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Theoretical study and modeling of low temperature and high pressure ethanol oxidation

Judit Zádor, Ravi X. Fernandes, Yuri Georgievskii, Leonard E. Jusinski, Giovanni Meloni, Craig A. Taatjes, James A. Miller

Combustion Research Facility, Mail Stop 9055, Sandia National Laboratories,
Livermore, CA 94551-0969 USA

Introduction

Ethanol is becoming an increasingly important component in fuel blends for automotive engines, in fact many countries have introduced ethanol as a compulsory component of gasoline. Understanding the low temperature and high pressure ignition properties of ethanol is crucial, especially for new engine technologies relying on chemical kinetics to time the ignition.

Aim

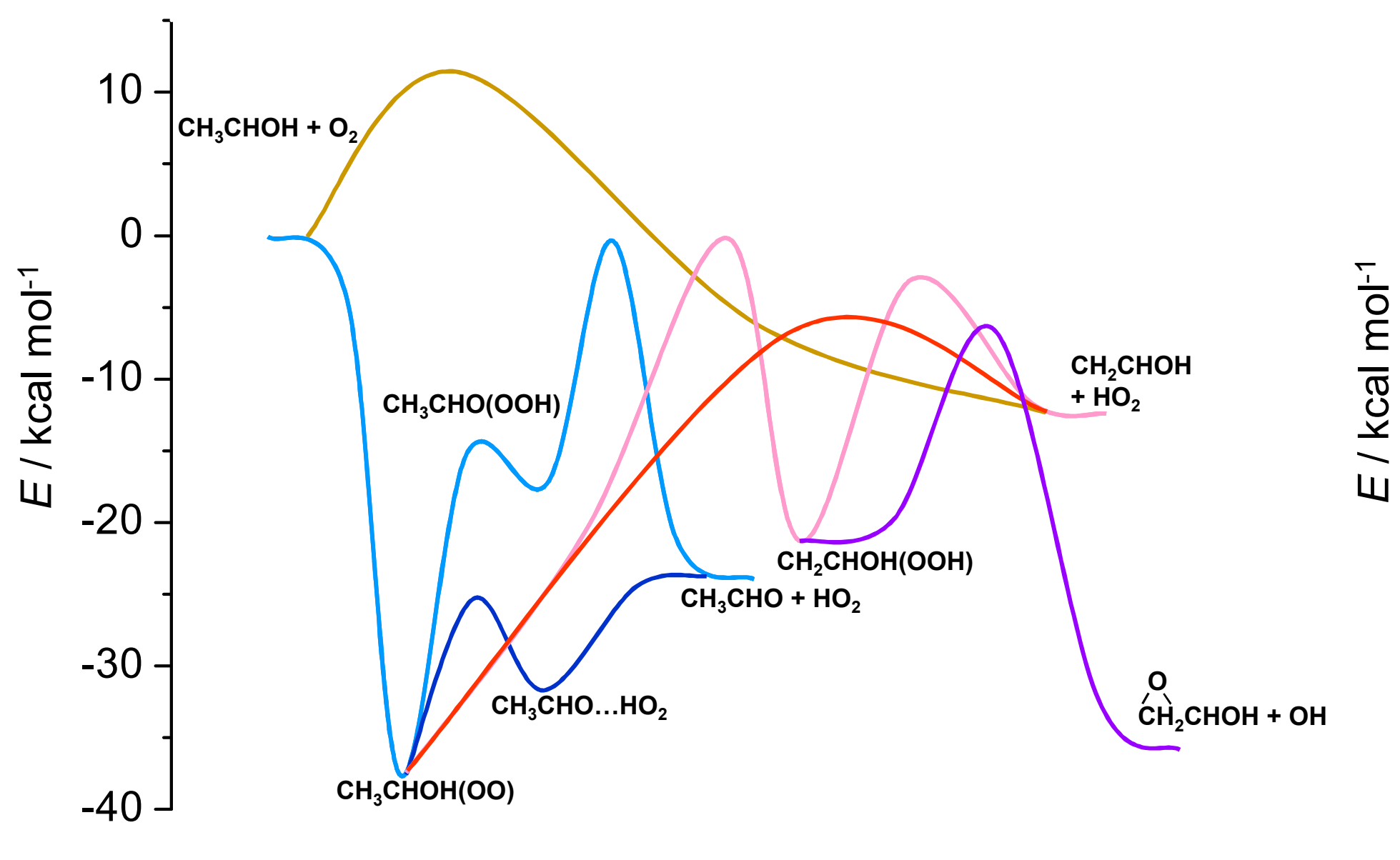
Our aim was to determine the bimolecular rate coefficient for reactions of the α- and β-hydroxyethyl radicals with oxygen in the ignition regime, as well as to characterize the product channels using ab initio methods.

$$CH_3CHOH + O_2 \rightarrow \text{Products} \qquad (\alpha)$$
$$CH_2CH_2OH + O_2 \rightarrow \text{Products} \qquad (\beta)$$

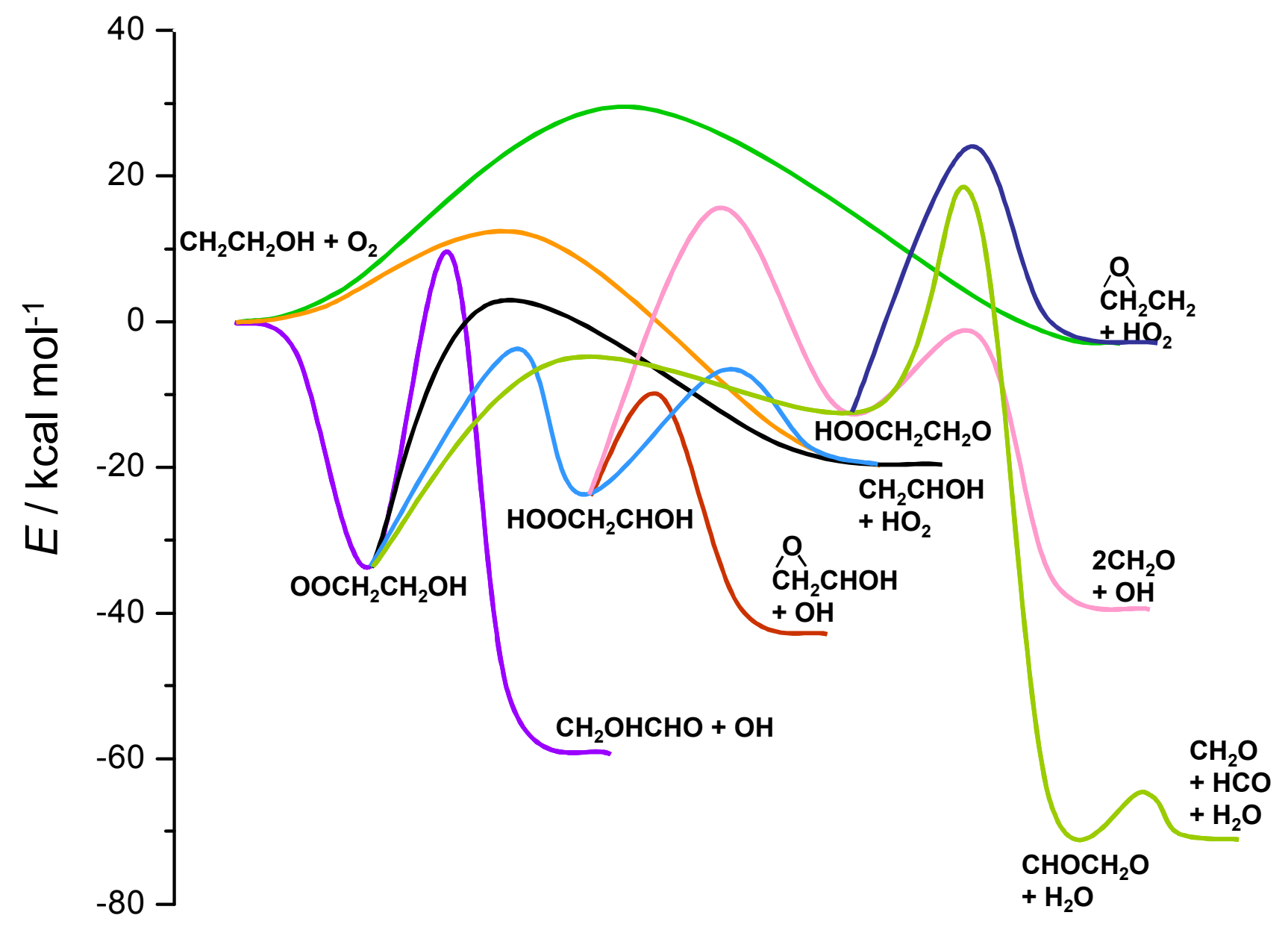
As a further development, experiments looking at these reactions will be carried out in a high-pressure cell designed specifically for this purpose.

Potential energy surfaces of reactions (*α*) and (*β*)

Geometries and frequencies were computed at the B3LYP/6-311++G(d,p) level of theory. Single point energies were calculated with the RQCISD(T) method using cc-pV*n*Z basis set, *n* = {T,Q}, extrapolated to the infinite basis set.



Stationary points on the *α*-hydroxyethyl + O_2 surface



Stationary points on the *β*-hydroxyethyl + O_2 surface

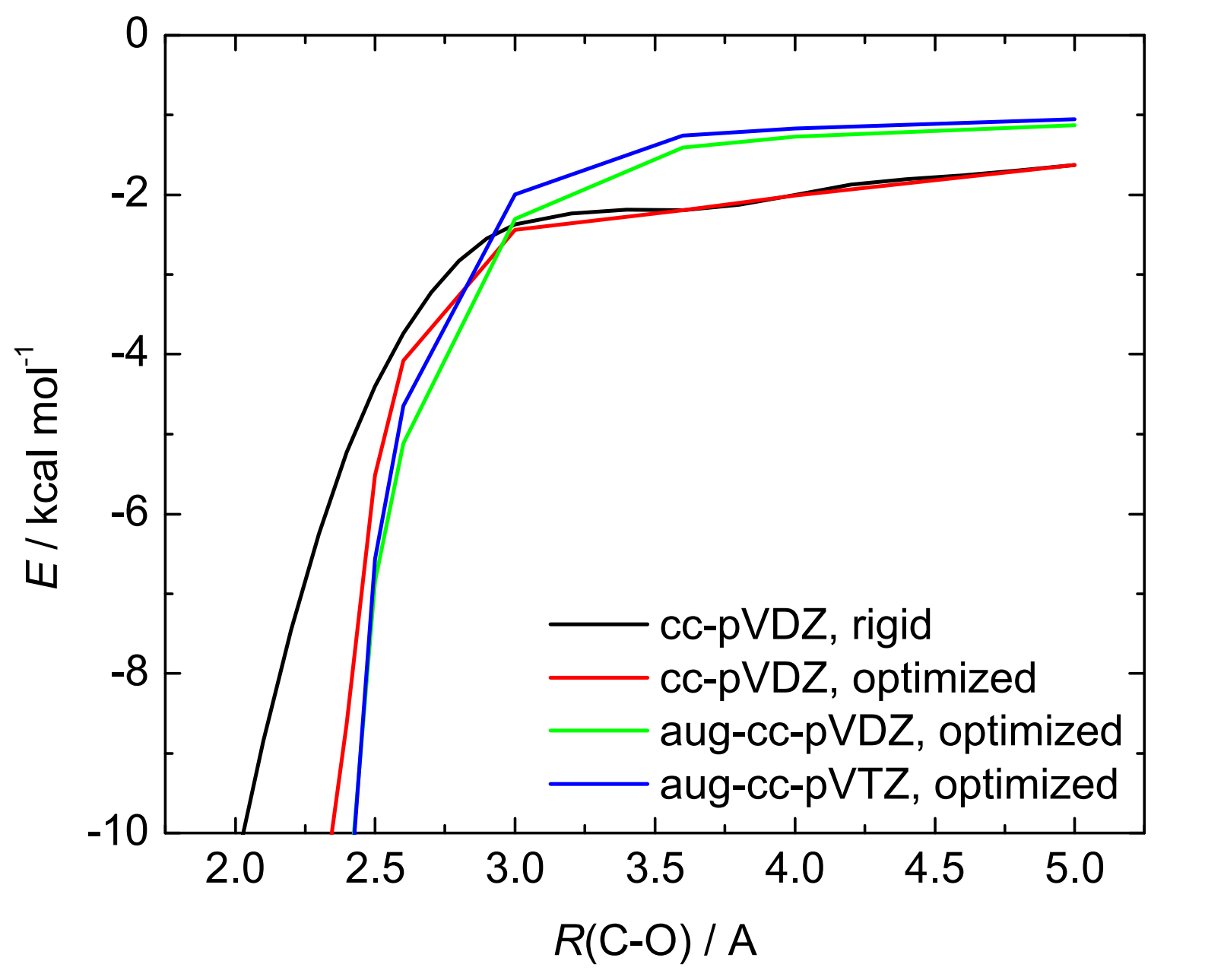
Calculation of rate coefficients

Rate coefficients are calculated using the eigenvalue-eigenvector based solution of the master equation, which can be given in the following form:

$$\frac{\mathrm{d}|w(t)\rangle}{\mathrm{d}t} = G|w(t)\rangle$$

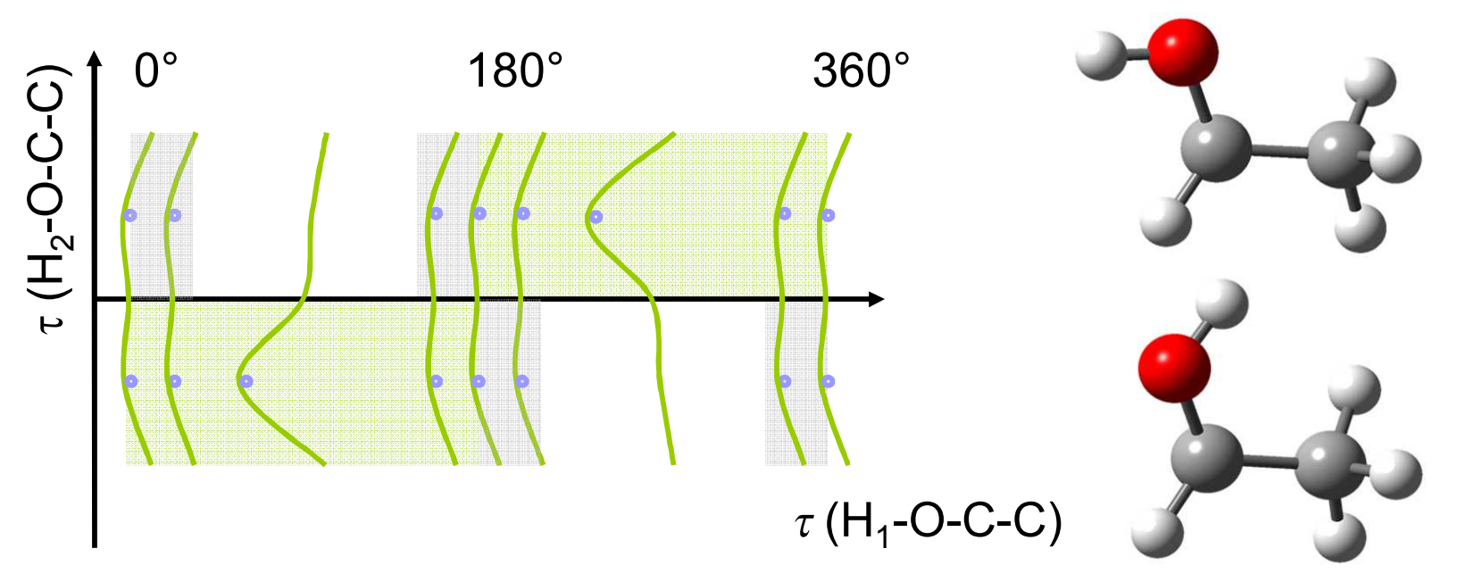
where matrix *G* describes the chemical exchange between different wells and also the *E* transfer during collisions, while $|w(t)\rangle$ contains the unknown populations. The phenomenological rate coefficient can be obtained from the eigenvalues out of which N_{well}+1 correspond to the chemically significant eigenmodes (CSE), and the rest to the internal-energy relaxation eigenmodes (IERE).

The entrance channels of both reactions are barrierless. The *E*,*J*-resolved number of states is calculated variationally using the direct variable reaction coordinate transition state theory (VRC-TST). The distance between the radical C atom and the bonding O atom is taken as a reaction coordinate and is allowed to change between 2.5 and 7.0 Angstrom. The potential energy is calculated "on the fly" using CASPT2(5e,5o)/VDZ. Using aug-cc-pVTZ basis set 1D potential correction is applied to correct for inaccuracies related to the basis set and the geometry relaxation.



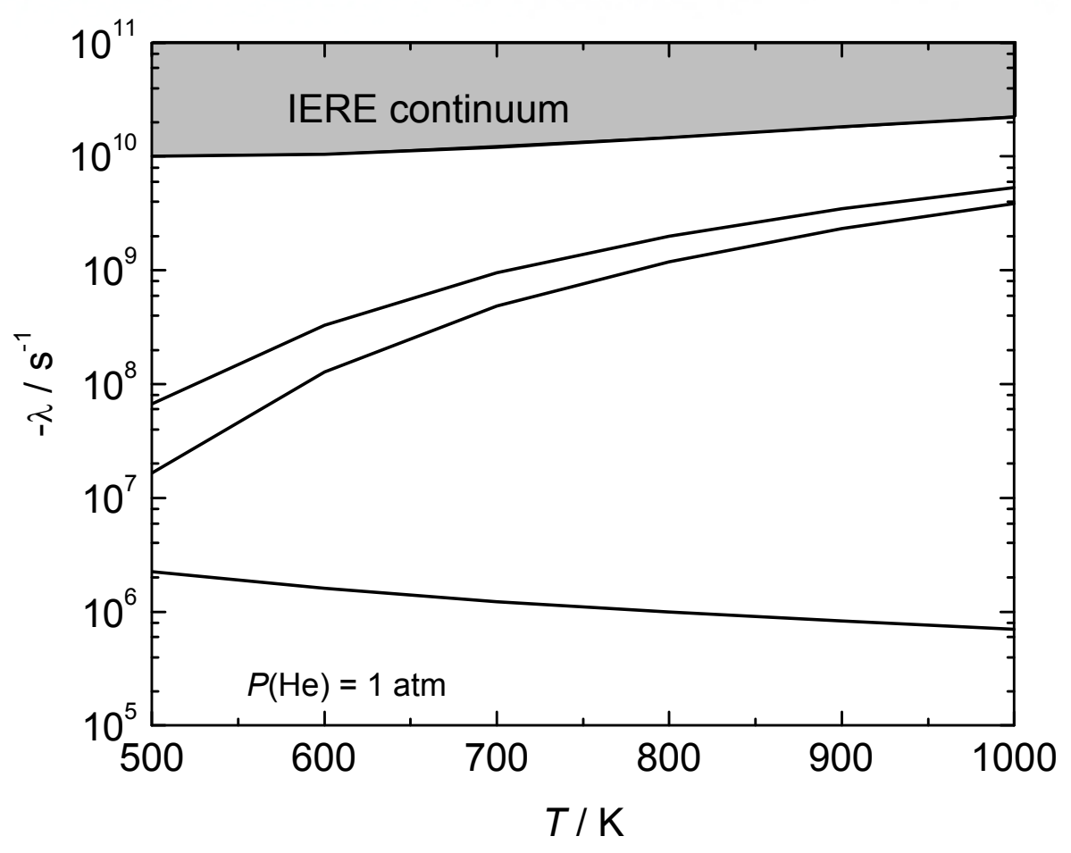
Energy along the minimum energy path calculated with various methods for the *α*-hydroxyethyl + O_2 system

Tunneling corrections are taken into account by asymmetric Eckart transmission probabilities. Internal rotors are treated using the Pitzer-Gwinn approximations by Fourier fits to the B3LYP potentials. For many of the radicals involved the internal rotors are strongly coupled, such as in the case of the α-hydroxyethyl radical.

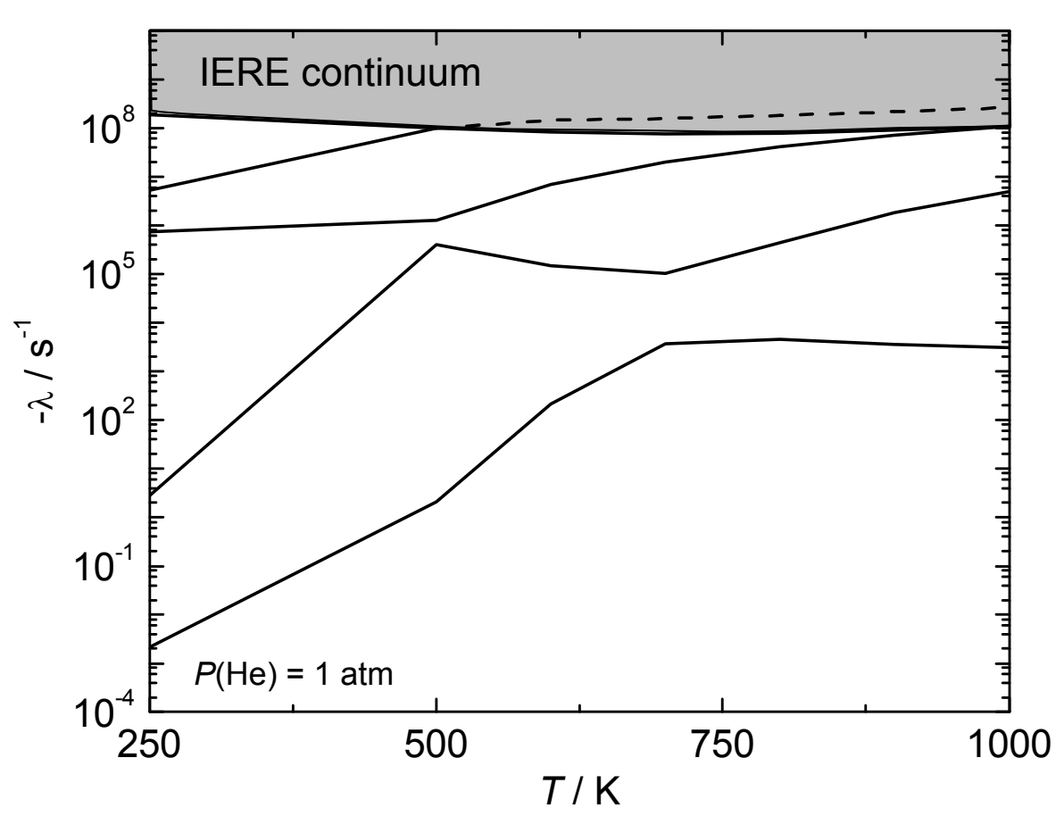


Eigenvalues

In the case of reaction (*α*) all three CSE contribute to the rate coefficient, while in the case of reaction (*β*) above 500 K the fastest, and above 1000 K the second fastest CSE merges in to the IERE continuum.



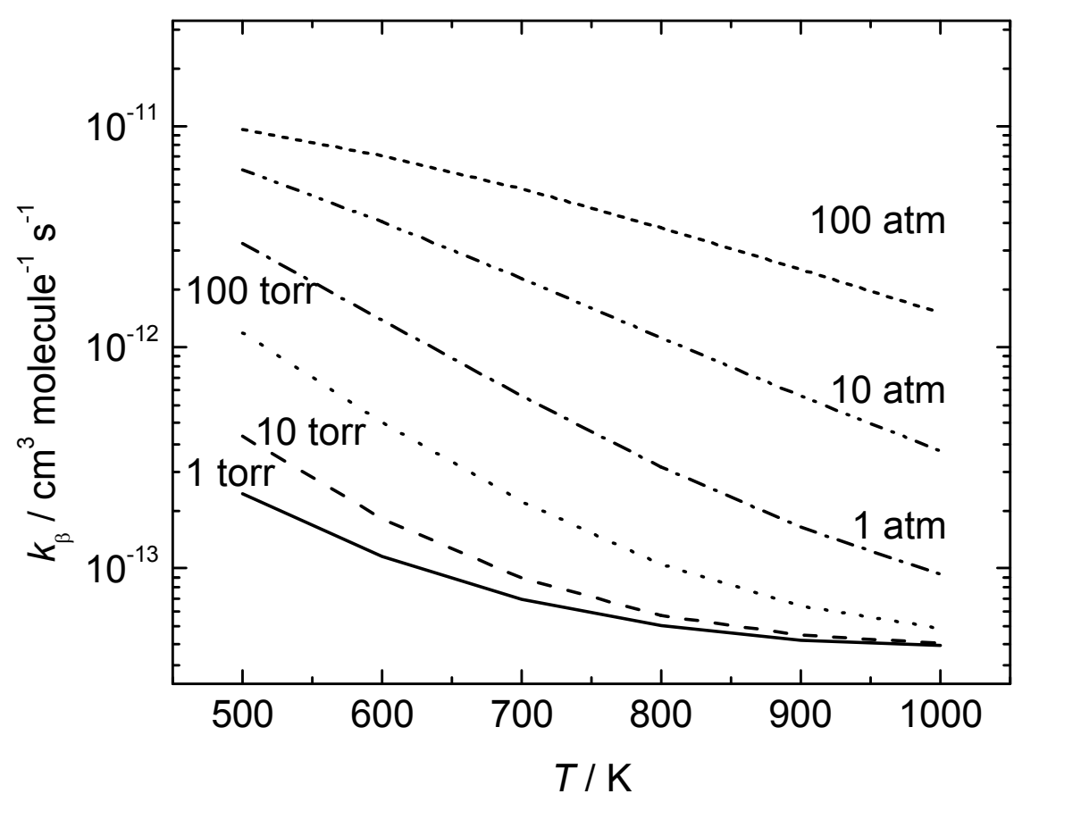
The CSEs as a function of temperature for the *α*-hydroxyethyl + O_2 system



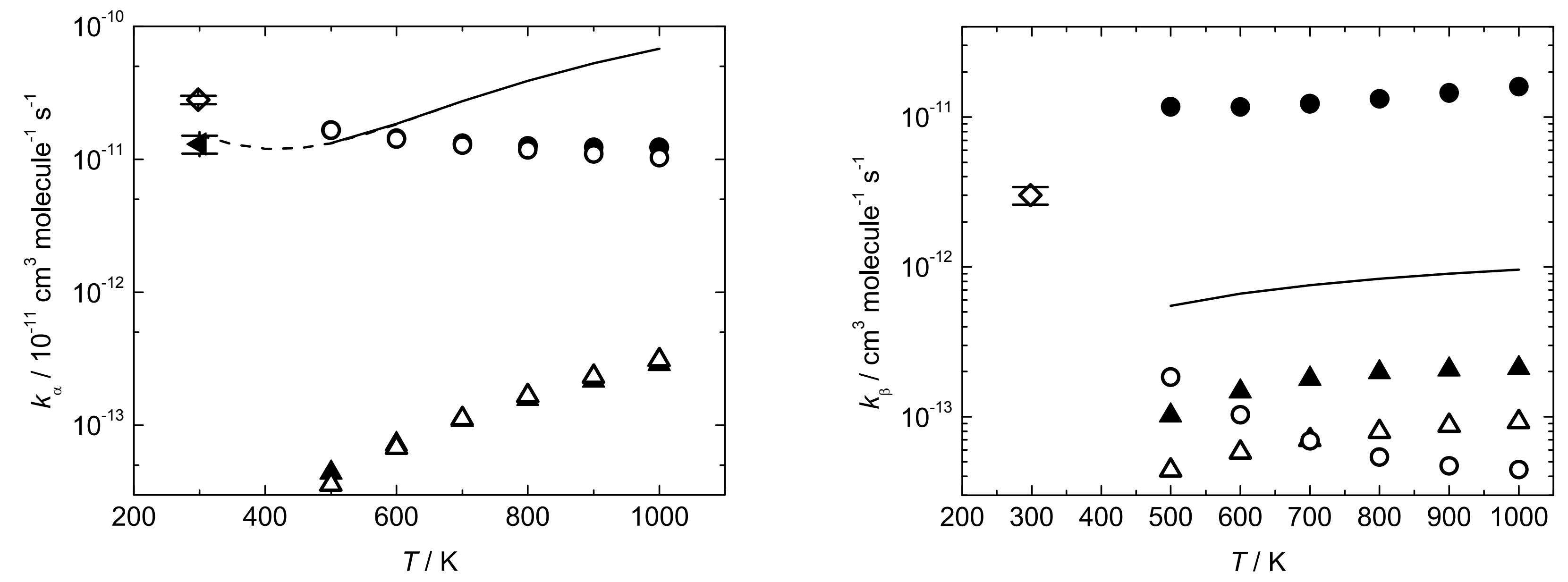
The CSEs as a function of temperature for the *β*-hydroxyethyl + O_2 system

Temperature and pressure dependence

k_α has a very small pressure dependence; on the contrary, the high and zero pressure k_β differs by two orders of magnitude. In both cases, our calculations are in good agreement with the available low temperature measurements; however, there are significant discrepancies between the high temperature ab initio calculations and estimates.



Pressure and temperature dependence of k_β

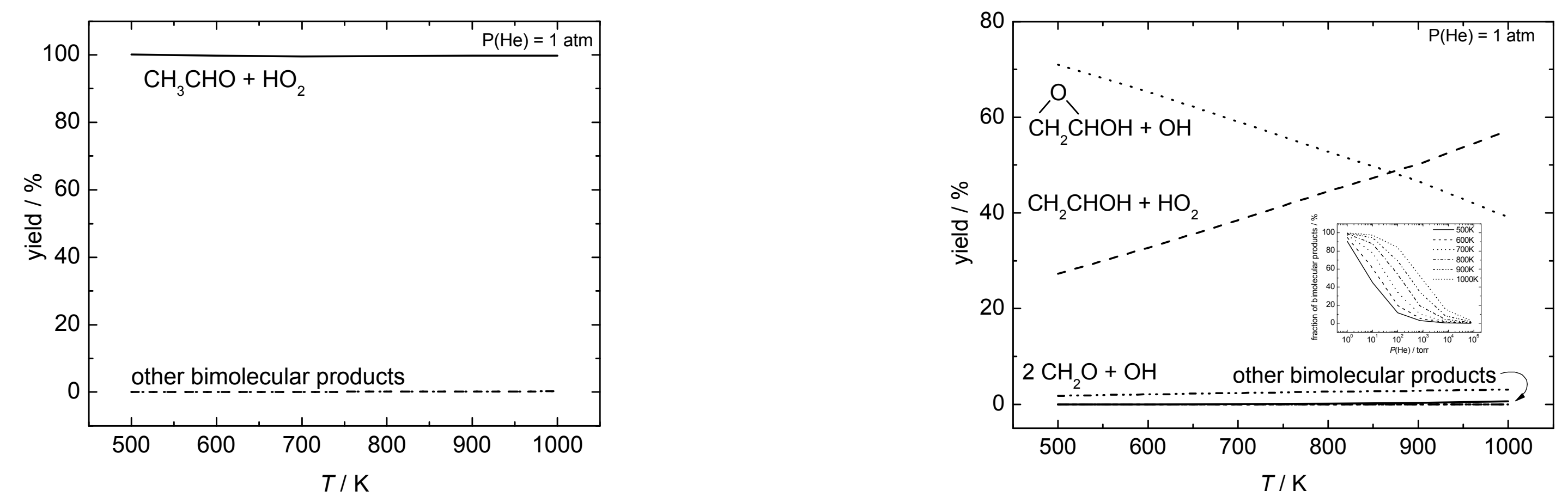


High and zero pressure limit of k_α (left) and k_β (right) and comparison to literature values.

● This work, k_{inf} , ○ This work, $k_{\text{collisionless}}$, —— Marinov [1], estimate, k_{inf}, ◇ Miyoshi [2], PLP-MS, *P* = 2-7 Torr
◀ Anastasi [3], PR-AS, *P* = 1 atm, ······ Grotheer [4], DF-MS, *P* = 0.8 Torr, ▲ da Silva [5], ab initio, *P* = 100 atm,
△ da Silva [5], ab initio, *P* = 0.001 atm

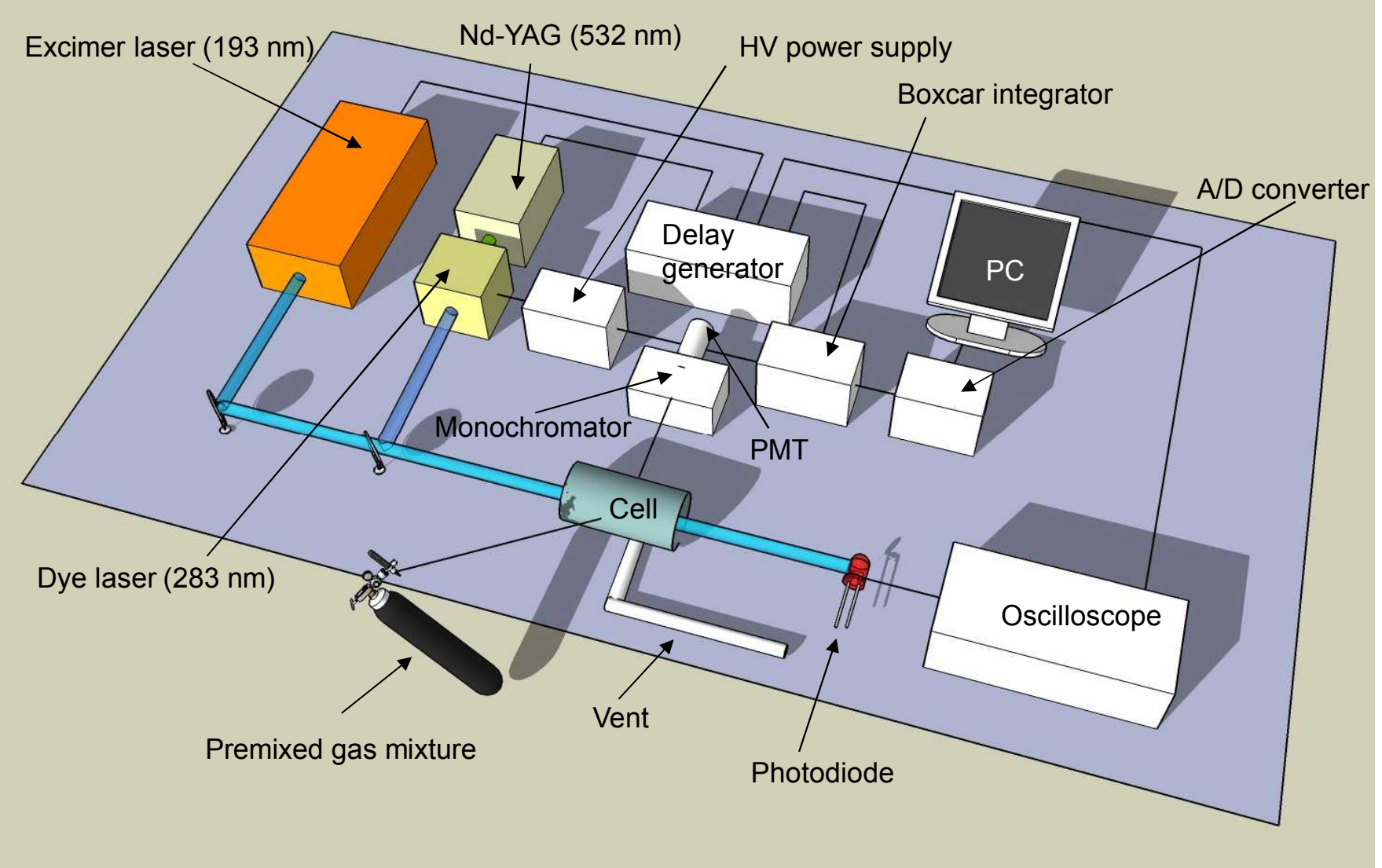
Product distribution

In reaction (*α*) the bimolecular channel is the only significant channel at all of the investigated pressures and temperatures producing HO_2 radical. In reaction (*β*) both OH and HO_2 radicals are produced, and the fraction of the bimolecular channel drops with pressure.



Relative yields of bimolecular channels in reaction (*α*) (left) and (*β*) (right)

Experimental setup to study the reactions



Possible radical sources:

$$CH_3COCO(OC)CH_3 \xrightarrow{193\text{ nm}} CH_3CHOH + CH_3CO$$
$$XCH_2CH_2OH \xrightarrow{193\text{ nm}} CH_2CH_2OH + X \qquad X = Cl, Br$$

$$Cl + CH_3CH_2OH \longrightarrow CH_2CH_2OH + HCl$$
$$\longrightarrow CH_3CHOH + HCl$$

Rate coefficients and products will be determined by detecting OH LIF signal.

Acknowledgement

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