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The role of radical + fuel-radical well-skipping reactions in ethanol and methylformate low-pressure flames

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Abstract

Although the reactions of fuel-radicals with other dominant flame radicals such as H and CH_3 are important reactions in low-pressure flames, they have not been well studied. These reactions may occur through either recombination to form stabilized molecular complexes or direct abstractions and chemically activated addition–eliminations to yield bimolecular products. Here, the role of such reactions in low-pressure flames of ethanol and methylformate is studied through a combination of theoretical characterizations of key reactions and detailed kinetic modeling. In particular, H and CH_3 + fuel-radical reactions have been characterized theoretically in this work and these are shown to make a pronounced impact on the formation of intermediates. Theoretical calculations for $H + CH_3CHOH$ and $CH_3 + CH_3CHOH$ predict that at low pressures recombinations are minor processes with well-skipping (addition–eliminations) dominating the reaction flux. Direct abstraction was also considered in $H + CH_3CHOH$ and theory suggests that abstraction at the CH_3-site forming CH_2CHOH is the only important channel. Notably, this result is counter to analogy based predictions that CH_3CHO should be the dominant abstraction product. Low-pressure ethanol flame simulations indicate that addition–elimination reactions from $H + CH_3CHOH$ and $CH_3 + CH_3CHOH$ are a major source for C_2H_4 and C_3H_6 profiles, respectively. Similar results are observed in simulations of a low-pressure methylformate flame, where addition–elimination reactions of $H + CH_2OCHO$ and $CH_3 + CH_2OCHO$ have a significant impact on CH_3OH and C_2H_4 mole fraction profiles, respectively. The present results suggest that the well-skipping reactions of relatively stable fuel-radicals with ubiquitous flame radicals such as H, O, OH, and CH_3 should be considered extensively in combustion models.

Keywords: Chemical kinetics; Ab initio; Theory; Rate constants; Biofuels

1. Introduction

The development of chemically accurate kinetic mechanisms is a central goal of combustion modeling, with low-pressure flame experiments providing important benchmark data for testing

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of such mechanisms. In recent years, laminar premixed flat-flame studies have been reported for a wide range of fuels and fuel mixtures. Such studies, when coupled with molecular beam mass spectrometry (MBMS), provide speciation data as a function of burner distance. These steady state species profiles for reactants, products, and intermediate species may even be isomer resolved with electron-impact [1] or synchrotron-photoionization (PI) [2,3] based detection schemes. These speciation data provide important tests for chemical mechanisms that are meant to describe how the reactants evolve into intermediates and subsequent products.

Mechanistic studies that interpret the speciation data from these premixed flames assume a nearly homologous sequence of steps that begin with fuel destruction largely due to hydrogen abstraction reactions. The fuel-radicals so formed then largely decompose via β-scission reactions, forming an unsaturated molecule and a radical species, which then helps perpetuate this abstraction and β-scission sequence. For example, mechanistic interpretations of an MBMS-flame study for ethanol [4] suggest 95% of the fuel is consumed by abstraction reactions, primarily forming CH_3CHOH, with a smaller fraction yielding the other two fuel-radicals, CH_2CH_2OH and CH_3CH_2O. The dominant fuel-radical, CH_3CHOH, then is consumed exclusively by β-scission to form acetaldehyde and H-atoms. In this particular case [4], unimolecular decomposition was shown to contribute only a minor fraction (5%) to fuel decay. But in other cases, unimolecular decompositions can play a larger role as was shown in a recent study [5] of a methylformate flame where 41% of fuel decomposition was attributed to unimolecular pathways. However, hydrogen abstractions still played the dominant role in contributing to methylformate destruction.

With most models relying on this sequence of abstraction followed by β-scission to describe fuel decomposition, predicted radical pools and intermediate products then become sensitive to the rate constants (and of course branching ratios to various channels) for these reactions. A recent ethanol flame study by Tran et al. [6] emphasized this sensitivity to rate constants and branching ratios for the $OH + C_2H_5OH$ reaction in predicting intermediates formation. In that study, predictions of C_2H_4 formation were improved by adjusting the branching ratio of abstraction at the primary C–H bond in ethanol giving CH_2CH_2OH, which then subsequently decomposes rapidly by β-scission to $OH + C_2H_4$. Interestingly, to match C_2H_4 profiles, the rate constants used in that study [6] for this abstraction channel are approximately a factor of 5 larger than the predictions from a recent experimental/theoretical study on $OH + C_2H_5OH$ [7]. Another recent theoretical analysis [8] predicts branching ratios more in line with the optimized model values [6]. However, a follow-up analysis suggests that the major channel may have been underestimated by about a factor of two [9].

Given the uncertainty in the appropriateness of the proposed branching ratios for the $OH + C_2H_5OH$ reaction, it is interesting to consider other possible sources for C_2H_4 in these flames. Relatively stable fuel-radicals, such as CH_3CHOH (in the case of ethanol), can build up to substantial amounts in these flames simply because unimolecular pressure fall-off inhibits β-scissions of these radicals in a low-pressure (<0.1 atm) environment. Consequently, bimolecular reactions of the relatively stable fuel-radicals with radicals present in the flame such as H, CH_3, and OH might provide an alternative source for intermediates. A probable candidate is the bimolecular reaction, $H + CH_3CHOH$, that can directly lead to products $C_2H_4 + H_2O$.

Well-skipping radical-molecule reactions such as $OH + C_2H_4$ have been shown to be the root cause for the elusive enol-intermediates first observed in the flame studies of Taatjes et al. [10]. However, there are limited theoretical/modeling studies on the role of radical–radical addition–eliminations in small oxygenates, particularly if the two radicals are energetically high-lying (from the well) such as the radicals (fuel-radical and H-atoms) produced in C–H bond fissions. Of course, the contributions of such chemically-activated reactions need to be assessed relative to other radical–radical recombinations (e.g. $CH_3 + CH_3 \rightarrow C_2H_6$) and well-skipping reactions (e.g. $CH_3 + CH_3 \rightarrow H + C_2H_5$) typically included in combustion models as indirect sources for C_2H_4 in ethanol flames. Additionally, the contribution of the fuel-radical + O_2 reaction to the fuel-radical decay should also be considered. In the particular case of the ethanol fuel-radicals this has been well characterized in a recent experiment/theory study [11].

In this work, we aim to accomplish three goals: (1) Identify flame-radical stable fuel-radical addition–elimination pathways, (2) theoretically characterize the kinetics of these addition–eliminations, (3) and demonstrate the effect of including these reactions in low-pressure flame models for simulating the evolution of intermediate species. To accomplish these goals, we have used ab initio electronic structure theory based master equation analyses to obtain kinetics estimates for well-skipping radical–radical reactions relevant to low-pressure flames for ethanol [12] and methylformate [5]. These rate constants are then used in a kinetic model to assess their potential contributions to C_2H_4 formation in these low-pressure flames [5,12]. In particular, it is observed that $H + CH_3CHOH$ (the most stable ethanol radical) is indeed an