

Kinetic modeling of the low temperature cool flames of acetaldehyde in a well stirred reactor

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Abstract

Due to the increasing interest in the use of biofuels such as alcohols in blend with fossil fuels, it is of great importance to better understand the combustion characteristics of species such as aldehydes, both in the high and in the low temperature regime. Starting from the high temperature mechanism for C₃-C₅ aldehydes recently developed at Politecnico di Milano (POLIMI), its extension to the low temperature conditions firstly requires to assess acetaldehyde and acetyl radical (CH₃•C=O) reactivity at low temperatures. Acetaldehyde low temperature mechanism is used in this paper to reproduce different oscillatory ignition regimes such as cool flames, experimentally observed in well stirred reactors.

Introduction

Considerable interest has been given to the kinetics of oxidation of aldehydes both in past and recent years. In the 80s Gray et al. [1] studied different behaviors of equimolar mixtures of acetaldehyde and oxygen in a well stirred non-isothermal reactor at very low temperatures (450-625 K) and pressures (50-150 torr), identifying five different regions in the pressure-temperature ignition diagram. Also the high temperature oxidation of acetaldehyde was extensively investigated [2]. More recently, due to the increasing interest in biofuels such as alcohols, research efforts have been made to understand and systematically model the oxidation of heavier aldehydes (propanal, *n*-butanal, *i*-butanal, and *n*-pentanal) [3-5] critically emerging as non-regulated pollutants from processing and combustion of both solid and liquid bio-fuels [6].

New and previously published experimental data were used to extensively validate the sub-mechanism developed to describe the high temperature oxidation of C₃-C₅ aldehydes by Pelucchi et al. [5]. This mechanism constitutes the basis for the extension to the low temperature regime discussed in this work.

Oscillatory cool flames of acetaldehyde in a well stirred reactor

As previously mentioned, Gray et al. [1] experimentally investigated the ignition and cool flame behavior of equimolar mixtures of acetaldehyde and oxygen in a continuous well stirred flow reactor at temperatures from 450 K to 625 K and

pressures from 50 to 150 torr. Nine different stable modes were characterized and grouped into five regimes [1]: R1) slow combustion (steady reaction without light emission), R2) stable oscillatory ignition with simple waveform, R3) stable oscillatory ignition with complex waveforms (five different types observed), R4) stable oscillatory cool flames, R5) steady rapid reaction accompanied by light emission (non-oscillatory cool flames). The five different regions are identified by the lines of Figure 1.

Numerical simulations were performed using the Perfectly Stirred Reactor solver included in the OpenSMOKE++ framework by Cuoci et al. [7]. To represent the open system, the energy balance with the usual heat exchange term ($Q=U\cdot S\cdot(T-T_{amb})$) was also solved. The heat exchange, therefore the heat transfer coefficients U , strongly affects the transition between regions where this dynamic behaviors are observed. The values suggested by Lignola et al. [8] were adopted.

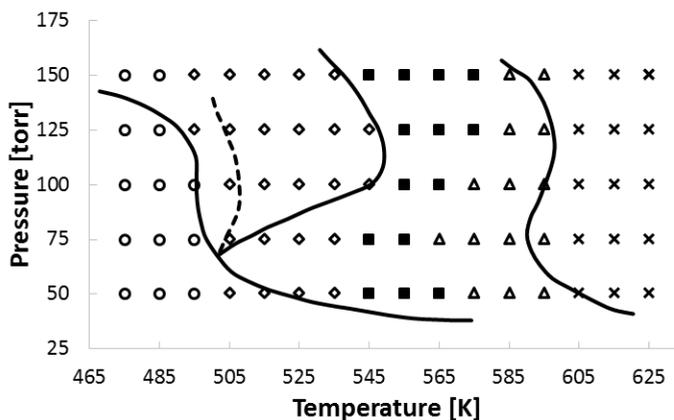


Figure 1. Ignition diagram of $\text{CH}_3\text{CO}/\text{O}_2/\text{N}_2$ (33%/33%/34%), $\tau=3.0$ s. Solid lines: experimental boundaries different dynamic behaviors [1], symbols: numerical simulations (circles: R1, diamonds: R2, squares: R3 (2 cool flames), triangles: R4, crosses: R5). U [$\text{W}/\text{m}^2/\text{K}$]: 11 (50 torr), 13 (75 torr), 15 (100 torr), 16.5 (125 torr), 18.0 (150 torr).

The POLIMI mechanism is able to reproduce the variety of regimes over the conditions explored. Examples of reactor temperature versus time profiles of the three oscillatory behaviors identified during the simulations at 100 torr pressure are reported in Figure 2. Despite a relatively small increase of initial temperature, the frequency of oscillations largely increases, while the amplitude (ΔT) sensibly decreases. As already stated by Gray et al. [1], the periodicity of cool flames depends on the self-quenching kinetics. In fact, the competition between the endothermic acetyl radical decomposition ($\text{CH}_3\cdot\text{CO}+\text{M}=\cdot\text{CH}_3+\text{CO}+\text{M}$) and the addition to oxygen to form acetyl-peroxide ($\text{CH}_3\cdot\text{CO}+\text{O}_2=\text{CH}_3\cdot\text{CO}_3$) explains the observed phenomena.

The evolution of the system can be clearly represented by phase plan diagrams, allowing to understand the role of intermediates in the observed oscillatory phenomena. Two examples are shown in Figure 3 for peracetic acid ($\text{CH}_3\text{CO}_3\text{H}$) and hydrogen peroxide (H_2O_2). Following the arrows from the initial temperature of 520 K to the limit cycle it can be easily understood how, during the induction time of a cool flame, the concentration of peracetic acid builds up and due to its instability at ~ 650 K rapidly decomposes through the branching reaction forming $\bullet\text{CH}_3$, CO_2 and $\bullet\text{OH}$. Conversely hydrogen peroxide reaches its maximum concentration during the cool flame quenching. At these temperatures (~ 650 K), $\text{CH}_3\bullet + \text{CO} + \text{M} = \bullet\text{CH}_3 + \text{CO} + \text{M}$ dominates over the addition to O_2 further enhancing termination reaction and self-quenching. The relative selectivities of acetyl radical towards the addition to O_2 and the decomposition are reported in Table 2 (POLIMI [5]).

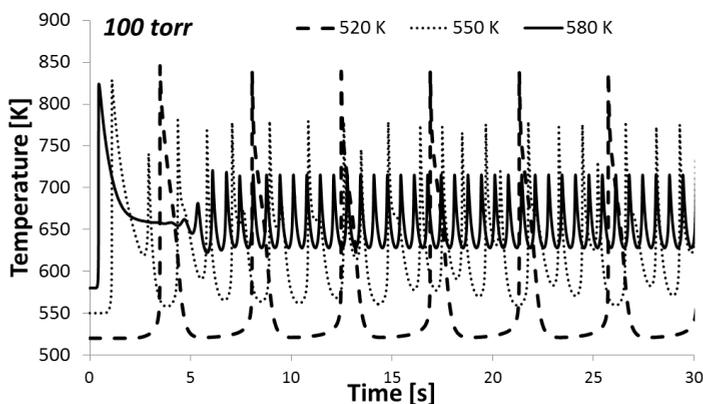


Figure 2. Simulation of periodic cool flames at $p=100$ torr and different initial temperatures.

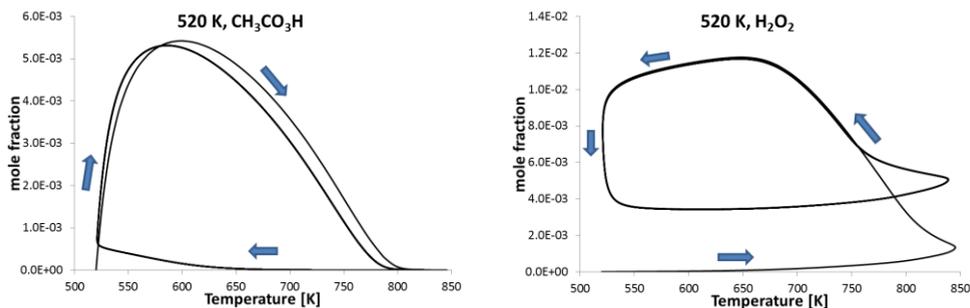


Figure 3. Phase plane plots of cool flame limit cycle, $T=520$ K, $P=100$ torr. Panel a) Peracetic Acid, $\text{CH}_3\text{CO}_3\text{H}$; b) Hydrogen peroxide, H_2O_2 .

Extension to heavier aldehydes

As clearly stated in the work previously mentioned [5], the dominating abstraction channel at high temperature conditions is that at the α site of the aldehydes, leading to the formation of carbonyl radicals $R_n\bullet C=O$ as reported in Table 1 for acetaldehyde, propanal and *n*-butanal. As reported in Table 2, differently from the more stable acetyl radical, larger carbonyl radicals ($R_n\bullet C=O$) very rapidly decompose forming CO, thus hindering the peracid path.

Table 1. Relative selectivities to H-abstraction reactions by $\bullet OH$ at 700 K for acetaldehyde, propanal and *n*-butanal [5].

CH ₃ CHO		CH ₃ CH ₂ CHO		CH ₃ CH ₂ CH ₂ CHO	
Acetaldehyde		Propanal		n-butanal	
CH ₃ •C=O	0.92	CH ₃ CH ₂ •C=O	0.77	CH ₃ CH ₂ CH ₂ •C=O	0.72
		CH ₃ •CHCHO	0.13	CH ₃ CH ₂ •CHCHO	0.12
				CH ₃ •CHCH ₂ CHO	0.11
•CH ₂ CHO	0.08	•CH ₂ CH ₂ CHO	0.10	•CH ₂ CH ₂ CH ₂ CHO	0.05

Table 2. Relative selectivities of carbonyl radicals (acetyl, 1-oxo-propyl) and propyl radicals addition (add.) to O₂ or decomposition (dec.) to CO and R_n alkyl radical.

	CH ₃ •C=O						CH ₃ CH ₂ •C=O		CH ₃ CH ₂ •CH ₂	
	POLIMI [5]		Veloo et al. [3]		[10]	[9]	[10]	[11]	POLIMI [12]	
<i>T</i> [K]	add.	dec.	add.	dec.	add.	dec.	add.	dec.	add.	dec.
450	0.47	0.53	0.64	0.36	0.99	0.01	0.68	0.32	1.00	0.00
500	0.15	0.85	0.24	0.76	0.93	0.07	0.22	0.78	1.00	0.00
600	0.02	0.98	0.02	0.98	0.40	0.60	0.01	0.99	1.00	0.00
700	0.00	1.00	0.00	1.00	0.06	0.94	0.00	1.00	1.00	0.00
800	0.00	1.00	0.00	1.00	0.01	0.99	0.00	1.00	0.97	0.03
900	0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.79	0.21
1000	0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.39	0.61

Relative selectivities shown in Table 2 are calculated assuming O₂ concentration equal to that of a stoichiometric oxidation of 0.15% fuel in nitrogen, at 10 atm pressure, to be consistent with the experimental data of Veloo et al. [3, 4]. Kinetics for the acetyl radical decomposition are those from Senosiain et al. [9], for its

addition to oxygen are from Lee et al. [10]. For sake of comparison also those in use in POLIMI mechanism [5,11,12] and Veloo et al. mechanism [3] are reported. Table 2 also reports the addition/decomposition branching ratio for *n*-propyl radical [12]. Carbonyl radicals preferentially undergo decomposition for temperatures above 500 K, while propyl radical addition to oxygen dominates up to 900 K.

Veloo et al. discussed the fate of carbonyl radicals for propanal [3] and *n*-butanal [4]. It has to be noted that, despite the same rate constants are used for carbonyl radicals from $\text{CH}_3\cdot\text{C}=\text{O}$ to $\text{C}_3\text{H}_7\cdot\text{C}=\text{O}$ by Veloo et al. [3, 4] (see Table 2), they reported some misleading results. In fact, at $T=655$ K and $p=10$ atm, while $\text{C}_2\text{H}_5\cdot\text{C}=\text{O}$ radical was found to be totally decomposed to form $\cdot\text{C}_2\text{H}_5$ and CO, $\text{C}_3\text{H}_7\cdot\text{C}=\text{O}$ was found to follow the peracid path ($\sim 70\%$). Due to the decreasing stability of $\text{R}_n\cdot\text{C}=\text{O}$ for increasing *n* as discussed by Pelucchi et al. [5], it seems more convenient to use different kinetic parameters.

Conclusions

The POLIMI mechanism was used to reproduce cool flames phenomena in well stirred reactor at low temperature and low pressure, giving satisfactory agreement in reproducing the ignition regimes experimentally detected [1]. Considering the dominant abstraction channel leading to the formation of carbonyl radicals in C_2 - C_4 aldehydes oxidation [5] and its subsequent fast decomposition, it is reasonable to assume that the low temperature oxidation of heavier aldehydes (R_nCHO) is mainly related to the low temperature branching path of the R_n alkyl radicals. These assumptions already allows satisfactory agreement with experimental measurements in JSR [3, 4]. It is worth mentioning that, despite aldehydes are key intermediates of hydrocarbon fuels oxidation and particularly in the case of biofuels [6], experimental data are still scarce, mainly at low temperatures and engine relevant conditions. This scarcity of experimental data prevents wide range validations of both the present mechanism and its extension to heavier aldehydes.

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