of reaction 1, there are still remaining issues that require attention. Recently, Troe presented an extended analysis of the dissociation – recombination kinetics of H_2O_2 .²⁶ The analysis of the pressure fall-off is consistent with the accepted value of the rate constant $k_{1a} =$ 1.45×10^{-12} at 298 K. However, the most recent direct measurements of Bahng and Macdonald ²⁷ are in significant, almost a factor of two, disagreement with this value (2.7×10^{-12}) . The experimental high pressure data that are used to create the pressure falloff curves for k_{1b} at elevated temperatures are sparse.⁴⁵

In addition, the turning point in the temperature dependence of the disproportionation channel 1a, which is expected from the combination of the low temperature and high temperature shock tube studies is never observed in a single experimental study. In the study of the reaction of methyl radicals with hydroxyl over extended temperature and pressure ranges the kinetic data for reaction 1 on an extended temperature and pressure grid is required. These reasons are the motivations for the current study of the OH+OH reaction.

4.2 Experimental

The experimental part consists of two sections. In the first section, the rate constant of overall reaction 1 is addressed and in the second section, investigation of Channel 1a is described. The experimental approach in both studies is based on excimer laser photolysis coupled to UV-vis transient absorption spectroscopy and a high-pressure flow system. The details of the experimental set-up and the design of the flow reactor are

presence of water at 193.3 nm (ArF excimer laser):

$$N_2O$$
 + $hv (193 \text{ nm}) \rightarrow O(^1D) + N_2$ (5a)

$$\rightarrow N(^{4}S) + NO(^{2}\Pi)$$
 (5b)

$$O(^{1}D) + H_{2}O \rightarrow 2OH(v=0,1)$$
 (6a)

$$\rightarrow$$
 O(³P) + H₂O (6b)

$$\rightarrow H_2 + O_2 \tag{6c}$$

The quantum yield of the major channel 5a is unity within 1%, the minor channel 5b is less than 0.8%.⁶⁶ The fraction of vibrationally excited hydroxyl radicals OH(v=1) formed in the reaction of O(¹D) + H₂O (reaction 4a) is 22 – 30% ⁶⁷⁻⁷⁰ A Fraction of O(¹D) formed in photolysis of N₂O reacts with N₂O:

$$O(^{1}D) + N_{2}O \rightarrow NO + NO$$
 (7a)

$$\Theta_2 + N_2 (7b)$$

$$\Rightarrow O(^{3}P) + N_{2}O \qquad (7c)$$

$$O + O_2 \rightarrow O_3 \tag{8}$$

In measurement of the total rate constant of reaction 1, the kinetics of hydroxyl radical decay is monitored by absorption in the UV (multiline at ca. 308 nm) using a low pressure Ar/H_2O DC voltage discharge lamp (Chapter 2). Helium is used as the bath gas in all measurements. The measurements are performed over the 1 - 100 bar pressure and 25 - 561 °C temperature range. In the second section, the disproportionation channel of

the self-reaction of hydroxyl radicals (reaction 1a), is studied over the 298 - 414 K temperature and 3 - 10 bar pressure ranges (bath gas He). To distinguish channel 1a from the recombination channel 1b, $OH + OH \rightarrow H_2O_2$ (1b), time resolved trapping of oxygen atoms, produced in channel 1a, is used. The ozone produced in the reaction of oxygen atoms (reaction 8) with molecular oxygen is measured using strong UV absorption at 253.6 nm. This allows circumventing experimental difficulties associated with the kinetic measurement of the self-reaction of hydroxyl radicals at low pressures, required for suppression of the recombination channel 1b. Provided that the trapping reaction ensures efficient conversion of oxygen atoms to ozone molecules, and the absolute concentration of hydroxyl radical is known, the approach provides reliable discrimination of the two channels in reaction 1 and independent determination of the rate constant of the disproportionation channel 1a.

To make the reaction of oxygen atoms with molecular oxygen (reaction 8) sufficiently fast to ensure efficient trapping of oxygen atoms, elevated pressures of the bath gas (3 - 10 bar) are required. The measurements are performed over the 25 - 141 °C temperature range and at pressure 3 and 10 bar. The upper temperature of the study is limited by the thermal stability of ozone. The 4-window configuration in the reactor to precisely define the path length of the reaction zone is employed.⁷¹ The gas flow rates are controlled by high pressure mass flow controllers (Brooks, model 5850). The total flow rates of the reactant mixtures with helium are in the range 20 - 75 sccs. Additional flush flows to the cold reactor windows are in the range 4.5 - 10 sccs. Liquid H₂O is injected into the high pressure system using a precision syringe pump (Harvard Apparatus, Model

PHD 4400). The flow of liquid H₂O in the range 6 - 18 μ L/min is flowing from the syringe pump through a capillary tube to an evaporator kept at 90 °C.

The concentrations of the precursors used are $(4.6 - 6.4) \times 10^{16}$ molecule cm⁻³ [N₂O], $(3.7 - 11.0) \times 10^{17}$ [H₂O] and $(3.9 - 5.5) \times 10^{17}$ [O₂]. The photolysis photon fluence inside the reactor is varied in the range $(4.6 - 8.9) \times 10^{15}$ photons cm⁻²pulse⁻¹. The initial concentrations of hydroxyl radicals are in the range $(4.7 - 8.4) \times 10^{13}$ molecule cm⁻³. The repetition rate of the laser was adequate to ensure complete replacement of the gas mixture in the reactor between the pulses (0.3 - 2 Hz depending on pressure).

Reagents. Helium used in the experiments is BIP®Helium from Airgas with 99.9999% purity with reduced oxygen content (<10 ppb). UHP oxygen is obtained from Matheson TriGas (99.98% purity). Certified mixture of N₂O in He (2.50%, accuracy \pm 2%) obtained from Matheson Tri-Gas is used. Purified water (Milli-Q®) with TOC less than 5 ppb) is degassed by freeze-pump-thaw cycles and used as a reactant supplied by a syringe pump (Harvard Apparatus PHD 4400) as well as in the low pressure H₂O/Ar discharge hydroxyl monitoring lamp. UHP Argon obtained from Matheson TriGas (99.999%) purity) is used in the H₂O/Ar lamp.

4.3 Result and Discussion

4.3.1 OH+OH \rightarrow products

Transient absorption profiles of OH are measured at 41 combinations of temperature and pressure. Examples of measured temporal profiles of absorption at 308 nm are shown in Figure 4.1. To determine the rate constant of reaction 1, a detailed reaction mechanism (Table 4.1) is used to model and fit the experimental profiles. Absorption profiles are fitted by numerical solutions of a system of differential equations corresponding to the

reaction mechanism using SCIENTIST software.⁷²



Figure 4.1 Sample temporal profiles of OH decay. Pressure – 100 bar (He). Temperatures – 714, 555 and 301 K, from upper to lower curves. Solid lines – fits by the reaction mechanism (see text). The residual is shown for 555 K. $[N_2O] = 8.93 \times 10^{16}$, 11.4×10^{16} , and 16.6×10^{16} molecule cm⁻³ for 714, 555 and 301 K, respectively.

The reaction mechanism used in the fits includes reactions 1 - 7 and additional reactions (Table 4.1). Reactions involving excited $O(^{1}D)$ atoms are completed within 50 nsec and are treated separately. The products of these reactions served as the initial reactants for the residual reactions in the mechanism occurring on the much longer (0.1 - 100 ms) time scale.

The UV absorption cross-sections and the rate constants, used in the fits, are either measured in the current work (*e.g.*, absorption of N_2O , absorption cross-section of

OH) or are taken from the literature. The reaction mechanisms as well as the kinetic parameters used in the model are listed in Table 4.1. The decay of hydroxyl radicals is almost entirely controlled by reaction 1 and subsequent fast reaction of oxygen atoms with hydroxyl radicals, reaction 2. Several other reactions also contribute into the decay rate. The rest of the reactions are considered to elucidate their potential role. Several of them play only a marginal (if any) role under the conditions of the current study. In addition to hydroxyl production in reaction 6a, formation of OH radicals and H atoms in direct photolysis of water at 193.3 nm with the cross-section $(1.51\pm0.15)\times10^{-21}$ cm²molecule⁻¹ (measured in this work) is also taken into account. Correction for the diffusion controlled wall loss of hydroxyl radical is performed by introducing first order rate constant $k_{w,OH} = 5.784 D_{OH-He}/R^2$, where the diffusion coefficient is expressed as $D_{OH-He} = D_{OH-He,296} (T/296 \text{ K}).^{1.6}$ The room temperature value of $D_{OH-He,296} = 662$ Torr $cm^2s^{-1} = 0.883$ bar cm^2s^{-1} is taken from the literature.⁶⁴ With the reactor insert internal radius of 0.38 cm, at the highest temperature 834 K this results in $k_{w,OH} = 183$, 61 and 18 s^{-1} for 1, 3 and 10 bar, respectively. The largest contribution of the wall loss to the decay rate of ca. 25% is at the highest temperature, 834 K, and the lowest pressure, 1 bar. At ambient temperature and 1 bar pressure the contribution is ca. 5%. At higher pressures the contribution is inversely proportionally smaller, and is completely negligible above 10 bar.

The results are listed in Table 4.2 and shown in Figure 4.2. The reaction mechanism which is used to fit the experimental profiles is shown in Table 4.1. In the last column of the table, the maximum reaction rate relative to the initial total rate of reaction

1 is given for a specific set of experimental conditions (low temperature 301 K and high pressure 100 bar).

Reaction	Reactants	Products	Rate Constant ^a Reference		Comments	Relative
						Rate ^b
1a	OH+OH	$O + H_2O$	$7.1 \times 10^{-13} \exp(210 \text{ K/T})$	Ref ⁴⁷	forT < 415	0.11
Iu	0111011	0 1 1120	,	1001.	K.Troe fit	0.11
					above 414 K	
1b		H_2O_2	fitted, this work		fitting	0.89
					parameter	
2a	OH+O	$O_2 + H$	$2.4 \times 10^{-11} \exp(110/T)$	Ref. ¹⁶		9.0x10 ⁻³
2b		HO ₂	$[M] 1.6 x 10^{-31} (T/298)^{-2.6}$	As for		9.4x10 ⁻²
				reaction		
				3b		
3a	OH+H	$H_2 + O$	$6.86 \times 10^{-14} (T/298)^{2.8} \exp(-1950/T)$	Ref. ⁷³		1.8x10 ⁻⁹
3h		H	$[M] 1.6 \times 10^{-31} (T/298)^{-2.6}$	Ref ⁷⁴		6.2×10^{-3}
6a	$O(^{1}D)+H_{2}$	OH+OH	$1.7 \times 10^{-10} \exp(36/T)$	Ref ⁷⁵		0.2410
6h	0	$O(^{3}\mathbf{D}) + \mathbf{H}$	<0.002 k	Dof ⁷⁶	Naglastad	
00	-	$0(P)+\Pi_2$ 0	$< 0.003 \text{ k}_{6a}$	Kel.	neglected	
6с		$H_2 + O_2$	$2.2 \cdot 10^{-12}$	Ref. ¹⁶		
7a	$O(^{1}D)+N_{2}$	NO + NO	8.37x10 ⁻¹¹	Branching	Average of	
	0			ratio of	three	
				0.62	studies, ⁷⁶⁻⁷⁸ as	
				Ref. ¹⁶	in Ref. ⁴³	
7b		$O_2 + N_2$	5.13x10 ⁻¹¹	Ref. ¹⁶		
7c		$O(^{3}P)+N_{2}$	1.3×10^{-12}	Ref. ⁷⁵	$k_{7c}/k_{7} < 0.01,^{75}$	
8	$OH \pm NO$	HONO	$k_{-1} = 6.0 \times 10^{-31} (T/300)^{-2.5}$	Ref ⁷⁹	Ref ⁷⁹	0.28
0		nono	$k_{8,inf} = 3.3 \times 10^{-11} (T/300)^{-0.}$	Kel.	Ker.	0.20
9	OH+HO ₂	H ₂ O+O ₂	4.8x10 ⁻¹¹ exp(250/T)	Ref. ⁸⁰		4.5×10^{-2}
10	HO ₂ + NO	OH+NO ₂	$4.0 \times 10^{-12} \exp(223/T)$	Ref. ⁸¹		4.5x10 ⁻⁴
11	OH+H ₂ O ₂	$H_2O +$	$2.9 \times 10^{-12} \exp(-109/T)$	Ref. ⁸²		1.3×10^{-2}
		HO_2				
12	$O + HO_2$	O ₂ +OH	$2.70 \times 10^{-11} \exp(224/T)$	Ref. ¹⁶		9.4x10 ⁻⁵
13	$O + H_2O_2$	$OH + HO_2$	$1.40 \times 10^{-12} \exp(-2000/T)$	Ref. ¹⁶		4.7×10^{-8}
14a	$H + HO_2$	$H_2 + O_2$	$7.11 \times 10^{-11} \exp(-710/T)$	Ref. ⁸³		1.2×10^{-6}
14b		2 OH	$2.81 \times 10^{-10} \exp(-440/T)$	Ref. ⁸³		1.1×10^{-5}
14c]	$H_2O + O$	$5.00 \times 10^{-11} \exp(-866/T)$	Ref. ⁸³		4.9x10 ⁻⁷
14d		$O(^{1}D)$	$3.29 \times 10^{-12} (T/298)^{1.55}$	Ref. ⁸⁴		7.5×10^{-7}
		$+H_2O$	exp(81/T)			

 Table 4.1 Reaction Mechanism used for Fitting of the Experimental Profiles

^aRate constants and concentrations units based on molecule, cm³ and sec.

.

^bMaximum reaction rate relative to the maximum (initial) total rate of reaction 1, for the experimental conditions at 301 K, 100 bar, $[OH]_0 = 1.50 \times 10^{14}$ molecule cm⁻³ (other relevant concentrations are listed in Table 4.2.

The relative importance of the reactions depends on temperature and pressure. However, the relative rates listed in the table provide some insight on the importance of specific reactions for the mechanism. It is quite clear, that at elevated pressures a number of recombination type reactions (such as 7b, 8b, 10) cannot be discarded, while being negligible at low pressures.

A completely negligible reaction of hydrogen atoms with hydroxyl radicals (reaction 3a) at 300 K might play a minor role at the highest temperatures of this study. Another feature should be stressed – at high pressures the reaction of recombination of hydroxyls with NO (reaction 8) plays significant role, and cannot be discarded. For the reaction of recombination of OH with O forming HO₂ (reaction 2b) no kinetic data is available. If the rate constant of this reaction is set as the rate constant of reaction 3b, then the simulations show a significant role of this reaction at elevated temperatures.

The impact of the reaction mechanism on the fitted rate constant is evaluated at 1 bar and 298 K, 100 bar and 301 K, and 100 bar and 714 K. The profiles are fitted with the complete mechanism listed in Table 4.1, the reduced mechanism of reactions 1a, 1b, 2a, and 8, and the limiting mechanism of reactions 1a, 1b, and 2a only. The maximum impact is found for 100 bar and 714 K. Using the reduced mechanism leads to the increase of k_1 by 17%, and additional removal of reaction 8 leads to additional increase of the rate constant by 17%. At 100 bar and 301 K, the increments are 7% and 12%, respectively. Finally, at 1 bar and 298 K, the increments are 7% and 6%, respectively

p / bar (He)	T / K	$[N_2O]_0/10^{16 a}$	[H ₂ O] ₀ / 10 ¹⁷	[O(³ P)] ₀ / 10 ¹¹	[NO] ₀ / 10 ¹²	Number density / 10 ²⁰	Photon fluence / 10 ¹⁵ photon cm ⁻²	[OH] ₀ / 10 ¹³	$\frac{k_{1} / 10^{-12}}{cm^{3}}$ molecule ⁻ $^{1}s^{-1}$
1.16	296	9.49	3.87	2.21	5.40	0.243	4.75	6.74	6.17
1.16	298	11.0	4.47	1.63	3.97	0.281	3.11	4.95	6.24
1.16	354	7.87	3.21	2.21	5.41	0.202	4.76	6.74	3.45
1.16	354	9.17	3.74	1.58	3.87	0.235	3.04	4.83	4.15
1.16	414	6.73	2.75	2.13	5.20	0.173	4.63	6.49	2.59
1.16	414	7.85	3.19	1.57	3.85	0.201	3.03	4.8	2.72
1.16	555	5.03	2.05	2.22	5.43	0.129	5.00	6.77	1.75
1.16	555	5.87	2.39	1.62	3.97	0.150	3.13	4.95	1.73
1.16	626	4.46	1.81	2.18	5.32	0.114	4.78	6.64	1.56
1.16	714	3.91	1.59	2.22	5.44	0.100	4.86	6.78	1.48
1.16	714	4.56	1.86	1.59	3.89	0.117	3.08	4.86	1.73
1.11	769	3.62	1.69	2.77	7.99	0.103	6.07	8.45	2.18
1.11	834	3.34	1.56	4.40	12.67	0.096	9.64	13.4	1.77
1.01	834	3.04	1.43	2.87	8.23	0.087	6.93	8.73	1.98
1.01	834	3.04	1.43	2.78	7.98	0.087	6.73	8.47	1.98
1.01	834	3.01	1.41	3.40	9.77	0.087	8.33	10.4	2.01
2.91	298	15.1	7.05	2.55	5.76	0.706	3.08	6.87	8.79
2.91	354	1.16	5.89	2.05	5.08	0.589	3.08	5.36	6.51
2.91	414	9.92	5.05	2.13	6.14	0.505	2.68	6.06	5.79
2.91	555	7.41	3.77	2.06	5.94	0.377	2.65	6.10	2.48
2.91	626	6.58	3.34	2.06	5.92	0.335	2.61	6.10	2.32
2.91	714	5.76	2.93	3.03	8.19	0.293	2.47	6.12	2.72
2.91	769	5.82	2.72	6.28	18.0	0.272	8.33	19.1	2.18
2.91	834	5.37	2.51	5.52	15.9	0.251	7.33	16.8	1.87
2.91	834	4.96	2.32	4.01	11.5	0.253	5.78	12.24	1.90
2.91	834	4.96	2.32	4.07	0.26	0.253	5.87	12.39	1.90
9.84	297	11.5	3.01	3.14	9.30	2.40	0.80	9.14	12.0
9.84	534 414	9.40	3.00	2.14	9.04	1.99	6.80	9.23	6.32
9.04	414 555	6.03	2.37	3.14	9.37	1.71	6.00	9.15	2.71
9.04	626	5.34	1.92	3.29	9.82	1.27	6.89	9.39	3.71
9.04	714	J.34 4.67	1.71	3.20	9.70	0.000	6.04	9.40	3.30
9.84	769	4.07	1.49	5.29	20.0	0.990	0.94	9.39	3.12
9.84	834	3.83	1.41	5.04	18.2	0.922	8 19	13.45	2 72
9.84	834	3.78	1.30	3.5	12.6	0.858	5 74	9 59	2.72
9.84	834	3.78	1.29	3.6	12.9	0.858	5.90	9.85	2.32
9.84	834	3.83	1.30	4.22	15.2	0.858	6.83	11.5	2.81
29.9	294	14.7	6.76	1.95	5.76	7.29	2.64	5.91	18.7
29.9	354	12.3	5.58	1.99	5.85	5.99	2.69	5.97	12.9
29.9	414	10.5	4.79	1.88	5.54	5.14	2.55	5.63	10.1
29.9	555	7.89	3.59	1.87	5.47	3.85	2.53	5.53	4.89
29.9	626	6.99	3.18	1.87	5.49	3.42	2.54	5.53	5.25
29.9	714	6.12	2.79	2.00	5.86	2.99	2.71	5.90	5.70
29.9	769	5.64	4.27	7.29	14.4	2.80	8.19	25.3	4.44
101	301	16.6	3.88	5.40	19.0	22.9	4.54	15.0	18.2
101	414	15.2	3.12	6.29	26.1	16.8	3.03	16.4	16.2
101	555	11.4	2.34	6.73	27.9	12.6	2.84	17.6	9.54
101	626	10.1	2.09	6.87	28.5	11.26	2.83	17.9	6.60
101	714	8.92	1.84	6.96	28.9	9.89	2.83	18.2	5.96

Table 4.2 The Experimental Conditions and the Rate Constants for Reaction 1 ($k_1 = k_{1a}+k_{1b}$)

^aAll concentrations in molecule cm⁻³



Figure 4.2 Pressure dependence of the rate constant of reaction 1 at different temperatures. Solid lines – fits using Troe expression (see text). Open squares - 299 K, solid circles - 354 K, open triangles up - 414 K, solid triangles down - 555 K, open diamonds - 626 K, solid triangles left - 714 K, open triangles right - 769 K, solid stars - 834 K.

At high temperatures, the reverse reaction -1b, reaction of dissociation of hydrogen peroxide, might become important. Estimates based on the equilibrium constant for reaction 1b show, however, that the rate constant of this reaction at the highest temperature of this study does not exceed 14 sec⁻¹, and can be neglected.

There are two major sources of errors in the measured rate constants. The first one is the uncertainty of the absolute concentrations of hydroxyl radicals. The accuracy of the N₂O cross-sections (ca. $\pm 6\%$), the O₃ determination (ca. $\pm 4\%$), and the uncertainties introduced by the ozone formation model (ca. $\pm 3\%$) contribute to the accuracy of the determination of the absolute concentrations of OH radical. The second source is the statistical error in the decay parameters of OH radicals ($\pm 12\%$ in the worst cases at 100 bar, negligible at 1 bar) and the uncertainties associated with the reaction model (estimated as $\pm 15\%$). Assuming that all these sources are independent, an overall estimate of the accuracy of the rate constants is $\pm 21\%$.

The rate constants measured in this work are in good agreement with the previous study at elevated pressures.^{28, 61} Direct comparison of data from Ref.^{28, 61} with the results of this study in a figure is not possible, because neither the temperature nor pressure grids coincide. The deviation at the lowest temperature of this study, 298 K, is ca. 8 - 16% at low pressures (1 - 3 bar), where the rate constants of this study are larger, and maximal at 100 bar, where the rate constant of this study is ca. 18% smaller than the mean value from the previous works.^{28, 61} However, this is still within the combined uncertainty of the two studies.

As it was pointed out by Troe,²⁶ irrespective of the impressive efforts and the temperature and pressure ranges covered in the experimental studies of reaction 1, the experimental data alone still is not sufficient to derive the reaction parameters, such as the low pressure limit and the high pressure limit rate constants, the fall-off broadening, etc. The case is further complicated by the presence of the pressure independent channel 1a as well as the controversial data on the kinetic parameters of this channel. Therefore,

the following strategy in the data processing is chosen. At the lowest temperature of this study (ambient), the pressure fall-off curve approaches the high pressure limit, and $k_{1b,inf}$ is used as a fitting parameter. However, at higher temperatures no reliable determination of the high pressure limit is possible, and theoretically derived temperature dependence of $k_{1b,inf}$ as well as the value of the temperature independent broadening factor ⁸⁵ ²⁶ are accepted:

$$k_{1b,inf}(T) = k_{1b,inf,298K} (T/298)^{-0.5}$$
 (4.1)

$$F_c = 0.37$$
 (4.2)

The situation is further complicated by the ambiguity of the literature data on the pressure independent channel 1a. The value recommended by IUPAC¹⁵ (based on the discharge flow study of Bedjanian et al.⁴⁷) is ca. factor of two lower than the most recent value of Bahng and Macdonald ²⁷ by laser photolysis – time resolved IR absorption. Except for one study all other temperature studies agree on the negative temperature dependence of reaction 1a near the ambient temperature, although in a pretty narrow temperature range.

Therefore, for the data processing over the temperature range 295 - 414 K we accepted the room temperature value as well as the negative temperature dependence for k_{1a} from the IUPAC recommendation, and used the values of the rate constant as fixed parameters. At higher temperatures, however, the information on k_{1a} is completely unavailable. Fortunately, at higher temperatures the pressure fall-off is strongly shifted towards high pressures, and the low pressure extrapolation becomes reliable. Therefore, at temperatures above 414 K the rate constant k_{1a} is used as a fitting parameter.

The data are fitted using Troe expression:⁸⁶
$$k_{1} = k_{1a} + k_{1b,\infty} \left(\frac{[M]/[M]_{c}}{1 + [M]/[M]_{c}}\right) 10^{\log(F_{c})/[1 + (\frac{\log([M]/[M]_{c})}{N})^{2}]}$$
(4.3)

$$[M] = p N_A / (ZRT) \tag{4.4}$$

$$N = 0.75 - 1.27 \log(F_c) \tag{4.5}$$

where $k_{1b,inf}$ is the rate constant of reaction 1b in the high-pressure limit, [M] is the number density of the gas, [M]_c is the density in the "center" of the pressure fall-off curve. The temperature independent broadening factor (F_c = 0.37) is accepted according to Ref.²⁶. Small non-ideality of helium (4.7% at 298 K and 100 bar) is taken into account via the compression factor Z (T, p):

$$Z = 1 + 0.00047 \text{ (p/bar)}(298 \text{ K/T})$$
(4.6)

The fits are shown in Figure 4.2 as solid lines. The center pressure of the fall-off curves p_c (defined as the pressure of ideal gas at the center number density $[M]_c$) as a function of temperature is shown in Figure 4.3.



Figure 4.3 Fitting parameter p_c (the center of the fall-off curves) plotted vs. temperature in the log-log coordinates. Filled squares are obtained with the recommended values: $k_{1b,inf} \sim T^n$, n = -0.5, Fc = 0.37. The resulting power dependence is: $p_c/bar = 1.12$ (T/300 K)^{4.0} The error bars are the standard deviations of the fits. Impact of the fall-off parameters variation: open triangles tip down, n = -0.75, Fc = 0.37; open triangles tip up, n = 0, Fc = 0.37; filled stars, n = -0.5, Fc = 0.74; open stars: n = -0.5, Fc = 0.19. Crosses are from the fits based on the Bahng and Macdonald data²⁷ using n = -0.5, Fc = 0.37.

$$p_c = ([M]_c/N_A)RT$$
(4.7)

Figure 4.4 shows the rate constant of the pressure independent channel 1a obtained from the fits at higher temperatures combined with the literature data^{29 47} at low temperatures. The rate constants are also summarized in Table 4.2.



Figure 4.4 Rate constant of the pressure independent channel 1a (OH + OH \rightarrow H₂O + O). Low temperature data (dotted squares) are taken from the literature.⁴⁷ Filled squares are obtained by short extrapolation of the data obtained in this work under the assumption $k_{1b,inf} \sim T^n$, n = -0.5, Fc = 0.37. Error bars are the standard deviations of the fits. Model variation: open triangles tip down, n = -0.75, Fc = 0.37; open triangles tip up - $k_{1b,inf}$ is temperature independent (n = 0, Fc = 0.37); filled stars, n = -0.5, Fc = 0.74; open stars: n = -0.5, Fc = 0.19. Crosses are the extrapolated k_{1a} based on the Bahng and Macdonald data²⁷ using the same approach (n = -0.5, Fc = 0.37).

The stability of the extrapolated rate constant of channel 1a to the parameters of the theoretical fall-off curve (parameter n in the temperature dependence $k_{1b,inf} \sim T^n$ and F_c) as well as to the low temperature data (where a significant discrepancy exists) is verified. The theoretically derived n = -0.5 and $F_c = 0.37$ are chosen as the base

parameters. First, it is determined that the derived values of k_{1a} at $T \ge 555$ K are almost independent of the accepted low temperature data. Using Bahng and Macdonald data²⁷ instead of the Bedjanian et al. data ⁴⁷ (which differ by a factor of 1.8) results in almost indistinguishable results (the difference is ca. 2%). Then at fixed $F_c = 0.37$ the parameter n in the temperature dependence is varied as n = 0, -0.5 and -0.75. In addition, at n = -0.5, F_c is varied by a factor of two, $F_c = 0.19$ and 0.74. All results are shown in Figure 4.4.

The results indicate that the extrapolated k_{1a} is quite stable with respect to the parameters variation. The most unstable value is at 555 K, where the center of the pressure fall-off curve is only ca. 13 bar. At higher temperatures the pressure fall-off shifts towards higher pressures (reaching ca. 70 bar at 834 K) making the low-pressure data of this work much closer to the low pressure limit, and, hence, the extrapolation much more reliable. At the highest temperature of this study, 834 K, the extracted rate constant k_{1a} is almost independent of the variations of the fall-off curve parameters outlined above (< ±6%). It should be stressed, that the positive temperature dependence above 555 K is confirmed for all evaluated combination of the fall-off parameters.

Moreover, the positive temperature dependence is already apparent from the data at 1 bar – the rate constant at 834 K is ca. 25 - 30% larger than at 626 and 714 K (Table 4.2). Together with the literature data, the results of this study indicate a turning point in the temperature dependence of k_{1a} in the range of 400 - 550 K. The positive temperature dependence of k_{1a} measured in this work in the 555 - 834 K temperature range correlates well with the shock tube studies of Sutherland et al.⁶⁴ and Wooldridge et al.⁶³ (Figure 4.5).



Figure 4.5 Rate constant of the disproportionation channel 1a compared to other experimental studies. Filled circle – Bahng and Macdonald, ²⁷ open triangle up – Bedjanian et al., ⁴⁷ horizontal bar – Wooldridge et al., ⁶³ vertical bar – Sutherland et al., ⁶⁴ cross – Wagner and Zellner, ⁵⁸ crossed circle – Farquharson and Smith, ⁵⁶ double cross – Ernst and Wagner, ⁶² star – Trainor and Von Rosenberg, ⁵⁷ filled pentagon – Del Greco and Kaufman, ⁴⁵ filled triangles – Sun and Li. ⁶⁰ Open dotted circles- this work.

The center pressure p_c as a function of temperature is shown in Figure 4.4 in the log-log

coordinates. The temperature dependence determined from the linear regression is:

$$p_c/bar = (1.12\pm0.40) (T/300)^{4.0\pm0.4}$$
 (4.8)

Therefore, for the low pressure limit rate constant $k_{1b,0}$:

$$k_{1b,0} = ([He]/[M]_c) k_{1b,inf} = [He] k_{1b,inf} RT/(p_c N_A) = [He] k_{1b,inf} 3.70 \times 10^{-20} (T/300)^{-3.0}$$
 (4.9)

The expression for the high-pressure rate constant $k_{1b, inf}$ with the 298 K value obtained from the fit and presumed temperature dependence of T^{-0.5} is:

$$k_{1b,inf} = (2.4 \pm 0.6) \times 10^{-11} (T/300)^{-0.5} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$
 (4.10)

At 300 K, this is 37% lower than that recommended by Troe, $3.8 \times 10^{-11} (T/300)^{-0.5}$.²⁶ and 28% lower than that calculated by Sellevag et al.⁶⁵, 3.34×10^{-11} cm³molecule⁻¹s⁻¹. Combination of equation 4.10 with 4.11 leads to the low pressure limit rate constant k_{1b,0}:

$$k_{1b,0} = (9.0 \pm 2.2) \times 10^{-31} (T/300)^{-3.5 \pm 0.5}$$
[He] cm³molecule⁻¹s⁻¹ (4.11)

At 300 K, Equation 4.11 gives factor of 2.2 higher value compared to that recommended by Troe and slightly stronger negative temperature dependence (the recommended low pressure limit rate constant with He as the bath gas is $4 \times 10^{-31} (T/300)^{-3.2}$.²⁶). Theoretical work of Sellevag et al.⁶⁵ predicts 3.22×10^{-31} cm³molecule⁻¹s⁻¹ for k_{1b,0} at 300 K, which is factor of 2.8 lower. Predicted temperature dependence over the temperature range of 300 – 800 K is k_{1b,0} ~ T^{-3.56}, in excellent agreement with our results (Figure 4.4).

The results also indicate existence of the turning point in the temperature dependence for the disproportionation channel 1a (Figure 4.5). The data suggest that the negative temperature dependence of the rate constant k_{1a} at low temperatures should switch to positive temperature dependence somewhere between 400 and 550 K. Such a

behavior is actually expected based on the comparison of low temperature low pressure data with the shock tube results, where positive temperature dependence of k_{1a} is observed (Figure 4.5). In the shock tube studies, due to much higher temperatures, the pressure fall-off region is shifted to much higher pressures, so that any observed rate constant must be assigned to channel 1a. Besides, the equilibrium in reaction 1b is shifted towards the reactants at T > 1000 K at realistic initial concentrations of OH, and hydrogen peroxide cannot be formed. Figure 4.5 shows that the temperature dependence of k_{1a} obtained in this study is consistent with other low and high temperature data.

Negative temperature dependence which switches to positive at ca. 500 K is quite typical for reactions with "negative barriers", i.e. reactions with the bottleneck on the potential energy surface having the "ground state" energy below the reactants ground state energy.⁸⁷ In reaction 1a in favorable orientations hydrogen bond is formed.^{18, 25, 65} Formation of a relatively long range and relatively strong attractive interaction results in a "negative barrier" condition by bringing the barrier below the reactants level.⁶⁵

4.2.2 OH +OH \rightarrow H₂O + O

The accurate values of the rate constant of reaction 1 as well as the branching ratios for the disproportionation channel 1a and recombination channel 1b are important. The disproportionation channel 1a is assumed to be pressure independent; however, the recombination channel is pressure dependent over the wide range of temperatures and pressures. In addition, the study detailed in previous section revealed a peculiar V-shaped temperature dependence of the rate constant of channel 1a, with negative temperature dependence at ambient and slightly elevated temperatures and positive at temperatures higher ca. 450 K.⁷¹

The temperature dependence of channel 1a near ambient temperature was a subject of minor controversy in the past. A positive temperature dependence is measured in one experimental study,⁷¹ although subsequent studies resulted in a small negative temperature dependences.⁶⁰ It appears that the negative temperature dependence of the disproportionation channel 1a is well established.

The absolute value of the rate constant of the disproportionation channel 1a is a subject of controversy. Bedjanian et al.⁴⁷, using discharge flow combined with mass-spectrometric detection obtained a slightly negative temperature dependence in the range 233 to 360 K at 1 Torr of He.⁴⁷ The measured apparent activation energy is -1.7 kJ mol⁻¹, and the room temperature rate constant 1.43×10^{-12} cm³molecule⁻¹s⁻¹. Both the room temperature value of 1.43×10^{-12} cm³molecule⁻¹s⁻¹ and the negative temperature dependence of Bedjanian et al. are currently accepted in the IUPAC recommendations.¹⁵ However, the most recent direct measurements of Bahng and Macdonald²⁷ using laser pulsed photolysis coupled to time-resolved IR absorption are in significant, almost a factor of two, disagreement with this value (2.7×10^{-12} cm³molecule⁻¹s⁻¹).

This section describes the effort to resolve this discrepancy using time resolved trapping of oxygen atoms, produced in channel 1a. The ozone produced in the reaction of oxygen atoms (reaction 8) with molecular oxygen is measured using strong UV absorption at 253.7 nm. This allows circumventing experimental difficulties associated with the kinetic measurement of self-reaction of hydroxyl radicals at low pressures, required for suppression of the recombination channel 1b.



Figure 4.6 Sample ozone and OH (insert) absorption profiles (2.91 bar, 295 K, $[N_2O] = 5 \times 10^{16}$, $[O_2] = 4.13 \times 10^{17}$, $[OH] = 4.12 \times 10^{13}$, $[H_2O] = 3.73 \times 10^{17}$ molecule cm⁻³). Solid line – fit by the reaction mechanism yielding $k_{1a}=1.12 \times 10^{-12}$. Dotted line is simulation using $k_{1a}=2.7 \times 10^{-12}$ cm³molecule⁻¹s⁻¹ (Ref.²⁷). The original curve taken with the time resolution of 3 usec and 2 usec/point is smoothed by a 50 points adjacent averaging.

Transient absorption profiles of OH and O_3 are measured at 23 combinations of temperature and pressure. Sample absorption temporal profiles at 308 nm and 253.7 nm are shown in Figure 4.6. The reaction mechanism and kinetic parameters used in the fit of

Reaction	Reactants	Products	Rate Constant ^a	Reference	Comment
					s
1a	OH+OH	$O + H_2O$	This work		
1b		HaQa	$[M] (1.4 \pm 0.5) \times 10^{-30} (T/300)^{-4.6 \pm 0.5}$	Ref ⁷¹	
2a	OH+O	$\Omega_2 + H$	$2.4 \times 10^{-11} \exp(110/T)$	Ref ¹⁶	
2h	01110	HO_2	$[M] 1.6x10^{-31} (T/298)^{-2.6}$	As for	
		1102		reaction	
				4b	
3	O+O ₂	O ₃	$[M] 3.4 \times 10^{-34} (T/300)^{-1.2}$	Ref. ⁸⁸	
4a	H+O ₂	OH+O	1.62x10 ⁻¹⁰ exp(-62110/8.31447/T)	Ref. ⁸⁹	
4b		HO ₂	$[M] 5.4 x 10^{-32} (T/298)^{-1.8}$		
5	HO ₂ +O ₂	OH+O ₃	0		Neglected
6	OH+O ₃	HO ₂ +O ₂	1.7x10 ⁻¹² exp(-7820/8.31447/T)	Ref. ¹⁶	
7	O+O ₃	O_2+O_2	8.0x10 ⁻¹² exp(-17130/8.31447/T)	Ref. ¹⁶	
8	H+O ₃	OH+O ₂	1.4x10 ⁻¹⁰ exp(3990/8.31447/T)	Ref. ⁹⁰	
9	HO ₂ +O ₃	OH+O ₂ +O ₂	$1.97 \times 10^{-16} \times (T/298)^{4.57} \exp(5760/8.31447/T)$	Ref. ¹⁶	
10a	OH+H	$H_2 + O$	$6.86 \times 10^{-14} (T/298)^{2.8} \exp(-1950/T)$	Ref. ⁷³	
10b	$O(^{1}D)+H_{2}O$	H ₂ O	$[M] 1.6x10^{-31} (T/298)^{-2.6}$	Ref. ⁷⁴	
11a	-	OH+OH	$1.7 \times 10^{-10} \exp(36/T)$	Ref. ⁷⁵	
11b		$O(^{3}P)+H_{2}O$	<0.003 k _{6a}	Ref. ⁷⁶	Neglected
11c	-	$H_2 + O_2$	2.2×10^{-12}	Ref. ¹⁶	
12a	$O(^{1}D)+N_{2}O$	NO + NO	8.37x10 ⁻¹¹	Branching	k _{total}
	· · · -			ratio of	average of
				0.62	three
				Ref. ¹⁶	studies, ⁷⁷⁻
					^{78, 90} Ref. ²⁷
12b		$O_2 + N_2$	5.13x10 ⁻¹¹	Branching	
				ratio of	
				0.38	
10		$O^{(3)}$	1.2.10-12	Ref. ⁷⁵	1 /1 .0
12c		$O(^{\circ}P)+N_{2}O$	1.3.10	Ref. ¹⁵	$K_{12c}/K_{12} < 0.$
					1.3×10^{-12}
13	$OH \pm NO$	HONO	$k_{\rm res} = -6.0 \text{ v} 10^{-31} (\text{T}/300)^{-2.5}$	R of ⁷⁹	F: fit of
15	OII + NO	nono	$k_{13,0} = 0.0 \times 10^{-11} (T/300)^{-0.3}$	KCI.	the data
			$F_{13,inf} = 0.60 \exp(91/T)$		from
					Ref. ⁷⁹
14	OH+HO ₂	H ₂ O+O ₂	$4.8 \times 10^{-11} \exp(250/T)$	Ref. ⁸⁰	
15	$HO_2 + NO$	OH+NO ₂	$4.0 \times 10^{-12} \exp(223/T)$	Ref. ⁷²	
16	OH+H ₂ O ₂	$H_2O + HO_2$	$2.9 \times 10^{-12} \exp(-109/\mathrm{T})$	Ref. ⁹¹	
17	$O + HO_2$	O ₂ +OH	$2.70 \times 10^{-11} \exp(224/T)$	Ref. ¹⁶	
18	$O + H_2O_2$	$OH + HO_2$	$1.40 \times 10^{-12} \exp(-2000/\mathrm{T})$	Ref. ¹⁶	
19a	$H + HO_2$	$H_2 + O_2$	$7.11 \times 10^{-11} \exp(-710/T)$	Ref. ⁹²	
19b		2 OH	$2.81 \times 10^{-10} \exp(-440/T)$	Ref. ⁹²	
19c		$H_2O + O$	$5x10^{-11}exp(-866/T)$	Ref. ⁹²	
19d		$O(^{1}D)$	$3.29 \times 10^{-12} (T/298)^{1.55} \exp(81/T)$	Ref. ⁹³	
		$+H_2O$			

 Table 4.3 Reaction Mechanism used for Fitting the Experimental Profiles

The decay of hydroxyl radicals is almost entirely controlled by reactions 1 and subsequent reaction of oxygen atoms with hydroxyl radicals. Several other reactions also contribute to the decay rate. At elevated pressures, reaction 2 is sufficiently fast to compete with the reaction of oxygen atoms with OH radicals and to provide efficient trapping of oxygen atoms. Typical trapping efficiencies in these experiments are in the range 0.73 - 0.85. The experimental absorption profiles of OH are converted into the hydroxyl concentration profiles based on the measured absorption cross-sections (Chapter 3). Then the hydroxyl concentration profiles are fitted using a smooth function with sufficient number of parameters to provide adequate fitting flexibility. These profiles are then explicitly used in the ozone absorption profiles fitting using the SCIENTIST software,⁷² where unknown rate constant k_{1a} is used as a fitting parameter.

The results are listed in Table 4.4 and shown in Figure 4.7. Sample simulated profile with the rate constant k_{1a} set as 2.7×10^{-12} (Ref.²⁷) is shown in Figure 4.6. It is apparent that the ozone yield cannot be reproduced with the rate constant of Bahng and Macdonald (Ref.²⁷), on the other hand, the results of current measurements are in perfect agreement with the study of Bedjanian et al.⁴⁷ (Figure 4.7). The highest temperature of the current study is limited by the equilibrium constant of the ozone formation reaction. At temperatures above ca. 450 K dissociation of ozone becomes important, and O-atoms cannot be efficiently converted to ozone.

The results of this study, combined with the results of Bedjanian et al.,⁴⁷ the results of previous measurements (Section 4.2.1) at elevated temperatures,⁷¹ and the latest shock tube measurements of Wooldridge et al.⁶³ are shown in Figure 4.8.



Figure 4.7 Rate constant of the disproportionation channel 1a compared to other experimental studies. Empty circles – Bahng and Macdonald.²⁷ Dotted line - Bedjanian et al.⁴⁷ Filled star - 3 bar and 10 bar; 295 K; filled circle - 10 bar, 354 K; filled square – 10 bar, 414 K; solid line – fit by the power dependence (see text) (this work). Each point is an average of several experiments from Table 4.4. The error bars are ± 2 st. dev. of the averaged values.

The results confirm the existence of the turning point in the temperature dependence of k_{1a} in the range 400 - 550 K.⁷¹ The V-shaped temperature dependence of k_{1a} based on combined current and previous studies in the temperature range of 233 – 2380 K is:

$$k_{1a} = (5.1 \exp(-T/190 \text{ K}) + 0.30(T/300 \text{ K})^{1.73}) \times 10^{-12} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$
(4.12)

p / bar	T / K	$[N_2O]_0 \\ / \ 10^{16a}$	[H ₂ O] ₀ / 10 ¹⁷	$\frac{[O_{2]0}}{10^{17}}/$	[NO] / 10 ¹²	[H] / 10 ¹²	Photonfluence / 10 ¹⁵	[OH] / 10 ¹³	[O] / 10 ¹²	$k_{1a}/10^{-12} \text{ cm}^3$ molecule ⁻¹ c ⁻¹
2.91	295	5.0	3.73	4.13	2.91	4.04	7.17	4.83	6.85	1.71
2.91	295	5.0	3.73	4.13	2.87	3.99	7.08	4.77	6.76	1.52
2.91	295	5.0	3.73	4.13	2.88	3.95	7.01	4.73	6.69	1.20
9.88	296	6.39	4.44	5.47	4.36	5.33	7.95	6.69	1.05	1.36
9.88	295	6.41	4.45	5.49	4.55	5.38	8.0	6.97	1.09	1.07
9.88	295	6.41	4.45	5.49	4.48	5.29	7.86	6.85	1.07	1.36
9.88	295	6.41	4.45	5.49	4.37	5.17	7.68	6.69	1.05	1.60
9.88	354	5.28	11.0	4.52	1.69	1.26	7.86	8.43	4.68	1.37
9.88	354	5.28	11.0	4.52	1.66	1.24	7.45	8.30	4.60	1.57
9.88	354	5.30	3.68	4.54	4.69	4.71	8.61	7.10	10.7	1.12
9.88	354	5.30	3.68	4.54	4.50	4.68	8.42	6.81	10.5	1.14
9.88	354	5.30	3.68	4.54	4.59	4.68	6.61	5.46	8.48	1.09
9.88	354	5.30	3.68	4.54	4.69	4.71	6.62	5.46	8.49	1.06
9.88	354	5.30	3.68	4.54	4.50	4.68	6.55	5.40	8.40	1.17
9.88	414	4.55	9.49	3.90	1.48	9.35	6.52	7.12	3.89	1.09
9.88	414	4.55	9.49	3.90	1.46	9.47	6.61	7.21	3.94	1.09
9.88	414	4.55	9.49	3.90	1.46	9.36	6.53	7.12	3.89	1.05
9.88	414	4.55	9.49	3.90	1.46	9.35	6.50	7.11	3.89	1.08
9.88	414	4.55	9.49	3.90	1.46	9.36	6.53	7.12	3.89	1.05
9.88	414	4.57	3.17	3.91	4.02	3.54	7.38	6.03	9.30	1.16
9.88	414	4.57	3.17	3.91	3.77	3.32	6.92	5.66	8.73	1.17
9.88	414	4.57	3.17	3.91	3.72	3.28	6.84	5.59	8.62	1.13
9.88	414	4.55	9.49	3.90	1.08	6.94	4.84	5.28	2.88	0.858

 Table 4.4 Experimental Conditions and the Rate Constant for reaction 1a



Figure 4.8 Rate constant of channel 1a (OH + OH \rightarrow H₂O + O). Filled squares – this work, dotted circles – Bedjanian et al.,⁴⁷ filled stars – Sangwan et al.,⁷¹ empty stars – Wooldridge et al.⁶³. Solid line – expression 4.12.

In fact, pressure independence of the disproportionation channel 1a is an assumption, which is typically made for "simple metathesis" reactions. V-shaped temperature dependences are likely for reactions with so-called "negative barriers", when the ground state of the "transition state" (the bottleneck position on the PES) lies below the ground state of the reactants. For such reactions pressure dependence of the rate constant might be anticipated (Krasnoperov et al.,⁹⁴). However, noticeable pressure

dependence is expected at low temperatures and high pressures (>100 bar). In this study, no impact of pressure is found within the experimental scatter between 3 and 10 bar of the bath gas pressure.

4.3 Conclusions

The rate constant of reaction 1 measured over an extended temperature (295 - 834 K) and pressure (1 - 100 bar) ranges is used to parameterize the pressure fall-off in the recombination channel 1b as well as to obtain independent data on the pressure independent disproportionation channel 1a at T > 450 K. The minor deviation in the high pressure rate constant for reaction 1b (-37%) and a substantial (factor of 2.2) deviation of the low pressure limit rate constant from the recommended values are reported. The lowpressure extrapolations of the rate constant k₁ suggest the existence of the turning point in the temperature dependence of reaction 1a in the 400 - 550 K range. The Rate constant of reaction 1a is measured over the temperature range 295 - 414 K at pressure 3 and 10 bar. The channel 1a is isolated using conversion of oxygen atoms, produced in the reaction, to ozone. The rate constants are determined based on the time-resolved ozone yield using explicit OH concentration profiles. The results are consistent with the measurements of Bedjanian et al.⁴⁷ which are currently recommended by IUPAC), and do not support the most recent measurement of Bahng and Macdonald.²⁷ Measured in this work, the rate constant of reaction 1a at 298 K is: $k_{1a} = (1.39 \pm 0.20) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with the temperature dependence of the rate constant of $k_{1a} = (1.38 \pm 0.20) \times 10^{-12} (T/300)^{-0.73}$ in the temperature range 295 - 440 K.

CHAPTER 5

CH₃+OH→products

5.1 Introduction

Reaction of methyl radicals with hydroxyl radicals plays an important role in combustion chemistry.²⁹⁻³¹ This reaction is a multi-channel reaction which proceeds via an intermediate complex.²⁹⁻³¹ The energetically open reaction channels are:²⁹⁻³⁰

CH ₃	+	OH	\rightarrow	¹ CH ₂	+	H_2O	(1a)
			\rightarrow	CH ₃ OH			(1b)
			\rightarrow	CH ₃ O	+	Н	(1c)
			\rightarrow	CH ₂ OH	+	Н	(1d)
			\rightarrow	cis-HCOH	+	H ₂	(1e)
			\rightarrow	trans-HCOH	+	H_2	(1f)
			\rightarrow	CH ₂ O	+	H ₂	(1g)

As suggested in previous studies^{29, 95-97}, channels 1a and 1b are the main reaction channels. However, relative importance of the reaction channels is temperature and pressure dependent.³³ Fockenberg et al.⁹⁸ reported that although at ambient temperature channels 1a and 1b are the major reaction channels, the relative contributions of channels 1e and 1f at an elevated temperature (610 K) are comparable to 1a and 1b.⁹⁸ They used time-of-flight mass spectrometer connected to a tubular flow reactor. The experiments were performed at pressures of a few Torr (gas density 1.2×10^{17} molecule cm⁻³) in helium as a bath gas. The methyl and hydroxyl radicals were produced by an excimer laser photolysis (193.3 nm) of acetone and nitrous oxide in the presence of excess water or

hydrogen. At 300 K the observations are consistent with singlet methylene (${}^{1}CH_{2}$) and water as the main reaction products, with a small contribution of methanol formation (channel 1b). However, at about 610 K the formaldehyde isomers and methanol are formed with yields comparable to channel 1a.

Sworski et al.⁹⁹ studied reaction 1 using flash photolysis of water vapor. Methyl radicals were produced in subsequent reaction of OH with CH₄. Methyl radicals were monitored using transient UV absorption at 216 nm. The profiles were fitted based on a reaction mechanism that included several important reactions of OH, CH₃ and H species. The absolute rate constant reported is $(9.2 \pm 4.6) \times 10^{-11}$ cm³molecule⁻¹s⁻¹ at pressure 700 Torr and temperature 300 K.

Anastasi et al.¹⁰⁰ employed pulsed radiolysis coupled with transient UV absorption at 1 bar pressure and ambient temperature. They used abstraction of H-atoms from CH₄ and H₂O by fluorine atoms in Ar/SF₆/CH₄/H₂O mixtures to generate CH₃ and OH radicals, respectively. The relative initial concentrations of CH₃ and OH radicals were controlled by varying the H₂O and CH₄ concentration ratio in the mixture. Kinetics of CH₃ was observed at 216.4 nm. The rate constant reported in this study is (9.4 \pm 1.3)x10⁻¹¹ cm³ molecule⁻¹s⁻¹at 1 bar and ambient temperature, which is in good agreement with the rate constant reported by Sworski et al.⁹⁹

Similar approach was used by Fagerstrom et al.¹⁰¹⁻¹⁰² to study the pressure dependence of the rate constant for reaction 1. Both CH_3 and OH radicals were monitored by using transient UV absorption (at 216.4 nm and 308 nm, respectively). The experiments were performed over the temperature range of 200 - 500 K and the pressure range of 85 - 1000 mbar. The temperature dependent high pressure rate constant reported

is $k_{1,\infty} = (1.44 \pm 0.15) \times 10^{-10} \exp(300/K)^{0.1} \text{ cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$ in the temperature range 200 - 500 K and pressure range 85 - 1000 mbar.

Grotheer with coworkers^{95,103-106} investigated the CH₃ + OH reaction using flow reactor coupled with mass-spectrometry over the pressure range 0.65 - 9.1 mbar and temperature range 300 - 700 K. Both reactants along with some products were monitored by mass spectrometry, methyl radical profiles served as the major observable quantity. However, at elevated temperatures good fit was achieved only after accepting the high pressure limit rate constant of reaction 1 of 1.7×10^{-10} . At the highest temperature (700 K), the total rate constant is separated into the contributions from individual channels. The reaction channels to CH₃O + H (1c) and to CH₂OH + H (1d) are not detected. The overall rate constant is found to be pressure dependent with a high pressure association rate constant $k_{1b,\infty} = 1.7 \times 10^{-10} \text{ cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$, temperature independent over the temperature range used.

Hughes et al.¹⁰⁷ employed laser photolysis to study reaction 1 at 290 K and 7 - 700 Torr pressure range. In this study, excess of CH₃ relative to OH was used. Hydroxyl radicals were generated by photolysis of HNO₃ and monitored by laser induced fluorescence at 308 nm. CH₃ radicals were produced by photolysis of acetone and monitored by absorption at 216.36 nm. The pressure dependence of the rate constant was fitted using inverse Laplace transformation to obtain the microcanonical rate constant, which is incorporated in a master equation model. The rate constant determined in this study has a weak pressure dependence over the 7 - 700 Torr pressure range. The high pressure limit rate constant reported is $(7.6 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$.

Pereira et al.²⁹ measured the rate constants of the CH₃ + OH reaction using laser flash photolysis combined with laser induced fluorescence at temperatures 290, 473 and 700 K over the pressure range of 7.6 - 678 Torr. Photolysis of acetone and traces of water at 193 nm produced CH₃ and OH radicals simultaneously; concentration of CH₃ was kept in large excess of the OH concentration. Laser induced fluorescence was used for monitoring of OH radicals, while CH₃ radical was monitored by UV absorption at 216.4 nm. The data were analyzed using master equation and the inverse Laplace transform resulted in the high pressure limit rate constant $k_{1,\infty}$ = (8.0±0.3)x10⁻¹¹(T/300 K)^{-0.79±0.009} cm³molecule⁻¹s⁻¹. A moderate pressure dependence of the rate constant over the experimental (7.6 - 678 Torr) pressure range is observed, as well as a slightly negative temperature dependence in the range 298 - 710 K.

Deters et al.¹⁰⁸ studied reaction 1 at ambient temperature over the pressure range of 0.7 - 467 mbar using laser photolysis - transient absorption (45 - 467 mbar) and discharge flow - laser magnetic resonance techniques (0.7 - 4 mbar). At higher pressures, the pressure independence of the overall rate constant of reaction 1 was observed, while over the low pressure range the rate constant increased slightly with pressure and approached the high pressure value obtained from the laser flash photolysis with transient UV absorption spectrometry experiments. The branching ratio of channel 1a determined as 0.89 at pressure 1.3 mbar and 298 K.

Reaction 1 is also studied at high temperatures using shock tubes. Bott and Cohen¹⁰⁹ studied reaction 1 at 1200 K and 1 atm pressure. Thermal dissociation of tertbutyl hydroperoxide in the shock wave is used for simultaneous production of OH and CH_3 radicals. The decays of OH radicals were monitored by UV absorption at ca. 309 nm. The rate constant reported is $(1.8 \pm 0.50)x10^{-11}$ cm³molecule⁻¹s⁻¹ at 1 atm and 1200 K.

Krasnoperov and Michael¹¹⁰ used shock tube coupled with a multipass absorption cell to study the CH₃ + OH reaction and the thermal dissociation of CH₃OH. The rate constant obtained is 1.74×10^{-11} exp (915 K/T) over the temperature range 834 - 2383 K and pressure range of 50 - 940 Torr. Thermal decomposition of tert-butyl hydroperoxide, di-tert-butyl peroxide, methanol, and methyl iodide were used as pyrolytic precursors of hydroxyl and methyl radicals. Similar reflected shock tube study performed later using a White multipass absorption cell with 56 number of passes (total path length of 4.9 m) for monitoring of OH radical at 308 nm by Srinivasan et al.¹¹¹ resulted in the rate constant of $(1.3 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ in the 1000 - 1200 K temperature range, about a factor of three lower than that reported by Krasnoperov and Michael.¹¹⁰

Most recently, reaction 1 has been studied at high temperatures by Vasudevan et al.¹¹² using a shock tube. Azomethane and methyliodide used as a source of CH₃ radicals and tert-butyl hydroperoxide used as a source for OH radicals. The overall rate constant is measured in the temperature range of 1081 - 1426 K. The rate constant reported in this study (2.98x10⁻¹¹ at 1192 K) is in excellent agreement with the earlier study of Krasnoperov and Michael,¹¹⁰ and ca. factor of three higher than that reported by Srinivasan et al.¹¹¹

Reaction 1 is extensively studied theoretically.^{30,96,113-114} Jordan et al.¹¹⁴ performed canonical variational transition state (cVTS) theory calculations using an extended Gorin model. The calculated high pressure limit association rate constant is $1.72 \times 10^{-10} (T/300 \text{K})^{0.27} \text{ cm}^3$ molecule⁻¹s⁻¹ with a weak positive temperature dependence.

Xia et al.³⁰ characterized the potential energy surface of the CH₃OH system by ab initio molecular orbital theory calculations at the G2M level of theory. The rate constant for CH₃ + OH was calculated using variational RRKM theory and compared with the available experimental data. They concluded that the bimolecular reaction of CH₃ and OH, the total rate constant and the relative branching ratios of the ¹CH₂ + H₂O and H₂ + HCOH channels at lower pressures (P <5 Torr) could be reasonably accounted for by the theory. For the reaction of ¹CH₂ with H₂O, both the yield of CH₃ + OH and the total rate constant could also be satisfactorily predicted theoretically. The production of ³CH₂ + H₂O by the singlet to triplet surface crossing was neglected in the calculations. The predicted high pressure rate constant k_{1,∞}(298 K) = $2.2x10^{-10}$ cm³molecule⁻¹s⁻¹ with a small negative temperature dependence.

Ing et al.¹¹³ calculated pressure and temperature-dependent rate constant of reaction 1 using quantum RRK theory combined with the master equation analysis for the pressure falloff. They predicted the high pressure rate constant of 1.5×10^{-11} with a positive temperature dependence over the 300 - 2500 K temperature range. In a recent theoretical study, Jasper et al.⁹⁶ used microcanonical two state model to describe the association rate constant over a broad temperature range as well as the master equation simulations for the pressure dependence of the rate constant of reaction 1. They predicted that the reaction is close to the high pressure limit at 298 K at 1000 Torr, variation of the rate constant over the pressure range 200 - 1000 Torr is ca. 15%. The computed high pressure limit rate constant at ambient temperature (9.82x10⁻¹¹) agrees well with the rate constant reported by Sworski et al.⁹⁹ and Anastasi et al.¹⁰⁰

Despite the large number of experimental studies on the reaction of CH_3 with OH, there is no experimental data on the pressure dependence of this reaction at elevated pressures and temperatures. All previous experimental studies have been performed at low to moderate pressures (0.0006 - 5 bar). In addition, there is still significant discrepancy in the absolute rate constants as well as in the temperature dependence at ambient as well as elevated temperatures.

5.2 Experimental Set-up

The experimental set-up is described in detail in Chapter 2, therefore only brief description critical for the current experiment is given here. The approach is based on the excimer laser photolysis coupled to UV-vis transient absorption spectroscopy and to a high-pressure flow system. Helium is used as a bath gas in all experiments. The measurements are performed over the 1 - 100 bar pressure and 21 - 441 °C temperature ranges. Two UV - grade quartz windows (12.7 diameter, 9.5 mm thick) are sealed at the end of the reactor at ambient temperature outside the high-temperature zone using Viton O-rings. The pre-heated reactant mixture entered the reactor tube in the center and left through the two outlets located on two sides 5 cm away from the center but within the uniform temperature zone. Additional flows of the bath gas (He) entered the reactor near the windows to flush gas from the windows towards the outlets. Two additional thick (9.5 mm) quartz windows, separated by a stainless steel insert, are placed without sealing inside the reactor near the reactor outlets. This "four windows" configuration prevented penetration of the reactants out of the observation zone, provided precise definition of the observation zone within the uniform temperature region and allowed avoiding of windows sealing at elevated temperatures. The length of the insert determined the optical path in the zone of reactants of 10.13 cm. To achieve uniform concentration profiles across the reactor cross-section, the laser beam is formed using a spherical lens (f = +30 cm, the distance from the reactor center 82 cm) and a cylindrical lens (f = +30 cm, the distance from the reactor center 35 cm). The beam profile is measured by scanning with a small orifice diaphragm (ca. 0.5 mm) combined with an energy meter. The beam uniformity across the reactor cross-section is \pm 7.3% from the mean value. The gas flow rates are controlled by high pressure mass flow controllers (Brooks, model 5850). The total flow rates of the reactant mixtures with helium are in the range 360 - 4,500 sccm (standard cubic centimeters per minute). Additional flush flows to the cold reactor windows are in the range 270 - 600 sccm.

Acetone - water mixtures are carefully degassed before loading in the stainless steel syringe. The mole fraction of acetone in water is varied from 0.02 to 0.04. Acetone - water mixtures are injected into the evaporator of the high pressure flow system using a precision syringe pump (Harvard Apparatus, Model PHD 4400) through a capillary tube. The temperature of the evaporator is kept at 90 °C, it is observed that this approach produce steady and stable flows of acetone-water mixtures over the pressure range 1 - 100 bar. The flow rate of acetone-water mixtures is varied in the range of 0.5 - 10 μ L/min depending upon the reactor pressure and temperature. The concentrations of the precursors used: (0.4 - 1.7)x10¹⁷ molecule cm⁻³ for N₂O, (0.93 - 14.6)x10¹⁵ for CH₃COCH₃ and (1.4 - 7.0)x10¹⁷ for H₂O. The laser photon fluence inside the reactor is varied in the range (2.4 - 11)x10¹⁵ photons cm⁻² pulse⁻¹. The initial concentrations of hydroxyl radicals are in the range (5 - 22)x10¹³ molecule cm⁻³. The pressure range is 1 -

100 bar (He), the temperature range is 295 - 714 K. The highest temperature is limited by the thermal stability of the precursors. The concentrations of the radicals precursors are monitored downstream the reactor by an on-line quadrupole mass-spectrometer (Finnigan 4021) at m/z = 43, 44 for N₂O, m/z = 58 for acetone, relative to the signal of argon added to the mixture (0.001 of argon, m/z = 40).



Figure 5.1 Thermal stability of the precursors (N₂O and acetone). The precursors are measured downstream the reactor using an on-line quadrupole mass-spectrometer at m/z = 43, 44 for N₂O, m/z = 58 for acetone, relative to the signal of argon added to the mixture (0.001 of argon, m/z = 40). N₂O flow rate= 1.5 sccm, acetone = 0.033 sccm, total flowrate = 450 sccm, p = 1 bar (He). Open circles – N₂O, closed circles – acetone, filled stars – the signal of acetone when the flow of N₂O is closed. Note different MS sensitivities for acetone and N₂O.

Noticeable depletion of the radical precursors (acetone and nitrous oxide) is observed above 714 K, probably due to a heterogeneous reaction of these species on the preheating tubing and reactor walls. These experiments are illustrated in Figure 5.1. Separately, two reactants are stable over the whole accessible temperature range (295 – 834 K), however, when mixed together they react at temperatures above 714 K. The repetition rate of the laser is set to ensure complete replacement of the gas mixture in the reactor between the pulses (0.1 - 4 Hz depending upon the reactor pressure).

5.3 Results and Discussion

Transient absorption profiles of OH and CH_3 are measured at 46 combinations of temperatures and pressures (Table 5.1). Sample absorption temporal profiles at 308 and 216 nm are shown in Figure 5.2. To determine the rate constant of reaction 1, a reaction mechanism (Table 5.2) is used to model and to fit the experimental profiles. Absorption profiles are fitted by numerical solutions of a system of differential equations corresponding to the reaction mechanism using SCIENTIST software.¹¹⁵

The UV absorption cross-sections and the rate constants, used in the fits, are either measured in this study (absorption cross sections of acetone and CH₃) or are taken from the literature and from current studies (Chapter 3). The reaction mechanism and the kinetic parameters used in the model are listed in Table 5.2. The decay of OH and CH₃ radicals is almost entirely controlled by reaction 1 as well as self-reactions of these radicals (reactions 5 and 7). Several other reactions also contribute into the decay rate. At typical experimental conditions, total contribution of all other reactions into the rate constant of reaction 1 returned from the fits is about 1% at 1 bar both at ambient temperature and 714 K. At 100 bar the contribution is ca. 15% at ambient temperature and ca. 8% at 669 K. The rest of the reactions in the mechanism are considered to elucidate their potential role as well as to introduce small corrections. Several of them play only a marginal role (if any) under the conditions of the current study.

p/bar (He)	T/K	$[N_2O]_0/$ 10 ¹⁶	[H ₂ O] ₀ / 10 ¹⁷	[(CH ₃) ₂ CO] ₀ / 10 ¹⁵	Photonfluence/ 10^{15} photon	$[CH_3]_0/$ 10 ¹³	[NO] ₀ / 10 ¹²	[OH] ₀ / 10 ¹³	$k_1 / 10^{-11}$ /cm ³ molecule
~ /					cm ⁻²				- ¹ s ⁻¹
1.01	296	9.68	3.95	1.90	3.67	4.76	4.27	5.30	12.8
1.01	297	9.50	3.87	0.93	4.13	2.26	4.71	5.87	12.4
1.01	298	9.43	3.85	1.85	4.23	5.36	4.80	5.99	12.7
1.01	355	8.03	3.28	1.57	3.64	4.67	4.22	5.26	12.2
1.01	355	7.87	3.21	1.54	4.21	5.30	4.78	5.97	10.5
1.01	414	6.87	2.80	1.35	3.39	4.28	4.0	4.90	11.6
1.01	497	5.73	2.34	1.12	3.56	4.12	4.12	5.15	9.22
1.01	555	5.03	2.05	0.987	4.04	4.34	4.59	5.72	9.08
1.01	588	4.85	1.97	0.950	3.65	3.88	4.24	5.28	7.63
1.01	626	4.46	1.81	0.875	3.93	3.93	4.46	5.56	7.98
1.01	669	4.17	1.70	0.818	3.98	3.82	4.52	5.64	6.82
1.01	669	4.24	1.71	0.830	3.16	2.67	3.65	4.55	6.07
1.01	714	3.91	1.59	0.767	4.08	3.73	4.63	5.77	5.83
2.91	298	12.6	3.10	2.47	5.82	3.25	7.95	9.92	11.5
2.91	294	12.8	3.10	0.752	6.16	3.85	14.1	10.5	12.2
2.91	298	12.2	3.44	7.11	11.2	59.3	23.0	19.1	12.2
2.91	355	10.2	2.86	5.92	9.51	48.1	19.3	16.0	11.8
2.91	414	8.78	2.47	5.11	10.9	54.6	22.5	18.6	12.1
2.91	555	6.88	1.93	4.01	10.2	50.9	22.2	18.3	11.5
2.91	626	5.81	1.63	3.38	10.5	43.6	21.9	18.0	11.0
2.91	669	5.43	1.52	3.15	9.46	36.1	18.4	16.1	10.3
2.91	714	5.09	1.43	2.96	8.87	36.6	19.6	15.1	9.22
9.84	297	11.3	3.61	1.74	4.84	5.27	8.06	7.88	12.1
9.88	355	9.40	3.0	1.44	5.03	2.81	8.37	8.18	9.05
9.84	355	11.3	3.61	1.74	4.03	2.71	8.06	7.88	12.1
9.84	414	8.05	2.57	1.24	4.95	5.05	8.24	8.05	10.2
9.88	414	8.05	2.56	1.24	4.95	5.05	8.24	8.05	10.2
9.84	497	6.64	2.10	1.02	4.90	4.57	8.03	7.85	9.62
9.84	555	6.01	1.91	0.924	4.90	4.36	8.14	7.96	8.0
9.84	555	6.02	1.91	0.924	4.90	4.36	8.15	7.96	8.0
9.84	588	5.61	1.79	0.862	4.90	4.19	8.09	7.85	6.89
9.84	626	5.27	1.68	0.81	4.94	4.04	8.13	7.94	9.06
9.84	669	4.92	1.56	0.754	4.50	3.32	7.38	7.21	6.77
29.9	294	15.9	6.76	1.59	4.86	6.70	9.16	11.8	12.3
29.9	298	15.5	7.03	14.6	6.65	106.4	11.6	16.1	12.5
29.9	355	12.9	5.86	12.1	7.10	99.1	12.4	17.2	10.8
29.9	414	11.1	5.03	10.4	7.10	89.9	12.5	17.3	11.5
29.9	555	8.28	3.77	7.82	9.26	93.6	16.4	22.5	10.8
29.9	626	7.24	3.30	6.85	8.60	76.7	15.0	20.6	6.16
29.9	669	6.87	3.13	6.49	8.54	73.7	15.2	20.8	5.91
29.9	714	6.44	2.94	6.09	8.25	67.2	14.7	20.1	9.01
101	294	16.9	4.37	2.0	6.25	22.3	19.6	15.4	11.9
101	414	12.2	3.12	1.45	4.61	12.5	14.7	11.6	7.79
101	555	9.14	2.34	0.551	5.23	4.84	16.8	13.2	7.68
101	626	8.14	2.10	0.492	5.28	4.17	17.0	13.4	11.1
101	669	7.61	1.95	0.922	5.20	7.36	16.7	13.2	8.49

Table 5.1. The Experimental Conditions and the Rate Constants of Reaction 1^a

^aAll concentrations in molecule cm⁻³.

Reactions of $O(^{1}D)$ (reactions 2 - 4, Table 5.2) are fast and the time required for these reactions completion (typically 10^{-8} sec) is very short comparable to the lifetimes of other transient species. Therefore in the kinetic modeling these reactions are treated separately. The role of these reactions is to produce the initial concentrations of OH radicals as well as small concentrations of NO, O and H, whose subsequent reactions are taken into account in the reaction mechanism. The initial concentrations of these species are calculated based on the rate constants and branching ratios of reactions 2 - 4. The transient species in the kinetic modeling are OH, O, NO, CH₃, H, CH₂, HONO, H₂O₂, and HO₂.

The concentrations of N₂O, H₂O, and (CH₃)₂CO, which are present in large excess of the transient species (30 to 4000 times), are considered to be constant during the course of the reaction. Photolysis of water ($\sigma_{H2O}(193.3) = 1.51 \times 10^{-21}$ cm²molecule⁻¹ ¹¹⁶), although does contribute to the initial concentrations of hydroxyl, when taken into account does contribute not more than 0.5% to the returned rate constants for reaction 1 at ambient temperature and 1 bar and 100 bar pressures, and maximum of 2 % at the highest temperature at 1 bar and 100 bar pressure, therefore it is neglected. This is caused by the only a minor role played by hydrogen atoms in the reaction mechanism, the absolute concentrations of hydroxyl radicals are accounted explicitly in the fits. The initial concentrations of CH₂, HONO, H₂O₂, and HO₂ are set to zero. The self-reactions of OH radicals and CH₃ radicals play significant role in the radical decays. In such cases, the rate constants resulting from the fits where all rate constants are allowed to vary are strongly correlated.¹¹⁷



Figure 5.2 Sample temporal profiles of OH and CH₃ decay. Solid lines: fits by the reaction mechanism (see text). The residual is shown for CH₃ absorption. Pressure = 1 bar (He), Temperature = 298 K, $[CH_3] = 5.3 \times 10^{13}$, $[OH] = 5.9 \times 10^{-13}$, $[N_2O] = 7.9 \times 10^{16}$, $[(CH_3)_2CO] = 1.85 \times 10^{15}$ molecules cm⁻³.

To circumvent this problem, the following approach is used. The experimental hydroxyl absorption profiles are converted into the hydroxyl concentration profiles based on the measured absorption cross-sections.¹¹⁶ Then the hydroxyl concentration profiles are fitted using a smooth function with sufficient number of parameters to provide sufficient fitting flexibility. These profiles are then explicitly used in the methyl radical absorption profiles fitting using the SCIENTIST software, where unknown rate constant

 k_1 as well as the initial concentrations of methyl radicals are used as fitting parameters.

In addition, to avoid the large cross-correlation of the fitted rate constants, this approach also allowed for drastic reduction of the sensitivity of the fits to the rate constants of all other elementary reactions involving hydroxyl radical. As it is mentioned in Ref.¹¹⁰, the ambiguity in the rate constant of reaction 13 (CH₂ + OH) might lead to a significant uncertainty in the determined rate constant of reaction 1 via the uncertainty in the apparent stoichiometric coefficient (up to a factor of two), when OH absorption profiles are used for the determination of the rate constant of reaction 1. The explicit accounting for the OH concentration temporal profiles and using CH₃ absorption profiles in the fits completely alleviates this problem. Moreover, it leads to a large reduction of the sensitivity to the branching ratio in reaction 1. To avoid complications associated with the cross-correlation of the rate constant of reaction 1 with the rate constant of reaction 7 (self-reaction of CH₃ radicals), this reaction is studied separately. The experiments are performed using acetone/water/He mixtures photolyzed at 193.3 nm. The absorption profiles at 216.4 nm of CH₃ are measured. The absorption cross-sections of CH₃ (more exactly, the products of the absorption cross-sections and the quantum yields of methyl radicals in the photolysis of acetone) are determined from the initial amplitudes of the absorption profiles. The rate constants of CH₃ recombination reaction 7 are used as fitting parameters. The rate constants for reaction 1 (OH + CH_3 reaction) are determined from the outcomes of two experiments, where photolysis of the same mixture N₂O/H₂O/(CH₃)₂CO/He is used. In the first experiment, OH profile is recorded using hydroxyl lamp at 308 nm.

Reaction	Reactants	Products	Rate constant ^a	Reference	Comment	Relative maximum rate ^b
1a	OH+CH ₃	$H_2O+^1CH_2$	To be determined			1.00
1b		CH ₃ OH				
2a	O(¹ D)+N ₂ O	2 NO	8.37x10 ⁻¹¹	Branching ratio of 0.62 (Ref. ¹⁶)	The total rate constant is the average of three studies ^{76, 78, 118} as discussed by Bahng and Macdonald. ²⁷	
2b		N_2+O_2	5.13×10^{-11}	Ref. ¹⁶		
2c		$O(^{3}P)+N_{2}O$	1.3×10^{-12}	Ref. ⁷⁵	$k_c/k_2 < 0.01$, ⁷⁵ set to 1.3×10^{-12}	
3a	$O(^{1}D)+H_{2}O$	2 OH	$1.7 \times 10^{-10} \exp(36/T)$	Ref. ⁷⁵		
3b		H_2+O_2	2.2×10^{-12}	Ref. ¹⁶		
3c		$O(^{3}P)+H_{2}O$	<0.003 k _{3a}	Ref. ⁷⁶	Neglected	
4	$O(^{1}D)+CH_{4}$	OH+CH ₃	1.3×10^{-10}	Ref. ¹⁵		
5a	OH+OH	H ₂ O+O	$7.1 \times 10^{13} \exp(210 \text{K/T})$	Ref. ⁴⁷	Literature for T<415 K, Troe fit above 414 K Ref. ¹¹⁶	0.05
5b		H ₂ O ₂	$\begin{array}{l} k_{\infty} = (2.4 \pm 0.6) x 10^{-11} \\ (T/300)^{-0.5} \\ k_{0} \ = \ [He] \ (9.0 \pm 2.2) x 10^{-31} \\ (T/300)^{-3.5 \pm 0.5} \\ F_{c \ = \ 0.37}. \end{array}$	Ref. ¹¹⁶		0.08
6	OH+CH ₄	H ₂ O+CH ₃	4.16x10 ⁻¹³ (T/298) ^{2.18} exp(- 1232/T)	Ref. ¹¹⁹		3x10 ⁻⁷
7	CH ₃ +CH ₃	C ₂ H ₆	This work		Separately determined for specific temperatures and pressures (see text).	0.16
8	OH+O	O ₂ +H	$2.4 \times 10^{-11} \exp(110/T)$	Ref. ¹⁶		4.5×10^{-3}

Table 5.2. Reaction Mechanism used to Fit the Experimental Profiles

Reaction	Reactants	Products	Rate constant ^a	Reference	Comment	Relative
						maximum
						rate ^b
9a	OH+H	H_2+O	$6.86 \times 10^{-14} (T/298)^{2.8} \exp(-10^{-14})$	Ref. ¹²⁰		$4x10^{-8}$
			1950/T)			
9b		H ₂ O	$[M] 1.6 x 10^{-31} (T/298)^{-2.6}$	Ref. ⁷⁴		0.18
10	CH ₃ +O	H ₂ CO+H	1.4×10^{-10}	Ref. ¹²¹		6.1x10 ⁻³
11	OH+NO	HONO	$k_0 = 6.0 \times 10^{-31} (T/300)^{-1}$	Ref. ⁷⁹	F_c : fit of the data from Ref. ⁷⁹	0.07
			$^{2.5}$ k _{inf} =3.3x10 ⁻¹¹ (T/300) ^{-0.3}			
			$F_c = 0.60 \exp(91/T)$			
12	CH ₃ +H	CH ₄	$6.2 \times 10^{-29} (T/298)^{-1.8}$	Ref. ²⁹		0.06
13	OH+CH ₂	CH ₂ O+H	$3x10^{-11}$	Ref. ⁷³		0.06
14	$OH+(CH_3)_2CO$	CH ₃ CH ₂ CO+H ₂ O	3.15×10^{-14}	Ref. ¹²²		0.03
			$x(T/300)^4 exp(453/T)$			
15	OH+H ₂ O ₂	H_2O+HO_2	$2.9 \times 10^{-12} \exp(109/T)$	Ref. ⁸²		4.0×10^{-4}
16	OH+HO ₂	H_2O+O_2	$4.8 \times 10^{-11} \exp(250/T)$	Ref. ⁸⁰		1.5×10^{-4}
17	HO ₂ +NO	OH+NO ₂	$4x10^{-12}exp(223/T)$	Ref. ⁸¹		4.1×10^{-6}
18	CH ₃ +NO	CH ₃ NO	$2.1 \times 10^{-30} (T/298 \text{ K})^{-1.87}$	Ref. ¹²³		0.011
19	CH ₃ +H ₂ O ₂	CH ₄ +HO ₂	$2x10^{-14}exp(300/T)$	Ref. ⁷³		3.2×10^{-6}

Table 5.2. Reaction Mechanism used to Fit the Experimental Profiles (Continued)

^aRate constants and concentrations unit based on molecule, cm³ and sec.

^bMaximum reaction rate relative to the maximum (initial) total rate of reaction 1 (1a+1b), for the experimental conditions at 294 K, 100 bar, $[CH_3]_0 = 7.32 \times 10^{13}$, $[OH]_0 = 1.54 \times 10^{13}$ molecules cm⁻³ (other relevant concentrations are listed in Table5.1).

In the second experiment, the monitoring light source is replaced with a xenon arc lamp, and absorption profiles are accumulated at 216.4 nm at the same experimental conditions. Sample absorption profiles obtained in this way are shown in Figure 5.2.

The data processing was performed in two steps. In the first step the absorption profile at 308 nm is fitted by a two-exponential function with a free term (a five parameter fitting function) and then converted to the OH concentration profile. In the second step the hydroxyl concentration profile, [OH](t), is transferred to the SCIENTIST fitting model as an explicit concentration profile (i.e., the differential equation for [OH] is omitted). The numerical solutions of the residual sets of ODE (for all transient spices except OH) with the proper initial conditions is used to fit the experimental absorption profile at 216.4 (where methyl is the major contributing species):

$$Abs_{216.4}(t) = l \left(\sigma_{CH3}[CH_3] + \sigma_{HONO}[HONO] + \sigma_{H2O2}[H_2O_2]\right)$$
(5.1)

where *l* is the path length (10.13 cm). The absorption cross-sections of CH₃ are measured in this work (Chapter 6). More exactly, the products of the apparent absorption cross-sections of CH₃ radical at 216.4 nm and the branching ratios of the photolytic channel 5a in the photolysis of acetone at 193.3 nm (leading to two CH₃ radicals), $\sigma_{216.4}$ (CH₃) x f_{5a}, are measured. The branching ratio of the acetone photolysis channel leading to two CH₃ radicals at low pressures is f_{5a}=0.95.¹²⁴ The cross-sections of HONO and H₂O₂ used are $\sigma_{216.4}$ (HONO) = 1.79x10⁻¹⁸ cm²molecule^{-1 125} and $\sigma_{216.4}$ (H₂O₂) = 2.96x10⁻¹⁹ cm²molecule^{-1.126} The rate constant k₁ and the initial concentration of CH₃ are used as fitting parameters. The results of the measurements are summarized in Table 5.1. It is assumed, that the branching ratio of the acetone photolysis channel 5a is pressure independent (f_{5a} =0.95). However, at higher pressures, the yield of methyl radicals in the photolysis of acetone might be quenched. Measurements of the integral intensity of the CH₃ absorption spectra did suggest, that such quenching (if exists), does not exceed 30% at 100 bar. The impact of possible pressure quenching of channel 5a on the rate constants returned by the fits is assessed.



Figure 5.3 Pressure dependence of the rate constant of reaction 1 at different temperatures. Filled squares - 298 K; open circles - 555 K; filled circles - 669 K.

Decreasing the branching ratio f_{5a} by 30 % lead to the increase of the returned rate constant k_1 by 5% at 294 K and 100 bar, and by 8% at 666 K and 100 bar. Such stability towards the methyl radical cross-section is again due to the explicit accounting for the

hydroxyl concentration temporal profiles in the fits of the methyl radical absorption profile. There are two main contributions to the experimental errors. The first one is the uncertainties in the OH concentrations; the second one is the statistical error of the rate constants determination based on the CH₃ profiles. The first contribution is estimated as \pm 5%, evaluated from the data scatter as well as cross-section uncertainties in the ozone actinometry procedure. The second contribution depends on the signal/noise ratio in the CH₃ profiles and is varied within ±5 to ±20%.

There are also minor contributions arising from the uncertainness in the rate constants of other reactions of CH_3 radical, mainly the $CH_3 + CH_3$ reaction (reaction 7). Numerical analysis of the sensitivity towards this rate constant in the typical experimental conditions resulted in $\delta(\ln k) = -0.34 \cdot \delta(\ln k_{CH3+CH3})$. Assuming the accuracy of the rate constants of about $\pm 20\%$, this adds about $\pm 7\%$ to the error. Considering these sources as estimate the uncertainties independent, we of the rate constants $\delta(\ln k) = \sqrt{5^2 + 5^2 + 7^2} = 10\%$ for the good signal to noise ratio profiles (low pressures, low temperatures), and $\delta(\ln k) = \sqrt{5^2 + 20^2 + 7^2} = 22\%$ for the lower signal to noise profiles (high pressure, high temperatures).



Figure 5.4 Pressure independent rate constant of reaction 1 as a function of temperature. The symbols are the average values at each temperature over the pressure range 1-100 bar (He). The solid line is the fit using the expression $k_1 = k_{1,300}(T/300)^n$.

Pressure dependences of the rate constant of reaction 1 are measured at all temperatures of the study. The representative samples are shown in Figure 5.3. Over the pressure range studied (1 - 100 bar, He), no pressure dependence is observed at all temperatures of thy study within the experimental error. Therefore, within the experimental error, the rate constants measured in this study are associated with the high pressure limit rate constant of reaction 1. The temperature dependence of the rate constant k_1 is shown in Figure 5.4. It is fitted with a power function (solid line):



Figure 5.5 Arrhenius plot for the CH₃ + OH → products (reaction 1). Symbols experimental studies, lines - theoretical studies. (●) this work, (☆) Krasnoperov and Michael 2004,¹¹⁰ (▲) Vasudevan et al. 2008,¹¹² (□) Srinivasan et al. 2007,¹¹¹ (⊗) Bott and Cohen 1991,¹⁰⁹ (★) Deters et al. 1998,¹⁰⁸ (★) Sworski et al. 1980,⁹⁹ (◇) Hughes et al. 1992,¹⁰⁷ (○) Fagerstorm et al.1993,¹⁰¹ (▽) Pereira et al. 1997,²⁹ (■) Hompfer et al. 1995,¹⁰⁴ (●) Hompfer et al. 1994,¹⁰⁵ (⊲) Oser et al. 1992,¹⁰⁶ Dashed line (−−) Ing et al. 2003,¹¹³ short dashed line (−−) Jasper et al. 2007,⁹⁶ dotted line (⁻⁻⁻) Jordan et al. 1991,¹¹⁴ solid line (−) Pereira et al. high pressure extrapolation 1997,²⁹ dash-dot-dash line (−•−) Xia et al. 2001.³⁰

$$k_1 = (1.20 \pm 0.20) \times 10^{-10} (T/300)^{-0.49} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$
(5.2)

In Figure 5.5 the results of the current study are plotted together with previous direct experimental determinations and theoretical studies. They are in perfect agreement with the shock tube studies of Krasnoperov and Michael¹¹⁰ as well as Vasudevan et al.¹¹² However, this observation could be misleading, because the shock tube studies are
performed at much lower pressures $(0.065 - 1.24 \text{ bar})^{110}$, and $(1.3 - 1.7 \text{ bar})^{112}$ and are expected to be in the pressure fall-off at this elevated temperatures.¹¹² However, a single experiment with pressure of ca. 5 bar did not reveal any increase in the rate constant at 1426 K compared with 1.2 bar.¹¹²

Jasper et al.⁹⁶ predict ca. 2.1 times rate constant increase with pressure between 1 bar and 100 bar at 700 K, which is not observed in this work. The absolute value of predicted rate constant by Jasper et al.⁹⁶ is in very good agreement with the current measurements. However, only very weak temperature dependence is predicted in this theoretical work. On the other hand, the temperature dependence measured in this work is in good agreement with that predicted by De Avilles Pereira et al.²⁹, although the predicted high pressure limit rate constant is ca. factor of 1.5 - 2 lower, than that measured in this work.

5.4 Conclusions

Reaction of methyl and hydroxyl radicals (reaction 1) is studied over extended temperature (294 - 714 K) and pressure (1-100 bar) ranges. The measured rate constants are independent of pressure within the pressure range of the study (1 – 100 bar, He) at all temperatures. The rate constant shows moderate negative temperature dependence, $k_1 \propto T^{-0.5}$.

CHAPTER 6

CH₃+CH₃→products

6.1 Introduction

The recombination reaction of methyl radical is of considerable interest to experimental and theoretical kineticists as well as modelers of combustion processes.³²

$$CH_3 + CH_3 \rightarrow C_2H_6$$
 (1a)

$$\rightarrow$$
 C₂H₅ + H (1b)

This reaction is a major termination reaction in pyrolysis and oxidation of hydrocarbons. It is frequently used as a reference reaction in kinetic studies and is considered a benchmark reaction for testing and improving statistical theories for radical - radical reactions.³² Therefore, this reaction has been studied extensively both experimentally and theoretically. There are close to 100 references in the NIST kinetics database for this reaction. Although this reaction has been studied over a wide range but very few studies has been done at high pressures. For current purpose, only direct experimental studies and a few theoretical studies are discussed here.

Clark et al.¹²⁷ studied reaction 1 between 1120 and 1400 K using mass spectrometry in a single-pulse shock tube. The temperature-independent rate constant measured in their study is $(1.4\pm0.6)\times10^{-11}$ cm³molecule⁻¹sec⁻¹. In another high temperature study, In another high temperature study, Held et al.¹²⁸ studied this reaction in a flow reactor at pressures between 10 and 80 Torr and at temperature 1005 K via optical absorption and gas chromatography. The limiting, high pressure rate constant for the recombination of CH₃ is estimated to be $10^{10.5\pm0.5} L \text{ mol}^{-1}\text{s}^{-1}$. In another study, Du et al.¹²⁹ used laser absorption in his high temperature study at pressure between 114 and 230 kpa. The rate constant for the recombination of methyl radicals, measured at 1.2 atm is in good agreement with previous measurements. The high pressure limit and low pressure limit rate constants obtained in this study are $k_{\infty}(T) = 1.53 \times 10^{-7} T^{1.203} \exp(-295/T(K))$ cm³molecule⁻¹s⁻¹and $k_0(T) = 1.70 \times 10^{-5} T^{-7.248} \exp(-2172/T(K)) \text{cm}^6$ molecule⁻²s⁻¹ respectively, with $F_c(T) = \exp(-T/506) \text{ cm}^6 \text{ s}^{-1}$ respectively, with $F_c(T) = \exp(-T/506)$ (Ref.¹³⁰).

Wang et al.¹³⁰ studied the temperature and pressure dependences of the rate constant of reaction 1 with helium as a bath gas using time-of-flight mass spectrometry over the temperature 300 - 700 K and pressure 0.6 - 10 Torr ranges. Methyl radicals were produced by the laser photolysis of acetone at 193 nm. They reported negative temperature dependence and falloff behavior for the rate constant of the recombination reaction. The reliability of the rate constant measurements were verified by determining the recombination rate constant with different bath gas (Ar) at room temperature and by analyzing the yield of the reaction product ethane. The calculated high-pressure rate constant reported is $k_{\infty}^{\text{Theory}}(T) = 7.42 \times 10^{-11} (T/298 \text{ K})^{-0.69} e^{-88K/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Troe's formulaism was used to describe the temperature and pressure dependences of the recombination rate constant, based on the data from their work and taken from the literature. The high-pressure limit rate constant calculated is given by expression $k_0(T) = 1.17 \times 10^{-25} (T/298 \text{ K})^{-3.75} e^{-494 \text{ K/T}} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \text{ and } F_c(T) = e^{-T/570K}$ (He as a bath gas).

Macpherson et al.¹³¹ measured absorption cross section of CH_3 and the rate constant of reaction 1 over the temperature range of 296 - 577 K and pressure 5.4 - 500

Torr. The experimental approached used in their study was laser photolysis coupled with UV absorption spectroscopy. The high pressure rate constant k_{∞} reported is $(6.47\pm0.20)\times10^{-11}$ cm³molecule⁻¹sec⁻¹. The temperature dependence of k_{∞} was expressed as $(4.09\pm0.36)\times10^{-11}$ exp(137/T).

In Another study, Slagle et al.¹³² employed two techniques to study reaction 1. In laser photolysis-photoionization mass spectrometry (LP-PIMS) study, the rate constant was measured over the temperature range 296 - 906 K and pressure range 1.2 - 10.6 Torr using argon as bath gas and over the temperature range 296 - 810 K and pressure 2.5-10.7 Torr using He as bath gas. In laser photolysis - UV absorption spectroscopy studies, the temperature range 296 - 906 K and pressure ranges 5.4 - 493 Torr (Ar as bath gas) were used. They reported the high pressure rate constant 6.0 x 10⁻¹¹cm³molecule⁻¹sec⁻¹ using both approaches. Various theoretical studies have been done on this reaction. The RRKM calculation by Wardlaw and Marcus¹³³ confirmed the negative temperature dependence of the rate constant, the predicted rate constant k_{∞} at 300 K is 7.1×10^{-11} cm³molecule⁻¹s⁻¹. Variational RRKM theory calculations by Wagner and wardlaw.¹³⁴ were performed in conjunction with study by Slagle et al.²⁹ There was good agreement in Wagner and wardlaw.¹³⁴ calculations and experimental results by Slagle et al.²⁹over the temperature range 296 – 806 K and pressure range 5.4 – 493 Torr.

Klippenstein and Harding¹³⁵ predicted the rate constant over a wide range of pressure (0.1 - 1000 Torr) and temperature range (200 - 1700 K). They reported the value of the rate constant as 6.4×10^{-11} cm³molecule⁻¹s⁻¹ which is in good agreement with the previous study. Hwang et al.¹³⁶ studied methyl radical recombination reaction behind reflected shock waves over the temperature range 1200 - 1600 K and the pressure range

10 to 240 bar using UV absorption spectroscopy at 216.5 nm. The reaction was in the falloff region under the conditions employed and the experimentally determined absorption cross sections of CH₃ were found to be slightly pressure dependent at a fixed temperature. The extrapolated high-pressure limit rate constants is represented by (in cm³/mol s), k_1^{∞} =1.15x10¹⁵T^{-0.6}, or k_1^{∞} =1.45x10¹³exp(330 K/T), or k_1^{∞} =5.36×10¹⁶T^{-1.1}exp(-320K/T). A negative temperature dependence of k_1^{∞} was confirmed.

Cody et al.¹³⁷ measured the rate constant of recombination reaction of methyl radical at low temperature using the discharge-flow kinetic technique coupled to mass spectrometric detection at temperature 202 and 298 K and pressure range 0.6 - 2.0 Torr. Methyl radicals were generated by the reaction of F with CH₄, with [CH₄] in large excess over [F], and detected by low energy (11 eV) electron impact ionization at m/z= 15. At 298 K, $k_{CH3+CH3}=(2.15 \pm 0.42)x10^{-11}$ cm³molecule⁻¹s⁻¹ at 0.6 Torr and $(2.44 \pm 0.52)x10^{-11}$ cm³molecule⁻¹s⁻¹ at 0.6 Torr and $(6.52 \pm 1.54)x10^{-11}$ cm³molecule⁻¹s⁻¹ at 2 Torr, indicating that the reaction is in the falloff region.

6.2 Experimental

Photolysis of acetone at 193.3 nm is used to produce CH_3 radicals. There are two other possible channels in the photolysis of acetone at this wavelength:

$$(CH_3)_2CO + hv(193 \text{ nm}) \rightarrow 2CH_3 + CO$$
 (2a)
 $\rightarrow CH_2COCH_3 + H$ (2b)

Detail description of generation and monitoring CH_3 radical is described in Chapter 2. Acetone - water mixtures are carefully degassed using freeze pump thaw cycle before loading in the stainless steel syringe. The mole fraction of acetone in water is varied from 0.02 to 0.04. Acetone - water mixtures are injected into the evaporator of the high pressure flow system using precision syringe pump (Harvard Apparatus, Model PHD 4400) through a capillary tube.

p / bar	T / K	Number density /10 ¹⁹	[(CH ₃) ₂ CO] / 10 ¹⁵	$[CH_3] / 10^{14}$	k ^b / 10 ⁻¹¹
1.01	292	2.49	1.9	1.03	5.89
1.01	354	2.04	0.93	1.02	5.87
1.01	414	1.74	1.85	1.17	4.71
1.01	558	1.31	1.57	1.02	4.62
1.01	626	1.16	1.54	8.87	4.15
1.01	669	1.09	1.35	7.72	4.22
1.01	714	1.02	1.12	7.55	3.83
2.88	293	7.04	4.44	8.73	5.65
2.88	354	5.89	3.73	8.48	4.55
2.88	414	5.05	3.19	7.95	4.61
2.88	497	4.21	2.66	7.09	4.15
2.88	555	3.77	2.38	6.64	3.86
2.88	626	3.35	2.12	5.93	3.18
2.88	669	3.13	1.98	5.63	3.19
2.88	714	2.93	1.85	5.47	3.36
9.84	294	24.5	6.76	2.01	5.67
9.84	414	17.3	4.78	1.82	4.81
9.84	555	12.9	3.58	1.56	4.62
9.84	626	11.5	3.18	1.38	4.36
9.84	669	10.7	2.97	1.31	4.31
9.84	714	10.1	2.78	1.30	4.29
30.51	294	74.1	5.06	1.51	5.78
30.51	354	61.2	4.17	1.56	4.86
30.51	414	52.5	3.58	1.70	4.42

Table 6.1. Experimental Conditions and Concentrations of Reactants^a

p / bar	T / K	Number density $/10^{19}$	[(CH ₃) ₂ CO] / 10 ¹⁵	[CH ₃] / 10 ¹⁴	k ^b / 10 ⁻¹¹
30.51	497	43.8	3.00	1.56	3.49
30.51	555	39.3	2.69	1.47	3.43
30.51	626	34.9	2.39	1.26	3.35
30.51	669	32.6	2.23	1.10	3.5
30.51	714	30.6	2.10	1.04	3.36
100.8	298	23.5	2.00	1.56	4.60
100.8	414	23.5	1.47	1.17	4.17
100.8	555	23.5	0.99	0.64	4.24
100.8	555	16.8	1.11	0.92	4.43
100.8	626	12.6	0.994	0.64	3.47
100.8	626	11.3	1.66	1.17	3.11
100.8	714	10.5	0.875	0.609	4.20
100.8	714	0.108	2.19	1.39	4.23

Table 6.1. Experimental Conditions and Concentrations of Reactants^a (Continued)

^aAll concentrations are in molecule cm⁻³.

^bRate constants and concentrations unit based on molecule, cm³ and sec.

The flow rate of acetone-water mixtures is varied in the range of 0.5 - 10 μ L/min depending upon the reactor pressure and temperature. The concentrations of the precursors used (0.93 - 14.6)x10¹⁵ molecule cm⁻³ for CH₃COCH₃ and (1.4 - 7.0)x10¹⁷ for H₂O. The laser photon fluence inside the reactor is varied in the range (2.4 - 11)x10¹⁵ photon cm⁻² pulse⁻¹. The pressure range is 1 - 100 bar (He). The conditions and concentrations of reactants are given in Table 6.1.

6.3 Results and Discussion

The products of the apparent absorption cross-sections of CH₃ radical at 216.4 nm and the branching ratios of the photolytic channel 2a in the photolysis of acetone at 193.3 nm (leading to two CH₃ radicals), $\sigma_{216.4}$ (CH₃) x f_{2a} are measured as follows. Mixtures of H₂O/acetone/He are photolyzed at 193.3 nm using a uniform laser beam. The transient profiles are recorded and processed according to the reaction mechanism (Table 6.3). The spectrograph with the focal length of 300 mm (Acton SpectraPro 300i) with a grating 1200 groove/mm is used. Both slit are 0.25 mm, which resulted in a triangular slit function with FWHM = 0.64 nm. A 75 W high pressure Xe arc lamp is used as the light source.



Figure 6.1 The products of the apparent absorption cross-sections of CH₃ radical at 216.4 nm and the branching ratios of the photolytic channel 5a in the photolysis of acetone at 193.3 nm (leading to two CH₃ radicals) as a function of temperature at different pressures. Open circles: 1 bar, filled circles: 3 bar, open triangles up: 10 bar, open squares: 30 bar, and filled stars: 100 bar (He) (this work). Solid lines are polynomial fits of the experimental data. Crosses and dotted line – the low pressure data of McPherson et al.¹³⁸ measured with a slightly narrower slit function (FWHM = 0.60 nm). The branching ratio of the acetone photolysis channel leading to two CH₃ radicals ratio at low pressures is f_{5a} =0.95.¹²⁴

A reflectance based band pass filter consisting of two dielectric mirrors with high reflectivity near 216 nm is used to cut off high intensity light with longer wavelengths, which otherwise being scattered inside the spectrograph produced a significant parasitic contribution to the PMT signal.⁹³ The ratios of the initial concentrations of CH_3 radicals and the branching ratios of the photolytic channel 2a in the photolysis of acetone at 193.3 nm are determined based on the photon fluence and the acetone absorption cross sections (Table 6.2). The least squares fits of the transient profiles according to the reaction mechanism yielded the product of the apparent absorption cross sections of CH_3 and the branching ratios f_{2a} (Figure 6.2) together with the rate constant of methyl radical recombination.





The photon fluences are determined in additional *in situ* actinometry experiments by measuring the ozone build-up in the $N_2O/N_2/O_2 + 193.3$ nm photolysis system at 1 bar and 298 K. In all experiments, the relative laser beam intensity is recorded with high accuracy using a pyroelectric sensor, due corrections for the laser power drift are introduced when needed. The results of the measurements are summarized in Table 6.2.



Figure 6.3 Methyl radical absorption spectrum broadening at 100 bar and 300 K. Note, the spectra are not normalized to the methyl radical concentrations which are different in the two experiments. The integrated absorption was used to estimate pressure quenching of CH_3 yield in the photolysis of acetone at 193.3 nm.

Reaction	Reactants	Products	Rate constant ^a	Reference
1	CH ₃ +CH ₃	C_2H_6	This work	
2a	(CH ₃) ₂ CO+hv ₁₉	2CH ₃ +CO		
2b	3	CH ₂ COCH ₃ +H		
2c		CH ₄ +CH ₂ O		
3a	$O(^{1}D)+H_{2}O$	2 OH	$1.7 \times 10^{-10} \exp(36/T)$	Ref. ⁷⁵
3b		H ₂ +O ₂	2.2×10^{-12}	Ref. ¹⁶
3c		$O(^{3}P)+H_{2}O$	<0.003 k _{3a}	Ref. ⁷⁶
4	$O(^{1}D)+CH_{4}$	OH+CH ₃	1.3×10^{-10}	Ref. ¹⁵
5a	OH+CH ₃	$H_2O+^1CH_2$	$1.2 \times 10^{-10} (T/300)^{0.49}$	
5b		CH ₃ OH		
6a	OH+OH	H ₂ O+O	(5.1exp(-T/190K)+	Ref. ¹³⁹
			$0.30(T/300 \text{ K})^{1.73})x10^{-12}$	
6b		H_2O_2	$k_{6b,\infty} = (2.4 \pm 0.6) \times 10^{-10}$	Ref. ¹¹⁶
			$^{11}(T/300)^{0.5}$	
			$k_{5b,0} = [He](9.0 \pm 2.2) \times 10^{-5}$	
			$^{31}(T/300)^{-3.5\pm0.5}$	
			$F_{c=0.37}$.	110
7	OH+CH ₄	H ₂ O+CH ₃	$4.16 \times 10^{-13} (T/298)^{2.18} \exp(-10^{-13})^{-13} \exp(-10^{-13})^{-13}$	Ref. ¹¹⁹
			1232/T)	1/
8	OH+O	O ₂ +H	$2.4 \times 10^{-11} \exp(110/T)$	Ref. ¹⁶
9a	OH+H	H ₂ +O	$6.86 \times 10^{-14} (T/298)^{2.8} \exp(-$	Ref. ¹²⁰
			1950/T)	
9b		H ₂ O	$[M] 1.6x10^{-31}(T/298)^{-2.6}$	Ref. ⁷⁴
10	CH ₃ +O	H ₂ CO+H	1.4×10^{-10}	Ref. ¹²¹
11	CH ₃ +H	CH ₄	$6.2 \times 10^{-29} (T/298)^{-1.8}$	Ref. ²⁹
12	OH+CH ₂	CH ₂ O+H	3x10 ⁻¹¹	Ref. ⁷³
13	$OH+(CH_3)_2CO$	CH ₃ CH ₂ CO+H	3.15×10^{-14}	Ref. ¹²²
		2 O	$x(T/300)^4 exp(453/T)$	
14	OH+H ₂ O ₂	H ₂ O+HO ₂	$2.9 \times 10^{-12} \exp(109/T)$	Ref. ⁸²
15	OH+HO ₂	H ₂ O+O ₂	$4.8 \times 10^{-11} \exp(250/T)$	Ref. ⁸⁰
16	CH ₃ +H ₂ O ₂	CH ₄ +HO ₂	$2x10^{-14}exp(300/T)$	Ref. ⁷³

 Table 6.2 Reaction Mechanism used to Fit the Experimental Profiles.

^aRate constants and concentrations unit based on molecule, cm³ and sec.

^bMaximum reaction rate relative to the maximum (initial) total rate of reaction 1 (1a+1b), for the experimental conditions at 294 K, 100 bar, $[CH_3]_0 = 7.32 \times 10^{13}$, $[OH]_0 = 1.54 \times 10^{13}$ molecules cm⁻³ (other relevant concentrations are listed in Table5.1).



Figure 6.4 Correlation of the apparent rate constant $k_{CH3+CH3}$ with the relative yield of methyl radicals in photolysis of acetone at 193.3 nm. Filled squares: the apparent rate constant ($k_{CH3+CH3}$) at different pressures at 298 K. Open circles: relative integral absorption of CH3 around 216nm.

The recombination rate constant of methyl radical shows negative temperature dependence. This observation is in agreement with the previous studies. However, there was small negative pressure dependence of the rate constant of reaction 1 at 298 K (Figure 6.4). This *negative* temperature dependence may be due to the quenching of the methyl radical yield in photolysis of acetone at 193 nm at high pressures (100 bar).

At high pressures quenching of CH_3 radical yield was indeed observed in this study (Figure 6.3). The quenching of CH_3 radical yield at 100 bar was estimated as 26% (±7%). From the integral absorption of CH_3 , if this correction in incorporated in the CH_3 yield at 100 bar then the rate constant of reaction 1 is independent of pressure. The experiments to assess the effect of temperature on the quenching are planned.

p/bar	1 bar	3 bar	10 bar	30 bar	100 bar
T/K					
298	3.55 ± 0.05	3.06 ± 0.05	3.36 ± 0.05	2.34 ± 0.05	1.27 ± 0.5
355	3.44 ± 0.05	2.86 ± 0.05		2.15 ± 0.05	
414	2.80 ± 0.05	2.75 ± 0.05	2.81 ± 0.05	2.18 ± 0.05	1.33 ± 0.05
497		2.53 ± 0.05		1.87 ± 0.05	
555	2.39 ± 0.05	2.36 ± 0.05	2.42 ± 0.05	1.76 ± 0.05	1.40 ± 0.05
626	2.17 ± 0.05	2.09 ± 0.05	2.10 ± 0.05	1.36 ± 0.05	1.18 ± 0.05
666	2.01 ± 0.05	2.14 ± 0.05	2.10 ± 0.05	1.35 ± 0.05	
714	1.91 ± 0.05	1.91 ± 0.05	1.77 ± 0.05	1.34 ± 0.05	1.10 ± 0.05

Table 6.3. The Products of the Apparent Absorption Cross-Sections of CH_3 Radical at 216.4 nm



Figure 6.5 Apparent rate constant $k_{CH3+CH3}$ (not corrected for CH_3 yield) at different pressures and different temperatures.

6.4 Conclusions

The rate constant of recombination reaction of methyl radical at room temperature is in agreement with the IUPAC recommended value and recent theoretical calculations. The negative temperature dependence of the rate constant is also confirmed.

CHAPTER 7

$CH_3+HO_2 \rightarrow products$

7.1 Introduction

The reaction of CH_3 and HO_2 radicals 1 plays an important role in hydrocarbon combustion.³⁴⁻³⁶ The importance of this reaction increases with pressure.³⁴ Recombination of hydrogen atoms (e.g., produced in dissociation of formyl radical, HCO) with molecular oxygen results in a relative unreactive hydroperoxy radical, HO_2 . However, subsequent reaction of HO_2 with CH_3 (e.g., in fuel rich mixtures) might lead to efficient chain propagation via reaction channel 1a. The sensitivity analysis of methane combustion ranks reaction 1 among the 5 most important reaction in the mechanism.³⁵⁻³⁶ The reaction is exothermic; there are several energetically allowed product channels:

Channel 1a is considered to be a chain propagation reaction in the high pressure methane oxidation,³⁷ whereas channel 1d is a chain termination step. The methoxy radicals produced in channel 1a easily dissociate to form H atoms and CH₂O. Therefore, at intermediate temperatures and high pressures reaction 1a is crucial in the mechanisms

of natural gas combustion.³⁷ Channels 1d and 1e are the direct abstraction reactions taking place on the triplet and singlet potential energy surfaces producing molecular oxygen in the ground and excited electronic states. Among channels 1d and 1e, channel 1d, proceeding on the triplet surface, dominates.³⁸⁻³⁹ The relative importance of other channels is assessed in previous theoretical studies.⁴⁰⁻⁴¹ The branching ratio of channels 1a and 1d is important for modeling ignition in high pressure combustion systems.⁴⁰

Despite the importance of reaction 1 in combustion mechanisms, only very limited experimental studies are performed. Baulch et al.¹⁴⁰ recommended the rate constant for channel 1a, $k_{1a} = 3x10^{-11}$ cm³molecule⁻¹s⁻¹, based on an indirect measurements of Colcket III et al.¹⁴¹ with an uncertainty of an order of magnitude.¹⁴¹. In another indirect experimental study, Scire et al.¹⁴²⁻¹⁴³ estimated the rate constant of reaction 1 at 1000 K by fitting stable species profiles from flow reactor experiments on moist CO oxidation perturbed with methane. They reported the rate constant of reaction $k_1 = 3x10^{-11}$ cm³molecule⁻¹sec⁻¹ at 1000 K with a significant uncertainty (a factor of 2.5). The uncertainties in the rate constant of the reactions CH₃+CH₃ and CH₂O +HO₂ are primary contributors to the uncertainty factor in reaction 1

Zhu and Lin³⁹ in a theoretical study using ab initio molecular orbital theory and variational RRKM calculations predicted the individual rate constants for different channels of reaction 1. The rate constants obtained for the individual channels are k_{1a} = 1.38x10⁻¹⁰ cm³molecule⁻¹ s⁻¹ and k_{1d} = 8.34x10⁻¹² cm³molecule⁻¹ s⁻¹ at 300 K. The predicted rate constant for the reaction 1 is ca. 2.3 times larger than the rate constant recommended by Baulch et al.¹⁴⁰ and determined by Scire et al.¹⁴³⁻¹⁴⁴

Recently, Jasper et al.³⁸ theoretically studied reaction 1 using variable reaction coordinate transition state theory coupled with high level multireference electronic structure calculations (VRC-TST). The reported calculated rate constant, $k_1 = 1.96 \times 10^{-11}$ cm³molecule⁻¹s⁻¹ at 1100 K is in reasonable agreement with the rate constant obtained in the indirect experimental studies by Scire et al.,¹⁴³⁻¹⁴⁴ $k_1 = 3x10^{-11}$ cm³molecule⁻¹ s⁻¹ and in excellent agreement with the recent direct shock tube study, 1.86x10⁻¹¹ cm³ molecule⁻¹ s⁻¹.³⁷

Direct experimental studies of reaction 1 are very sparse; only one high temperature shock tube study is performed (Hong et al.³⁷). In this study, the reaction is initiated using H₂O₂/CH₄/Ar mixtures shock-heated to temperatures between 1054 and 1249 K at about 3.5 atm. Hydroperoxy and methyl radicals are produced in reactions of hydroxyl radicals (produced from thermal dissociation of H₂O₂) with H₂O₂ and CH₄, respectively. The decay profiles of H₂O, OH and HO₂ are recorded using laser absorption spectroscopy behind reflected shock waves. The determined rate constant of reaction 1a is $k_{1a} = 1.13 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ with an uncertainty factor of 1.4, the rate constant of channel 1d is $k_{1d} = 7.31 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, with an uncertainty factor of 2.1 in the temperature range 1072 - 1139 K. The measured rate constant of reaction 1 is in good agreement with the rate constant calculated by Jasper et al.³⁸ at these temperatures.

There are no direct experimental measurements at ambient temperature for this very important reaction. An effort to measure the rate constant of reaction 1 using photolysis of CH_3CHO/O_2 mixtures at 248 nm is mentioned, although no rate constant have been yet reported.¹⁴⁵

In this work, a direct study of reaction 1 at ambient temperature and pressure 1 bar, using photolysis of $N_2O/H_2O/CH_4/H_2O_2/He$ mixtures at 193.3 nm, by recording temporal profiles of methyl radicals via transient UV absorption at 216 nm.

7.2 Experimental

The experimental set-up is described in details in Chapter 2, therefore, only brief description critical for the current experiments is given here. The approach is based on the excimer laser photolysis coupled to the UV-vis transient absorption spectroscopy. Helium is used as a bath gas in all experiments. The measurements are performed at 295 K and ca. 1 bar pressure. Stainless steel flow reactor with the path length 10.17 cm is used. Two UV - grade fused silica windows (12.7 diameter, 9.5 mm thick) are sealed at the end of the reactor and two additional thick (9.5 mm) fused silica windows, separated by a stainless steel insert, are placed without sealing inside the reactor near the reactor outlets. To achieve uniform concentration profiles across the reactor cross-section, the laser beam is formed using a spherical lens (f = +30 cm, the distance from the reactor center 35 cm). The gas flow rates are controlled by mass flow controllers (Brooks, model 5850). The total flow rates of the reactant mixtures with helium are in the range 4,200 – 4,500 sccm (standard cubic centimeters per minute).

Solutions of H_2O_2 in H_2O are freshly prepared before every measurement and calibrated using an UV spectrophotometer (Perkin Elmer EZ150) at 253.6 nm using the extinction coefficient of hydrogen peroxide in aqueous solutions $\varepsilon_{253.6}$ (aqueous solution, base 10) = 19.6 ± 0.3 L mol⁻¹cm⁻¹.¹⁴⁶ The solutions of H_2O_2 in H_2O are carefully degassed before filling in the precision syringe. The mixtures of H_2O_2 and H_2O are

supplied to the reactor using a precision syringe pump (Harvard Apparatus, Model PHD 4400). The liquid solutions of H₂O₂ in H₂O are flowing from the syringe pump through a capillary tube to an evaporator kept at 90 °C. The flow rate is in the range of 6 – 18 μ L/min. To ensure that H₂O₂ reached the reactor without losses, the concentration of H₂O₂ is monitored at the reactor exhaust. The exhaust of the reactor is connected to a 10 cm gas absorption flow cell placed in a UV-vis spectrophotometer (Perkin Elmer EZ150). The concentrations of H₂O₂ in the reactor are determined based on the measured absorbance of H₂O₂ at 200 nm (ε_{200} (gas phase, base 10) = 140 L mol⁻¹cm⁻¹.¹⁴⁶ Due to the low absorbance (ca. 0.013) these measurements have only a limited accuracy (ca. ± 7%), and are performed to verify whether there are any losses of hydrogen peroxide in the stated accuracy with the expected based on the flow rates, the latter are used in the calculations, as being more accurate.

The concentrations of the reactants used are $(1.5 - 2.0) \times 10^{16}$ molecule cm⁻³ (N₂O), $(1.2 - 3.5) \times 10^{17}$ molecule cm⁻³ (H₂O), $(2.8 - 6.6) \times 10^{17}$ molecule cm⁻³ (CH₄) and $(2.3 - 7.4) \times 10^{15}$ molecule cm⁻³ (H₂O₂). The photolysis laser photon fluence inside the reactor is varied in the range $(4.3 - 8.0) \times 10^{15}$ photon cm⁻²pulse⁻¹. The initial concentrations of hydroxyl radicals are in the range $(2.8 - 6.6) \times 10^{13}$ molecule cm⁻³. The experimental conditions are listed in Table 7.1. The repetition rate of the laser is adequate to ensure complete replacement of the gas mixture in the reactor between the pulses.

In situ actinometry. To determine accurately the radicals concentrations it is necessary to know the photon fluence inside the reactor. In this work, the absolute concentrations of HO_2 and CH_3 radicals are calculated based on the photon flux inside the

reactor, the reactants concentrations, and the absorption cross-sections of N₂O, H₂O₂ and H₂O at 193.3 nm. The efficiency of conversion of O(¹D) atoms produced in the photolysis of N₂O to CH₃, HO₂ and OH radicals is evaluated using a detailed reaction mechanism (Table 7.2). The absorption cross-section of N₂O at 193.3 nm is accurately known at 298 and 1 bar $(8.50 \pm 0.20) \times 10^{-20}$,¹⁴⁷ The absorption cross section of H₂O₂ (6.01 $\pm 0.12) \times 10^{-19}$ is obtained from literature.¹⁴⁷ The major source of errors is in the determination of the laser light intensity inside the reactor. The *in situ* laser light actinometry based on the stable molecule formation with very well characterized cross-section at a monitoring wavelength. Specifically, ozone formation, monitored at 253.7 nm, in the photolysis of N₂O/O₂/N₂ mixtures at 1 bar and 298 K, is used. Details of this technique can be found in Chapter 2.

Typically, two such determinations are performed, before and after a series of measurements. Simultaneously, the readout of the pyroelectric detector measuring laser pulse energy after the reactor is recorded.¹¹⁶ The readout of the pyroelectric detector is then used to introduce proper corrections for the drift of the laser energy during a series of experiments in the kinetic measurements.

Reagents. Helium used in the experiments is BIP®Helium from Airgas with 99.9999% purity with reduced oxygen content (<10 ppb). UHP oxygen is obtained from Matheson TriGas (99.98% purity). N₂O obtained from Matheson Tri-Gas with 99.999% purity is used. Nitrogen for purging the window is obtained from Matheson Tri-Gas with 99.998% purity. H₂O₂ is obtained from Fluka Chemika(>35%). Purified water (Milli-Q®) with TOC less than 5 ppb is used to prepare solution of H₂O₂.

Radicals (CH₃ and HO₂) generation and monitoring. CH₃ and HO₂ radicals are generated in pulse photolysis of N_2O in the presence of water at 193.3 nm (ArF excimer laser):

The quantum yield of the major channel 2a is unity within 1%, the minor channel 2b is less than 0.8%.⁹³ The quantum yields of OH in photolysis of hydrogen peroxide at 193.3 nm (channel 3a) is 1.5, the quantum yield of H-atoms is 0.16.¹⁴⁸⁻¹⁴⁹

The yield of vibrationally excited hydroxyl radicals OH(v=1,2) formed in the reaction of $O(^{1}D) + H_{2}O$ (reaction 6a) is 22 - 32%.⁶⁷⁻⁷⁰ A fraction of $O(^{1}D)$ formed in photolysis of N₂O reacts with N₂O:

$$O(^{1}D) + N_{2}O \rightarrow NO + NO$$
 (8a)





Figure 7.1 Sample temporal profiles of the absorptions at 216.4 nm (mainly CH₃), 224 nm and 308 nm (insert). Solid lines with noise – experimental absorption profiles. Solid smooth line - fit by the reaction mechanism (see text). Dash-dotted line – simulation of the absorption at 224 nm. Dashed line is the simulation of the transient absorption at 216.4 nm with rate constant k_1 set to zero at the same conditions. Experimental conditions: 1 bar (He), 295 K, $[CH_3]_0 = 2.79 \times 10^{13}$ (the "initial" concentrations of transient species refer to the concentrations after completion of the reactions of $O(^1D)$, see text), $[HO_2]_0 = 1.87 \times 10^{13}$, $[OH]_0 = 7.47 \times 10^{13}$, $[H_2O_2] = 3.76 \times 10^{15}$, $[N_2O] = 1.9 \times 10^{16}$ molecule cm⁻³.

The methyl and hydroperoxy radicals decays are monitored by absorption at 216.4 nm and 224 nm (1200 groove/mm grating, 300 mm focal distance, both slits 0.25 mm,

triangle slit function, FWHM = 0.64 nm) using xenon arc lamp combined with an imaging spectrograph (Acton 300i).

$[N_2O]_0/10^{16}$	$[H_2O]_0/\\10^{17}$	$[H_2O_2]_0/\\10^{15}$	Photon fluence/10 ¹⁵ photon cm ⁻²	Number density/10 ²⁰	[CH ₄] ₀ / 10 ¹⁷	$k_1 / 10^{-11}$ cm ³ molecule ⁻¹ s ⁻¹
1.49	3.51	7.24	8.0	0.243	4.29	3.40
1.49	3.51	3.76	3.17	0.248	4.29	3.46
2.04	1.22	2.34	6.48	0.248	2.76	3.60
2.04	1.21	4.68	5.53	0.248	2.76	3.07
2.00	1.19	2.30	4.30	0.248	6.67	4.50
2.00	1.20	2.30	5.35	0.248	6.64	5.83
2.00	1.22	2.34	4.25	0.248	2.76	5.50
1.49	1.20	15.3	4.30	0.248	4.29	1.46
2.00	1.20	2.30	4.30	0.248	6.64	4.00
2.00	1.20	2.30	4.30	0.248	6.64	2.68
						Average 3.7 ± 1.8

Table 7.1 The Experimental Conditions and the Rate Constants of Reaction 1^a (1.01 barHe, 295 K)

^aAll concentrations are in molecule cm⁻³

7.3 Results and Discussion

Temporal profiles of both reactants (CH₃ and HO₂ radicals) are recorded via UV absorption at 216.4 and 224 nm, respectively. The experimental conditions are listed in Table 7.1. The UV absorption of HO₂ is significantly weaker than absorption of methyl radical, and might be contaminated by the absorption of N₂O photolysis products. Due to these reasons, although a reasonable agreement between the calculated and measured traces at 224 nm is observed, the kinetic data are extracted exclusively from the absorption profiles at 216.4 nm, where methyl radical contribution dominates. Sample absorption profiles at 216.4 nm and 224 nm are shown in Figure 7.1. The parasitic absorption by ozone formed outside the reactor is completely suppressed by purging the

overlapping areas of the photolysis and the monitoring beams with nitrogen. Small "baseline shift" caused by the mirrors reflectivity change after a laser pulse, is accurately measured in the absence of the reactants and taken into account in the profiles processing. To determine the rate constant of reaction 1, a comprehensive reaction mechanism is used to model and to fit the experimental profiles (Table 7.2).



Figure 7.2 Simulated temporal profiles of OH, HO_2 , CH_3 , CH_3O and C_2H_6 (the same conditions as in Figure 7.1).

Absorption profiles are fitted by numerical solutions of a system of differential equations corresponding to the reaction mechanism using SCIENTIST software.¹¹⁵ Simulated profiles of OH, HO₂, CH₃, CH₃O and C₂H₆ are shown in Figure 7.2. About

95% of hydroperoxy is formed from the reaction $OH + H_2O_2$, about 5% from the reaction of $O(^1D) + H_2O_2$. Methyl radicals are formed almost exclusively from the reaction $O(^1D) + CH_4$. Hydroxyl radicals react on a short timescale (< 200 µsec), while methyl radical profiles are sensitive to the rate constant of reaction 1 in the range 0.7 - 2 msec.

The UV absorption cross-sections (Table 7.3) and the rate constants, used in the fits, are either measured in previous work^{71, 116, 139, 150} (rate constant of OH+OH and CH₃+OH) or are taken from the literature. The detailed reaction mechanism and the kinetic parameters used in the model are listed in Table 7.2. The branching ratio of the channels 1a and 1d is set to 0.78 based on the theoretical study of Jasper et al.³⁸ The results are not sensitive to this branching ratio. Setting the branching ratio to 0.3 leads to +4% change of the returned rate constant, while setting the branching ratio to 0.9 leads to a -3% change. The kinetics of methyl radicals is mainly controlled by the cross reactions CH₃ and OH (reaction 10), self reaction of methyl radicals (reaction 12), reaction of CH₃ and HO₂ (reaction 1).

The approximate distributions of the contributions of these reactions into the methyl radical decay are as follows. At zero time, the contributions of reactions 10, 7, 12 and 17 are ca. 50%, 26%, 19% and 4%, respectively. At 0.5 ms, when hydroxyl is almost depleted, the contributions of reactions 1, 12, 7, 17 and 10 are 25%, 23%, 19%, 12% and 7%, respectively. At ca. 1 ms, when the profiles are sensitive to reaction 1, reaction 1 (reaction under study, $CH_3 + HO_2$), contributes ca. 30%. Next contribution is coming from reaction 7 ($OH + CH_4$), ca. 23%. Self-reaction of CH_3 (reaction 12), the reaction $CH_3 + H$ (reaction 17) and the reaction $CH_3 + H_2O_2$ (reaction 21) contribute ca. 15%, 8%,

and 6%, respectively. There are minor reactions which have only a minor impact on the rate constant of reaction 1.



Figure 7.3 Rate constant of the reaction $CH_3 + HO_2 \rightarrow \text{products.} (\blacksquare)$ this work, (★) Hong et al.³⁷, (★) Scire et al.,¹⁴³⁻¹⁴⁴ dotted line: Zhu and Lin³⁹, solid line: Jasper et al.³⁸.

These reactions were considered to elucidate their potential role as well as to introduce small corrections. Several of them play only a marginal role under the conditions of the current study. HO₂ radical production is controlled by the reactions of $O(^{1}D)$, OH and CH₃ with H₂O₂. Methyl radicals, CH₃, are produced mainly by reactions of $O(^{1}D)$ and OH with methane. Reactions of $O(^{1}D)$ atoms, (reactions 4 – 6, 9) are very fast and are completed within 10^{-8} sec, the timescale much shorter compared to the

lifetimes of other transient species. Therefore, in the kinetic modeling these reactions were treated separately. The role of these reactions is to produce the "initial" concentrations of HO_2 , CH_3 and OH radicals as well as small concentrations of NO, O and H, whose subsequent reactions are taken into account in the reaction mechanism.

The initial concentrations of the transient species were calculated based on the rate constants and branching ratios of reactions of $O(^{1}D)$ with the reactants. The transient species in the kinetic modeling were OH, HO₂, CH₃, O, H, H₂O₂, O₃, NO, CH₂, HONO, and CH₃O. The concentrations of N₂O, H₂O, and CH₄, which were present in large excess of the transient species, were considered to be constant during the course of the reaction after the laser pulse. The experimental methyl absorption profiles are fitted by the reaction mechanism (Table 7.2). The life time of HO₂ radical is much longer than the life time of methyl radicals, in turn the lifetime of hydroxyl radicals is shorter than the lifetime of methyl radicals (Figure 7.2). Therefore, as it is shown by numerical simulations, the decay profiles are sensitive to the rate constant of reaction 1 at the late stage of the decay (Figure 7.1), which allowed extraction of k₁ from the fits based on the reaction mechanism.

The results of the measurements are summarized in Table 7.1. The average value of the rate constant is $(3.7 \pm 1.8) \times 10^{-11}$ cm³molecule⁻¹s⁻¹ (295 K, 1bar, He). Figure 7.3 shows comparison of this measurement with the previous data. The rate constant of reaction 1 measured in this study is factor of 3.7 lower than that predicted in theoretical study of Zhu and Lin³⁹, and is in a very good agreement with the recent theoretical study by Jasper et al.³⁸

Reaction ^a	Reactants	Products	Rate constant ^b	Reference	Comment	Variation in the rate	Change in
						constant, %	k1 returned
							by the fit,
							%
1a	CH ₃ +HO ₂	CH ₃ O+OH	This work				
1b	-	CH ₂ O+H ₂ O					
1c	-	CH ₃ OOH	-				
1d		$CH_4+^3O_2$					
1e		$CH_4+^1O_2$					
2a	N ₂ O+hv(193	$O(^{1}D)+N_{2}$			$\phi(O^1D)=1$		
2b	nm)	$N(^{4}S)+NO(^{2}\Pi)$					
3a	$H_2O_2 + hv(193)$	2OH		Ref. ¹⁴⁸⁻¹⁴⁹	φ(OH)=1.5		
3b	nm)	other products		Ref. ¹⁴⁸⁻¹⁴⁹	φ(H)=0.16		
4	$O(^{1}D)+H_{2}O_{2}$	OH+HO ₂	5.2×10^{-10}	Ref. ¹⁵¹		+23	
5	$O(^{1}D)+CH_{4}$	OH+CH ₃	1.3×10^{-10}	Ref. ¹⁵		+23	< 0.002
ба	$O(^{1}D)+H_{2}O$	2 OH	$1.7 \times 10^{-10} \exp(36/T)$	Ref. ⁷⁵		+23	+5
6b		H_2+O_2	2.2×10^{-12}	Ref. ¹⁶		+23	+5
6с	-	$O(^{3}P)+H_{2}O$	<0.003 k _{6a}	Ref. ⁷⁶	Neglected		
7*	OH+CH ₄	H ₂ O+CH ₃	$4.16 \times 10^{-13} (T/298)^{2.18} \exp(-1232/T)$	Ref. ¹¹⁹		+12	+17
8	OH+H ₂ O ₂	H ₂ O+HO ₂	$2.9 \times 10^{-12} \exp(109/T)$	Ref. ⁸²		+23%	+5
9a	$O(^{1}D)+N_{2}O$	2 NO	8.37x10 ⁻¹¹	Branching	$k_8 = 1.35 \times 10^{-10}$ is	+23	+3

Table 7.2. Reaction Mechanism used to Fit the Experimental Profiles (Continued)

Reaction ^a	Reactants	Products	Rate constant ^b	Reference	Comment	Variation in the rate	Change in
						constant, %	k1 returned
							by the fit,
							%
				ratio of 0.62	the average of		
				based on Ref. ¹⁶	three studies ⁷⁰ , 78, 118		
9b		N ₂ +O ₂	5.13x10 ⁻¹¹	Branching ratio of 0.38 Ref. ¹⁶		+23	+5
9c*		O(³ P)+N ₂ O	1.3x10 ⁻¹²	Ref. ⁷⁵	$k_{8c}/k_8 < 0.01,^{75}$ set to 1.3×10^{-12}	+23	+6
10a*	OH+CH ₃	H ₂ O+ ¹ CH ₂	$1.2 \times 10^{-10} (T/300)^{-0.49}$	Ref. ¹⁵⁰		+26	-10
10b		CH ₃ OH					
11a	OH+OH	H ₂ O+O	$(1.38 \pm 0.20) \text{x} 10^{-12} (\text{T}/300)^{-0.76}$	Ref. ¹³⁹		+15	±0.01
11b		H ₂ O ₂	$K_{11b,\infty} = (2.4 \pm 0.6) \times 10^{-11} (T/300)^{-0.5}$ $K_{11b,0} = [He] (9.0 \pm 2.2) \times 10^{-31} (T/300)^{-10}$ $K_{11b,0} = [He] (9.0 \pm 2.2) \times 10^{-31} (T/300)^{-10}$	Ref. ¹¹⁶		+25	±0.02
12	CH ₃ +CH ₃	C ₂ H ₆	5.92x10 ⁻¹¹	Ref. ¹⁵⁰		+5	+4
13	OH+O	O ₂ +H	$2.4 \times 10^{-11} \exp(110/T)$	Ref. ¹⁶		+40	+0.02
14a*	OH+H	H ₂ +O	6.86x10 ⁻¹⁴ (T/298) ^{2.8} exp(-1950/T)	Ref. ¹²⁰		+23%	+6
14b*		H ₂ O	$[M] 1.6x10^{-31} (T/298)^{-2.6}$	Ref. ⁷⁴		+23%	+6
15*	CH ₃ +O	H ₂ CO+H	$1.4 \mathrm{x} 10^{-10}$	Ref. ¹²¹		+67%	+10
16	OH+NO	HONO	$\begin{array}{c} k=6.0 \times 10^{-31} (T/300)^{-2.5} \\ k_{inf}=3.3 \times 10^{-11} (T/300)^{-0.3} \\ exp(91/T) \end{array} F_{cent}=0.60 \end{array}$	Ref. ⁷⁹	$F_{17,cent}$: fit of the data from Ref. ⁷⁹	+40%	+3
17*	CH ₃ +H	CH ₄	$6.2 \times 10^{-29} (T/298)^{-1.8}$	Ref. ²⁹		+40%	+10
18	OH+CH ₂	CH ₂ O+H	3x10 ⁻¹¹	Ref. ⁷³		+37%	+5

Table 7.2. Reaction Mechanism used to Fit the Experimental Profiles (Continued)

Reaction ^a	Reactants	Products	Rate constant ^b	Reference	Comment	Variation in the rate	Change in
						constant, %	k1 returned
							by the fit,
							%
19*	OH+HO ₂	H ₂ O+O ₂	$4.8 \times 10^{-11} \exp(250/T)$	Ref. ⁸⁰		+23%	-9
20*	CH ₃ +NO	CH ₃ NO	2.1x10 ⁻³⁰ (T/298 K) ^{-1.87}	Ref. ¹²³		+23%	-6
21*	CH ₃ +H ₂ O ₂	CH ₄ +HO ₂	$2x10^{-14}exp(300/T)$	Ref. ⁷³		+40%	-8
22	HO ₂ +NO	OH+NO ₂	$4x10^{-12}exp(223/T)$	Ref. ⁸¹		+5%	+3
23	O+HO ₂	O ₂ +OH	$2.7 \times 10^{-11} \exp(224/T)$	Ref. ¹⁶		+40%	+4
24	O+H ₂ O ₂	OH+HO ₂	$1.4 \times 10^{-12} \exp(-2000/T)$	Ref. ¹⁶		factor 2.5	+0.01
25a	H+HO ₂	H ₂ +O ₂	$7.11 \times 10^{-11} \exp(-710/T)$	Ref. ⁹²		+40%	+3
25b	-	O(¹ D)+H ₂ O	$3.29 \times 10^{12} (T/298)^{1.55} \exp(81/T)$	Ref. ⁸⁴		+40%	+3
25*c	-	2OH	$2.8 \times 10^{-10} \exp(-440/\mathrm{T})$	Ref. ⁹²		+40%	+7
25d		H ₂ O+O	$5.00 \times 10^{-11} \exp(-433/\mathrm{T})$	Ref. ⁹²			+3
26	H+H ₂ O ₂	H ₂ +HO ₂	$2.81 \times 10^{-12} \exp(-1889/T)$	Ref. ⁹²			+3
27	O+O ₂	O ₃	$[M] 3.4 x 10^{-34} (T/300)^{-1.2}$	Ref. ⁸⁸			+3
28a	H+O ₂	OH+O	$1.62 \times 10^{-10} \exp(-7470/\mathrm{T})$	Ref. ⁸⁹			+3
28b		HO ₂	$[M] 5.4 \times 10^{-32} (T/298)^{-1.80}$	Ref. ⁹¹			+3
29	HO ₂ +O ₂	OH+O ₃	0				
30	O+O ₃	O ₂ +O ₂	8x10 ⁻¹² exp(-2060/T)	Ref. ¹⁵²			+3
31	H+O ₃	OH+O ₂	$1.4 \times 10^{-10} \exp(-480/T)$	Ref. ⁹⁰			+2
32	HO ₂ +O ₃	OH+O ₂ +O ₂	$1.97 \times 10^{-16} (T/298)^{4.57} \exp(693/T)$	Ref. ¹⁶			+1
33	HO ₂ +HO ₂	H ₂ O ₂ +O ₂	$2.2 \times 10^{-13} \exp(-600/T)$	Ref. ¹⁶			-3
34	O ₃ +NO	NO ₂ +O ₂	1.8×10^{-14}	Ref. ¹⁶			

Table 7.2. Reaction Mechanism used to Fit the Experimental Profiles (Continued)

Reaction ^a	Reactants	Products	Rate constant ^b	Reference	Comment	Variation in the rate	Change in
						constant, %	k1 returned
							by the fit,
							%
35a	CH ₃ O	CH ₂ OH	$1 \times 10^{13} \exp(-13110/T)$	Ref. ¹⁵³			+0.02
35b	-	CH ₂ O+H	9x10 ⁻¹¹ exp(-6791/T)	Ref. ¹⁵⁴			+0.02
36	CH ₃ O+N ₂ O	PRODUCT	1.66x10 ⁻¹⁴	Ref. ¹⁵⁵			+1
37	CH ₃ O+H ₂ O ₂	CH ₃ OH+HO ₂	5x10 ⁻¹⁵ exp(-1300/T)	Ref. ¹⁵⁶			-2
38	CH ₃ O+HO ₂	CH ₂ O+H ₂ O ₂	5x10 ⁻¹³	Ref. ⁷³			-2
39	CH ₃ O+CH ₄	CH ₃ OH+CH ₃	$2.2 \times 10^{-10} \exp(-7579/T)$	Ref. ¹⁵⁷			-2
40a	CH ₃ O+CH ₃	CH ₂ O+CH ₄	4x10 ⁻¹¹	Ref. ⁷³			-2
40b	-	(CH ₃) ₂ O	5.5x10 ⁻¹¹	Ref. ¹⁵⁸			-3
41a	CH ₃ O+CH ₃ O	CH ₃ OH+CH ₂ O	3.85x10 ⁻¹¹	Ref. ¹⁵⁸			+1
41b		(CH ₃ O) ₂	3x10 ⁻¹²	Ref. ⁷³			+1
41c		CH ₂ O+H ₂ O					+0.1
42a	CH ₃ O+OH	CH ₂ O+H ₂ O	3x10 ⁻¹¹	Ref. ⁷³			
42b	-	CH ₃ OOH	Unknown				+0.1
43a	CH ₃ O+O	CH ₂ O+OH	1x10 ⁻¹¹	Ref. ¹⁵⁶			+0.1
43b		CH ₃ OO	0				+0.2
44a	CH ₃ O+H	CH ₂ O+H	$3.3_{\rm X}10^{-11}$	Ref. ¹⁵⁹			
44b		CH ₃ OH	Unknown				

Table 7.2. Reaction Mechanism used to Fit the Experimental Profiles (Continued)

^a Asterisk labels the main reactions in the mechanism (when variation of the rate constants leads to >5% variation in the rate

constant k_1 returned by the fits) ^bRate constants and concentrations units are based on molecule, cm³ and sec.

r	oss -Sections.			
	216.4 nm	224 nm	Reference	

2.25x10⁻¹⁹

 0.037×10^{-20}

 2.99×10^{-19}

 1.21×10^{-19}

Table 7.3. Relev	ant Absorption Cr	oss -Sections.	
Absorption	102.2	216.4	

193.3nm

 6.01×10^{-19}

8.70x10⁻²⁰

 1.51×10^{-21}

3.90x10⁻¹⁹

 1.55×10^{-19}

Cross Section^a

 H_2O_2

 N_2O

 H_2O

CH₃

 HO_2

HONO

^aAbsorption cross section in cm² molecule⁻¹

7.4 Conclusions

2.93x10⁻¹⁹

 0.20×10^{-20}

 3.55×10^{-17}

3.73x10⁻¹⁹

 1.76×10^{-19}

It is demonstrated, that reaction of methyl and hydroperoxy radicals can be successively studied using simultaneous production of these species from hydrogen peroxide and methane in reactions of photolytically produced $O(^{1}D)$ atoms and, subsequently, OH radicals. In this work, the reaction is studied at 295 K and ambient pressure. The measured rate constant is in excellent agreement with the recent theoretical study by Jasper et al.³⁸ Extension of the measurements on higher temperatures and pressures is planned

Ref.^{126, 160-162}

Ref.⁷¹

Ref.¹³⁹

Ref.¹⁵⁰

Ref.¹⁶³

Ref.¹⁶⁴

CHAPTER 8

CONCLUSIONS

This dissertation describes a systematic fundamental study on the kinetics and mechanisms of several elementary reaction of combustion importance over extended temperature and elevated pressure ranges. A fully functional experimental set-up that incorporates several novel features (such as a high-pressure flow reactor and direct introduction of liquid at high pressure in reactor) was modified and reassembled. The experimental approaches as well as the procedures of the data processing and interpretation are validated in the studies of elementary reactions of free radicals (OH, CH_3 , and HO_2). Chapter 4 describes the self reaction of OH radical. Experimental data on the rate constant of this reaction measured over an extended temperature (295 - 834 K)and pressure (1 - 100 bar) ranges is used to parameterize the pressure fall-off in the recombination channel (formation of H_2O_2) as well as to obtain independent data on the pressure independent disproportionation channel (OH+OH \rightarrow H₂O+H) at T > 450 K. The minor deviation in the high pressure rate constant for recombination channel (-37%) and a substantial (factor of 2.2) deviation of the low pressure limit rate constant from the recommended values are observed. The low-pressure extrapolations of the rate constant suggest the existence of the turning point in the temperature dependence of disproptionate channel in the 400 - 550 K range. In a separate study, the rate constant of reaction $OH+OH \rightarrow H_2O+H$ is measured over temperature over the range 295 – 414 K at 3 and 10 bar to resolve the discrepancy in the IUPAC recommended value and recent reported by Bahng and Macdonald.²⁷ The disproportionation (presumably pressure independent)

channel of reaction 1, OH + OH \rightarrow H₂O + O, is isolated using conversion of oxygen atoms, produced in the reaction, to ozone. The rate constants are determined based on the time-resolved ozone yield using explicit OH concentration profiles. The results are consistent with the measurements of Bedjanian et al.⁵⁴ (which is currently recommended by IUPAC), and do not support the most recent measurement of Bahng and Macdonald.²⁷ Measured in this work, the rate constant of reaction OH+OH \rightarrow H₂O+H at 298 K is: k = (1.39 ± 0.20) x10⁻¹² cm³molecule⁻¹s⁻¹, with the temperature dependence of the rate constant is (1.38 ± 0.20) x10⁻¹² (T/300)^{-0.73} in the temperature range 295 – 440 K. A turning point in the temperature dependence of k_{OH+OH₂H2O+H} in the temperature range of 400 - 500 K is confirmed. Such behavior is anticipated for reactions with "negative barriers" (Krasnoperov et al.).⁷¹ The V-shaped temperature dependence of k_{OH+OH₂H2O+H} based on combined current and previous studies in the temperature range of 233 – 2380 K is k_{OH+OH₂H2O+H = (5.1exp(-T/190 K) + 0.30(T/300 K)^{1.73})x10⁻¹² cm³molecule⁻¹s⁻¹.}

The study of reaction of the methyl and hydroxyl radicals over extended temperature (294 - 714 K) and pressure (1-100 bar) ranges is described in Chapter 5. The measured rate constants are independent of pressure within the pressure range of the study (1 – 100 bar, He) at all temperatures. The rate constant shows moderate negative temperature dependence, $k_{CH3+OH} \propto T^{-0.5}$. Self-reaction of CH₃ radicals is discussed in Chapter 6, the recombination rate constant is independent of pressure, and it has negative temperature dependence. The room temperature rate constant k _{CH3+CH3}=5.94x10⁻¹¹ cm³molecule⁻¹s⁻¹ is in excellent agreement with the IUPAC recommended value.

Initial experiments on the kinetics of the reaction of methyl and hydroperoxy radicals $(CH_3 + HO_2)$ are described in Chapter 7. The reaction is studied at 295 K and

ambient pressure. The measured rate constant is in excellent agreement with the recent theoretical study by Jasper et al.³⁸ Extension of the measurements on higher temperatures and pressures is planned. Current approach is limited by observed decomposition of H_2O_2 (the source of HO_2 radicals) on the walls of the preheating tubing of the flow reactor at elevated temperatures. An alternative source of HO_2 (one that does not use H_2O_2) for kinetics studies at elevated temperatures and pressures is to be developed.

APPENDIX A

CALIBRATION OF MASS FLOW CONTROLLER

The mass flow controllers used in this study are Brooks 1050 series. Depending upon the flow rate requirement different mass flow controllers have been used for the reactant gases. The mass flow controllers have been routinely calibrated.

Mass flow controller #6 (S/N 5142): This mass flow controller has been used for supply N_2O and N_2O /He mix to the reactor. The calibrations of the mass controllers with different gases are shown in Figure A1 – A5.



Figure A.1 Calibration of mass flow controller # 6 (S/N 5142) with N₂O mix (2.5%).


Figure A.2 Calibration of mass flow controller # 6 (S/N 5142) with Pure N_2O .



Figure A.3 Calibration of mass flow controller # 6 (S/N 5142) with helium

Mass flow controller #2 (S/N 8122): This mass flow controller is used for supply of Oxygen to the reactor in this study. The calibration of mass controller with different gases is following



Figure A.4 Mass flow controller #2 (S/N B90HCOB80212) calibrations for oxygen.



Figure A.5 Mass flow S/N B90HCOB80212 calibrations using helium and methane as a career gas.

Mass flow controller #4 (S/N 27257001): This mass flow controller is used for supply of helium to the reactor in this study.



Figure A.6 Mass flow controller #4 (S/N 27257001) calibrations used for heliu

Appendix B

SCIENTIST MODEL

The sample model used for the processing of profiles in $OH + OH \rightarrow H_2O$ study

//oh v4.eqn. OH proviles processing, version 4. L Krasnoperov, 01/25/12
//modified 1/31/12 to include the diffusion limited wall rate constant
// for OH loss
// as a longest exponential (lambda = 5.748 D/R^2)
//This model fits OH absorption
//and produces the rate constant OH+OH --> H2O + O, k4a
//based on OH absorption profiles and SigmaOH
//Based on the version of E Chesnokov "oh_oh_based_on_Mcdonald.eqn"
//Photolysis of N2O/H2O mixtures at 193 nm.

 $\label{eq:linear_line$

// Time should be in the 1-st column, signal (absorbance) - in 2-nd and 3-rd

IndVars: TIME, SIGNAL1 DepVars: SIGNAL Params: kwOH,OHini,ZeroShift

//Only information between the two dashed lines may be changed // from experiment to experiment //_____

//Time Window for fit (all in sec) t1=0.2e-3 t2=30e-3

//Conditions: //Exp 020812 Exp.4 He, 1.012 bar

T=769 p=1.012 M=9.528e18 N2O=3.303E+16 //OHini=1.235E+13 Oini=5.11e10 NOini=1.129E+12 SigmaN2O=2.20e-19 SigmaH2O=1.51e-21

SigmaOH=4.07e-17 Hini=2.274e11 HONOini=0 H2O2ini=0 HO2ini=0 //ZeroShift=0 // D(OH in He)= 0.88 bar cm2s-1 according to Ivanov et al at 296 // Temperature dependence T^1.6 is ASSUMED //0.146 is R^2 (R =0.76 cm/2) //kwOH = (5.784/0.146)*(0.88/p)*(T/296)^1.6 //kwOH=0 //Pass length (cm) L=10.12 // Wavelength 216 nm (just for reference) //SigmaCH3=4.36e-17 //SigmaH2O2=2.96e-19 //SigmaHONO=1.79e-18 //

//Reaction Mechanism based on Macdonald J.Phys.Chem. A 2007, 111, 3850-3861

// N2O + hv>O(1D) + N2 // O(1D)+N2O> 2 NO // O(1D)+N2O> N2 +O2 //O(1D)+H2O> 2 OH // OH + OH> H2O+O		(1a) (1b) (2) (4a)	(0)
// OH + OH> H2O2 //OH + O> O2 +H //OH + H> H2O	(8b)	(4b) (7)	
//OH + H> H2 + O // OH + NO> HONO // OH + H2O2> H2O + HO2	()	(8a) (10) (14)	
// OH + HO2> H2O + O2 // HO2 + NO> OH + NO2 //Rate constants:		. ,	(15) (16)
// k4a: OH+OH> H2O + O // k4a to be fitted //k4a=2.6e-12*(298/T)		(4)	
k4a=1.75e-12 //k4b: OH+OH> H2O2 // at high T and not very high p k4b	is negle	(4b) cted	
//OH + O> O2 +H // 2004 ATK/BAU k7=2 4e-11*exp(109/T)		(7)	
//OH + H> H2O //77 ZEL/ERL k8b=M*1 6e-31*(T/298)^(-2 6)	(8b)		
//OH + H> H2 + O //86TSA/HAM k8a = 6.86e-14*(T/298)^2.8*exp(-1	950/T)	(8a)	
// OH + NO> HONO k010=3.9e-31*(T/298)^(-2.6) kinf10=3.3e-11		(10)	
Fcent10=1.23*exp(-T/815) x10=k010*M/kinf10 c10=-0.4-0.67*Log10(Fcent10) N10=0.75-1.27*Log10(Fcent10)			
d=0.14 y10=Log10(x10)+c10 LF10=Log10(Fcent10)/(1+(y10/(N1 F10=10^LF10	0-d*y10))^2)	

k10=kinf10*F10*x10/(1+x10) // OH + H2O2 --> H2O + HO2 (14) //2004JIM/GIE k14=2.9e-12*exp(-109/T) // OH + HO2 --> H2O + O2 (15) //1988KEY k15=4.8e-11*exp(250/T) // HO2 + NO --> OH + ŃO2 (16) //2003BAR/BAC k16=4e-12*exp(223/T) //Species transient: OH, O, H, NO, HONO, H2O2,HO2 //Species stable: N2O, H2O, //Equations: r4a=k4a*OH*OH r4b=k4b*OH*OH r7=k7*OH*O r8a=k8a*OH*H r8b=k8b*OH*H r10=k10*OH*NO r14=k14*OH*H2O2 r15=k15*OH*HO2 r16=k16*HO2*NO OH'=-2*r4a-2*r4b-r7-r8a-r8b-r10-r14-r15+r16-kwOH*OH O'=r4a-r7+r8a H'=r7-r8a-r8b NO'=-r10-r16 HONO'=r10 H2O2'=r4b-r14 HO2'=r14-r15-r16 Absorption = L*SigmaOH*OH+ZeroShift F1=SIGNAL1 F2=Absorption gate=UNIT(TIME-t1)*UNIT(t2-TIME) SIGNAL=(1-gate)*F1+gate*F2 //Initial Conditions TIME=0 OH=OHini O=Oini NO=NOini H=Hini HONO=HONOini H2O2=H2O2ini HO2=HO2ini //Initial Parameters and Constraints //k4a=2e-12 kwOH=200 OHini=3e13 ZeroShift=-2e-4

The sample model used for the processing of profiles in CH₃ + OH study

//CH3 v1 explicit OH based on McDonald.eqn. CH3 profiles processing, version 1. L Krasnoperov, //12/04/09 //This model produces the rate constant OH+CH3 //based on CH3 absorption profiles //and explicit OH profiles under THE SAME EXPERIMENTAL CONDITIONS

//and explicit On profiles under the SAME EXPERIMENTAL CONDITIONS //Based on the version of E Chesnokov "ch3_(oh_explicit)_based_on_Mcdonald.eqn" //Photolysis of N2O/H2O/acetone mixtures at 193 nm.

 $\label{eq:linear_line$

// Time should be in the 1-st column, signal (light intensity) - in 2-nd and 3-rd

IndVars: TIME,SIGNAL1 DepVars: SIGNAL Params: CH3ini, k, shift

//Only information between the two dashed lines may be changed // from experiment to experiment //_____

//Time Window (all in sec)

t1=5e-6 t2=3e-3

//Exp 04/21/10 Exp.6 He 9.84 bar //Conditions: T=558 M=1.27777E+20 N2O=6.01981E+16 CH4=0 Acetone=9.24E+14 OHini=7.96122E+13 //CH3ini=4.36E+13 Oini=2.73713E+11 NOini=8.14874E+12

Hini=0 CH2ini=0 HONOini=0 H2O2ini=0 HO2ini=0

//Explicite profile of OH expressed as double-exponential with shift //Laser energies when CH3 and OH were measured (mJ on Molectron), respectively

ELaserCH3=.600

ELaserOH=.604

EnergyCorr=ELaserCH3/ELaserOH

OH=EnergyCorr*(0.00907*exp(-TIME/0.00058)+0.00379*exp(-TIME/0.00011)+0.00085)/SigmaOH/L

//Branching ratio in the reaction OH + CH3, fixed. Alpha is the fratcion of the H2O + CH2(S) channel. // (1-alpha) is the fraction of the stabilization channel, CH3OH.

(6)

alpha=0.1

//Rate constant of CH3 recombination: depends upon pressure and temperature

//k6: CH3 + CH3 --> C2H6

//T=298 //1 bar 6.29e-11 //10 bar 6.42e-11 //100 bar 6.47e-11

//k6=6.42e-11 k6=5.54e-11*(T/300)^(-0.31)

//Cross-section of OH at ca. 308 - pressure and lamp dependent! Obtained from the OH profile fit

SigmaOH=1.67e-17

//Pass length (cm) L=10

// Cross-sections at 216 nm
 // Cross-section of CH3 is pressure dependent! (Temperature too!)
 //From Krasnoperov, Mehta for Sigma(216.51), correction for triangular slit function
 //0.6 nm as x1.019 (Grebenkin, Krasnoperov), and p-dependence as in Mehta, et al.

//for T=298K
//pHe=1 bar SigmaCH3 = 3.59e-17
//pHe= 3 bar SigmaCH3 = 3.51e-17
//pHe=10 bar SigmaCH3 = 3.27e-17
//pHe=30 bar SigmaCH3 = 2.73e-17
//pHe=100 bar SigmaCH3=1.74e-17
// Pilling temperature dependance corrected /1.33

SigmaCH3=1e-17*(4.35-0.0035*T)

//SigmaCH3=4.36e-17 - this is the value used by E Chesnokov for 30 bar???

SigmaH2O2=2.96e-19 SigmaHONO=1.79e-18

//

//Reaction Mechanism based on Macdonald J.Phys.Chem. A 2007, 111, 3850-3861

(0)

// N2O + hv>O(1D) + N2	
// O(1D)+N2O> 2 NO	(1a)
// O(1D)+N2O> N2 +O2	(1b)
//O(1D)+H2O> 2 OH	(2)
//O(1D)+CH4> OH + CH3	(3)

// OH + OH> H2O+O // OH + OH> H2O2 // OH + CH3> H2O + CH2 // OH + CH3> CH3OH //OH + CH4> H2O + CH3 //CH3 + CH3> C2H6 //OH + O> O2 +H //OH + H> H2O //OH + H> H2O // OH + H> H2O + H // OH + NO> H2OO + H // OH + CH2> CH2O + H // OH + CH2> CH2O + H // OH + CH2> H2O + HO2 // OH + H2O2> H2O + HO2 // OH + H2O2> H2O + HO2 // OH + HO2> OH + NO2 // CH3 + NO> CH3NO //CH3 + H2O2> CH4 + HO2 // CH3 + H2O2> CH4 + HO2 //CH3 + H2O2> CH4 + HO2 //CH3 + H2O2> CH4 + HO2 //Rate constants: ka=alpha*k kb=(1-alpha)*k //k4b obtained from OH profile fits k4b=2.75e-12 //k4a: OH+OH> H2O + O //2007McDon // k4a decrese with temperature.	(8) 2)CO+H2((4a) (4b) (Xa) (Xb) (6) (7) (8b) (9) (10) (11) (12) (14) (17) (18) (4) endence	ka kb (5) (13) (15) (16) arbitrary	ka+kb=k
k4a=2.6e-12*(298/T)				
//k4b: OH+OH> H2O2		(4b)		
//OH + CH4> H2O + CH3 k5 =4.16e-13*(T/298)^2.18*exp(-12	232/T)		(5)	
//OH + O> O2 +H // 2004 ATK/BAU k7=2.4e-11*exp(109/T)		(7)		
//OH + H> H2O //77 ZEL/ERL k8=M*1.6e-31*(T/298)^(-2.6)	(8)			
//OH + H> H2 + O //86TSA/HAM k8b = 6.86e-14*(T/298)^2.8*exp(-1	950/T)	(8b)		
// CH3 + O> H2CO		(9)		
// OH + NO> HONO		(10)		
k010=3.9e-31*(T/298)^(-2.6) kinf10=3.3e-11 Fcent10=1.23*exp(-T/815) x10=k010*M/kinf10 c10=-0.4-0.67*Log10(Fcent10) N10=0.75-1.27*Log10(Fcent10) d=0.14 y10=Log10(x10)+c10 LF10=Log10(Fcent10)/(1+(y10/(N1	10-d*y10))	y^2)		

F10=10^LF10 k10=kinf10*F10*x10/(1+x10)

r4a=k4a*OH*OH r4b=k4b*OH*OH

// CH3 + H --> CH4 (11)//Pilling1997 k011=6.2e-29*(T/298)^(-1.8) kinf11=3.5e-10 Fcent11=0.638*exp(-T/3231) x11=k011*M/kinf11 c11=-0.4-0.67*Log10(Fcent11) N11=0.75-1.27*Log10(Fcent11) d=0.14 y11=Log10(x11)+c11 LF11=Log10(Fcent11)/(1+(y11/(N11-d*y11))^2) F11=10^LF11 k11=kinf11*F11*x11/(1+x11) // OH + CH2 --> CH2O + H (12)//1986TSA/HAM k12=3e-11 // OH + (CH3)2CO -->(CH3)(CH2)CO+H2O (13)//2003YAM/TAY k13=3.15e-14*(T/300)^4*exp(453/T) // OH + H2O2 --> H2O + HO2 (14) //2004JIM/GIE k14=2.9e-12*exp(-109/T) // OH + HO2 --> H2O + O2 (15) //1988KEY k15=4.8e-11*exp(250/T) // HO2 + NO --> OH + NO2 (16)//2003BAR/BAC k16=4e-12*exp(223/T) //CH3 + NO -->CH3NO (17)//1991 Pilling Ar //A.H.Langer,A.M.Bass.Int.J.Chem.Kin.V.7,639-648(1975) kHe=kAr k017=6.9e-32*exp(1430/T) kinf17=1.5e-11*exp(-60/T)Fcent17=5*exp(-T/120) x17=k017*M/kinf17 c17=-0.4-0.67*Log10(Fcent17) N17=0.75-1.27*Log10(Fcent17) d=0.14 y17=Log10(x17)+c17 LF17=Log10(Fcent17)/(1+(y17/(N17-d*y17))^2) F17=10^LF17 k17=kinf17*F17*x17/(1+x17) //CH3 + H2O2 --> CH4 + HO2 (18) //1986TSA k18=2e-14*exp(300/T) //Species transient: OH, CH3, O, H, NO, CH2, HONO, H2O2, HO2 //Species stable: N2O, ACETONE, CH4 //Equations:

r5=k5*OH*CH4 ra=ka*OH*CH3 rb=kb*OH*CH3 r6=k6*CH3*CH3 r7=k7*OH*O r8=k8*OH*H r8b=k8b*OH*H r9=k9*CH3*O r10=k10*OH*NO r11=k11*CH3*H r12=k12*OH*CH2 r13=k13*OH*ACETONE r14=k14*OH*H2O2 r15=k15*OH*HO2 r16=k16*HO2*NO r17=k17*CH3*NO r18=k18*CH3*H2O2

//OH'=-2*r4a-2*r4b-r5-ra-rb-r7-r8-r8b-r10-r12-r13-r14-r15+r16 CH3'=r5-ra-rb-2*r6-r9-r11-r17-r18 O'=r4a-r7+r8b-r9 H'=r7-r8-r8b+r9-r11+r12 NO'=-r10-r16-r17 CH2'=ra-r12 HONO'=r10 H2O2'=r4b-r14-r18 HO2'=r14-r15-r16

Absorption = L*(SigmaCH3*CH3+SigmaHONO*HONO+SigmaH2O2*H2O2)+shift

F1=SIGNAL1 F2=Absorption gate=UNIT(TIME-t1)*UNIT(t2-TIME) SIGNAL=(1-gate)*F1+gate*F2 ***

//Initial Conditions

TIME=0 CH3=CH3ini O=Oini NO=NOini H=Hini CH2=CH2ini HONO=HONOini H2O2=H2O2ini HO2=HO2ini

//Initial Parameters and Constraints

CH3ini=2.37e13 k=1.306e-10 shift=0

The sample model used for the processing of profiles in CH₃ + CH₃ study

//This model produces the rate constant CH3+CH3 and SigmaCH3

// Time should be in the 1-st column, signal (light intensity) - in 2-nd and 3-rd

IndVars: TIME,SIGNAL1 DepVars: SIGNAL Params: k6, SigmaCH3, shift

//Only information between the two dashed lines may be changed
// from experiment to experiment
//

//Time Window (all in sec)

t1=9e-6 t2=3e-3

//Exp 06/03/10 Exp1He 100bar //Conditions: T=837 M=8.57667E+20 N2O=451836446 CH4=0 Acetone=1.59E+15 OHini=792484.9166 CH3ini=7.08E+13 Oini=2161.322505 NOini=0.000732628 Hini=0 CH2ini=0 HONOini=0 H2O2ini=0 HO2ini=0

OH=0

//Rate constant of CH3 recombination: depends upon pressure and temperature

//k6: CH3 + CH3 --> C2H6

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//T=298 //1 bar 6.29e-11 //10 bar 6.42e-11 //100 bar 6.47e-11

//Pass length (cm) L=10

// Cross-sections at 216 nm
 // Cross-section of CH3 is pressure dependent! (Temperature too!)
 //From Krasnoperov, Mehta for Sigma(216.51), correction for triangular slit function
 //0.6 nm as x1.019 (Grebenkin, Krasnoperov), and p-dependence as in Mehta, et al.

//for T=298K //pHe=1 bar SigmaCH3 = 3.59e-17 //pHe= 3 bar SigmaCH3 = 3.51e-17 //pHe=10 bar SigmaCH3 = 3.27e-17 //pHe=30 bar SigmaCH3 = 2.73e-17 //pHe=100 bar SigmaCH3=1.74e-17 // Pilling temperature dependance corrected /1.33 1bar /1.8 100bar

//SigmaCH3=1e-17*(7.58-1.29e-2*T+7.28e-6*T*T)/1.8

SigmaH2O2=2.96e-19 SigmaHONO=1.79e-18

//_____

//Reaction Mechanism based on Macdonald J.Phys.Chem. A 2007, 111, 3850-3861

// N2O + hv>O(1D) + N2 // O(1D)+N2O> 2 NO // O(1D)+N2O> N2 +O2 //O(1D)+H2O> 2 OH //O(1D)+CH4> OH + CH3 // OH + OH> H2O+O // OH + OH> H2O2	(1a) (1b) (2) (3) (4a) (4b)	(0)	
<pre>// OH + CH3> H2O + CH2 // OH + CH3> CH3OH //OH + CH4> H2O + CH3 //CH3 + CH3> C2H6 //OH + O> O2 +H //OH + H> H2O //OH + H> H2CO + H // OH + NO> HONO // CH3 + H> CH4 // OH + CH2> CH2O + H // OH + CH2> CH2O + H // OH + (CH3)2CO>(CH3)(CH2 // OH + HO2> H2O + HO2 // OH + HO2> H2O + O2 // OH + HO2> OH + NO2 // CH3 + NO> CH3NO //CH3 + H2O2> CH4 + HO2</pre>	(Xa) (Xb) (5) (6) (7) (8) (8b) (9) (10) (11) (12) 2)CO+H2O(13) (14) (15) (16) (17) (18)	ka kb	ka+kb=k
//Rate constants:			
ka=alpha*k kb=(1-alpha)*k			
//k4b obtained from OH profile fits			
k4b=3.9e-12			
//k4a: OH+OH> H2O + O	(4)		
//2007McDon // k4a decrese with temperature.	1/T dependence	arbitrary	introdused
k4a=2.6e-12*(298/T)			
//k4b: OH+OH> H2O2	(4b)		
//OH + CH4> H2O + CH3 k5 =4.16e-13*(T/298)^2.18*exp(-1	232/T)	(5)	
//OH + O> O2 +H // 2004 ATK/BAU k7=2.4e-11*exp(109/T)	(7)		

//OH + H --> H2O (8) //77 ZEL/ERL k8=M*1.6e-31*(T/298)^(-2.6) //OH + H --> H2 + O (8b) //86TSA/HAM $k8b = 6.86e - 14^{*}(T/298)^{2.8} \exp(-1950/T)$ // CH3 + O --> H2CO + H (9) //1992ATK k9= 1.4e-10 // OH + NO --> HONO (10)k010=3.9e-31*(T/298)^(-2.6) kinf10=3.3e-11 Fcent10=1.23*exp(-T/815) x10=k010*M/kinf10 c10=-0.4-0.67*Log10(Fcent10) N10=0.75-1.27*Log10(Fcent10) d=0.14 y10=Log10(x10)+c10 LF10=Log10(Fcent10)/(1+(y10/(N10-d*y10))^2) F10=10^LF10 k10=kinf10*F10*x10/(1+x10) // CH3 + H --> CH4 (11) //Pilling1997 k011=6.2e-29*(T/298)^(-1.8) kinf11=3.5e-10 Fcent11=0.638*exp(-T/3231) x11=k011*M/kinf11 c11=-0.4-0.67*Log10(Fcent11) N11=0.75-1.27*Log10(Fcent11) d=0.14 y11=Log10(x11)+c11 LF11=Log10(Fcent11)/(1+(y11/(N11-d*y11))^2) F11=10^LF11 k11=kinf11*F11*x11/(1+x11) // OH + CH2 --> CH2O + H (12) //1986TSA/HAM k12=3e-11 // OH + (CH3)2CO -->(CH3)(CH2)CO+H2O (13)//2003YAM/TAY k13=3.15e-14*(T/300)^4*exp(453/T) // OH + H2O2 --> H2O + HO2 (14)//2004JIM/GIE k14=2.9e-12*exp(-109/T) // OH + HO2 --> H2O + O2 (15) //1988KEY k15=4.8e-11*exp(250/T) // HO2 + NO --> OH + NO2 (16)//2003BAR/BAC k16=4e-12*exp(223/T) //CH3 + NO -->CH3NO

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//1991 Pilling Ar //A.H.Langer,A.M.Bass.Int.J.Chem.Kin.V.7,639-648(1975) kHe=kAr k017=6.9e-32*exp(1430/T) kinf17=1.5e-11*exp(-60/T) Fcent17=5*exp(-T/120) x17=k017*M/kinf17 c17=-0.4-0.67*Log10(Fcent17) N17=0.75-1.27*Log10(Fcent17) d=0.14 y17=Log10(x17)+c17 LF17=Log10(Fcent17)/(1+(y17/(N17-d*y17))^2) F17=10^LF17 k17=kinf17*F17*x17/(1+x17) //CH3 + H2O2 --> CH4 + HO2 (18)

//1986TSA k18=2e-14*exp(300/T) alpha=0.1 k=1.2e-10

//Species transient: OH, CH3, O, H, NO, CH2, HONO, H2O2,HO2 //Species stable: N2O, ACETONE,CH4 //Equations:

r4a=k4a*OH*OH r4b=k4b*OH*OH r5=k5*OH*CH4 ra=ka*OH*CH3 rb=kb*OH*CH3 r6=k6*CH3*CH3 r7=k7*OH*O r8=k8*OH*H r8b=k8b*OH*H r9=k9*CH3*O r10=k10*OH*NO r11=k11*CH3*H r12=k12*OH*CH2 r13=k13*OH*ACETONE r14=k14*OH*H2O2 r15=k15*OH*HO2 r16=k16*HO2*NO r17=k17*CH3*NO r18=k18*CH3*H2O2

//OH'=-2*r4a-2*r4b-r5-ra-rb-r7-r8-r8b-r10-r12-r13-r14-r15+r16 CH3'=r5-ra-rb-2*r6-r9-r11-r17-r18 O'=r4a-r7+r8b-r9 H'=r7-r8-r8b+r9-r11+r12 NO'=-r10-r16-r17 CH2'=ra-r12 HONO'=r10 H2O2'=r4b-r14-r18 HO2'=r14-r15-r16

Absorption = L*(SigmaCH3*CH3+SigmaHONO*HONO+SigmaH2O2*H2O2)+shift

F1=SIGNAL1 F2=Absorption gate=UNIT(TIME-t1)*UNIT(t2-TIME) SIGNAL=(1-gate)*F1+gate*F2 *** //Initial Conditions

TIME=0 CH3=CH3ini O=Oini NO=NOini H=Hini CH2=CH2ini HONO=HONOini H2O2=H2O2ini HO2=HO2ini

//Initial Parameters and Constraints

k6=7e-11 SigmaCH3=3e-17 shift=0

The sample model used for the processing of profiles in CH₃ + HO₂ study

//CH3_HO2.eqn. v.1. L. Krasnoperov, 07/31/12 // Reaction CH3+ HO2 //Photolysis of N2O/H2O/H2O2/CH4/(CH3)2CO/He at 193.3 // Observation at 216.4 and 224 nm //Reversible reaction O + O2 <=> O3 //Explicit HO2 concentration profiles // Obtained via absorption at 224 nm // Calculation of the initial concentartion of transients is here //This model is for N2O/H2O/H2O2/CH4/Acetone/He photolysis at 193 //Recording at 216.4 nm (mainly CH3), 224 nm (HO2) and 253.6 nm

//

//Troe Formalizm Functions Definitions:

// It looks like that User Defined Functions do not work properly!!!!!!!!!!!

```
//This is for the reference only:
//c(y)=-0.4-0.67*Log10(y)
//N(y)=0.75-1.27*Log10(y)
//d=0.14
//LF(x,y)=Log10(y)/(1+((Log10(x)+c(y))/(N(y)-d*(Log10(y)+c(y))))^2)
//F(x,y)=10^LF(x,y)
//_______//
```

// Time should be in the 1-st column, signal (absorbance) - in 2-nd and 3-rd

IndVars: TIME, A216_1, A224_1 DepVars: A216 Params: k1ad

//Cross-sections and O(1D) reactions

```
// Photolysis of water at 193.3 nm (1.51e-21, our measurements, 03/22/11)
// Photolysis of O2 at 193.3 nm (ca. 3e-22, our rough estimate)
// Photolysis of N2O at 193.3 at 1 bar, 298 K 8.77e-20
//O(1D)+H2--> OH(all)+H 1.35e-10 (Vranckx et al, PCCP, 2010, 9213)
// The following rate constants for O(1D)+N2O are averages of three recent //determinations, as discussed
by
//Macdonald
//Shaun Avondale Carl, PCCP,2005,7,4051-4053, E.J.Dunlea, Ravishankra
//PCCP,2004,6,2152-2161,
// K. Takahashi, Yukari Takeuchi, Yutaka Matsumi Chem. Phys. Lett. //410(2005),196-200.
// However, these recent study do not distinguish between the two channels,
// and it is accepted the branching ratios as 7.2/11.6=0.62 for 2 NO and 1/4.4/11.6=0.38 for N2+O2
// Accepting total as 1.35e-10, this results in
// O(1D) + N2O -> 2 \text{ NO } 8.37e - 11  (1)
//O(1D)+N2O->N2+O25.13e-11(2)
// Quenching on N2O is kg/k=0.056 (Carl, 2005) => kg(N2O)=0.756e-11 (3)
//O(1D)+H2O--> 2 OH (1) 1.7e-10exp(36/T) (Vranckx et al.PCCP, 2010
//O(1D)+H2O--> H2 +O2 (2) 2.2 e -12
// Quenching on water is < 0.003 of the total (Carl, 2005), and is neglected.
//O(1D)+O2 -> O(3P) + O2 3.3e-11 \times exp(55/T) k298 = 3.95e-11 JPL 2011
```

//O(1D)+CH4 --> OH + CH3 1.0e-10 (IUPAC online) (1) // O(1D)+CH4 --> CH2O+H2 7.5 e-12 (IUPAC online) (2) // O(1D)+CH4--> CH3O or CH2OH + H 3.4e-11 (IUPAC online) (3) // IUPAC branching recomendation is based on Hippler's paper // Here is accepted: Total rate constant is 1.57e-10 (Amimoto et al., 1979) // Branching ratio to channel 1 is 0.9 //Branching ratio to channel 3 is 0.1 (into CH2OH, CH3O is negligible) // Channel 2 is neglected

//O(1D)+H2--> OH(all)+H 1.35e-10 (Vranckx et al.PCCP, 2010, 12) // O(1D)+Acetone--> OH + CH3COCH2 Rate constant???? Arbitrarily set to // 5e-10 (typical for C-H bond) // O(1D)+H2O2 --> OH + HO2 5.2e-10 1976FLE/HUS

kN2Och1=8.37e-11 kN2Och2=5.13e-11 kN2Och3=0.756e-11 kH2Och1=1.7e-10 kH2Och2=2.2e-12 kO2=3.95e-11 kCH4ch1=1.41e-10

kCH4ch2=0 kCH4ch3=1.57e-11 kH2=1.35e-10

kAcetone=5e-10 kH2O2=5.2e-10

//Only information between the two dashed lines may be changed // from experiment to experiment

//Cross-sections: 193=193.3 nm, 216=216.4 nm, 224=224 nm, 254=253.6

```
//Cross-sections of H2O2 at 1 bar, 298 K (JPL-15)
sH2O2at193=60.1e-20
sH2O2at216=29.3e-20
sH2O2at224=22.5e-20
sH2O2at230=18.2e-20
sH2O2at254=7.1e-20
```

//Cross-sections of HO2, at 1 bar, 298 K (JPL-15) sHO2at193=390e-20 sHO2at216=373e-20 sHO2at224=299e-20 sHO2at230=230e-20 sHO2at254=32.4e-20

//Cross-sections of N2O, at 1 bar, 298 K (JPL-15) sN2Oat193=8.70e-20 sN2Oat216=0.205e-20 sN2Oat224=0.0375e-20 sN2Oat230=0.00955e-20

```
sN2Oat254=0
```

// Cross-sections of H2O //Our measurement, 02/16/12/ exp 11 sH2Oat193=1.51e-21 // Cross-sections of O2 sO2at193=1.72e-22 // Cross-section of O3 (JPL-15, actually - narrow bands, see JPL-15) sO3at193=42.9e-20 sO3at216=118e-20 sO3at224=255e-20 sO3at224=255e-20 sO3at230=490e-20 sO3at254=1148e-20*(T/298)^(-0.2303) // Cross-section of HONO at 1 bar, 298 K (JPL-15)

sHONOat193=155e-20 sHONOat216=176e-20 sHONOat224=121e-20

sHONOat230=84.5e-20 sHONOat254=15.0e-20

// Cross-sections of acetone at 1 bar, 298 K
// Our measurements
sAcetoneat193=334e-20
//old our measurement (paper with Kashyap Mehta):0.18e-16
// Gierczak et al., 1998
sAcetoneat216=0.186e-20
sAcetoneat224=0.346e-20
sAcetoneat230=0.584e-20
sAcetoneat254=2.82e-20

// Cross-sections of CH3 at 1 bar, 298 K
// Our measurements
sCH3at216=3550e-20
sCH3at224=0
sCH3at230=0
sCH3at254=0

```
//___
```

// **Conditions**//Time Window for fit (all in sec) t1=60e-6 t2=7e-3 t3=60e-6 t4=7e-3

CH3iniFactor=0.91

//Path length (cm) L=10.16 // Conditions: // Date 10/09/12 Exp 10091207-08 // N2O/H2O/H2O2/CH4/He 1.014bar // Pressure in bar

```
p=1.014
T=295
H2O_0=1.218e17
N2O_0=2.004e17
H2O2_0=2.337e15
CH4_0=2.758e17
Acetone_0=0
H2_0=0
O2_0=0
```

//PhotonFluence216.4=4.25e15
//PhotonFluence224= 4.20e15
PhotonFluence=4.25e15
Zeroshift224=2.99e-5
Zeroshift216=-2.44e-4
//Zeroshift224=0
//ZeroShift216=0

M=p*2.429e19*298.15/T

//___

//Initial Conditions Calculations

```
QuenchN2O = (kN2Och1+kN2Och2+kN2Och3)*N2O_0
QuenchH2O = (kH2Och1+kH2Och2)*H2O 0
QuenchH2O2=kH2O2*H2O2_0
QuenchO2=kO2*O2_0
QuenchH2=kH2*H2_0
QuenchCH4=(kCH4ch1+kCH4ch2+kCH4ch3)*CH4_0
QuenchAcetone=kAcetone*Acetone_0
Quench1 = QuenchN2O+QuenchH2O+QuenchO2+QuenchH2O2
Quench2=QuenchH2+QuenchCH4+QuenchAcetone
TotalOuench=Ouench1+Ouench2
fN2Och1=kN2Och1*N2O_0/TotalQuench
fN2Och2=kN2Och2*N2O_0/TotalQuench
fN2Och3=kN2Och3*N2O_0/TotalQuench
fH2Och1=kH2Och1*H2O_0/TotalQuench
fH2Och2=kH2Och2*H2O_0/TotalQuench
fO2=kO2*O2_0/TotalQuench
fH2=kH2*H2_0/TotalQuench
fCH4ch1=kCH4ch1*CH4_0/TotalQuench
fCH4ch2=kCH4ch2*CH4_0/TotalQuench
fCH4ch3=kCH4ch3*CH4_0/TotalQuench
fH2O2=kH2O2*H2O2 0/TotalQuench
fAcetone=kAcetone*Acetone 0/TotalQuench
fTotal1= fN2Och1+fN2Och2+fN2Och3+fH2Och1+fH2Och2+fO2+fH2+fCH4ch1
fTotal2=fCH4ch2+fCH4ch3+fH2O2+fAcetone
fTotal=fTotal1+fTotal2
```

//

```
//Quantum Yields
```

//Photolysis of N2O at 193, quantum yield O(1D)=1

//Photolysis of H2O2 at 193. Quantum yield of OH =1.5 (JPL-15) //Quantum yield of O-atoms is 0.16 (JPL-15) // H2O2 +hnu(193) --> 2 OH Fi(OH)=1.5 (JPL-15) // --> H2O + O (Okabe), Fi(O) =0.16 (JPL-15) //Photolysis of acetone at 193 nm, Fi(CH3)=0.95x2 // Photolysis of water at 193 nm, Fi(H)=1, Fi(OH)=1,(JPL-15) //Photolysis of oxygen at 193 nm. Both atoms are ground state O-atoms. //(Okabe). Fi(O)=2. // Methane, of course, does not absorb anywhere close

O1Dini=PhotonFluence*sN2Oat193*N2O_0

delN2O=-PhotonFluence*sN2Oat193*N2O_0-O1Dini*(fN2Och1+fN2Och2) delH2O=-PhotonFluence*sH2Oat193*H2O_0-O1Dini*(fH2Och1+fH2Och2) delH2O2=-PhotonFluence*sH2O2at193*H2O2_0-O1Dini*fH2O2 delO2=-PhotonFluence*sO2at193*O2_0 delAcetone=-PhotonFluence*sAcetoneat193*Acetone_0-O1Dini*fAcetone delCH4=-O1Dini*(fCH4ch1+fCH4ch2+fCH4ch3)

OHfromH2O2=PhotonFluence*sH2O2at193*H2O2_0*1.5 OHfromH2O = PhotonFluence*sH2Oat193*H2O_0 HfromH2O=OHfromH2O HfromH2O2=PhotonFluence*sH2O2at193*H2O2_0*0.16 OfromH2O2=PhotonFluence*sH2O2at193*H2O2_0*0.02 OfromO2 = PhotonFluence*sO2at193*O2_0*2 CH3fromAcetone=PhotonFluence*sAcetoneat193*Acetone_0*2*0.95

N2O=N2O_0+delN2O H2O=H2O_0+delH2O O2=O2_0+delO2 CH4=CH4_0+delCH4

OHini1=O1Dini*(2*fH2Och1+fCH4ch1+fH2+fAcetone+fH2O2) OHini2=OHfromH2O+OHfromH2O2 OHini=OHini1+OHini2 Hini= O1Dini*(fCH4ch3+fH2)+HfromH2O+HfromH2O2 Oini= O1Dini*(fN2Och3+fO2)+OfromO2+OfromH2O2 //CH3ini=O1Dini*fCH4ch1+CH3fromAcetone

CH3ini=(O1Dini*fCH4ch1+CH3fromAcetone)*CH3iniFactor HO2ini=O1Dini*fH2O2 NOini=O1Dini*2*fN2Och1 HONOini=0 CH2ini=0 H2O2ini=H2O2_0+delH2O2 Acetoneini=Acetone_0+delAcetone O3ini=0 CH3Oini=0

//_

//Wall Reactions

// Diffusion coefficient 0.88 bar cm2 s-1 according to Ivanov et al at 296 // Temperature dependence T^1.6 is ASSUMED // 0.146 is R^2 (R =0.76 cm/2)

kwOH = (5.748/0.146)*(0.88/p)*(T/296)^1.6 kwO=0 kwH=0 kwHO2=0

//___

// Reaction Mechanism

//CH3 + HO2> CH3O + OH	(1a)	
//CH3 + HO2> CH2O + H2O	(1b)	
//CH3 + HO2> CH3OOH		(1c)
//CH3 + HO2> CH4 + O2		(1d)
//CH3 + HO2> CH4 + O2(1 Delt	a)	(1e)
//OH + CH3 - > H2O + CH2	(3a)	
$//OH + CH3 \rightarrow CH3OH$	(3a)	
// OH + OH -> H2O + O	(30)	
// OH+OH -> H2O2	(4a)	
// OH + CH4> H2O + CH3	(10)	
//CH3 + CH3> C2H6	(6)	
//OH + O -> O2 + H	(7a)	
//OH + O -> HO2	(7a) (7b)	
//OH + H> H2 + O	(8a)	
//OH + H> H2O	(8b)	
//CH3 + O> H2CO + H	(9)	
// OH + NO> HONO	(10)	
// CH3 + H> CH4	(11)	
// OH + CH2> CH2O + H	(12)	
// OH + (CH3)2CO>(CH3)(CH	(2)CO+H2O	(13)
// OH + H2O2> H2O + HO2	(14)	
// OH + HO2> H2O + O2		(15)
// HO2 + NO> OH + NO2		(16)
// CH3 + NO>CH3NO	(17)	
// CH3 + H2O2> CH4 + HO2	(18)	
// O + HO2>O2+OH	(19)	
// O + H2O2> OH + HO2		(20)
// H + HO2> H2 +O2	(21a)	
// H + HO2> 2 OH	(21b)	
// H + HO2> H2O + O	(21c)	
// H + HO2> O(1D) +H2O		(21d)
// H + H2O2> H2 +HO2	(22)	
//0 + 02 = 03	(30) reversible	
//H + O2 -> OH + O	(31a)	
//H + O2 -> HO2	(31b)	
// HO2 + O2> OH + O3	(32)	
// OH + O3 - > HO2 + O2	(35)	
// O + O3> O2 + O2	(36)	
//H + O3> OH + O2	(37)	

// HO2 + O3> OH + O2 + O2	(38)	
// HO2 + HO2>H2O2+O2		(39)
// O3 + NO> NO2 + O2	(40)	

//CH3 + CH3COCH3 --> CH4 + CH3COCH2

(50)

//Reactions	of Methoxy	Radical,	CH3O
	<i><u><u></u></u></i> <u></u>		

······································		
// CH3O> CH2OH	(60a)	
// CH3O> CH2O + H	(60b)	
// CH3O + N2O> products	(61)	
// CH3O + H2O2> products	(62)	
// CH3O + CH4> CH3OH + CH3	(63)	
// CH3O + HO2> CH2O + H2O2	(64)	
// CH3O + CH3> CH2O + CH4	(65a)	
// CH3O + CH3> (CH3)2O	(65b)	
// CH3O + CH3O> CH3OH + CH2O		(66a)
// CH3O + CH3O> (CH3O)2	(66b)	
// CH3O + OH> CH2O + H2O	(67a)	
// CH3O + OH> CH3OOH		(67b)
// CH3O + O> CH2O + OH	(68a)	
// CH3O + O> CH3 + O2		(68b)
// CH3O + O> CH3OO	(68c)	
// CH3O + H> CH2O + H2	(69a)	
/ CH3O + H> CH3OH	(69b)	

//Rate Constants

//CH3 + HO2> CH3O + OH	(1a)	
//CH3 + HO2> CH2O + H2O	(1b)	
//CH3 + HO2> CH3OOH		(1c)
//CH3 + HO2> CH4 + O2		(1d)
//CH3 + HO2> CH4 + O2(1 Delta)		(1e)

// According to Jasper et al., 2009, the only important channels are // channel 1a, 1c and 1d.

// This is reaction under study. k1=k1a+k1b+k1c+k1d+k1e

// According to Jasper et al., 2009, the branching ratio between 1a and 1d // is k1a/(k1a+k1d)=0.7 at 300 K (obtained approximately from Figures). // for now we will leave only these two channels, 1a and 1d //k1ad=3e-11 k1a=k1ad*0.7 k1b=0 k1c=0 k1d=k1ad*0.3

k1e=0

k1=k1a+k1b+k1c+k1d+k1e

// OH + CH3 --> H2O + CH2 (3a) // OH + CH3 --> CH3OH (3b) // Our work 2012, pressure independent 1 - 100 bar k3=1.2e-10*(T/300)^(-0.49)

 $\label{eq:constraint} \begin{array}{ll} // \ OH+OH \ --> \ H2O \ + \ O & (4a) \\ // \ Low \ T \ <\!\!420K \ 1999 \ Bedjanian \ et \ al, \ high \ T \ >\!\!550K \ - \ our \ data \ 2011 \\ // \ fit \ of \ the \ data \ that \ were \ submitted \ in \ the \ final \ version \\ //k4a = 1.07e \ -12*(1 + 1.0e \ -4*((T \ -483)^2))^{0.2} \end{array}$

// Our study, 2012. For 298 k, 1 bar, He k4a=1.44e-12 // OH+OH --> H2O2 (4b) // 2011 Sangwan et al. //k04b=9.0e-31*(T/300)^(-3.5) //kinf4b=2.4e-11*(T/300)^(-0.5) //Fcent4b=0.37 //x4b=k04b*M/kinf4b //c4b=-0.4-0.67*Log10(Fcent4b) //N4b=0.75-1.27*Log10(Fcent4b) //d=0.14 //y4b=Log10(x4b)+c4b //LF4b=Log10(Fcent4b)/(1+(y4b/(N4b-d*y4b))^2) //F4b=10^LF4b //k4b=kinf4b*F4b*x4b/(1+x4b) //This generates k4b=4.4e-12 at 1 bar 1nd 298 K // Our direct value is (6.2-1.4)e-12 // Our study, 2012. For 298 k, 1 bar, He k4b = 4.73e - 12// OH + CH4 --> H2O + CH3 (5) // 2005SRI/SU k5=4.16e-13*(T/298)^2.18*exp(-1232/T) // CH3 + CH3 = C2H6(6)// Our study 2012, for 1 bar k6=5.92e-11*(T/300)^(-0.45) //OH + O --> O2 +H (7a) // 2004 ATK/BAU k7a=2.4e-11*exp(109/T) // OH + O --> HO2 (7b) // No data, set as OH+H k7b=M*1.6e-31*(T/298)^(-2.6) //OH + H --> H2 + O (8a) //86TSA/HAM $k8a = 6.86e - 14*(T/298)^2.8*exp(-1950/T)$ //OH + H --> H2O (8b) //77 ZEL/ERL k8b=M*1.6e-31*(T/298)^(-2.6) // CH3 + O --> H2CO + H (9) //1992ATK k9=1.4e-10 // OH + NO --> HONO (10)k010=3.9e-31*(T/298)^(-2.6)

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kinf10=3.3e-11 Fcent10=1.23*exp(-T/815) x10=k010*M/kinf10 c10=-0.4-0.67*Log10(Fcent10) N10=0.75-1.27*Log10(Fcent10) d=0.14 y10=Log10(x10)+c10 LF10=Log10(Fcent10)/(1+(y10/(N10-d*y10))^2) F10=10^LF10 k10=kinf10*F10*x10/(1+x10)

// OH + CH2 --> CH2O + H (12) //1986TSA/HAM k12=3e-11

// OH + (CH3)2CO -->(CH3)(CH2)CO+H2O (13) //2003YAM/TAY k13=3.15e-14*(T/300)^4*exp(453/T)

// OH + H2O2 --> H2O + HO2 (14) //2004JIM/GIE k14=2.9e-12*exp(-109/T)

// OH + HO2 --> H2O + O2 (15) //1988KEY k15=4.8e-11*exp(250/T) // HO2 + NO --> OH + NO2 (16) //2003BAR/BAC k16=4e-12*exp(223/T)

//CH3 + NO -->CH3NO (17) //1991 Pilling Ar //A.H.Langer,A.M.Bass.Int.J.Chem.Kin.V.7,639-648(1975) kHe=kAr k017=6.9e-32*exp(1430/T) kinf17=1.5e-11*exp(-60/T) Fcent17=5*exp(-T/120) x17=k017*M/kinf17 c17=-0.4-0.67*Log10(Fcent17) N17=0.75-1.27*Log10(Fcent17) d=0.14 y17=Log10(x17)+c17 LF17=Log10(Fcent17)/(1+(y17/(N17-d*y17))^2) F17=10^LF17 k17=kinf17*F17*x17/(1+x17) //CH3 + H2O2 --> CH4 + HO2 (18) //1986TSA k18=2e-14*exp(300/T)

//O + HO2-->O2+OH (19) //2004ATK/BAU k19= 2.70E-11*exp(1860/8.31447/T)

//O + H2O2--> OH + HO2 (20) //2004ATK/BAU k20 =1.40E-12*exp(-16630/8.31447/T)

//H + HO2 --> H2 +O2 (21a) //1992 BOU/COB k21a=7.11E-11*exp(-5900/8.31447/T)

//H + HO2 --> 2 OH (21b) //1992Bau/COB k21b=2.81E-10*exp(-3660/8.31447/T)

//H + HO2 --> H2O + O (21c) //1992 BAU/COB k21c=5.00E-11*exp(-7200/8.31447/T)

//H + HO2 --> O(1D) +H2O (21d)
//2007MOU/SAH1901-1913
// A theoretical paper - important reaction, thou!
// Will be used as H + HO2 --> 2OH +H2O
k21d=3.29E-12*(T/298)^1.55*exp(670/8.31447/T)

// H + H2O2 --> H2 +HO2 (22) // 1992 BAU/COB k22=2.81e-12*exp(-15710/8.31447/T)

// O + O2 --> O3 (30) // Hippler, Rahn, Troe 1990 (on He) k30 = M*3.4e-34*(T/300)^(-1.2)

//Equilibrium constant from dHf298(O3)=141.746 kJmol-1 //(from Active Thermo Tables), O and O2 fro GRI, and // the rest for ozone from NIST WebBook. Keq30=4.0007e-9*(T/298)^(-1.37313)*exp(14123.53/T) kfkr30=Keq30*10*8.31451*T/6.022e23

// H + O2 --> OH + O (31a) //1994 Bau/Cob //Plays role only at high T k31a = 1.62E-10*exp(-62110/8.31447/T)

// H + O2> HO2 // 1997ATK/BAU (for N2): k31b = M*5.4E-32*(T/298)^(-1.80)	(31b)
<pre>// HO2 + O2> OH + O3 // This reaction is ENDOTHERMIC by ca. 1 // Play absolutely no role k32=0</pre>	(32) 80 kJ mol-1
// OH +O3> HO2 + O2 // 2004 ATK/BAU k35 = 1.7E-12*exp(-7820/8.31447/T)	(35)
// O + O3> O2 + O2 // 2001 ATK/BAU k36=8.0E-12*exp(-17130/8.31447/T)	(36)
// H + O3> OH + O2 // 1989 ATK/BAU k37=1.4E-10*exp(-3990/8.31447/T)	(37)
// HO2 + O3> OH + O2 + O2 // 2004 ATK/BAU k38 =1.97E-16 *(T/298)^4.57*exp(5760/8.3	(38) 1447/T)
// HO2 + HO2>H2O2+O2	(39)
<pre>//2004 A1K/BAU k39=2.2e-13*exp(4990/8.31447/T) // O3 + NO> O2 + NO2 // 2004 Atk/Bau k40 at 298 = 1.80E-14 // Does not play any role at 298 // Not taken into account k40=0</pre>	(40)
//CH3 + CH3COCH3> CH4 + CH3COCH // my fit from NIST database k50= 1.06e-12*exp(-42720/8.31447/T)	I2 (50)
// CH3O> CH2OH // 1981 BAT/BUR k60a = 1e13*exp(-109000/8.31447/T)	(60a)
// CH3O> CH2O + H // 1994 BAU/COB k60b = 9e-11*exp(-56460/8.31447/T)	(60b)
// CH3O + N2O> products //1980 SUN/BUT k61 < 1.66e-14 at 298 K //k61=1.66e-14 k61=0	(61)
// CH3O + H2O2> CH3OH + HO2 // 1987 TSA k62 = 5e-15*exp(-10810/8.3144 k62 = 5e-15*exp(-10810/8.31447/T)	(62) 47/T)
// CH3O + CH4> CH3OH + CH3	(63)

$\frac{1}{1989}$ wAN/OLD k63 = 2.2e-10*exp(-63020/8.31447/T)		
// CH3O + HO2> CH2O + H2O2 // 1986 TSA k64=5e-13	(64)	
// CH3O + CH3> CH2O + CH4 // 1986 TSA/HAM k652-4e 11	(65a)	
// CH3O + CH3> (CH3)2O // 1979 HAS/KOS k65b=5.5e-11	(65b)	
// CH3O + CH3O> CH3OH + CH2O // 1979 HAS/KOS k66a=3.85e-11		(66a)
// CH3O + CH3O> (CH3O)2 // 1986 TSA/HAM k66b=3e-12	(66b)	
// CH3O + OH> CH2O + H2O // 1986 TSA k67a=3e-11	(67a)	
// CH3O + OH> CH3OOH // not known k67b=0		(67b)
// CH3O + O> CH2O + OH // 1987 TSA k68a=1e-11	(68a)	
// CH3O + O> CH3 + O2 //1987 ZEL k68b=2.5e-11		(68b)
// CH3O + O> CH3OO // not known k68c=0	(68c)	
// CH3O + H> CH2O + H2 //1991 DOB/BER k69a=3.3e-11	(69a)	
// CH3O + H> CH3OH // not known k69b=0 //	(69b)	

//System of Ordinary Differential Equations

//Species "transient": CH3, HO2, OH,O, H,O3,NO,HONO,CH2, H2O2,CH3O
// Acetone, N2O
//Species initially present: N2O, H2O, CH4, H2O2, Acetone

r30=k30*(O*O2-O3/kfkr30) r31a=k31a*H*O2 r31b=k31b*H*O2 r32=k32*HO2*O2 r35=k35*OH*O3 r36=k36*O*O3 r37=k37*H*O3 r38=k38*HO2*O3 r39=k39*HO2*HO2 r40=k40*O3*NO

r22=k22*H*H2O2

r11=k11*CH3*H r12=k12*OH*CH r13=k13*OH*Acetone r14=k14*OH*H2O2 r15=k15*OH*HO2 r16=k16*HO2*NO r17=k17*CH3*NO r18=k18*CH3*H2O2 r19=k19*O*HO2 r20=k20*O*H2O2 r21a=k21a*H*HO2 r21b=k21b*H*HO2 r21c=k21c*H*HO2 r21d=k21d*H*HO2

r10=k10*OH*NO

r9=k9*CH3*O

r8a=k8a*OH*H r8b=k8b*OH*H

r7a=k7a*OH*O r7b=k7b*OH*O

r5=k5*OH*CH4 r6=k6*CH3*CH3

r4a=k4a*OH*OH r4b=k4b*OH*OH

r3=k3*OH*CH3

r1=k1*CH3*HO2

r1a=k1a*CH3*HO2 r1b=k1b*CH3*HO2 r1c=k1c*CH3*HO2 r1d=k1d*CH3*HO2 r1e=k1e*CH3*HO2

//Reaction Rates:

r50=k50*CH3*Acetone

r60a=k60a*CH3O r60b=k60b*CH3O r61=k61*CH3O*N2O r62=k62*CH3O*H2O2 r63=k63*CH3O*CH4 r64=k64*CH3O*HO2 r65a=k65a*CH3O*CH3 r65b=k65b*CH3O*CH3 r66a=k66a*CH3O*CH3O r66b=k66b*CH3O*CH3O r67a=k67a*CH3O*OH r67b=k67b*CH3O*OH r68a=k68a*CH3O*O r68b=k68b*CH3O*O r68c=k68c*CH3O*O r69a=k69a*CH3O*H r69b=k69b*CH3O*H

rOH1=r1a-r3-2*r4a-2*r4b-r5-r7a-r7b-r8a-r8b-r10-r12-r13-r14-r15+r16+r19 rOH2=r20+2*r21b+r21d*2*fH2Och1+r31a+r32-r35+r37+r38-r67a-r67b+r68a // ODE System

OH'=rOH1+rOH2-kwOH*OH CH3'=-r1-r3+r5-2*r6-r9-r11-r17-r18-r50+r63-r65a-r65b+r68b HO2'=-r1+r7b+r14-r15-r16+r18-r19+r20-r21a-r21b-r21c-r21d+r22+r31b-r32+r35-r38-2*r39-r64

O'=r4a-r7a-r7b+r8a-r9-r19-r20+r21c-r30 +r31a-r36-r68a-r68b-r68c-kwO*O H'=r7a-r8a-r8b+r9-r11+r12-r21a-r21b-r21c-r21d-r22-r31a-r31b-r37+r60b-r69a-r69b-kwH*H H2O2'=r4b-r14-r18-r20-r22+r39-r62+r64 Acetone'=-r13-r50 O3'=r30+r32-r35-r36-r37-r38-r40 NO'=-r10-r16-r17-r40 HONO'=r10 //for CH2 it is assumed that reaction 3 produces CH2 ONLY CH2'=r3-r12

rCH3O1=r1a-r60a-r60b-r61-r62-r63-r64-r65a-r65b-2*r66a-2*r66b rCH3O2=-r67a-r67b-r68a-r68b-r68c-r69a-r69b CH3O'=rCH3O1+rCH3O2

//

```
// Transient Absorptions
```

N2Otrans= delN2O H2O2trans=H2O2-H2O2_0 Acetonetrans=Acetone-Acetone_0

 $\label{eq:abs216c1=L*(sCH3at216*CH3+sHO2at216*HO2+sH2O2at216*H2O2trans)} \\ Abs216c2=L*(sH0NOat216*H0NO+sN2Oat216*N2Otrans+sO3at216*O3) \\ Abs216c3=L*(sAcetoneat216*Acetonetrans) \\ Abs216=Abs216c1+Abs216c2+Abs216c3 \\ \end{tabular}$

Abs224c1=L*(sCH3at224*CH3+sHO2at224*HO2+sH2O2at224*H2O2trans)

$$\label{eq:second} \begin{split} Abs224c2 = L^*(sHONOat224*HONO+sN2Oat224*N2Otrans+sO3at224*O3)\\ Abs224c3 = L^*(sAcetoneat224*Acetonetrans)\\ Abs224 = Abs224c1 + Abs224c2 + Abs224c3 \end{split}$$

$$\label{eq:scharge} \begin{split} Abs230c1=L*(sCH3at230*CH3+sHO2at230*HO2+sH2O2at230*H2O2trans)\\ Abs230c2=L*(sHONOat230*HONO+sN2Oat230*N2Otrans+sO3at230*O3)\\ Abs230c3=L*(sAcetoneat230*Acetonetrans)\\ Abs230=Abs230c1+Abs230c2+Abs230c3 \end{split}$$

```
\label{eq:abs254c1=L*(sCH3at254*CH3+sHO2at254*HO2+sH2O2at254*H2O2trans)} \\ Abs254c2=L*(sHONOat254*HONO+sN2Oat254*N2Otrans+sO3at254*O3) \\ Abs254c3=L*(sAcetoneat254*Acetonetrans) \\ Abs254=Abs254c1+Abs254c2+Abs254c3 \\ \end{tabular}
```

//

F216_1=A216_1 F216=Abs216+ZeroShift216

F224_1=A224_1 F224=Abs224+ZeroShift224

```
gate1=UNIT(TIME-t1)*UNIT(t2-TIME)
gate2=UNIT(TIME-t3)*UNIT(t4-TIME)
A216=(1-gate1)*F216_1+gate1*F216
A224=(1-gate2)*F224_1+gate2*F224
```

*** //Initial Conditions

TIME=0

CH3=CH3ini HO2=HO2ini OH=OHini O=Oini H=Hini

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