Contents lists available at ScienceDirect





Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

# The impact of roaming radicals on the combustion properties of transportation fuels



#### Richard H. West<sup>a,\*</sup>, C. Franklin Goldsmith<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering, Northeastern University, Boston 02115, USA <sup>b</sup> School of Engineering, Brown University, Providence, RI 02912, USA

#### ARTICLE INFO

Article history: Received 24 August 2017 Revised 6 October 2017 Accepted 18 May 2018

Keywords: Chemical kinetics Roaming radicals Combustion Ignition delay Laminar flame speeds

#### ABSTRACT

A systematic investigation on the effects of roaming radical reactions on global combustion properties for transportation fuels is presented. New software was developed that can automatically predict all the possible roaming pathways within a given chemical kinetic mechanism. This novel approach was applied to two mechanisms taken from the literature, one for heptane and one for butanol. Ignition delay times and laminar flame speeds were computed over a broad range of conditions, while testing varying degrees of roaming. As the degree of roaming is increased, the ignition delays increased, consistent with the hypothesis that roaming decreases the reactivity of the system. The percent increase in the ignition delay is strongly temperature dependent, with the largest effect seen in the negative temperature coefficient regime. Outside of this temperature range, the effect of roaming on global combustion properties is small, on the order of a few percent for ignition delays and less than a percent for flame speeds. The software that was used to create the new mechanisms and test the effects of roaming on combustion properties are freely available, with detailed tutorials that will enable it to be applied to fuels other than heptane and butanol.

© 2018 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

#### 1. Introduction

Broadly speaking, traditional statistical models for unimolecular decomposition of a closed-shell species may be characterized into one of two classes of reactions: homolytic cleavage to form two radicals, and some type of molecular elimination to form two closed-shell products; the transition state for the former typically has no maximum along the minimum energy path and must be determined variationally, whereas the transition state for the latter typically occurs at or near a first-order saddle point in potential energy. In 2004, a third pathway was discovered: the roaming reaction [1]. A roaming reaction is a dynamical process in which unimolecular dissociation begins as homolytic cleavage to produce two radicals, but at long inter-atomic distances at which the covalent bond is effectively broken but the potential is otherwise still attractive, the radicals reorient themselves to facilitate an Hatom transfer, thereby producing two closed-shell products. Thus, the radicals roam around the otherwise high-energy, entropically disfavored tight transition state for molecular elimination.

*E-mail addresses:* r.west@northeastern.edu (R.H. West), franklin\_goldsmith@brown.edu (C.F. Goldsmith).

https://doi.org/10.1016/j.combustflame.2018.05.020

0010-2180/ $\ensuremath{\mathbb{C}}$  2018 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Since the work of Townsend et al., [1] there has been an explosion of interest in roaming reactions [2–40]. Most of the initial attention to roaming focused on formaldehyde [1–4,6–8,40] and acetaldehyde [5,10,11,15,34,38,41], but more recent studies considered larger carbonyls [12,13,27,32,39], alkanes [14,20,24], ethers [19,26], and NO<sub>2</sub> -containing compounds [22,29,30,33,35,37]. Collectively, these experimental and theoretical studies suggest that the roaming mechanism is nearly universal in gas-phase chemical kinetics, and that the branching fraction between roaming and homolytic bond fission typically is between 1 and 10% under combustion conditions. The magnitude of the branching fraction is highly dependent on the underlying potential energy surface (PES), particularly the energy of the roaming saddle point relative to the two radical fragments at infinite separation.

Despite the ubiquitous nature of roaming, the implications of the roaming mechanism on global combustion properties have not been thoroughly investigated. Presumably, this absence is due to the computational cost associated with a detailed investigation, and not due to a lack of interest or awareness. A truly quantitative prediction of roaming necessitates multireference theory calculations in the PES around the roaming saddle point, followed by some variant of molecular dynamics; at the time of publication, this process typically requires  $10^3 - 10^5$  CPU-hours, depending upon the size of the molecule and complexity of the

<sup>\*</sup> Corresponding author.

active space in the CASSCF calculations. Given that there could be hundreds of roaming reactions in transportation fuels, a reactionspecific investigation for transportation fuels is computationally unrealistic.

The aim of this manuscript is to provide a systematic investigation of the impact of roaming on the ignition delay and laminar flame speed of transportation fuels. To that end, we have selected two literature mechanisms: the n-heptane mechanism (v3.1) [42], and the butanol mechanism [43], of Lawrence Livermore National Laboratory. Given the experimental and computational challenges associated with measuring and/or predicting the roaming branching fractions, treating each bond-fission reaction in these mechanisms individually is not feasible. Instead, we make a global approximation: we assume that each bond-fission reaction in the mechanism has the potential for roaming if it has an appropriately situated H atom, and that the resulting branching fraction between bond fission and roaming is the same for all molecules. We consider roaming branching fractions of 0, 1, 5, and 10%. To perform this test, we have written an interpreter that reads the literature mechanism, finds all the bond fission reactions, automatically determines all the feasible roaming pathways, and generates a new mechanism that includes these new reactions.

This global approach is a useful first pass to determine whether or not roaming reactions have a significant effect on the combustion properties of transportation fuels under industrially relevant conditions. One outcome of this work will be to suggest which roaming pathways should be investigated in greater detail.

#### 2. Methods

### 2.1. Automated discovery of roaming pathways in literature mechanisms

The overview is to take each kinetic model, in the CHEMKIN format in which it was published, and generate a new, modified kinetic model with all the roaming pathways added and bond fission reactions adjusted accordingly, then perform ignition and flame simulations to determine the impact of the roaming pathways. To automate this workflow as much as possible (there are over 7000 reactions to check for roaming potential and we end up adding over 300 roaming pathways to the two mechanisms) we make extensive use of the open-source Python software Reaction Mechanism Generator (RMG) [44,45]. The steps are described here in further detail:

#### 2.1.1. Identify species

The first task is to identify the molecular structure of each of the named species in the CHEMKIN files. For example, the name IC4H800H-T02 corresponds to the species with the SMILES string CC(C)(CO0)0[0], IIC4H7Q2-T is C[C](CO0)CO0, and the molecule with the SMILES CC(=0)CO0 is called both C3KET21 and CH3C0CH202H. To aid with this task we have developed a tool that uses RMG's understanding of how molecules ought to react, to help a user identify the molecular structures of species in a kinetic model based on how that model says the species react [46].

The "importer tool" source code [47] and a database of kinetic models from the literature with species identified [48] are freely available online; potential users are invited to contact the authors for assistance. With the help of this tool, we uniquely identified the molecular structures of all the species in both the butanol and the n-heptane models. The original butanol mechanism contains 431 species and 2346 reactions; the original heptane mechanism contains 654 species and 4846 reactions.

(a) Radical recombination

$$^{1}R$$
 +  $^{2}R$   $\implies$   $^{1}R$   $-^{2}R$ 

(b) Homolytic Fission

$$^{1}R \xrightarrow{(}^{2}R \rightarrow ^{1}R + ^{2}R$$

(c) Pseudo hydroperoxide decomposition

$$^{3}H$$
  $^{1}O$   $^{2}O$   $^{4}R$   $^{5}R$   $\rightarrow$   $^{3}H$   $^{1}O$   $^{2}O$   $^{4}R$   $^{5}R$ 

(d) Buggy hydroperoxide decomposition

$$^{3}H - ^{1}O - ^{1}O + ^{2}O - ^{4}R - ^{5}R \rightarrow ^{3}H - ^{1}O + ^{2}O = ? + ?$$

(e) Radical Roaming

$$\begin{array}{c} 2R \xrightarrow{3}R \\ 1_R \xrightarrow{4} \\ 1_R$$

(f) Radical Roaming Alpha

$$^{1}R \xrightarrow{C_{2}} _{4H} ^{3}O \longrightarrow ^{1}R \xrightarrow{-4}H + ^{2}C \stackrel{3}{=} ^{3}O$$

Fig. 1. Reaction templates and recipes. From Ref. [55].

#### 2.1.2. Filter reactions

The next task is to filter the thousands of reactions in the kinetic model and determine which reactions might have alternate roaming pathways. The first filter is based simply on the stoichiometry: at first we only consider unimolecular dissociation (one reactant, two products) or its reverse, bimolecular recombination (two reactants, one product), because we are looking for homolytic fission reactions.

The next filter is to see if the reaction can be reproduced using the "Radical Recombination" reaction family in RMG. A reaction family in RMG contains a template and a recipe. In this case, the template is simply: two reactants, each with an atom that has one unpaired electron (which will be given labels when the template matches). The recipe says: form a single bond between the two labeled atoms, and decrease the unpaired electron (radical) count on each of them. This is illustrated in Fig. 1a. The reverse template and recipe, for homolytic fission of a single bond (Fig. 1b), is generated automatically by RMG so the reactions can be detected or generated in either direction. When matching a reaction template, via a subgraph isomorphism algorithm, RMG labels the atoms that are part of the reaction (the superscript numbers in Fig. 1), importantly labeling the atoms either side of the bond that is being broken. Usually these labels are removed as soon as they have been used to generate an estimate of the reaction kinetics, but we modified the RMG code to preserve these labels, so they could be used to generate roaming pathways in the subsequent step.

In the butanol model, 185 of the 272 unimolecular dissociation (or bimolecular recombination) reactions fail this reaction family test; in the heptane model 465 of the 667 are filtered out. Reactions filtered out here are mostly radical addition to a multiple bond, but with some cycloaddition, Diels Alder, and other recombination and addition reaction families. Download English Version:

## https://daneshyari.com/en/article/6593504

Download Persian Version:

https://daneshyari.com/article/6593504

Daneshyari.com