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Investigation of the Flame Structure of Dichloromethane-doped nonpremixed Methane-Flames by Laser Induced Fluorescence

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Abstract

A detailed understanding of the combustion of chlorinated hydrocarbons is of major importance as it leads to a deeper insight in flame chemistry and formation of pollutants like polychlorinated dibenzodioxines and furanes (PCDD/PCDF). Furthermore, the knowledge of the structure of chlorinated hydrocarbon flames allows optimizing designs of technical burners and combustion chambers to inhibit pollutant formation. This requires a full investigation on various ongoing physico-chemical effects as well as stable and short-lived species in the flame. In this paper, laser-induced fluorescence (LIF) is applied to investigate the flame structure of the non-premixed combustion of mixtures of dichloromethane (DCM) and methane, stabilized with a model burner. Measurements of the fluorescent emissions from excited OH and CCl radicals at different concentrations of DCM provide an insight in the flame structure and mechanism of the thermal conversion. These LIF profiles give preliminary information for a general understanding of the combustion of chlorinated hydrocarbons and therefore help towards decreased toxic emissions from combustion of these compounds.

Introduction

The combustion of chlorinated hydrocarbons plays an important role in several technical applications, e.g. thermal decomposition of waste material. The knowledge of the impact of chlorine species to the overall combustion process and especially to the flame structure is very limited. The chlorine species lead to formation of harmful emissions and act as a precursor for the formation of polychlorinated dibenzodioxines and furanes (PCDD/PCDF) [1,2]. In addition to these highly toxic species, combustion of chlorinated hydrocarbons may lead to the formation of byproducts like Cl_2 , CO [3] and soot [4], while HCl is the desired oxidation product of the chlorine atoms. A deeper understanding of the chemistry of flames containing chlorinated hydrocarbons may improve applications in fields like hazardous waste disposal, fire suppression, and laser decontamination of toxic coatings [5] towards complete oxidation of the chlorinated species.

In the past, Chelliah et al. [6] have done detailed experimental and numerical studies on the global and detailed kinetics of the premixed and non-premixed chloromethane-doped flames and concluded that the influences of chlorine content on the responses of premixed and non-premixed flames are similar. Brukh et al. [7] studied pathways of methylene chloride destruction and pointed out the significant role of various radicals.

The CCl radical has been long known to exist in chlorinated hydrocarbon flames [8]. First detections of this radical were performed using microwave spectroscopy [8] and other spectroscopic methods like FTIR [9,10], but Devynck et al. [11] showed first quenching measurements of CCl under flame conditions by laser-induced fluorescence. In Figure 1, the laser emission spectrum of a CH_2Cl_2 -seeded methane flame is

shown. It can be seen, that the emission of the CCl radical is at $278 \text{ nm} \pm 1 \text{ nm}$ in the Q1(0-0) band.

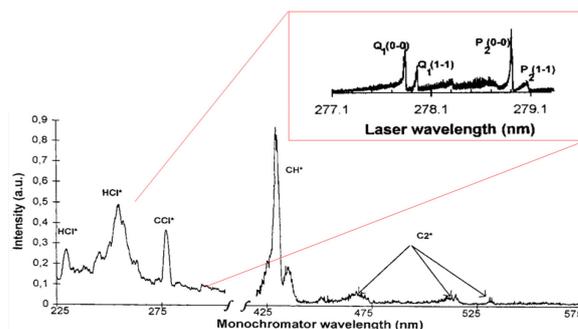


Figure 1. Laser emission spectrum of a CH_2Cl_2 -seeded methane-flame [11].

To our knowledge, no simultaneous planar LIF-based measurements of reactive species like OH and CCl in flames containing chlorinated hydrocarbons to investigate the flame structure have been performed. This paper focuses on the flame structure of a non-premixed laminar flame of methane mixed with different concentrations of dichloromethane.

Approach

The non-premixed combustion of different concentrations of dichloromethane in methane was carried out using a model burner. The desired mixture of DCM and methane flows through a vertical steel tube with an inner diameter of 10.0 mm. The air flows as a co-flow from the annular region between the fuel tube and a 102 mm inner diameter concentric tube. This co-flow is stabilized by a perforated ceramic plate that is fitted in the outer tube of the burner. This burner is derived from the design of the co-flow model "Gülder" burner [12]. Methane and air flows were controlled by

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thermal mass flow controllers (EL-Flow[®], Bronkhorst B.V.) with an uncertainty of 1 % of the reading value, while DCM was controlled by a coriolis mass flow controller (mini-CORI-Flow[™], Bronkhorst B.V.) with an uncertainty of 0.2 % of the reading value. Because DCM is in liquid phase at ambient conditions, it needs to be evaporated (atmospheric boiling point of 39.6 °C). Therefore, methane was added directly downstream of the coriolis mass flow controller and the consequent pipe towards the burner was heated up to 100 °C to ensure complete evaporation and mixing of the two components.

Table 1. Investigated flows of methane and DCM. Co-flow constant at 200 l_N/min. (normal conditions 1.01325 bar, 293 K).

ϕ DCM	Volumetric flow rate	
	Methane [l _N /min]	DCM [l _N /min]
0 % (reference)	0.1500	0
10 %	0.1350	0.0150
15 %	0.1275	0.0225
20 %	0.1200	0.0300
25 %	0.1125	0.0375
30 %	0.1050	0.0450
35 %	0.0975	0.0525
36 %	0.0960	0.0540
37 %	0.0945	0.0555
40 %	0.0900	0.0600

The flow of the gaseous fuel (methane + DCM) was set constant to a value of 0.15 l_N/min to ensure constant flow velocities. Methane was substituted by different amounts of DCM to study its influence on the combustion. The co-flow was fixed to 200 l_N/min air. Therefore, the flow velocity of the fuel was 0.032 m/s and 0.413 m/s for the co-flow. All investigated flows of methane and DCM are listed in Table 1. The piping and instrumentation is shown in a schematic flow-sheet in Figure 2.

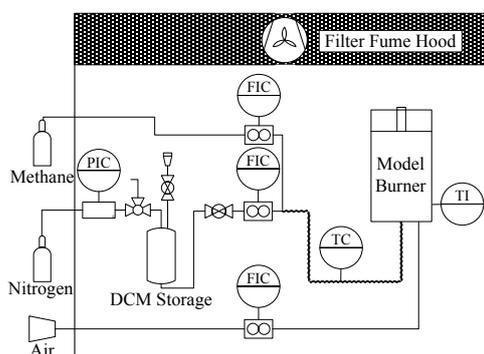


Figure 2. Schematic representation of the burner setup.

Because of the harmful nature of the DCM and its combustion products, the whole setup for the burner was placed in a ductless filtering fume hood which is equipped with synthetic fused silica SQ1 (Sico

Technology Ltd.) windows to guarantee optical access for the laser induced fluorescence measurements.

To investigate the flame structure of DCM-seeded methane-flames, the laser induced fluorescence of the OH radicals and the CCl-radicals were recorded. The laser system consists of a 10 Hz repetition rate frequency-doubled Nd:YAG (Quantel Brilliant b) pumping a dye laser (Quantel TDL90). The laser beam was stretched and focused to form a light-sheet using two lenses. The thickness of this so formed light sheet was around 100 μm and its vertical focus was directed through the center of the flame.

The A-X transition of the OH-radical's Q1(6)-band was excited at 282.927 nm with an energy of approximately 2 mJ per laser pulse. The selected band is chosen for the high probability of transition, and the relatively low energy needed for excitation. The resulting fluorescence signal of the OH transition has been selectively filtered to detect with a 12 bit intensified CCD camera (Dantec Dynamics HiSense MKII camera and Hamamatsu C9546-03L intensifier) at 308 nm (FWHM 25 nm) with a resolution of the two-dimensional images of 1280 x 1024 px at right angle to the light-sheet. 200 shots were averaged for each measurement. These measurements were corrected by subtracting the recorded emissions when the laser is detuned to a wavelength of 282.8 nm while maintaining laser energy constant. At this wavelength, OH-radicals will not absorb emission leading to fluorescence; hence subtracting these emissions will eliminate all background noise and scatter (PAK-fluorescence, possible LII and Rayleigh scattering etc.).

The CCl-radical was excited at 277.84 nm with the same laser system but different dye – here it was Rhodamine 560 Chloride solved in methanol. For this wavelength, pulse energies were limited to approximately 1 mJ. The resulting fluorescence was filtered using a short-pass filter (50 % cut-off wavelength: 280 nm) and recorded around 278 nm using the same camera system and recording parameters as for the OH-LIF.

Results and Discussion

The resulting planar LIF distributions of the OH radicals at different concentrations of DCM are given in Figures 5-7. Substituting methane by DCM leads to a stable combustion up to about 39 % DCM, while the total length of the OH-zone contracts with increased concentrations of DCM – the flame gets smaller. For concentrations above 35 % DCM, the contraction of the flames OH-zone in length is increased, as well as an increased lift-off of the flame from the burner outlet. Also, the width of the OH-profile decreases with increased DCM-concentrations.

At 40 % DCM the flame blows off, due to the flame-retardant nature of chlorinated hydrocarbons.

The length of the OH-zone and the lift-off height for the investigated concentrations of dichloromethane in methane are shown in Figure 3. These values were derived from the planar LIF measurements. The OH-

zone length is determined from the planar OH-distributions where the top of the zone is defined as the pixel with maximum y-coordinate showing 10 % of the respective maximum intensity of the image. Analog procedure applies for the determination of the lift-off height, with the pure methanol flame as reference case.

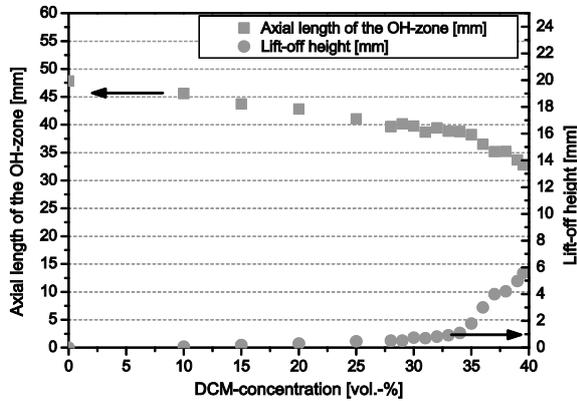


Figure 3. Length of the OH-zone and lift-off height as a function of DCM concentration in methane.

The CCl radical was detected in the upper center of the flame. Figure 4 gives the axial positions of the CCl-zones as well as the OH-zones. These dimensions were determined like the dimensions given in Figure 3.

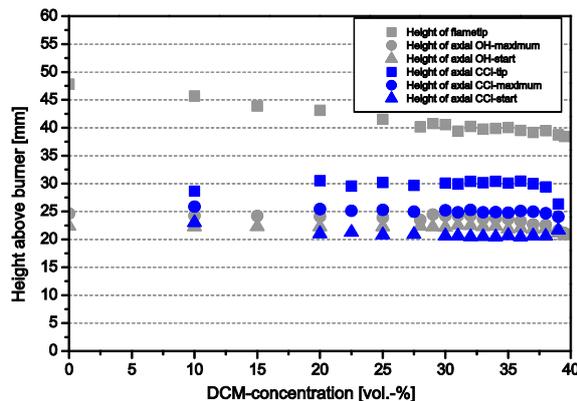


Figure 4. Characteristic axial positions of OH and CCl radicals as a function of DCM concentration.

For all concentrations investigated, the CCl-zone in axial direction is in the lower half of the OH zone. Peak concentrations of CCl were found downstream of axial OH peak concentrations. For concentrations greater than 20 %, CCl radicals begin to form upstream of OH-radicals.

The axial OH-zone dimension contracts almost linearly with the DCM-concentration, so the increased contraction of the total axial length of the OH-zone for concentrations above 35 % DCM comes from flame lift-off. In contrast, the axial length of the CCl-zone is almost constant for DCM-concentrations between 20 and 36 %, but contracts for concentrations higher than 36 % significantly. More than 36 % DCM affect the whole structure of the CCl-zone, even the point of the axial CCl intensity maximum.

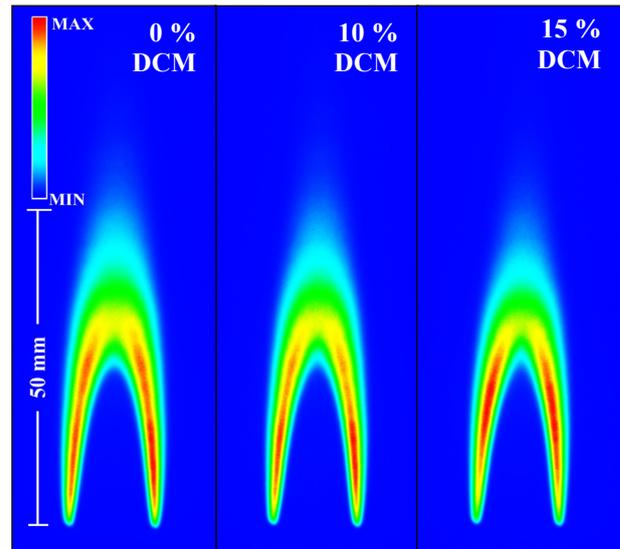


Figure 5. OH-distribution at 0 %, 10 %, and 15 % DCM in methane.

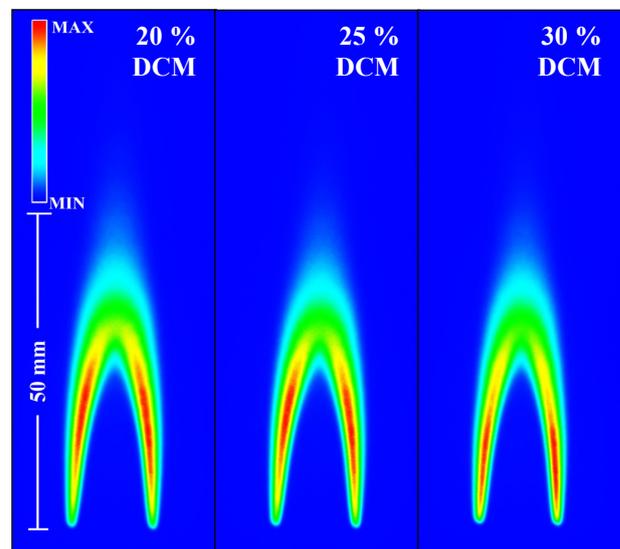


Figure 6. OH-distribution at 20 %, 25 %, and 30 % DCM in methane.

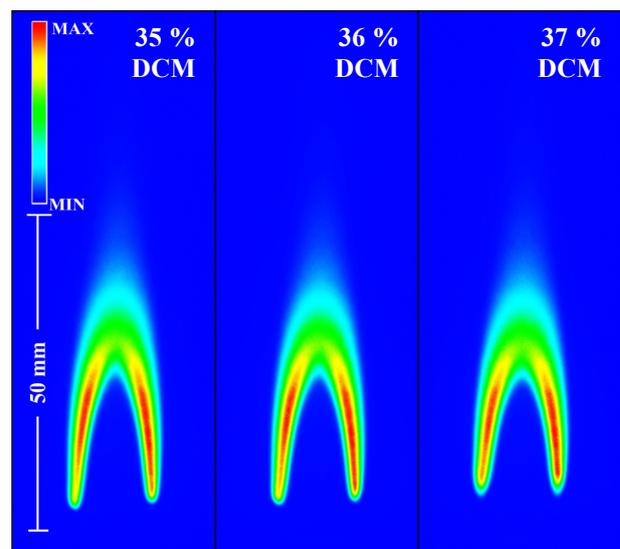


Figure 7. OH-distribution at 35 %, 36 %, and 37 % DCM in methane.

An explanation for the decrease in length of the axial OH-zone with an DCM increase is the consumption of OH-radicals due to chlorine (CCl, Cl, etc.) radicals. Also, the overall H-balance decreases with increased DCM, because hydrogen is substituted by chlorine.

Figure 8 shows that the CCl-signal is strongly dependent on the DCM-concentration. The maximum in intensity can be found around 35 % DCM, higher concentrations lead to strongly decreasing signals.

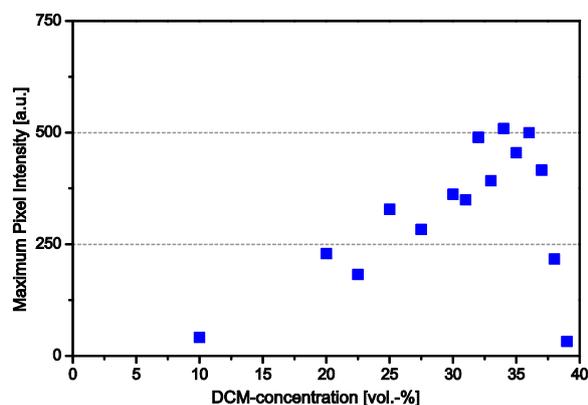


Figure 8. Maximum intensity of CCl-LIF signal vs. DCM concentration.

Conclusions

Our investigations on the non-premixed combustion of methane and dichloromethane using laser induced fluorescence show a strong influence of the DCM-concentration on the flame structure. The OH-zone contracts in its vertical as well as horizontal dimensions with increased DCM-concentrations. At 35 % DCM, an increased lift-off from the burner nozzle reduces the whole flame zone additionally. At 40 % DCM in methane, the flame blows off.

CCl radicals could be detected in the inner part of the flame. The structure of the CCl-zone for concentrations of DCM between 20 and 36 % is far more stable than the structure of the OH-zone. The concentration of CCl radicals within this zone is affected by the DCM concentration because the signal of these radicals strongly depends on the DCM concentration, with peak intensity – and therefore a peak in CCl radical concentration – around 35 % DCM in methane.

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References

- [1] Stanmore, B.R. (2004): The formation of dioxins in combustion systems. In: *Combustion and Flame* 136 (3), pp. 398-427.
- [2] Gullett, B.K.; Sarofim, A.F.; Smith, K.A.; Procaccini, C. (2000): The Role of Chlorine in

Dioxin Formation. In: *Process Safety and Environmental Protection* 78 (1), pp. 47-52.

- [3] Wang, B.; Chi, Y.; Yan, J.-H.; Ni, M.-J. (2009): Experimental study on CO oxidation inhibited by chlorine. In: *Zhongguo Dianji Gongcheng Xuebao/Proceedings of the Chinese Society of Electrical Engineering* 29 (2), pp. 58-62.
- [4] Leylegian, J.C. (2008): Soot formation in aerodynamically strained methane–air and ethylene–air diffusion flames with chloromethane addition. In: *Combustion and Flame* 152 (1-2), pp. 144–153.
- [5] Anthofer, A.; Lippmann, W.; Hurtado, A. (2013): Development and testing of a laser-based decontamination system. In: *Optics & Laser Technology* 48, pp. 589-598.
- [6] Chelliah, H.K.; Yu, G.; Hahn, T.O.; Law, C.K. (1992): An experimental and numerical study on the global and detailed kinetics of premixed and nonpremixed flames of chloromethane, methane, oxygen and nitrogen. In: *Symposium (International) on Combustion* 24 (1), pp. 1083-1090.
- [7] Brukh, R.; Mitra, S.; Barat, R. (2004): Pathways to methylene chloride destruction at low and high concentrations. In: *Combustion Science and Technology* 176 (4), pp. 531-555.
- [8] Endo, Y.; Saito, S.; Hirota, E. (1982): Microwave Spectroscopy of the CCl Radical. In: *Journal of Molecular Spectroscopy* 94, pp. 199-207.
- [9] Burkholder, J.B.; Sinha, A.; Hammer, P.D.; Howard, C.J. (1988): High-resolution Fourier transform infrared spectroscopy of the CCl radical ($X^2\Pi_{3/2, 1/2}$). In: *Journal of Molecular Spectroscopy* 127 (1), pp. 61-69.
- [10] Xiang, T.; Liu, K.; Shi, C.; Su, H.; Kong, F. (2007): Experimental and theoretical studies of the CCl + O₂ reaction. In: *Chemical Physics Letters* 437, pp. 8-13.
- [11] Devynck, P.; Desgroux, P.; Gasnot, L.; Therssen, E.; Pauwels, J.F. (1998): CCl, CH, and NO LIF measurements in methane-air flames seeded with chlorinated species: Influence of CH₃Cl and CH₂Cl₂ on CCl and NO formation. In: *Proceedings of the 1998 27th International Symposium on Combustion*, pp. 461-468.
- [12] Gülder, Ö.L.; Intasopa, G.; Joo, H.I.; Mandatori, P.M.; Bento, D.S.; Vaillancourt, M.E. (2011): Unified behavior of maximum soot yields of methane, ethane and propane laminar diffusion flames at high pressures. In: *Combustion and Flame* 158 (10), pp. 2037-2044.