Towards a quantitative understanding of the role of non-Boltzmann reactant distributions in low temperature oxidation

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Abstract

An essentially universal assumption of chemical kinetics is that bimolecular reactions only occur between reactants of rovibrational energy described by a Boltzmann (thermal) distribution. Given that the O_2 mole fraction is roughly 20% under nearly all relevant low-temperature combustion situations, there is significant potential for molecules to undergo reactive collisions with O_2 on the same time scale as the energy-transferring collisions necessary to achieving a Boltzmann distribution. Within the context of low-temperature combustion, this phenomenon conceivably gives rise to an entirely non-Boltzmann sequence involving multiple reactions of fuel-derived radicals with O_2 to produce multiple OH radicals. Given the complex interplay among simultaneous internal isomerizations, energy-transferring collisions, dissociations and reactive collisions across multiple reaction surfaces, estimating the extent of deviations from conventional thermal assumptions is not straightforward. A novel methodology is presented for coupling multiple master equations and deriving effective phenomenological rate constants for thermal sets of reactants to thermal sets of products in chemically activated sequences that proceed across multiple reaction surfaces. The methodology is used to establish a better understanding of the nature of non-Boltzmann reactant distribution effects and quantify their magnitude. As a case study, we implement the methodology to explore the effect of non-Boltzmann reactants on product branching fractions of the $QOOH^* + O_2$ reaction from *n*-propyl oxidation as well as its associated dependence with O_2 mole fraction, temperature, and pressure. While it appears that the effect of non-Boltzmann reaction sequences will be considerably smaller at higher pressures (at least for propane), it appears that consideration of non-Boltzmann reaction sequences is likely required for interpretations of experimental measurements commonly used to investigate the $R + O_2$ and $QOOH + O_2$ reactions central to engine-relevant ignition behavior. With regard to observable signatures of these effects in experiments, the presence of a stronger-than-usual O_2 mole fraction dependence may be a likely indicator of non-Boltzmann behavior.
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1. Introduction

Low-temperature combustion (LTC) is central to advanced engine technologies [1,2]. In contrast to more conventional engines that are largely governed by fluid mechanics, these advanced engine concepts are very sensitive to fuel chemistry. As a result, modeling has become a considerable subject of attention, focused on creating detailed kinetic models to predict engine-relevant behavior. The reactions $RO_2 = QOOH$, $QOOH + O_2 = O_2$ $QOOH$, and decomposition of their subsequent products (ketohydroperoxides, $OQ'OOH$) have long been recognized as key reactions involved in low-temperature chain branching, and the rates of those reactions have been demonstrated to be essential to high-accuracy predictions of both 0-D [3–5] and engine [6] systems for a wide variety of fuels. Accordingly, a great number of studies have been devoted to characterizing these reactions and/or reaction sequences. For example, we have been applying our multi-scale informatics approach [7,8] to quantitatively inform a low-temperature propane oxidation model by *ab initio* theoretical calculations [9] and measurements of OH, HO_2, and Multiplexed Photo-Ionization Mass Spectrometry measurements under conditions intended to isolate $R + O_2$ and $QOOH + O_2$ pathways [8,10–12]. Interpretation of those and other kinetic measurements as well as prediction of ignition behavior depend on a fundamental kinetic assumption, which may require further investigation (e.g. Fig. 2 as discussed below).

An essentially universal assumption of chemical kinetics is that bimolecular reactions only occur between reactants of rovibrational energy described by a Boltzmann (thermal) distribution. In other words, if an ensemble of molecules is initially formed with an energy distribution that differs from the Boltzmann distribution (non-Boltzmann), as is relatively commonplace, the molecular ensemble is assumed to undergo sufficiently many energy-transferring (thermalizing) collisions to establish a Boltzmann distribution prior to subsequent bimolecular reaction.

Given that the O_2 mole fraction, X_{O_2}, is ∼20% under nearly all relevant low-temperature combustion situations (and may even reach ∼100% in elementary reaction studies of LTC reactions, e.g. [13]), there is significant potential for molecular ensembles to undergo reactive collisions with O_2 on the same time scale as thermalizing collisions. The potential for such a phenomenon calls to question the abovementioned thermal distribution assumption and provides the possibility for entirely different kinetics processes to dominate oxidation behavior. Indeed, this phenomenon is becoming increasingly more recognized within atmospheric chemistry, where many studies (e.g. [14–19]) have found that substantial fractions of molecules react with O_2 prior to stabilization –

consequently yielding different products than reactants in a Boltzmann distribution.

Within the context of low-temperature combustion, there similarly appears to be potential for non-Boltzmann reaction processes to significantly affect the evolution of the system (Fig. 1). R can react with O_2 to form a rovibrationally excited RO_2^*, which in turn can isomerize to an excited $QOOH^*$. (Throughout the text, unstarred species names and numbered subscripts, e.g. QOOH and $k_{3 \to 4}$, refer only to molecular ensembles in the Boltzmann distribution; starred species names and numbered subscripts, e.g. $QOOH^*$ and $k_{3* \to 4*}$, refer to molecules at a particular energy or molecular ensembles that may or may not be in the Boltzmann distribution. "Excited" states are used to describe rovibrational, not electronic, excitation.) $QOOH^*$ formed in this manner can react with O_2 before stabilization to form an excited O_2QOOH^*. O_2QOOH^* at higher energies decomposes more rapidly to $OH + OQ'OOH^*$. $OQ'OOH^*$ at sufficiently high energies can decompose directly to $OH + OQ'O^*$. Combining the above steps, there is potential for an entirely non-Boltzmann sequence involving multiple reactions with O_2 to produce multiple radicals: $R + O_2 + O_2 = OH + OH + OQ'O$. It further seems that there is potential for an amplification mechanism (e.g. Fig. 4 below) – excited reactants are more likely to form excited products. Clearly, such processes could have a significant impact on low-temperature fuel oxidation if/when they are occurring to a sufficient extent.

We initially became interested in quantifying these non-Boltzmann processes because an uncertainty screening procedure for non-Boltzmann effects suggested that they may play a crucial role in the interpretations of fundamental OH measurements [8]. Figure 2 shows the script-generated model predictions using our multi-scale informatics code [8] under two limiting assumptions for the fate of the chemically activated pathway, $R + O_2 + O_2$, where excited $QOOH^*$ formed from $R + O_2$ reacts with O_2 prior to stabilization. Simulations that assume that $R + O_2 + O_2$ yields the same product branching fractions as thermal $QOOH + O_2$ predict orders of magnitude less OH than simulations that assume that all $R + O_2 + O_2$ proceeds directly to $OH + OH + OQ'O$. Consequently, interpretation of these OH measurements that ignores uncertainties due to non-Boltzmann reactants may suggest false constraints on the model parameters, such that model extrapolation from those conditions to engine-relevant conditions may be flawed. Quantifying deviations from traditional kinetics assumptions is therefore crucial to meaningful interpretations of LTC reactions at the conditions commonly employed to characterize them.

Furthermore, one may additionally be concerned that non-Boltzmann reaction processes