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Effect of non-thermal product energy distributions on ketohydroperoxide decomposition kinetics

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Abstract

The decomposition of ketohydroperoxides (OQ'OOH) to two radicals is commonly predicted to be the key chain branching step in low-temperature combustion. The possibility of a direct decomposition of the OQ'OOH from its initially produced energy distribution is studied with a combination of master equation (ME) and direct trajectory simulations. The temperature and pressure dependent rate constants for the thermal decomposition of a ketohydroperoxide, HOOCH₂CH₂CHO, to four product channels were computed using RRKM/ME methods. Direct dynamics calculations were initiated from a transition state in the O₂ + QOOH reaction network to understand the fraction of energy in that transition state that is converted into the internal energy of the OQ'OOH. A novel approach to solving the master equation is used to determine the probability that a vibrationally hot OQ'OOH either will be stabilized to a thermal distribution or will react to form new products. Under most conditions, the majority of vibrationally excited OQ'OOH will be quenched into a thermal distribution. At higher internal energies and lower pressures, however, a significant fraction of the hot OQ'OOH will decompose rather than thermalize. Proper interpretation of low-pressure experiments may require inclusion of vibrationally hot intermediates, particularly if a chemical kinetic mechanism is optimized against the low-pressure data.

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1. Introduction

In the low-temperature oxidation of alkanes, an alkyl radical, R, reacts with molecular oxygen to form an alkylperoxy radical, RO₂. Depending upon the temperature and pressure, some of the

RO₂ will decompose to form a mixture of HO₂ + alkene, OH + cyclic-ether, or OH + carbonyls. In the context of chain branching, however, the most important product from RO₂ is a transient hydroperoxyalkyl radical, QOOH, which is formed via internal H-abstraction. A second oxygen molecule can add to the QOOH, thereby forming a hydroperoxyalkylperoxy radical, O₂QOOH. When this O₂QOOH undergoes a similar internal H-abstraction reaction, TS₁ in Fig. 1, the incipient alpha-hydroperoxy structure is not stable and immediately dissociates to form a ketohydroperoxide

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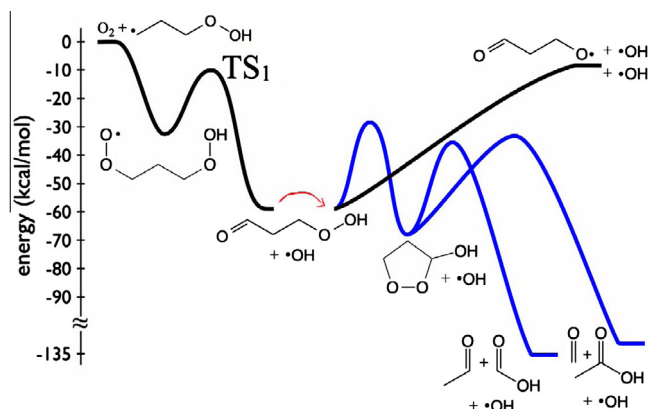


Fig. 1. Combined $C_3H_7O_4$ and $C_3H_6O_3$ (+OH) potential energy surfaces. The chain branching pathway is shown in black; the Korcek pathway is shown in blue. Direct dynamics simulations were initiated from TS_1 . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

+ OH. The O–O bond in the ketohydroperoxide (OQ'OOH) is relatively weak – typically on the order of 40–45 kcal/mol – and thus the OQ'OOH dissociates to form a ketoalkoxy radical + OH (OQ'O + OH). This final reaction is chain branching. For a review of low-temperature oxidation, see Ref. [1].

The OQ'OOH dissociation products are exothermic relative to the $O_2 + QOOH$ reactants. For the *n*-propyl oxidation system, the zero-point corrected electronic energy of $HOOCH_2CH_2CHO + OH$ channel is 61 kcal/mol below $O_2 + CH_2CH_2CH_2OOH$, and the energy for the corresponding $OCH_2CH_2CHO + 2OH$ products is 17 kcal/mol below the same reactants [2]. Although the preceding reactions were described sequentially, chemically activated reactions can skip some of the intermediate steps, e.g. $R + O_2 \rightarrow QOOH$, and $O_2 + QOOH \rightarrow OQ'OOH + OH$. In fact, owing to the exothermicity of the final products, some of the $O_2 + QOOH$ may go directly to the three radicals in a single step: $O_2 + QOOH \rightarrow OQ'O + 2OH$.

Under typical conditions for low-temperature compression ignition engines (e.g. 700 K and 10 atm), several intermediates in the preceding reactions will reach a pseudo-steady state in which the net rate of destruction equals the net rate of formation [3,4]. First, the concentration of QOOH increases until the net rate for $O_2 + QOOH \rightarrow$ products equals the net rate for $RO_2 \rightarrow QOOH$; at the same time, the concentration of R builds up until the net rate for $R + O_2 \rightarrow$ products equals the net rate for $RH + OH \rightarrow R + H_2O$; next, the concentration of O_2QOOH increases until the net rate of $O_2QOOH \rightarrow OQ'OOH + OH$ equals the net rate of $O_2 + QOOH \rightarrow O_2QOOH$; lastly, the concentration of OQ'OOH builds up until its net rate of thermal decomposition equals the net rate of O_2QOOH dissociation. Once this final stage has

occurred, the sequence reaches a tipping point and becomes autocatalytic in radical production: the net result is two OH and one OQ'O formed for one OH consumed. Using a low-temperature propane oxidation mechanism [5], Merchant et al. developed a simple-yet-accurate analytic model for first-stage ignition from these pseudo-steady state assumptions [3]. This model highlights the centrality of OQ'OOH in the low-temperature chain branching sequence and indicates that thermal decomposition of OQ'OOH is even the rate-determining step in first-stage ignition under some conditions.

The mechanism utilized in Ref. [3] does not include other reactions for OQ'OOH destruction. If there were competing reactions that consumed OQ'OOH prior to its thermal decomposition to OQ'O + OH, then these reactions could have a profound impact on the time constant for the first-stage ignition. Recently Jalan et al. discovered such a reaction [6]. The same ketohydroperoxide resulting from the *n*-propyl system, $HOOCH_2CH_2CHO$, can isomerize to form a cyclic peroxide, *c*-CH(OH)OOCH₂CH₂ (CP), which subsequently decomposes to a mixture of carboxylic acids and carbonyls, e.g. the blue lines in Fig. 1.

This pathway, originally hypothesized by Korcek, is important in liquid-phase hydrocarbon oxidation [6,7]. The barrier height for isomerization from OQ'OOH to CP is 15 kcal/mol below the dissociation limit for the competing OQ'O + OH chain branching pathway. Furthermore, the OQ'OOH \rightarrow CP isomerization reaction can be catalyzed by carboxylic acids, with a bimolecular barrier height of 1 kcal/mol [6], so once a critical concentration of acids is obtained, the isomerization reaction becomes autocatalytic. However, both the unimolecular and the acid-catalyzed isomerization reactions involve the coordinated shuttling of two hydrogen atoms, which requires double ring-like structures, and

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