Alkyl radicals rule the low temperature oxidation of long chain aldehydes

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Abstract

A detailed knowledge of aldehydes oxidation at high and low temperatures is of concern in exploring the viability of biofuels such as alcohols. A reliable and simple approach for the description of aldehydes low temperature oxidation is proposed based on fundamental studies available in the literature, previous high temperature kinetic studies and acetaldehyde low temperature cool flames. The high reactivity of the weakly bound aldehydic H-atom leads to the predominant formation of carbonyl radicals. While acetyl-radical addition to oxygen is a key step in the low temperature reactivity of acetaldehyde, heavier carbonyl radicals are rapidly decomposed to CO and alkyl radicals. Therefore, the observed reactivity of C_3–C_4 aldehydes is ruled by the well established low temperature branching pathways of the corresponding alkyl radicals. Based on these assumptions, a comparison of the relative reactivity of alkanes and aldehydes is also discussed. The approach and the kinetic mechanism here presented are supported by several comparisons with experimental data in Jet Stirred Reactor, and allow easy extension to heavier aldehydes.
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Keywords: Aldehydes; Low temperature kinetics; Cool flames; Jet stirred reactor; Kinetic modeling

1. Introduction

Long chain alcohols (C_3–C_6) are considered amongst the most promising alternative fuels for transport due to their high energy density and to the compatibility of their physical–chemical properties with existing infrastructures [1]. While the use of alcohols has been largely proved to reduce CO, nitrogen oxides, and particulate matter emissions,

an increased release of harmful carbonyl compounds such as aldehydes and ketones is observed [2]. As clearly summarized in a recent review paper by Sarathy et al. [1], the presence of the hydroxyl moiety in alcohol molecules, causes the reactive path proceeding toward aldehydes formation to be of key importance both at high and low temperatures. For these reasons, a detailed knowledge of aldehydes oxidation kinetics is needed for exploring the viability of alcohol fuels in terms of combustion properties and pollutants emissions. Pelucchi et al. [3] recently reported a comprehensive kinetic study of the high temperature pyrolysis and oxidation of n-C_3–C_5 aldehydes in shock tubes. Based

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on the low temperature oxidation of acetaldehyde, the global POLIMI kinetic mechanism [4] has been extended to describe propanal, *n*- and *iso*-butanal oxidation at low temperatures. The experimental data of Veloo et al. [5,6] in isothermal jet stirred reactor (JSR) are very useful for this goal. In the same studies an interpretative kinetic model was also reported. This low temperature mechanism [5,6] constitutes the only one proposed in the literature at present. Moving from these data, the aim of this study is to provide a general and simple approach for the characterization of the low temperature kinetics of C_3–C_4 and heavier aldehydes (R_nCHO). The main oxidation pathway rising from the H-abstraction at the aldehydic site forms the carbonyl radical R_n–CO. Due to its fast decomposition to the corresponding alkyl radical (R_n) and CO, the low temperature mechanism of aldehydes is mainly ruled by the successive and well established low temperature reactions of alkyl radicals. The oxidation pathways of the remaining primary radicals again follow the rate rules of alkanes.

2. Kinetic mechanism

2.1. H-abstraction reactions

At low temperatures ($T < 1000$ K), aldehydes are mainly consumed via H-abstraction from the weakly bound aldehydic $R_n(CO)$–H site by OH and HO_2 radicals. Mendes et al. [7] systematically investigated the H-abstractions by H, OH, HO_2 and CH_3 from aldehydes (C_1–C_3 and *iso*-butanal) between 500 K and 2000 K, using conventional transition state theory. Wang et al. [8] presented direct measurements of the total H-abstraction rate constant by OH for C_1–C_4 aldehydes in shock tubes, in the temperature range of 950–1400 K. Fig. 1 shows a comparison among different abstraction rate constants from the carbonyl site of propanal, by OH (a) and HO_2 (b), according to different authors [3,5–7]. The rate constants discussed by Pelucchi et al. [3] and adopted in this work were estimated by reducing the activation energy of the reference H-abstraction of a primary H-atom of alkanes by 4.5 kcal/mol [9]. As a further comparison, Fig. 1 also reports the total rate of abstraction by OH on propanal as measured by Wang et al. [8].

Fig. 2 shows the relative selectivities of H-abstraction reactions by OH on the different H-sites for propanal (a) and butanal (b), at $T = 650$ K. The weakly bound H-atom at the carbonyl site is largely the more likely to be abstracted. In propanal, it accounts for ∼70–80%, and even up to ∼99% according to Mendes [7]. Despite the reported uncertainty of ∼2.5 in the calculations [7], the selectivity of the aldehydic H-site seems excessive. Referring to *n*-butanal, the selectivity of the aldehydic hydrogen accounts for ∼60–70% and, of course, it is expected to decrease for larger
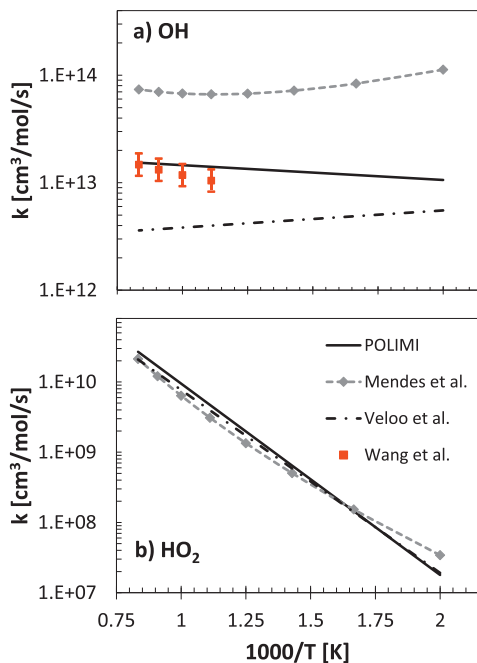

Fig. 1. Rate constant of H-abstraction of the aldehydic H-atom by OH (a) and HO_2 (b) [3,5–7]. Experimental rate constant for OH+propanal: symbols [8].
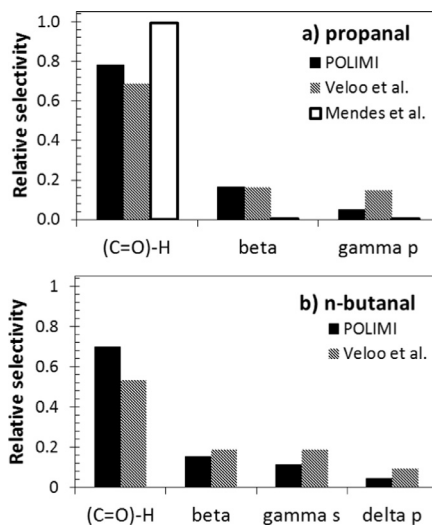

Fig. 2. Comparison between relative selectivities to the different H-abstraction positions by OH in (a) propanal and (b) *n*-butanal. Present study and literature values [5–7].

aldehydes. This predominance becomes even larger for abstractions by HO_2, not reported in Fig. 2.

The influence of the carbonyl group on the adjacent β-site results in a correction factor of 1.25, with respect to the corresponding H-atoms