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Experimental and modeling study of the oxidation of *n*-butane in a jet stirred reactor using cw-CRDS measurements

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Abstract

The gas-phase oxidation of *n*-butane has been studied in an atmospheric jet-stirred reactor (JSR) at temperatures up to 950 K. For the first time, continuous wave cavity ring-down spectroscopy (cw-CRDS) in the near-infrared has been used, together with gas chromatography (GC), to analyze the products formed during its oxidation. In addition to the quantification of formaldehyde and water, which is always difficult by GC, cw-CRDS allowed as well the quantification of hydrogen peroxide (H₂O₂). A comparison of the obtained mole fraction temperature profiles with simulations using a detailed gas-phase mechanism shows a good agreement at temperatures below 750 K, but an overestimation of the overall reactivity above this temperature. Also, a strong overestimation was found for the H₂O₂ mole fraction at higher temperatures. In order to improve the agreement between model and experimental results, two modifications have been implemented to the model: (a) the rate constant for the decomposition of H₂O₂ (+M) \rightleftharpoons 2 OH (+M) has been updated to the value recently proposed by Troe (Combust. Flame, 2011, 158, 594–601) and (b) a temperature dependent heterogeneous destruction of H₂O₂ on the hot reactor walls with assumed rate parameters has been added. The improvement (a) slows down the overall reactivity at higher temperatures, but has a negligible impact on the maximal H₂O₂ mole fraction. Improvement (b) has also a small impact on the overall reactivity at higher temperatures, but a large effect on the maximal H₂O₂ mole fraction. Both modifications lead to an improved agreement between model and experiment for the oxidation of *n*-butane in a JSR at temperatures above 750 K.

Introduction

In a previous study of the *n*-butane oxidation¹ in an atmospheric jet-stirred reactor (temperature from 550 to 800 K), the combined use of gas chromatography with different detection systems and of tunable synchrotron vacuum ultraviolet (SVUV) photoionization mass spectrometry with molecular-beam sampling has shown to be a powerful tool to analyse a wide range of stable species from water and carbon oxides up to C₄ ketohydroperoxides, olefins, aldehydes, ketones and cyclic ethers. However, species cannot be quantified with accuracy when their photoionization cross sections are not known with precision. This is the case for hydrogen peroxide, a key product of alkane oxidation:² its decomposition is a degenerate branched chain reaction and leads to the formation of the very reactive OH radicals, finally driving the system to ignition. Unfortunately, hydrogen peroxide mole fractions presented by Herbinet et al.¹ were calculated using an estimated cross section and are therefore not accurate.

Despite its importance in the occurrence of autoignition, H₂O₂ has been rarely quantified under conditions close to those observed near this phenomenon. Only recently, two papers have shown some quantitative measurements of this species. Guo et al.³ have measured H₂O₂ during dimethyl ether oxidation in an atmospheric flow reactor from 490 K to 750 K, using molecular beam electron-ionization mass spectrometry. The H₂O₂ mole fraction was calibrated by vaporizing liquid H₂O₂ solution into a heated helium flow; the vapor was then used for calibration. The authors observed a fast surface decomposition of H₂O₂ into O₂ and H₂O, and the O₂ signal measured during the calibration was used to correct and to calculate the actual H₂O₂ concentration. A temperature mole fraction profile in reasonable agreement with literature models for dimethyl ether oxidation⁴⁻⁶ was obtained.

Bahrini et al.⁷ have quantified H₂O₂ during *n*-butane oxidation in a jet-stirred reactor under conditions very close to those used by Herbinet et al.¹ using continuous wave cavity ring-down spectroscopy (cw-CRDS) in the near-infrared. CRDS is an absolute absorption technique, and therefore no calibration is needed when the absorption cross section is known. However, absorption cross sections in the near infrared region are not known in the literature and have therefore been obtained in the present work from separate experiments using laser photolysis coupled to cw-CRDS. Using these absorption cross sections, the obtained temperature mole fraction profile was in good agreement with the prediction of a literature model for *n*-butane oxidation⁸ below 750 K, but important deviations appear at higher temperatures. Compared to the work of Guo et al.,³ the more direct calibration method used by Bahrini et al.⁷ seems to be independent of the uncertainty in the H₂O₂ concentration when handling the unstable H₂O₂.

The purpose of the present paper is to present all stable species which have been measured using cw-CRDS during the oxidation of *n*-butane in a jet-stirred reactor. The profiles obtained by cw-CRDS are compared, when possible, with gas chromatography (GC) measurements. Simulations are presented using a kinetic model taking into account a temperature dependent wall loss reaction of

H₂O₂ as well as a recently improved rate constant⁹ for the decomposition of H₂O₂. A sensitivity analysis on the kinetic model has been performed to evaluate the impact of uncertainties of some reaction rate constants as well as wall effects on the origin of the observed deviation between experimental profiles and simulations.

Experimental and modeling details

The study has been accomplished in a spherical fused silica jet-stirred reactor (JSR) with a volume of 90 cm³ coupled to a detection of stable species by cw-CRDS. For comparison purposes and also for obtaining profiles for a large number of species, analyses using GC with flame ionization detection (GC-FID) have also been performed, either in separate experiments or simultaneously.

The isothermal JSR is attached to a quartz annular preheating zone in which the temperature of the gas is increased up to the reactor temperature. The gas mixture residence time inside the annular preheater is very short compared to its residence time inside the reactor (a few percent). Both the spherical reactor and the annular preheating zone are heated by means of Thermocoax resistances rolled up around the reactor. The reaction temperature was measured using a thermocouple located inside the intra-annular space of the preheating zone; its extremity being placed at the level of the injection jets.

All experiments have been performed using a stoichiometric mixture of 0.023 *n*-butane–0.15 O₂–0.827 He at a total pressure of 1 atm in the temperature range 550–950 K, total gas flows have been adapted in order to always obtain a residence time within the reactor of 6 s. The set-up has already been described in detail in earlier works,^{10,11} so only a brief description will be given here.

Coupling JSR – cw-CRDS

The cw-CRDS measurements are carried out in a 80 cm long cell, well separated from the JSR: a strong pressure drop between JSR (atmospheric pressure) and cw-CRDS cell (below 10 Torr) is established, mainly for decreasing the pressure broadening of the absorption spectra and thus achieving a more selective detection of the different species. The cw-CRDS cell consists of two glass tubes (outer diameter 8 mm, length 40 cm each), held together in the center by a stainless steel Swagelok T-fitting. The third outlet of the T takes a 6 mm diameter fused silica tube with its second extremity thinned out to a very small orifice. This second end of the tube is connected to the JSR such that the orifice is placed in the center of the JSR. Pumping on both ends of the cw-CRDS cell leads to the pressure drop between the JSR reactor and the cw-CRDS cell. The gas flow through the cw-CRDS cell is around 100 ccm STP min⁻¹, leading to a residence time in the cw-CRDS cell of less than 1 second. Cw-CRDS measurements have been carried out using a DFB laser, tunable in the range 6620–6644 cm⁻¹. From the ring-down time measured in the absence of the absorbing species A (τ_0) and in the presence of the species A (τ), the absorption coefficient α can be determined as:

$$\alpha = [A] \times \sigma = \frac{R_L}{c} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (1)$$

where R_L is the ratio between the cavity length L , i.e. the distance between the two cavity mirrors, to the length L_A over which the absorber is present (this ratio has been determined as 0.92 in independent experiments, for details see Bahrini et al.¹⁰), and c is the speed of light. If the absorption cross section σ is known for the species A, its concentration can be calculated using equation (1). More details of the cw-CRDS technique can be found in earlier works.^{10,12}

Coupling JSR – GC/FID

Gas chromatographic analyses have already been used for the study of the oxidation of large alkanes and details can be found in recent papers.^{1,11,13–15} Briefly, analyses were performed using two online gas chromatographs equipped with a six-gate sampling valve for the introduction of samples taken from the outlet of the jet-stirred reactor.

The first gas chromatograph (Shimadzu 14) is equipped with a Carbosphere packed column, a thermal conductivity detector (TCD), and a flame ionization detector (FID). It was used for the quantification of O₂, CO, CO₂, methane, ethylene, acetylene and ethane. Amongst the products which are known to be important for hydrocarbon oxidation, only water and hydrogen were not quantified.

The second gas chromatograph (Agilent 7890) was fitted with a Plot Q capillary column and a FID preceded by a methanizer, which increases the sensitivity of the detection of carbon oxides compared to thermal conductivity detectors, as well as improves the quantification of formaldehyde, and was used for the quantification of C₁–C₅ hydrocarbons and small oxygenated compounds.

The calibration of the gas chromatographs was performed using gaseous standard cylinders of well defined and calibrated composition provided by Air Liquide. The maximum relative uncertainty in the mole fractions was estimated to be ±5% with a detection limit of around 5 ppm for hydrocarbons and C₂₊ oxygenated compounds. The maximum relative uncertainty in the mole fraction was estimated to be ±20% for formaldehyde (due to the tail of the peak and the co-elution with other species) with a detection limit around 10 ppm.

Coupling of laser photolysis – cw-CRDS/LIF

Absorption cross sections for H₂O₂ in the near-infrared region have already been measured in an earlier work,¹⁶ however all experiments had been performed at a total pressure of 50 Torr while

cw-CRDS measurements in this work have been carried out at around 10 Torr. The main advantage of carrying out the cw-CRDS measurements at low pressure is to limit the pressure broadening of the absorption spectra of all species, leading to a less digested spectrum and thus a better selectivity. Absorption lines in the wavelength range covered in this work suffer from pressure broadening, therefore it is indispensable to know the broadening coefficient of the selected line in order to calculate the absorption cross section at different pressures in a given bath gas. Unfortunately, broadening coefficients for H₂O₂ in the near-infrared region are not known in the literature and thus we have preferred to directly measure absorption cross sections of a few selected lines at the working pressure of 10 Torr.

Modeling details

The purpose of the present study is mainly an experimental one, but a detailed kinetic model has been used in order to test its performance in reproducing these new results, and to possibly point out important deviations. The model used in this work, which is available on request, is based on the mechanism recently proposed by Battin-Leclerc et al.⁸ It is based on a mechanism automatically generated by software EXGAS, such as described by Buda et al.¹⁷ and by Biet et al.¹³ The updated rate constant for the reaction H₂O₂ (+M) ⇌ 2 OH (+M), recently proposed by Troe,⁹ has been implemented to this model. Also, a temperature dependent wall loss of H₂O₂ has been introduced into the model in order to explain the experimentally observed H₂O₂ profiles.

Experimental results

The mole fraction profiles such as obtained in this work from experimental and model calculations are presented in Figures 1 and 2 and Figures S1–S4 (supplementary material): Figure 1 shows the products quantified by cw-CRDS (CH₂O, H₂O, C₂H₄ and H₂O₂, whereby CH₂O and C₂H₄ were also quantified by GC), Figure 2 shows other major products linked to the reactivity (*n*-butane, O₂, CO, CH₃CHO, OH and HO₂ radicals, whereby the last two species have not been quantified experimentally), Figures S1–S4 (supplementary material) finally show the profiles of 20 other products quantified by GC only. In all figures, the results of three different models are shown: the dashed lines show the results from the original model such as proposed by Battin-Leclerc et al.,⁸ the full lines show the results from the model improved with the new rate constant for the decomposition of H₂O₂,⁹ while the dotted lines show the model including additionally the heterogeneous decomposition of H₂O₂. Compared to the previous study of Herbinet et al.¹ in the same type of JSR, the temperature range has been extended in this study up to 950 K allowing the investigation of the reactivity of this alkane above 800 K. The only studies in the literature dealing with the oxidation of *n*-butane in this intermediate range of temperature are from Chakir et al.¹⁸ and Minetti et al.,¹⁹ both having observed significantly less products. Figures 1 and 2 and Figures S1–S4 (supplementary material) show for all analyzed species the characteristic behavior with two distinct reactivity zones, an increase in reactivity at low temperature (T ≈ 600 K), followed by a decrease in reactivity in the so-called negative temperature zone (T > 650 K) and another increase in reactivity at higher temperatures (T > 800 K).²⁰

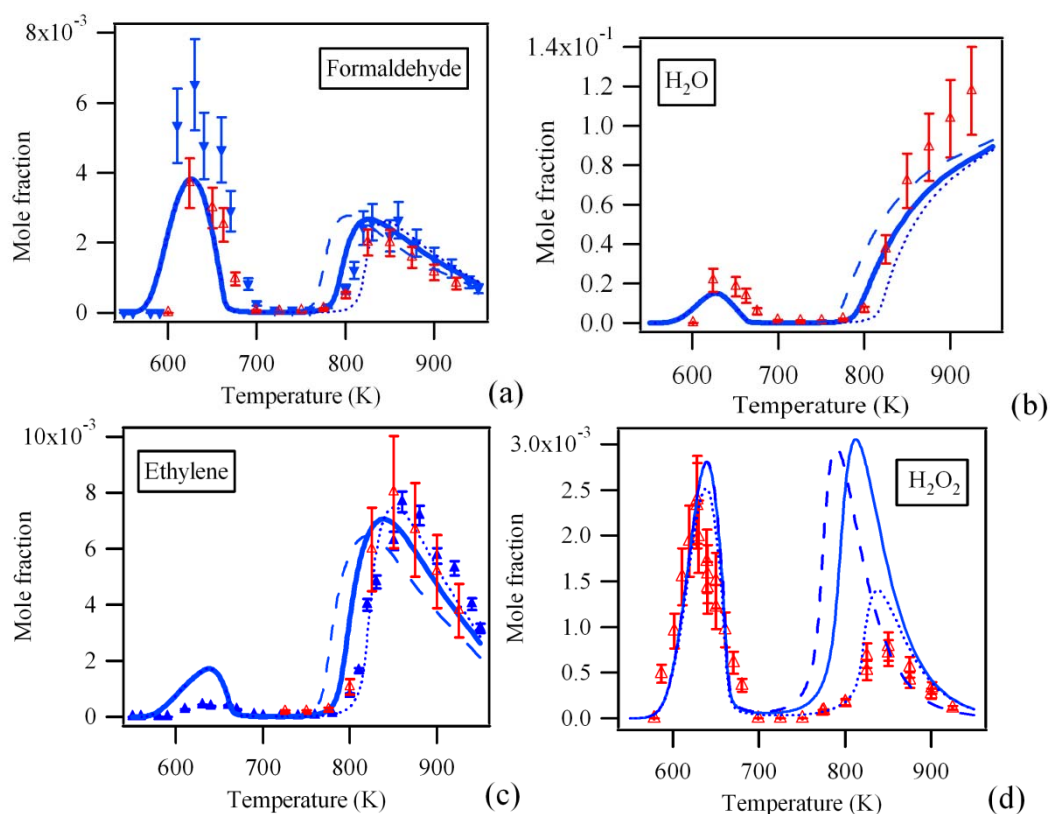


Figure 1: Profiles of CH_2O (a), H_2O (b), C_2H_4 (c) and H_2O_2 (d). Full blue symbols: GC measurements. Open red symbols: experimentally obtained mole fractions by averaging the mole fractions obtained from different CRDS absorption lines. Dashed lines: gas phase model such as from Battin-Leclerc et al.⁸ Full lines: gas phase model with the revised rate constant for H_2O_2 decomposition. Dotted lines: gas phase model as a full line, but with additional H_2O_2 wall destruction.

The absorption spectrum of the gas mixture exiting the JSR reactor has been analyzed by cw-CRDS between 6620 to 6644 cm^{-1} , i.e. the range accessible by the DFB laser. In Figure 3 is shown the portion of the spectrum in the wavelength range between 6638 and 6641 cm^{-1} , the full spectrum can be found as supplementary material (Figure S5). In these figures, the spectrum is shown such as obtained at the exit of the JSR at two different temperatures, 875 K (second from top) and 638 K (bottom); the spectra are represented as ring-down time τ as a function of wavenumber. These temperatures have been chosen because they represent the maxima of product formation in the two temperature domains (see Figures 1 and 2). Butane itself does absorb in this wavelength range, but it does not exhibit any structured absorption feature, i.e. it only leads to an overall decrease in ring-down time. This is illustrated in Figure 4, showing the baseline recorded before admitting *n*-butane to the reactor (upper red line, $\tau \approx 300\text{ }\mu\text{s}$), the baseline with *n*-butane, but the reactor still at ambient temperature (lower green line, $\tau \approx 100\text{ }\mu\text{s}$), as well as a typical spectrum obtained with the reactor at 825 K and a residence time of 6 s (blue dots), where around 60% of the *n*-butane has been consumed. From the decrease in ring-down time after admission of *n*-butane at ambient temperature (red and green line), an absorption cross section of *n*-butane of $\sigma = (2.5 \pm 0.3) \times 10^{-23}\text{ cm}^2$ over the entire wavelength range can be calculated. Therefore, the structured spectrum

obtained from the gas mixture at the exit of the JSR such as shown in Figure 3 is solely due to absorption by reaction intermediates.

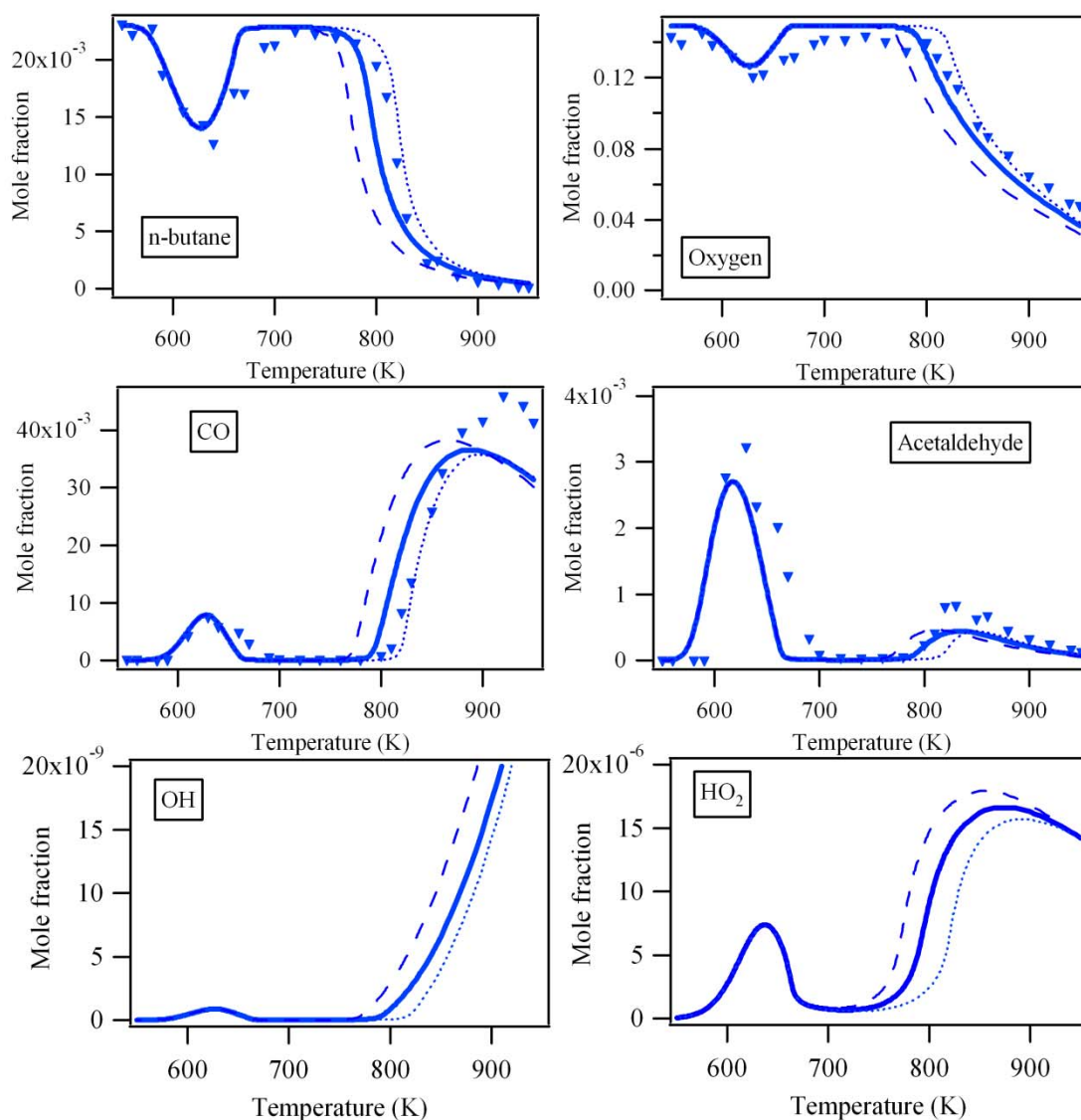


Fig.

Figure 2: Mole fraction profiles of reactants, main products and some important radicals which cannot be observed by CRDS. Symbols: GC measurements. Lines are the same as Figure 1.

Four species have been identified being mostly responsible for the structured absorption observed in this wavelength range: C_2H_4 , H_2O , H_2O_2 and CH_2O . The individual spectra of these four species have therefore been added for comparison in Figure 3 and Figure S5 (supplementary material): C_2H_4 as the top panel, H_2O (as a dashed line) and a mixture of H_2O and H_2O_2 in the center and CH_2O as the second panel from the bottom. The spectra of C_2H_4 , H_2O and H_2O_2 have been obtained during this work by flowing a diluted mixture of the species via the JSR at room temperature into the cw-CRDS cell: C_2H_4 has been taken as a pure gas from a cylinder (99.95% purity, Air Liquide) and has been diluted with a known flow of helium prior to entering the JSR, H_2O has been obtained by bubbling a fraction of the

He-flow through liquid water, H_2O_2 has been obtained by bubbling through a solution of 50% H_2O_2 – H_2O and hence consists of the sum of both spectra, H_2O and H_2O_2 . The spectrum of CH_2O has been taken from Staak et al.,²¹ however absolute absorption cross sections used in this work have been taken from Morajkar et al.²² The absorption spectra for the individual species are relatively dense (except for H_2O , which has well-defined and separated lines), and hence the spectrum of the gas mixture at the exit of the JSR, a convolution of the individual spectra weighted by the concentration of each species, is also very dense. In order to extract reliably the concentration of each species, isolated absorption features need to be identified, i.e. lines that are as little as possible perturbed by absorption lines from other species. The procedure for extracting absolute concentrations for each individual species from the convoluted product spectrum is detailed in the following sections.

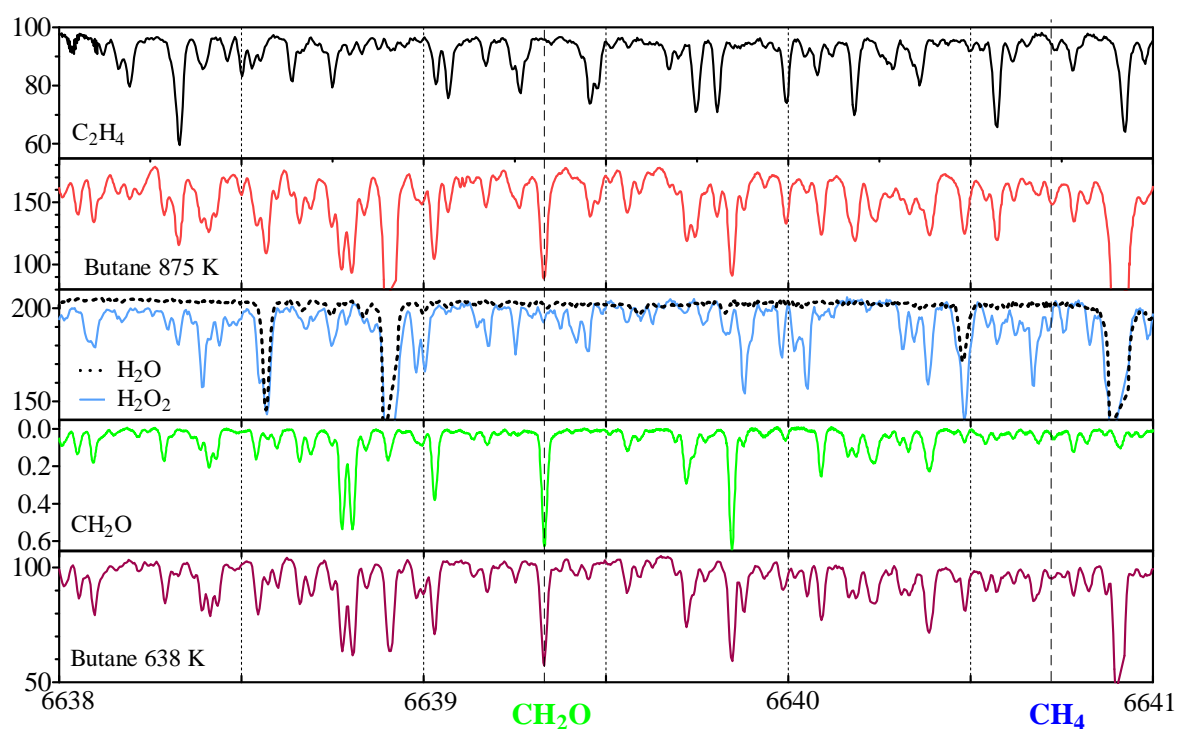


Figure 3: Absorption spectrum in the range 6638 – 6641 cm^{-1} for the major absorbing reaction products (ring down time as a function of wavenumber for H_2O_2 , H_2O and C_2H_4 , absorption cross sections of 20^{-21} cm^2 taken from Staak et al. for CH_2O) as well as the spectrum as observed from the oxidation of *n*-butane at 638 K and 875 K. The CH_4 line at 6640.72 cm^{-1} is shown as a blue dotted line, and the CH_2O line at 6639.33 cm^{-1} is shown as a green dotted line.

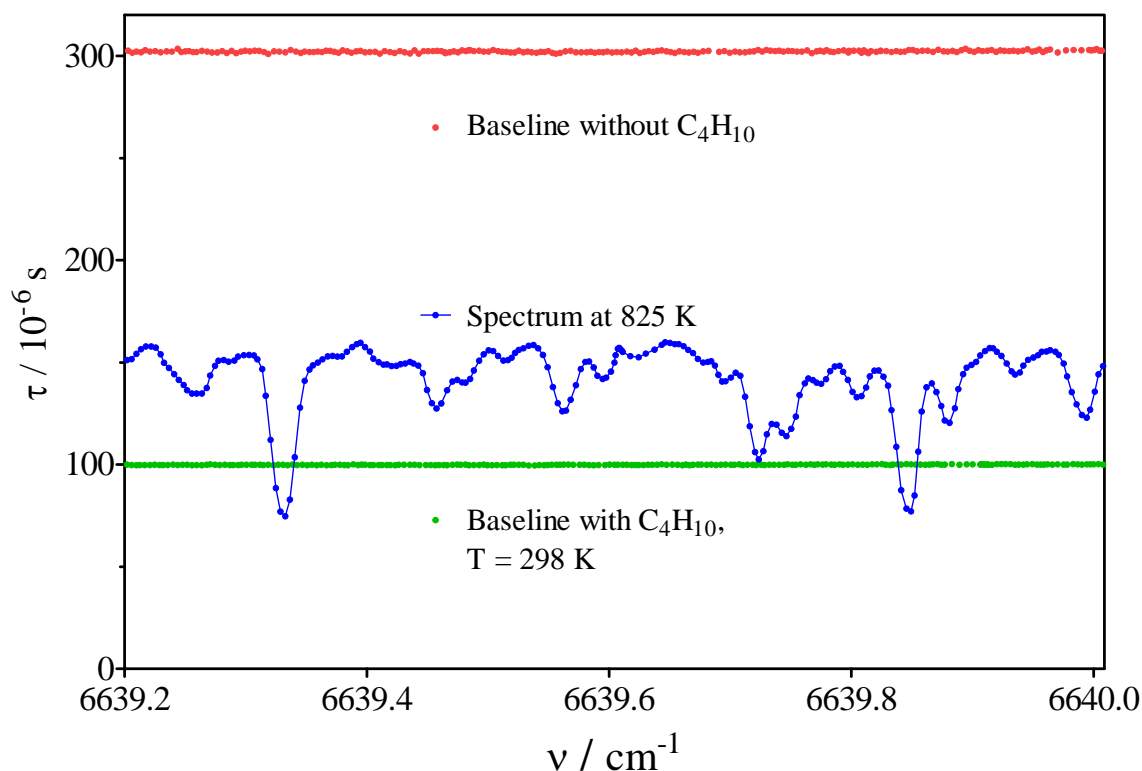


Figure 4: Absorption of *n*-butane: base line with helium only (red), with the presence of $9.7 \times 10^{15} \text{ cm}^{-3}$ *n*-butane (green) and oxidation products at 825 K (blue).

Quantification of CH_2O

CH_2O has already been quantified by the same technique in an earlier study by Bahrini et al.¹⁰ on the oxidation of CH_4 . Four different lines (6638.77, 6638.804, 6641.674 and 6642.355 cm^{-1}) were chosen for the quantification of CH_2O due to their relatively good isolation from CH_4 and H_2O absorption lines, the only other species exhibiting a structured absorption spectrum in that previous study. In the current work, the fuel, *n*-butane, has, in contrast to CH_4 , only a broadband absorption feature in this wavelength range and thus does not perturb the measurement, but leads only to a shift of the baseline. Therefore, lines that have not been considered in the CH_4 -study due to strong overlap with a CH_4 absorption line, might be very well appropriate for a quantification of CH_2O in this study, while lines that have been chosen in the CH_4 study can be perturbed by either H_2O_2 or by C_2H_4 , two species that were not present in significant amounts in the CH_4 oxidation study. The absorption of CH_4 itself as a reaction product in the oxidation of *n*-butane is very small due to its low absorption cross sections and its low concentrations (see Figure S1, supplementary material). The position of the strongest CH_4 absorption line in our wavelength range ($\sigma = 2.05 \times 10^{-23} \text{ cm}^2$ at 6640.72 cm^{-1} , obtained from Campargue et al.²³ by considering a Voigt profile) is indicated by a blue, dashed line in Figure 3. The absorption due to CH_4 explains well the small absorption feature observed at this wavelength in the 875 K spectrum (maximal CH_4 concentration) of Figure 3, but underlying small absorption features of C_2H_4 and CH_2O make it impossible to determine a reliable CH_4 -concentration. Besides, the determination of CH_4 concentration by GC is very reliable. A small contribution of CH_4 absorption has

also been identified in the vicinity of the strongest HO₂ absorption line (see Figure 5 and the discussion on the absence of HO₂ below).

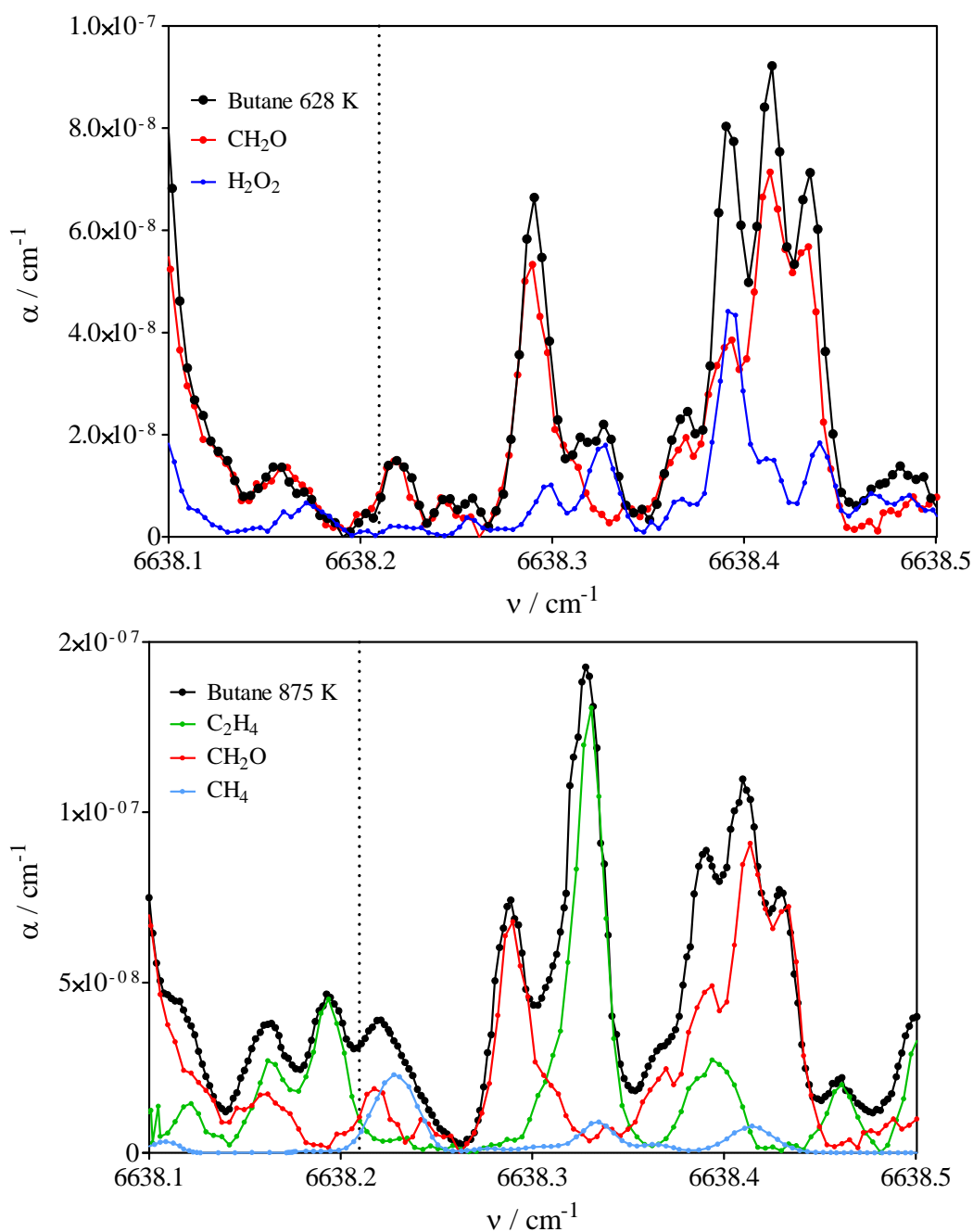


Figure 5: The graph demonstrating the absence of HO₂ within the cw-CRDS cell. The black line represents the spectrum obtained from *n*-butane oxidation: the upper panel at 628 K, the lower panel 875 K. The red line represents the CH₂O spectrum, the blue line in the upper panel represents H₂O₂, the green line in the lower panel represents C₂H₄, the blue line in the lower panel represents the CH₄ spectrum. The dotted line indicates the position of the strongest absorption line of HO₂ at 6638.21 cm⁻¹ from Ibrahim et al.³⁷ Spectra of individual species have been scaled to match the spectrum from *n*-butane oxidation products.

A major source of uncertainty for the reliable quantification of species during this study is the determination of the baseline τ_0 , i.e. the ring-down time in the absence of the absorbing species. Due to the broad absorption of *n*-butane itself, the baseline varies with temperature with the change in *n*-butane concentration (see Figure 4). Besides this problem, it can be seen from Figure 3 and Figure S5 (supplementary material) that the spectra of the reaction mixtures are very dense and it is generally not possible to identify isolated strong absorption lines with the baseline next to the absorption line free of any perturbation by other absorbing species. A rigorous way out of this problem could be the fitting of the product spectra through convolution of the individual spectra using an appropriate program such as Fityk.²⁴ This option however is not straightforward either, because the measured raw data (ring-down time as a function of wavenumber) need to be converted into absorption spectra (absorption coefficient α as a function of wavenumber) using equation (1): it can be seen that again the baseline τ_0 is needed. From these considerations, we have adopted a pragmatic approach: the average of the highest ring-down time in the right and left vicinity of the absorption line has been used as τ_0 . In order to check for systematic errors, different absorption lines have been analyzed for each species and the obtained concentrations have been compared for consistency. For CH₂O, the following 6 lines have been analyzed (see Table 1): 6624.78, 6625.25, 6639.33 (indicated by a green dashed line in Figure 3), 6641.67, 6642.35 and 6642.49 cm⁻¹.

Table 1: CH₂O concentrations extracted from the full spectrum as shown in Figure S5 (supplementary material) using 6 different lines with either absorption cross sections as obtained directly by Morajkar et al.²² at 10 Torr or divided by 1.7 as obtained from Staak et al.²¹ (see the text)

Line no	Wavenumber/cm ⁻¹	$\sigma/10^{-22}$ cm ²	628 K			875 K				
			τ/μ s	τ_0/μ s	[CH ₂ O]/10 ¹⁴ cm ⁻³	τ/μ s	τ_0/μ s	[CH ₂ O]/10 ¹⁴ cm ⁻³		
1	6624.78	5.34	45.61	102.14	8.23	70.70	177.80	5.78		
2	6625.25	3.20	60.02	103.74	7.95	96.00	177.60	5.42		
3	6639.33	3.60	58.28	103.50	7.54	90.10	175.60	5.44		
4	6641.67	4.59	52.05	100.05	7.28	81.42	166.40	4.95		
5	6642.35	4.24	53.80	99.50	7.30	81.96	171.62	5.45		
6	6642.49	1.52	74.20	99.95	8.28	118.7	171.33	6.17		
Average									7.8 ± 0.3	5.5 ± 0.2

The absorption cross sections for CH₂O at around 6640 cm⁻¹ used in the former study on the oxidation of CH₄ were taken from Staak et al.,²¹ the only data available in the literature at that time. Using these values, the experimentally obtained CH₂O profile did not agree well with model calculations: the CH₂O concentrations obtained from the experiment were roughly two times lower than predicted by the model. Following that study, we have measured CH₂O absorption cross sections of two selected lines in the near infrared region (6624.78 and 6625.25 cm⁻¹, indicated by dashed green lines in Figure S5, supplementary material):²² we have used, similar to the measurement of the H₂O₂ absorption cross sections presented further down in this work, the well-known rate constant²⁵ for the reaction of OH-radicals with CH₂O for quantifying the CH₂O concentration in situ. Line strengths were found to be two times smaller compared to Staak et al. for

both lines. From this result and taking into account the corresponding broadening factors for CH₂O (0.918 cm⁻¹ atm⁻¹)²¹ and helium (0.04 cm⁻¹ atm⁻¹)²² we have adopted for this study (8 ± 2 Torr helium) peak absorption cross sections for all lines 1.7 times smaller than published by Staak et al.

Table 1 summarizes the CH₂O concentrations extracted from the spectra shown in Figure S5 (supplementary material) for both temperatures, using all six lines. The absorption cross sections for the first two lines are those directly determined by Morajkar et al.,²² while the absorption cross sections for the last four lines are those obtained by dividing the peak absorption cross sections of Staak et al.²¹ by 1.7. It can be seen that there is overall consistency between the concentrations from all six lines for both temperatures, giving confidence that the analysis procedure can be considered free from systematic errors.

It was also possible to quantify formaldehyde by gas chromatographic analyses using the flame ionization detector thanks to the use of a methanizer located before the detector. The methanizer causes the catalytic hydrogenation of carbonyl functions transforming formaldehyde into methane and making the detection of this species much more sensitive. However the formaldehyde peak using the Plot Q capillary column has a very long tail which results in a co-elution with the peaks of methanol, acetaldehyde and ethylene oxide. Thus the relative uncertainty in the mole fractions obtained using this method is larger than that of other species and is estimated to be ±20%.

The mole fraction profiles for CH₂O are shown in Figure 1a: the open red symbols represent the average such as obtained by cw-CRDS from the different absorption lines, the blue symbols represent the results obtained by GC. The experimental mole fractions obtained by cw-CRDS are in good agreement with the predicted ones. The mole fractions derived from GC measurement are somewhat higher than the values obtained by cw-CRDS, especially in the low temperature range, supporting the lack of accuracy in the values obtained by gas chromatography for this oxygenated species.

Quantification of H₂O

H₂O is obviously a major reaction product in the oxidation of hydrocarbons and has already been detected by cw-CRDS in the earlier study on the oxidation of CH₄. H₂O has a well-structured and well-known absorption spectrum in the near infrared region and an extended list of line strengths has been published. Line strengths²⁶ in the wavelength range covered in this work span over several orders of magnitude and peak absorption cross sections under our conditions vary from around 10⁻²³ to 10⁻²⁹ cm². Thus it is possible to choose lines having a suitable absorption cross section depending on the H₂O concentration to be measured: lines with a large absorption cross section can be appropriate for a reliable quantification of H₂O in the low temperature range while the same transition might be saturated at higher temperatures, where the *n*-butane oxidation is more advanced and thus the H₂O concentration is higher. Another criterion for choosing a suitable

absorption line, besides the line strength, is again the absence of interfering lines from other reaction products. Taking into account these requirements, 12 absorption lines have been selected and are listed in Table 2, 9 lines have been used for quantification in the low and high temperature range. Peak absorption cross sections under our conditions (8 ± 2 Torr helium) have been calculated from line strengths such as published by Macko et al.²⁶ supposing a Voigt profile with a unique broadening coefficient of $0.1 \text{ cm}^{-1} \text{ atm}^{-1}$ for all lines.²⁷ As explained above, not all absorption lines can be used at all temperatures. From Table 2 it can be seen that, even though the scatter of the concentrations obtained from individual lines is larger than for CH_2O , the statistical error from the obtained average concentration (95% confidence interval) is satisfactory. In Figure 1b is presented the H_2O mole fractions as a function of temperature, the data point at each temperature being obtained from the average of several individual absorption lines. The computed profiles are in good agreement with the experimental data.

Table 2: H_2O concentrations extracted from the full spectrum as shown in Figure S5 (supplementary material) using 12 different lines with the absorption cross sections obtained from the line strength as published by Macko et al.,²⁶ a unique broadening factor of $0.1 \text{ cm}^{-1} \text{ atm}^{-1}$ has been used for all lines for calculating the peak absorption cross section

Line no	Wavenumber/ cm^{-1}	$\sigma/10^{-23} \text{ cm}^2$	628 K			875 K		
			$\tau/\mu\text{s}$	$\tau_0/\mu\text{s}$	$[\text{H}_2\text{O}]/10^{15} \text{ cm}^{-3}$	$\tau/\mu\text{s}$	$\tau_0/\mu\text{s}$	$[\text{H}_2\text{O}]/10^{16} \text{ cm}^{-3}$
1	6628.24	20.5	32.9	101.6	3.63			
2	6628.42	0.35				120.4	183.9	2.97
3	6631.88	2.10	14.5	101.7	2.12	53.5	168	2.20
4	6625.87	1.27	91.5	103.1	3.51	73.5	177.9	2.28
5	6626.47	18.6	42.8	100.3	2.61			
6	6636.84	0.918				83.1	171.9	2.45
7	6638.90	4.46	63.7	102.2	4.80	28.6	168.6	2.36
8	6640.48	0.254				128.7	171.2	2.75
9	6640.90	16.0	33.9	90.95	4.19			
10	6641.26	1.82	84.8	100.2	3.61	60.3	173.0	2.15
11	6642.84	1.62	87.4	99.8	3.18	59.6	171.8	2.45
12	6643.06	1.13	91.6	98.2	2.37	78.8	168.2	2.17
Average					3.3 ± 0.4			2.4 ± 0.1

Quantification of C_2H_4

C_2H_4 has been identified as one of the major absorbing species in the higher temperature range, while its concentration is below the CRDS-detection limit in the lower temperature range. To our knowledge, the absorption spectrum of C_2H_4 in the wavelength range used in this work has not been published and therefore its spectrum has been measured in the wavelength range $6620\text{--}6644 \text{ cm}^{-1}$. For the spectrum shown in Figure 3 and Figure S5 (supplementary material), a concentration of $5.92 \times 10^{15} \text{ cm}^{-3}$, calculated from flow meter measurements, has been used at a total pressure of 6.1 Torr, and the obtained peak absorption cross sections of the eleven most intense absorption lines in this wavelength range are tabulated in Table 3. Only six of these lines have been used to quantify the

C₂H₄ concentration, because the other lines do overlap with absorption lines from CH₂O. As can be seen in Table 3, the concentrations extracted from the 875 K-spectrum in Figure S5 (supplementary material) using the six lines are in good agreement and the C₂H₄ mole fractions at higher temperature, shown in Figure 1c, are also in good agreement with the mole fractions such as obtained by GC/FID as well as with the predicted ones. However, absorption spectroscopy in this wavelength range is certainly not the most appropriate method for a sensitive detection of C₂H₄.

Table 3: 11 most intense absorption lines of C₂H₄ obtained from the spectrum shown in Figure S5 (supplementary material)

Line no	ν/cm^{-1}	$[\text{C}_2\text{H}_4] = 5.75 \times 10^{15} \text{ cm}^{-3}$			875 K		
		$\tau/\mu\text{s}$	$\tau_0/\mu\text{s}$	$\sigma/10^{-23} \text{ cm}^2 \text{ at 10 Torr He}$	$\tau/\mu\text{s}$	$\tau_0/\mu\text{s}$	$[\text{C}_2\text{H}_4]/10^{15} \text{ cm}^{-3}$
1	6623.37	59.70	90.75	3.61	125.9	170.20	2.07
2	6623.48	60.83	91.05	3.44	116.2	169.30	2.84
3	6627.90	70.06	91.74	2.13	139.4	183.2	2.92
4	6633.22	70.00	93.50	2.26	137.7	171.3	2.28
5	6635.01	76.60	96.05	1.67	146.6	171.1	2.13
6	6637.09	70.60	97.30	2.49	134.2	174.0	2.49
7	6622.38	61.78	89.72	3.18			
8	6637.96	70.15	97.25	2.50			
9	6638.33	59.50	96.30	4.05			
10	6640.57	65.68	94.90	4.66			
11	6641.23	56.15	96.07	2.95			
Average							2.46 ± 0.24

Quantification of H₂O₂

The quantification of H₂O₂ has already been described in a separate paper,⁷ for completeness the concentration profile such as presented in the earlier work is shown as Figure 1d. In this work we briefly describe the measurement of the absorption cross sections used for the analysis of the spectra and discuss possible reasons for the disagreement between measurement and model in the high temperature range.

Preparing a mixture containing a known concentration of H₂O₂ is rather difficult, because H₂O₂ is unstable and tends to decompose heterogeneously.³ Therefore, the absorption cross sections at 10 Torr total pressure have been determined using laser photolysis coupled to a simultaneous detection of OH and HO₂ radicals. Advantage can be taken of the well-known rate constant²⁸ for the reaction of OH-radicals with H₂O₂ to deduce the H₂O₂ concentration from experimental OH decays, measured by LIF under pseudo-first order conditions. Simultaneous measurement of absolute HO₂ profiles, measured by cw-CRDS, allows taking into account secondary chemistry. More details of this method can be found in Parker et al.,¹⁶ where the measurement of absorption cross sections of H₂O₂ at 50 Torr total pressure has been described. The absorption cross sections obtained in such a way for 5

different lines at 10 Torr helium are summarized in Table 4. In Table 5 are listed the ring-down times and the corresponding absorption coefficients α for the 18 most intense lines of H_2O_2 in the current wavelength range, obtained from the spectrum shown in Figure S5 (supplementary material). The absolute absorption cross sections from Table 4 can then be used to convert the absorption coefficients into absorption cross sections: plotting σ from Table 4 against α from Table 5 for the 5 lines calibrated by laser photolysis leads to the H_2O_2 concentration used in Figure 3/Figure S5 (supplementary material) and can then be used as a calibration factor of $\sigma = \alpha/[\text{H}_2\text{O}_2] = \alpha/(3.41 \pm 0.2) \times 10^{14} \text{ cm}^2$.

Table 4: Absorption cross sections of H_2O_2 lines at 10 Torr helium in the near infrared region from LP/LIF/cw-CRDS measurements

ν/cm^{-1}	$\sigma/10^{-23} \text{ cm}^2$ at 10 Torr He
6639.25	7.49 ± 0.44
6639.45	7.79 ± 0.47
6640.02	7.89 ± 0.13
6640.06	13.8 ± 0.48
6642.14	8.55 ± 0.23

Table 5: Absorption cross sections of H_2O_2 lines in the near infrared region obtained from Figure S5 (supplementary material) and calibrated using absorption cross sections from Table 4 ($\sigma = \alpha/[\text{H}_2\text{O}_2] = \alpha/(3.41 \pm 0.2) \times 10^{14} \text{ cm}^2$). Bold lines are the same as in Table 4. The error is estimated to be $\pm 20\%$ and includes uncertainties in σ (from Table 4) as well as in τ and τ_0 obtained from Figure S5 (supplementary material)

ν/cm^{-1}	$\tau/\mu\text{s}$	$\tau_0/\mu\text{s}$	$\alpha/10^{-8} \text{ cm}^{-1}$	$\sigma/10^{-23} \text{ cm}^2$ at 10 Torr He
6621.99	161.19	187.25	3.15	9.22 ± 1.8
6624.10	165.96	185.21	2.28	6.68 ± 1.3
6631.81	153.31	189.79	4.57	13.4 ± 2.7
6633.57	167.70	192.30	2.78	8.15 ± 1.6
6635.11	157.95	191.59	4.05	11.9 ± 2.4
6635.84	149.56	192.21	5.41	15.8 ± 3.1
6635.95	149.25	192.75	5.51	16.1 ± 3.2
6639.25	175.13	200.16	2.60	7.62 ± 1.5
6639.45	179.20	203.31	2.41	7.06 ± 1.4
6639.88	154.32	202.29	5.60	16.4 ± 3.3
6640.02	176.91	201.30	2.50	7.32 ± 1.5
6640.06	158.50	200.60	4.83	14.1 ± 2.8
6640.38	159.00	201.19	4.81	14.1 ± 2.8
6640.67	158.84	201.29	4.84	14.2 ± 2.8
6641.71	159.17	205.41	5.15	15.1 ± 3.0
6641.80	176.41	205.78	2.95	8.65 ± 1.7
6642.14	175.24	205.52	3.06	8.97 ± 1.8
6643.43	160.42	210.99	5.45	16.0 ± 3.2

Absence of HO₂

HO₂ is an important intermediate in the oxidation of hydrocarbons and models predict concentrations of up to around 20 ppm under the conditions of this work. HO₂ has a well structured absorption spectrum in the wavelength range investigated in this work,²⁹ with the strongest line at around 6638.21 cm⁻¹. The portion of the absorption spectrum around this wavelength range, such as obtained from the oxidation of *n*-butane at 628 K (upper panel) and 875 K (lower panel) is shown in Figure 5 as black symbols and line. For the lower temperature, CH₂O and H₂O₂ are the major absorbers in this wavelength range, while it is CH₂O and C₂H₄ at the higher temperature, with small contributions of CH₄. Therefore, the spectra obtained from the two (three) corresponding species are plotted in the same figures with their intensities being scaled such that the sum of the individual spectra roughly matches the absorbance obtained from *n*-butane oxidation. It can be seen that the *n*-butane oxidation spectrum at the lower temperature shows only very weak absorption ($\alpha < 1 \times 10^{-8} \text{ cm}^{-1}$) around the strongest HO₂ line (indicated by a dotted, vertical line) and can be very well reproduced by the sum of the corresponding stable species alone. The absorption is slightly higher at the higher temperature ($\alpha = 3 \times 10^{-8} \text{ cm}^{-1}$), where C₂H₄, CH₂O and CH₄ have weak absorption lines near the HO₂ absorption line. When matching characteristic absorption features for both stable products (C₂H₄ and CH₂O), the missing absorption around the HO₂ line matches very well with an absorption coefficient corresponding to a CH₄ mole fraction of around 4×10^{-3} .

The maximal HO₂ concentration such as predicted by the models (mole fractions up to 5 and 15×10^{-6} in the low and high temperature range, respectively) would lead to an absolute concentration in the cw-CRDS cell (around 10 Torr) of around $2/6 \times 10^{12} \text{ cm}^{-3}$. Estimating an absorption cross section for HO₂ at 10 Torr of $\sigma = 3 \times 10^{-19} \text{ cm}^2$, such concentrations would result in absorption coefficients of $\alpha = 0.6/1.8 \times 10^{-6} \text{ cm}^{-1}$, to be compared with the overall observed absorbance of $0.007/0.03 \times 10^{-6} \text{ cm}^{-1}$. From these observations it can be concluded, that over the entire temperature range the HO₂ concentration in the cw-CRDS cell is less than 1% of what is predicted by models. The same total absence of HO₂ has already been observed in an earlier work¹⁰ on the oxidation of CH₄ and no obvious explanation could be given. We have very recently coupled a JSR to a detection of HO_x radicals by FAGE (Fluorescence Assay by Gas Expansion: details of the instruments are described elsewhere³⁰⁻³² and will not be repeated here): preliminary results show that the HO₂ concentration measured by this technique is in good agreement with model calculations. Because the self-reaction of HO₂ radicals in the gas phase is too slow to explain the decrease of at least 99%, we suspect a heterogeneous loss of HO₂ radicals during sampling into the cw-CRDS cell. It is known that HO₂ radicals recombine easily by heterogeneous reaction on glass surfaces,³³ so we are left with the suspicion that this process is efficient enough to decrease the HO₂ concentration below our detection limit.

Discussion

It has already been shown in an earlier work⁷ and it can be seen from Figure 1d, that the H₂O₂ mole fraction profile is in excellent agreement with the one predicted by the current model⁸ in the low temperature range ($T < 750 \text{ K}$); at higher temperatures however, the model overestimates the H₂O₂

mole fraction by up to a factor of 4. This is especially surprising since the agreement for the maximum mole fractions is generally very good for other species in this range of temperature. The following discussion aims therefore at trying to understand the deviation between experiments and predictions which is observed for the H_2O_2 mole fraction profile above 750 K. Two modifications to the current model will be discussed: (a) implementation of the recently revised rate constant for the unimolecular decomposition of H_2O_2 and (b) considering the possibility of heterogeneous destruction of H_2O_2 on hot reactor walls.

(a) Improvement of gas phase chemistry

Figure 6 shows a sensitivity analysis on the influence of the rate parameters of gas phase reactions on the predicted H_2O_2 mole fraction at 800 K. The most sensitive reaction for the consumption of H_2O_2 is the reaction: $\text{H}_2\text{O}_2 (+\text{M}) \rightleftharpoons 2 \text{OH} (+\text{M})$. Fortuitously, Troe⁹ has recently proposed a new value for this rate constant, decreasing it by a factor 2.7 at 800 K at 1 atm compared to the value from Baulch et al.,³⁴ which was used in the initial model. The influence of this latter rate constant on the profiles of all species can be seen by comparing simulations obtained with the initial mechanism using the Baulch et al.³⁴ value (the dashed line in Figures 1 and 2 and Figures S1–S4 in supplementary material) with profiles from the improved model incorporating the value by Troe⁹ (full line in Figures 1 and 2 and Figures S1–S4 in supplementary material). The lower value from Troe induces a shift of around 20 K toward the higher temperatures for the consumption of *n*-butane and the formation of H_2O_2 as well as for the formation of all other products. This is in good agreement with experiments: the initial model tends to overestimate the reactivity in the high temperature range. However, the maximum value of the H_2O_2 mole fraction is barely influenced by this new rate constant and remains much too high compared to experiments. The influence of the kinetic parameters of the other reactions on both the consumption of *n*-butane and the H_2O_2 formation are all almost negligible and therefore it is concluded, that gas phase chemistry alone cannot explain the strong overestimation of H_2O_2 .

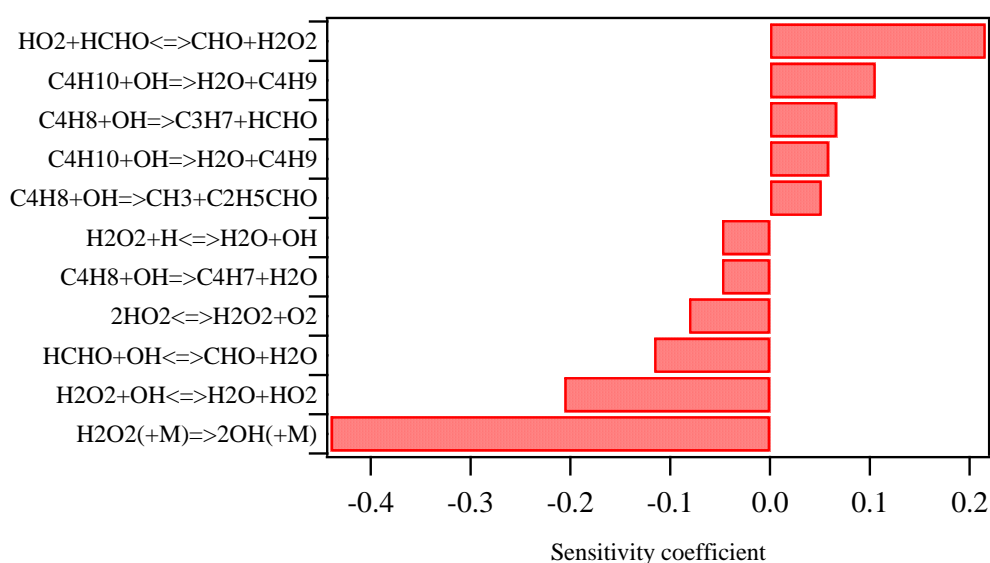


Figure 6: Sensitivity analysis showing the reactions of importance for the H_2O_2 mole fraction at 800 K.

(b) Heterogeneous loss of H_2O_2

H_2O_2 is a thermally rather stable molecule: for example its decomposition rate at 800 K and 1 bar N_2 is only around 0.7 s^{-1} , thus H_2O_2 concentrations predicted by models stem mostly from the continuous formation of this species as a product of *n*-butane oxidation. On the other hand, H_2O_2 might decompose heterogeneously on the hot reactor walls. In order to test for this possibility, we have admitted H_2O_2 into the JSR by bubbling helium through a 50% H_2O_2 - H_2O solution, maintaining the same residence time as in the *n*-butane experiments. We have measured its concentration at the exit of the JSR using cw-CRDS. The result is presented in Figure 7 as a 3-D plot of the absorption spectra obtained at different temperatures up to 625 K in the JSR. It can be clearly seen, that the H_2O_2 concentration strongly decreases with increasing temperature, while the H_2O concentration (admitted together with H_2O_2 to the reactor) is constant, as can be seen from the stable H_2O absorption lines at 6638.57 and 6638.9 cm^{-1} . Above 600 K, the H_2O_2 concentration falls below the detection limit, even though from gas phase kinetic considerations its concentration should be nearly stable. This is a clear hint that H_2O_2 is destroyed heterogeneously in a temperature dependent reaction and that this loss should be taken into account in the model in order to improve the agreement of experimentally obtained H_2O_2 profiles with model predictions.

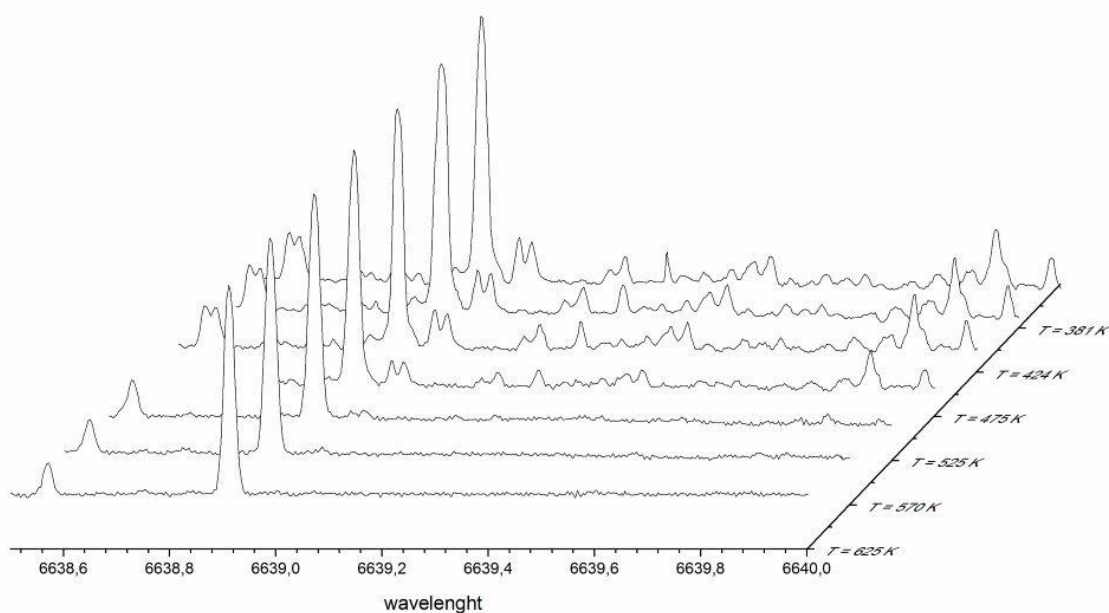


Figure 7: Destruction of H_2O_2 concentration when passed through the heated JSR: an H_2O_2 - H_2O mixture diluted in helium was passed through the JSR reactor with a residence time of 6 s. The spectrum was measured at different reactor temperatures: all lines are due to H_2O_2 except the two lines at 6638.57 and 6638.91 cm^{-1} , which are due to H_2O .

An earlier study by Porter et al.³⁵ has already shown the influence of wall reactions of H_2O_2 and HO_2 radicals and its significant influence on oxidation phenomena in the case of *n*-butane, confirming older experimental results obtained in static reactors coated with different types of oxides.³⁶ A simulation under our conditions using temperature independent wall reactions such as proposed by Porter et al. for both H_2O_2 and HO_2 radicals would lead to no reactivity at all for *n*-butane for temperatures below 950 K. A simulation using the same wall reactions as Porter et al. but only for H_2O_2 would lead to a displacement of the reactivity of *n*-butane of about 100 K toward higher temperatures, and to a mole fraction of H_2O_2 reduced by more than a factor of 10 over the whole temperature range, i.e. much below the observed experimental profiles. Therefore, the wall reactions under the condition of a JSR are probably significantly more limited than those considered by Porter et al. Also, it is clear from the experimental observations (in very good agreement in the low temperature range as well as temperature dependent H_2O_2 destruction presented in Figure 7) that the mechanism in this work exhibits strong temperature dependence and that a model including a temperature independent wall loss will not be able to reproduce the observations.

As a tentative method to reduce possible wall reactions, we have used for some experiments a reactor such as shown in Figure 8. The walls of this reactor have been entirely covered by an inert coating: SilcoNert™ 2000, provided by SilcoTek. Such surface treatment is known to eliminate adsorption of active compounds on surfaces such as steel, glass, ceramic and carbon surfaces. Figure 9 presents two CRDS spectra: one was obtained using a reactor with the walls coated by the SilcoNert™ 2000 surface treatment (full black line) and one with uncoated walls (dashed red line). Characteristic H_2O_2 absorption features in this wavelength range are marked with a star, and it can be seen that no significant difference is observed between these two spectra.

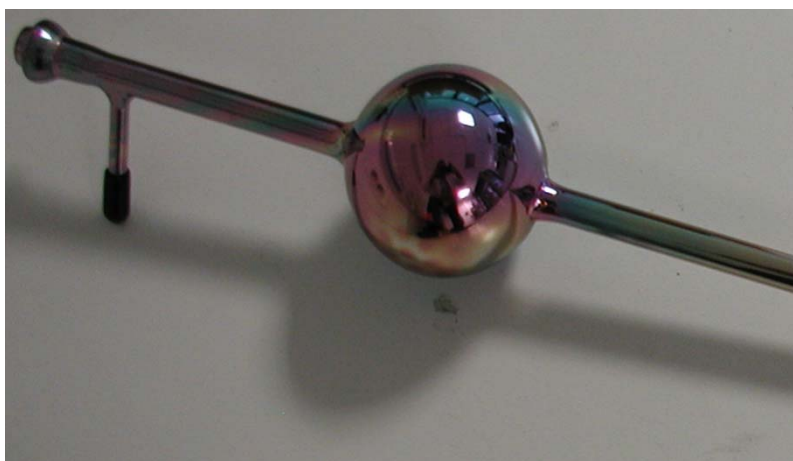


Figure 8: Photography of the JSR, coated with SilcoNert™ 2000.

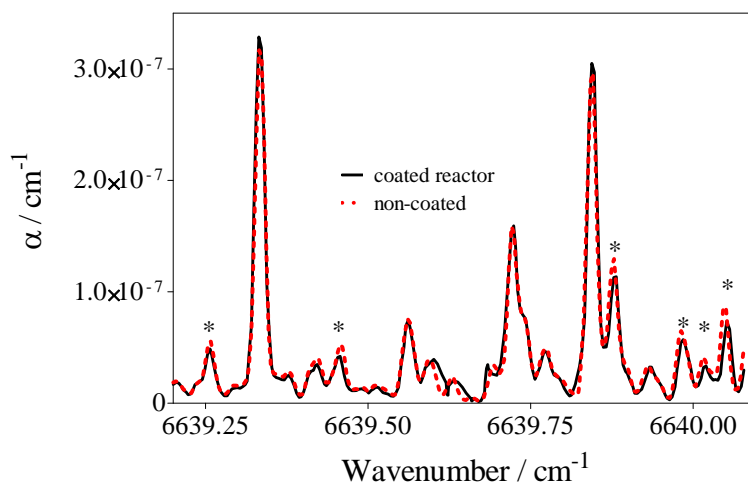


Figure 9: CRDS spectra obtained with reactor walls fully covered by the SilcoNert™ 2000 surface treatment and with reactor walls without any special treatment.

In order to best reproduce the experimental H_2O_2 mole fraction profile, we have then included a temperature dependent wall destruction of H_2O_2 into the model. The rate constant of this possible wall reaction was adjusted in order to match the maximum H_2O_2 mole fraction observed in the experiments:

$$k_{\text{wall}} = 3.5 \times 10^3 \exp(-7550/T) \text{ s}^{-1},$$

This rate constant is about ten times lower than that proposed by Porter et al.³⁵ The activation energy used in this expression has no physical meaning but only indicates the temperature dependence of this process. The results of simulations using this wall reaction in addition to the improved gas-phase only model are shown as dotted lines in Figures 1 and 2 and Figures S1–S4 (supplementary material). While the implementation of a wall reaction has a major impact on the H_2O_2 mole fraction at high temperature (see Figure 1d), its influence on the reactivity of *n*-butane and the formation of carbon containing products and radicals (including HO_2 radicals) can be seen as only a slight shift (about 20 K) towards higher temperature between 800 and 850 K, thus improving even more the agreement between model and experimental results.

The experiment in Figure 7 cannot be well reproduced with the same rate constant: a nearly complete loss of H_2O_2 is already observed experimentally at 625 K, while the above rate constant predicts only a decay of the H_2O_2 concentration during the 6 s residence time of 12%. But such comparison is not straightforward, because in the Figure 7 experiment the H_2O_2 has also to pass the preheating zone before entering the reactor, a zone with a large surface to volume ratio where a partial destruction of H_2O_2 can already take place.

The present study has been carried out at a residence time within the JSR of 6 s, which is rather long: it can be seen from Figure 10a that under such conditions the impact of the wall loss on the H_2O_2 mole fraction is particularly high: the wall loss decreases the maximum H_2O_2 mole fraction by more than 50%, while at a residence time of 2 s the mole fraction is decreased by only 37%. Not surprisingly, the wall loss seems rather independent of the inlet fuel concentration: it causes always the same minor shift in reactivity at around 800 K while H_2O_2 mole fraction drops off by around a factor of 2 for all concentrations (see Figure 10b).

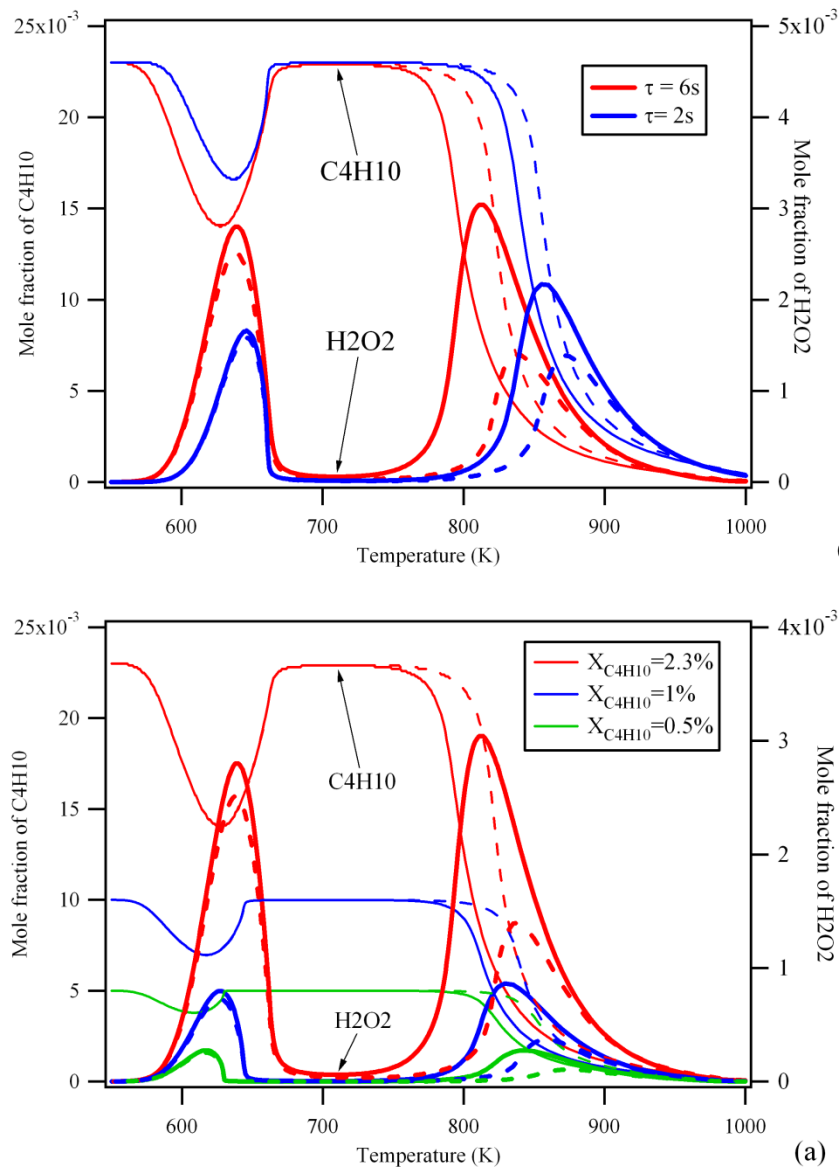


Figure 10: Influence of the wall reactions on the simulated consumption of *n*-butane (thin lines) and the formation of H_2O_2 (thick lines) for (a) different residence times (τ) for an initial fuel mole fraction of 2.3% and (b) different initial fuel mole fractions for a residence time of 6 s and (b) different residence times (τ) for an initial fuel mole fraction of 2.3%. Full lines represent the simulation with the initial gas-phase mechanism; dotted lines represent simulations considering wall reactions.

Wall destruction of H_2O_2 within the JSR, mainly significant above 800 K, is therefore a hypothesis which cannot be discarded. Fortunately, the influence of this wall reaction seems to remain very limited on the fuel reactivity and product formation and does not diminish the value of jet-stirred reactor experiments, an experimental technique that allows the analysis of a wide range of stable oxidation products and is an irreplaceable tool to validate detailed kinetic models.

Conclusion

New results on the low temperature oxidation of *n*-butane have been presented using two complementary detection techniques: cw-CRDS and GC. Two of the stable reaction products can be detected using both techniques: C_2H_4 and CH_2O . While GC is much more adapted for the detection of C_2H_4 , it has been observed that the quantification of CH_2O with GC is not fully accurate due to a long tail in the peak and co-elution with other species. A major breakthrough in the application of cw-CRDS to combustion systems is the quantification of H_2O_2 , a key species in the development of auto-ignition. It has been observed that the temperature profile of this species is in excellent agreement with current models at low temperature, but that models overpredict its concentration at higher temperature. Gas phase reactions as reason for this disagreement have been excluded through sensitivity analysis and it is now suspected that H_2O_2 is destroyed through heterogeneous reactions on the hot reactor wall. The major impact of adding a temperature dependent wall loss reaction of H_2O_2 to the model is a shift in the reactivity of around 20 K in the high temperature range, inducing the same shift in the profiles of most oxidation products, which interestingly leads to a better agreement between model and experiment.

Acknowledgements

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