Kinetics of hydrogen abstraction from propanol and the subsequent unimolecular dissociation of the C_3H_7O radicals

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Introduction

- **Alcohols** are important components of modern transportation fuels.
- **Butanol** is a promising fuel alternative with more similar properties to traditional gasoline ➔ can be used in unmodified internal combustion engines.
- Butanol combustion is intricate due to the isomers arising from the parent molecules and the possible H-abstraction sites ➔ **16 possible C_4H_9O isomers**
- In this work **propanol** is investigated (**7 possible C_3H_7O isomers**). Our calculations are compared to the experimental data available in the literature on the elementary reaction kinetics of propanol + OH.
- Here we present high-level electronic structure calculations coupled to RRKM-based master equation (ME) methodology to study the initial steps of propanol combustion.

H-abstraction by H, OH and HO_2 [1]

$[C_3H_7]OH + H \rightarrow [C_3H_7O] + H_2$ (1)
$[C_3H_7]OH + OH \rightarrow [C_3H_7O] + H_2O$ (2)
$[C_3H_7]OH + HO_2 \rightarrow [C_3H_7O] + H_2O_2$ (3)

Unimolecular dissociation of the resulting radicals

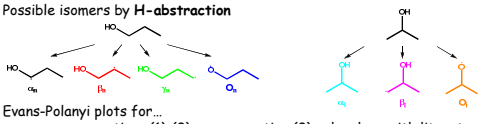
$[C_3H_7O] \rightarrow$ products (4)

[1] the [] means that all relevant isomers are considered

Energetics of the *n*/*i*-propanol + H/OH/HO_2 reactions and C_3H_7O dissociation/isomerization

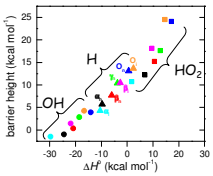
QCISD(T)/cc-pV∞Z//B3LYP/6-311++G(d,p) level

Possible isomers by **H-abstraction**

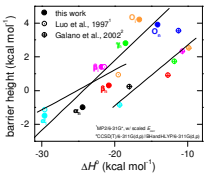


Evans-Polanyi plots for…

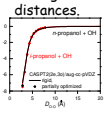
… reactions (1)-(3)



… reaction (2) only, along with literature data

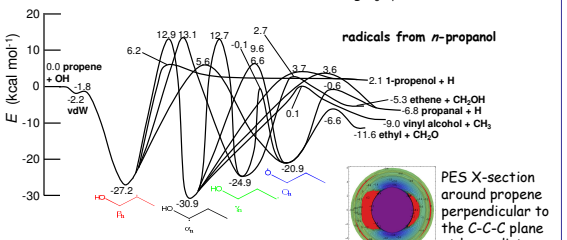


MEP for propanol + OH at large distances.

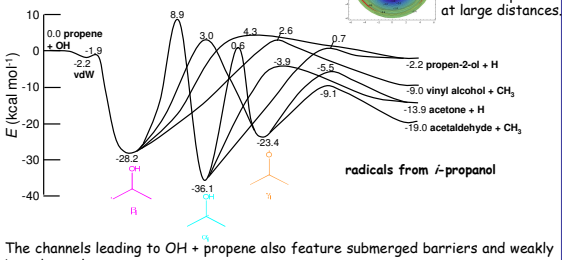


For reactions (2) and (3) weakly bound complexes exist on both the reactant and the product side. From a kinetic point of view only the reactant complexes of reaction (2) are important, due to the low-lying transition states. The well depth of the OH–propanol van der Waals complexes is ~7 kcal mol^{-1}.

Possible channels for the **dissociation** of the resulting C_3H_7O radicals



PES X-section around propene perpendicular to the C-C-C plane at large distances.



The channels leading to OH + propene also feature submerged barriers and weakly bound complexes.

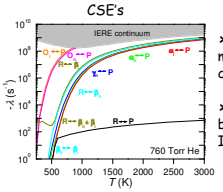
Calculation of rate coefficients

- Rate coefficients are calculated using **RRKM-based ME**, given in the form $\frac{d|w(t)\rangle}{dt} = G|w(t)\rangle$, where **G** describes the chemical exchange between different wells and also the *E* transfer during collisions, while $|w(t)\rangle$ contains the unknown populations. The master equation is solved using VARIFLEX 2.0.
- At low enough temperatures chemical reactions are related to the slow, chemically significant eigenvalues (**CSE**'s), while the fast ones are the internal energy relaxation eigenvalues (**IERE**'s).
- At higher temperatures CSE's get closer to, and eventually merge into IERE's ➔ phenomenological rate coefficients are undefined here.
- Two methods to obtain rate coefficients from the ME:
  Initial-rate method: applicable as long as the IERE >> CSE
  Long-time method: applicable as long as IERE > CSE
- When one or more CSE's merge into the IERE's, rate coefficients related to the unmerged CSE's can be only obtained by **reducing the number of chemical species** in the problem by merging equilibrating species into a "superspecies".
- **Tunneling** corrections are taken into account by asymmetric Eckart transmission probabilities. **Internal rotors** are treated using the Pitzer-Gwinn-like approximations by Fourier fits to the relaxed B3LYP potentials.
- For barrierless channels the *E*,*J*-resolved number of states is calculated variationally using the **direct variable-reaction-coordinate transition-state theory**. The distance between the center of mass of the fragments is taken as a reaction coordinate. The potential energy is calculated using CASPT2(5e,4o)/aug-cc-pVDZ in the case of propene + OH, and CASPT2(2e,3o)/aug-cc-pVDZ for propanol + OH. The VaReCoF program is used to obtain capture rate constants.
- The barrierless entrance channel, the van der Waals well and the submerged barriers are represented by an effective **two-transition-state model at the microcanonical, *J*-resolved level** with the general form of:

$$N^E_{i,\mathrm{eff}}(E,J) = \frac{N^E_{\mathrm{outer}}(E,J) \times N^E_{\mathrm{inner},i}(E,J)}{N^E_{\mathrm{outer}}(E,J) + \sum_k N^E_k(E,J)}$$

Temperature and pressure dependent unimolecular dissociation of the C_3H_7O radicals

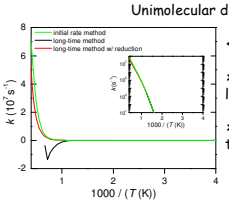
CSE's



>850 K: two eigenvalues merge into the IERE continuum.

>1500 K: separation between most CSE's and IERE is small

Unimolecular dissociation *k* of β_n using different methods

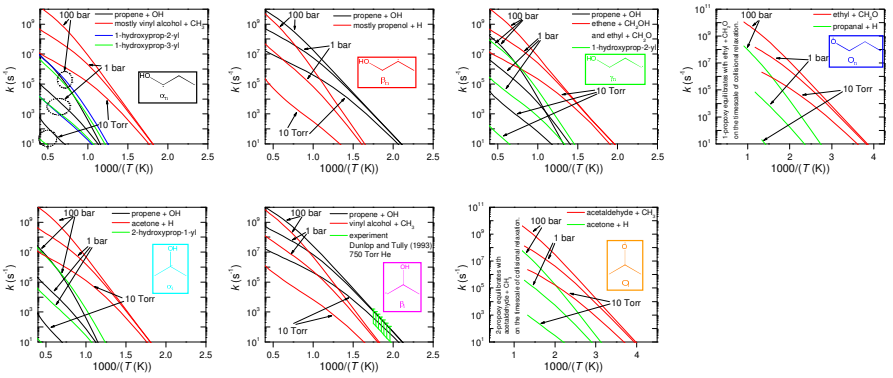


<850 K: all methods result in the same *k*

>850 K: the initial-rate method and the long-time method without reduction fail

>1000 K: only the long-time method with the reduction of species gives good *k*'s

Unimolecular dissociation rate coefficients and product channels for hydroxypropyl radicals



Catalytic dehydration of *n*/*i*-propanol via β-hydrogen abstraction by OH. The hydroxyl radical is regenerated, leading to increased reactivity under low-temperature combustion conditions.

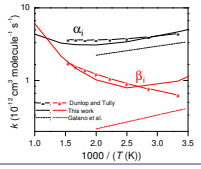
$CH_3CH_2CH_2OH + \mathbf{OH} \rightarrow CH_3CHCH_2OH + H_2O$
$CH_3CHCH_2OH \rightarrow CH_3CHCH_2 + \mathbf{OH}$
$CH_3CHOHCH_3 + \mathbf{OH} \rightarrow CH_3CHOHCH_2 + H_2O$
$CH_3CHOHCH_2 \rightarrow CH_3CHCH_2 + \mathbf{OH}$

Well-skipping (formally direct) channels persist even at high pressures. In this case, these channels do not originate from chemical activation, but from isomerization reactions, where collisional stabilization in the intermediate wells is ineffective. E.g. the reaction
$CH_2CH_2CH_2OH \rightarrow C_2H_5 + CH_2O$
takes place to a significant extent without stabilization in the intermediate propoxy well.

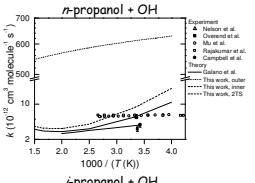
Vinyl alcohol is formed from various dissociation channels. Vinyl alcohol has been identified as an intermediate in 1- and 2-propanol flames using electron ionization and VUV-photoionization molecular-beam mass spectrometry. The concentration of vinyl alcohol was reported to be 10x more in 1-propanol flames compared to 2-propanol ones, which is qualitatively in line with our dissociation and H-abstraction rate coefficients.

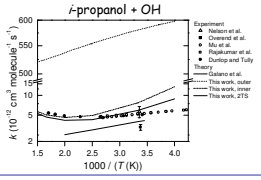
Abstraction rate coefficients

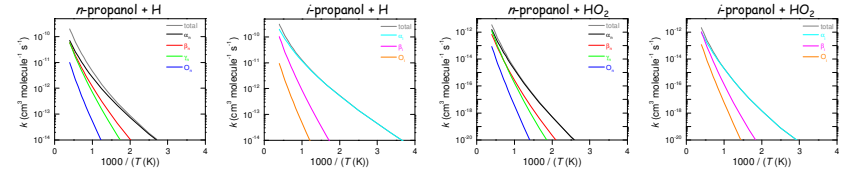
- Experimental data is available for OH + *n*/*i*-propanol, and branching fractions only for OH + *i*-propanol.
- To achieve good agreement with the experiments, barrier-heights were modified by <1 kcal mol^{-1}.
- The remainder discrepancy requires further investigation. In doing so, Dunlop and Tully's measurements on the KIE are expected to be instrumental.



branching for *i*-propanol + OH







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