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MEASUREMENTS OF PRODUCT FORMATION IN THE REACTION OF CYCLOHEXYL RADICALS WITH O_2

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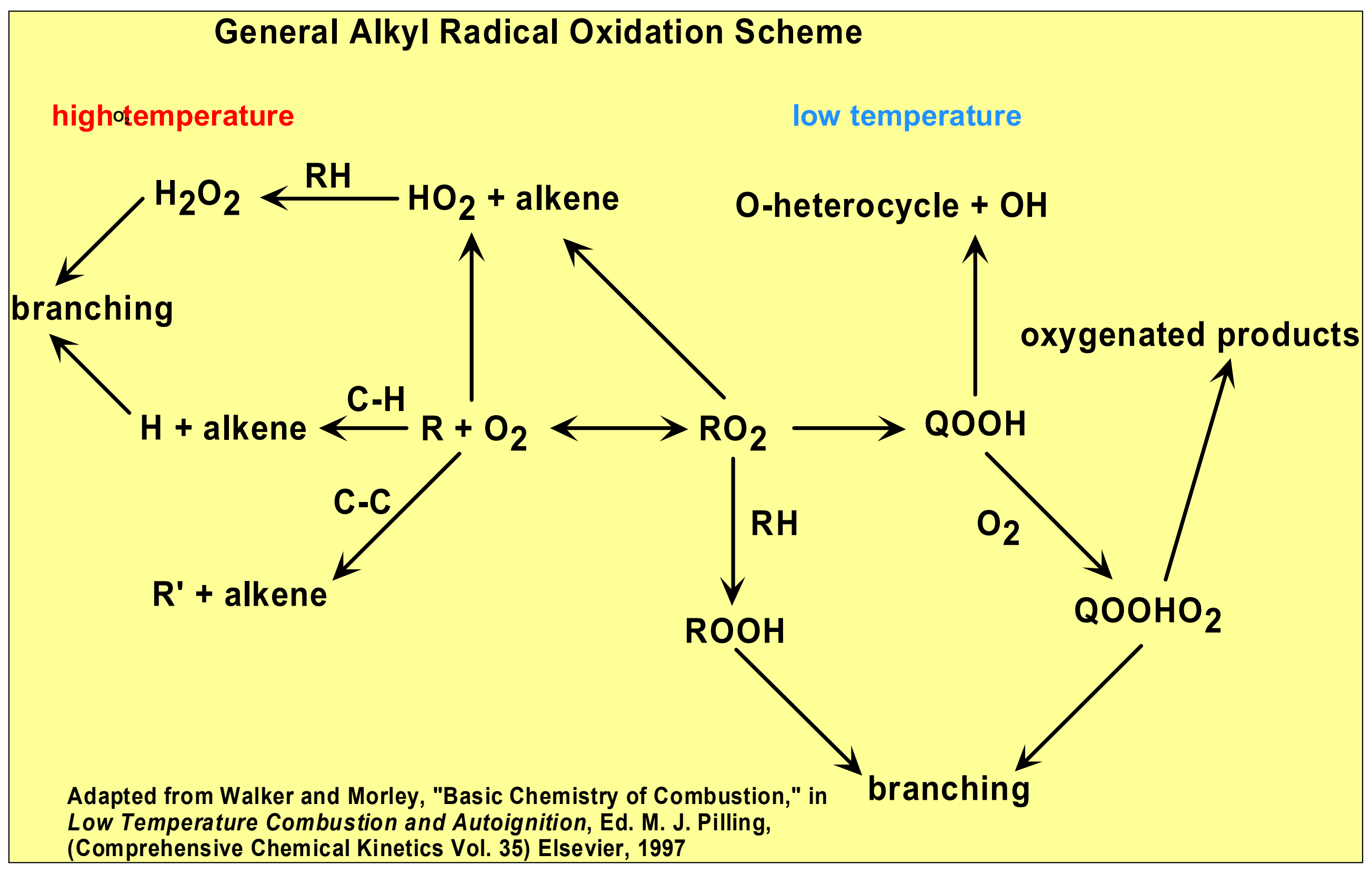
Reactions of Alkyl Radicals with O_2 Are Central to Low Temperature Hydrocarbon Oxidation


General Alkyl Radical Oxidation Scheme

high temperature

low temperature

H_2O_2 $\xleftarrow{RH}$ HO_2 + alkene

O-heterocycle + OH

branching

oxygenated products

H + alkene $\xleftarrow{C-H}$ R + O_2 ⟷ RO_2 ⟶ QOOH

C-C

R' + alkene

RH

ROOH

O_2

$QOOHO_2$

branching

Adapted from Walker and Morley, "Basic Chemistry of Combustion," in *Low Temperature Combustion and Autoignition*, Ed. M. J. Pilling, (Comprehensive Chemical Kinetics Vol. 35) Elsevier, 1997

Motivation

- •Despite the fact that many fuels contain cyclic alkanes, the oxidation of this class of molecules has received less attention than that of straight-chain alkanes

- •Cyclohexane is also interesting because it possesses the six-membered ring of benzene, the formation of which is thought to be the rate-limiting step of formation of polycyclic aromatic compounds

- •HO_2 and OH are two important radical products of this oxidation, and the time behavior of their formation can be observed by absorption spectroscopy

- •The results of these experiments can be compared with the predictions of detailed kinetic modeling and previous measurements on R + O_2 systems

Measurement of product formation in R + O_2 uses Cl-initiated alkane oxidation

- •Photolysis of Cl_2 initiates reaction:

Cl_2 (355 nm) → 2 Cl
Cl + c-C_6H_{12} → HCl + c-C_6H_{11}
c-C_6H_{11} + O_2 → c-C_6H_{10} + HO_2
c-C_6H_{11} + O_2 → $C_6H_{10}OOH$ → epoxy/aldehdye/ketone + OH

- •Probe A-X transition of HO_2 in near infrared
- •HO_2 yield determined by comparison to a reference system with 100% yield

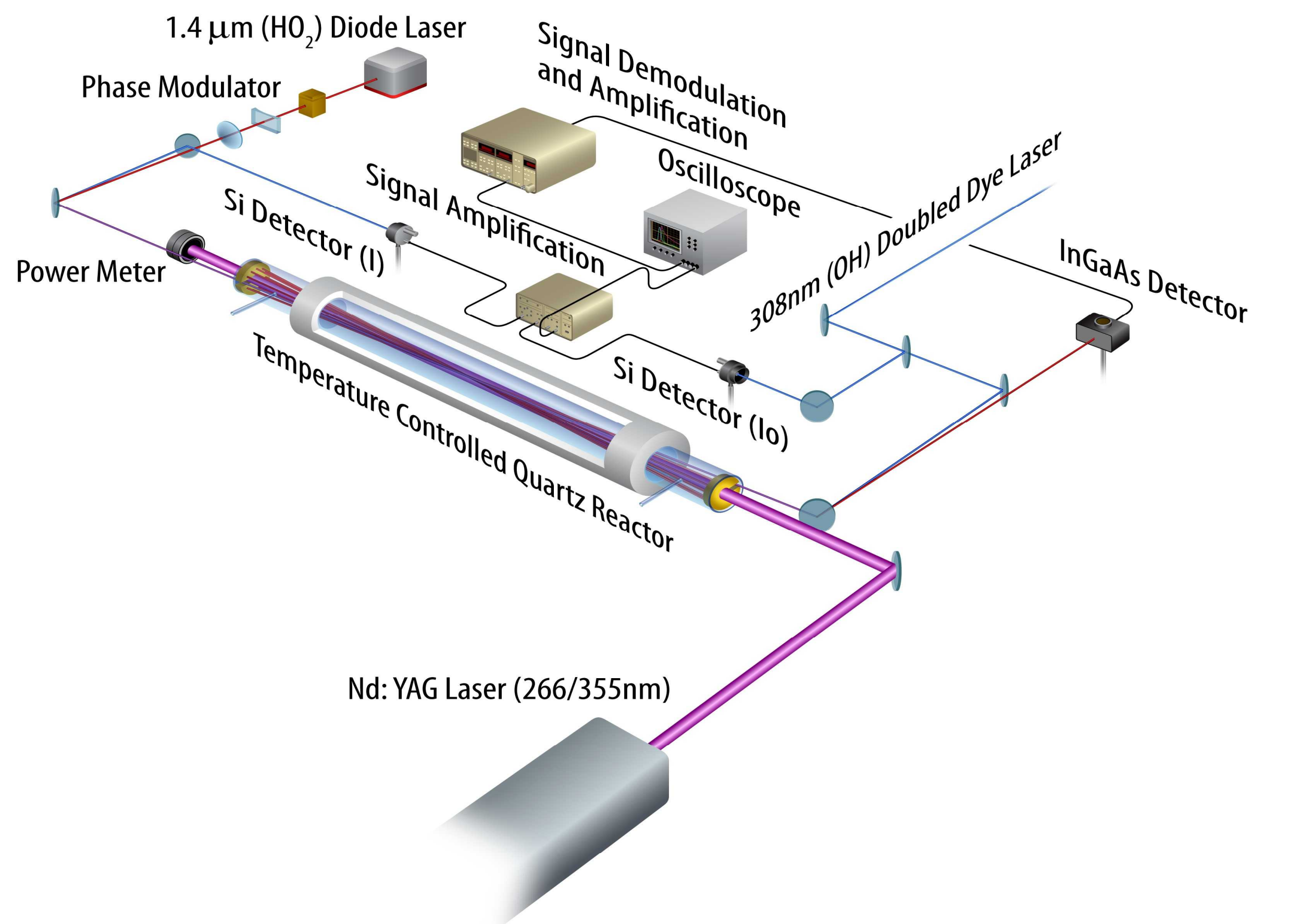
Cl + CH_3OH → HCl + CH_2OH
CH_2OH + O_2 → CH_2O + HO_2 (100%)

- •OH experiment use oxalyl chloride as Cl atom source:

$(ClCO)_2$ (266 nm) → 2Cl + 2CO
Cl + c-C_6H_{12} → HCl + c-C_6H_{11}

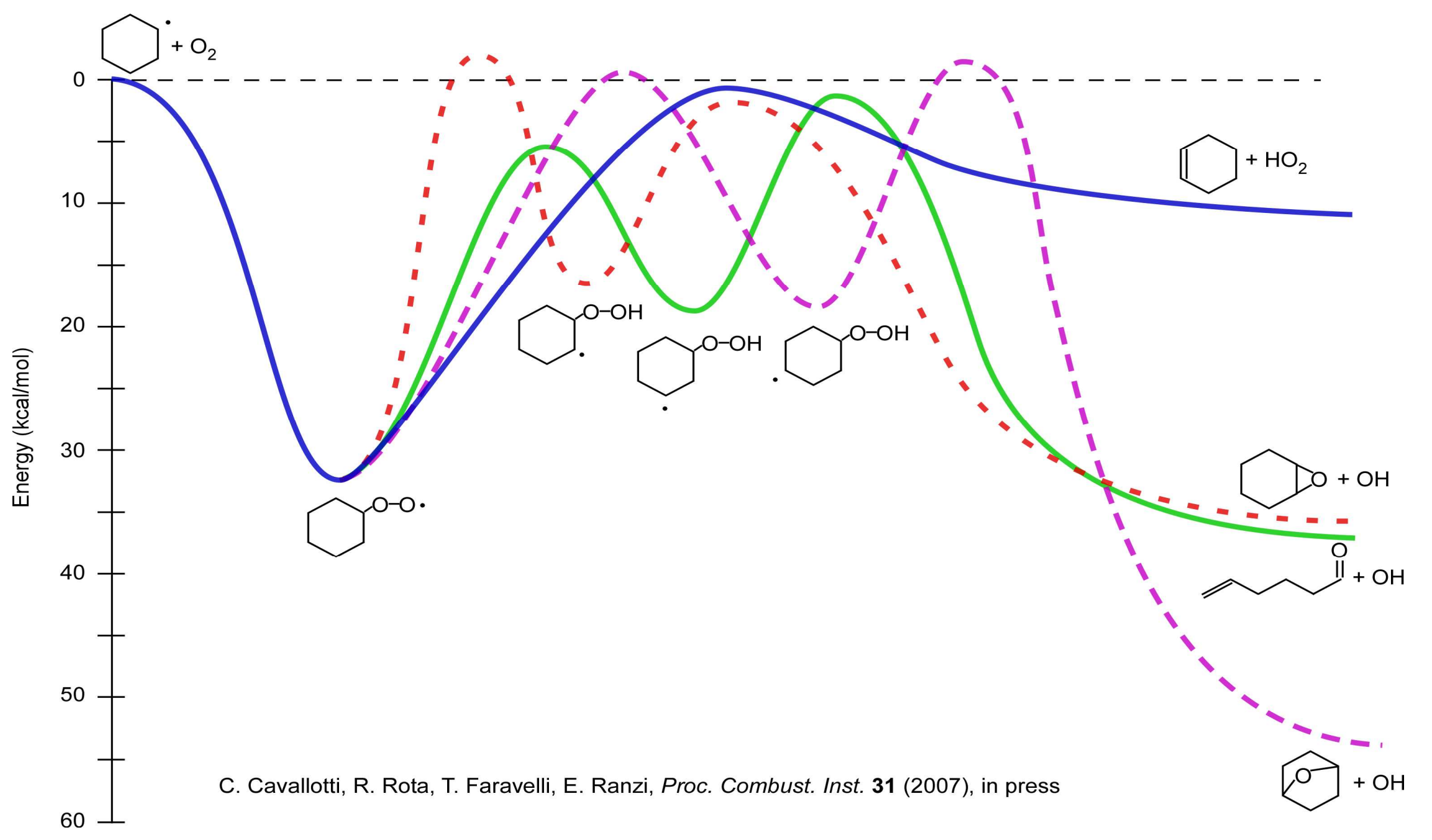
- •Probe A-X transition of OH at 308 nm

Product Formation Monitored by Long-Path Absorption



- •Cl_2, cyclohexane, O_2, and helium (total density of 8.5 x 10^{17} cm^{-3})
- •Oxygen concentration maintained ~ 30 times greater than Cl_2 to minimize competing chlorination
- •Oxalyl chloride photolysis allows use of lower O_2 concentrations
- •Herriott-type multipass cell increases effective path length

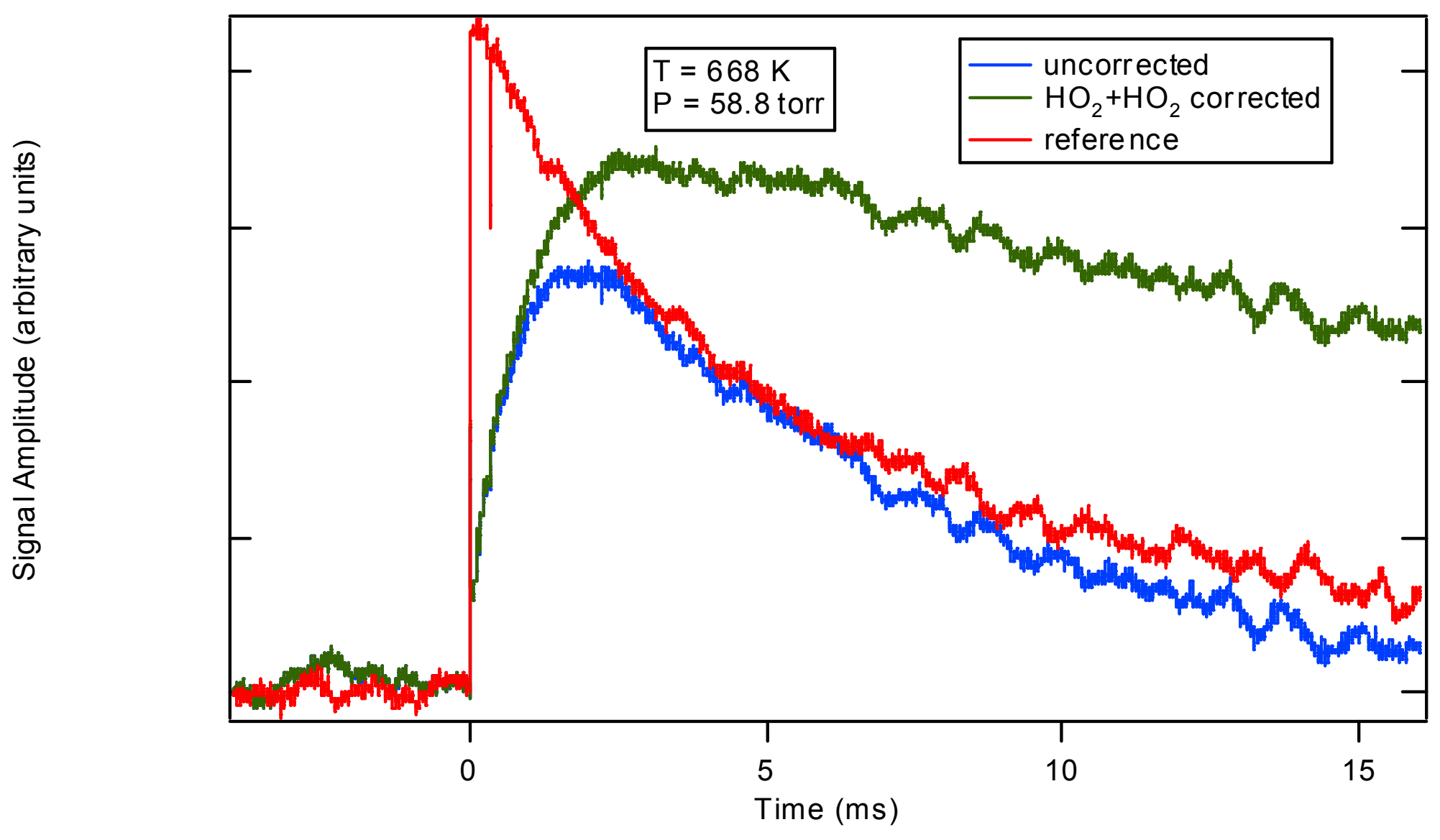
Potential Energy Surface Diagram of c-C_6H_{11} + O_2



C. Cavallotti, R. Rota, T. Faravelli, E. Ranzi, *Proc. Combust. Inst.* **31** (2007), in press

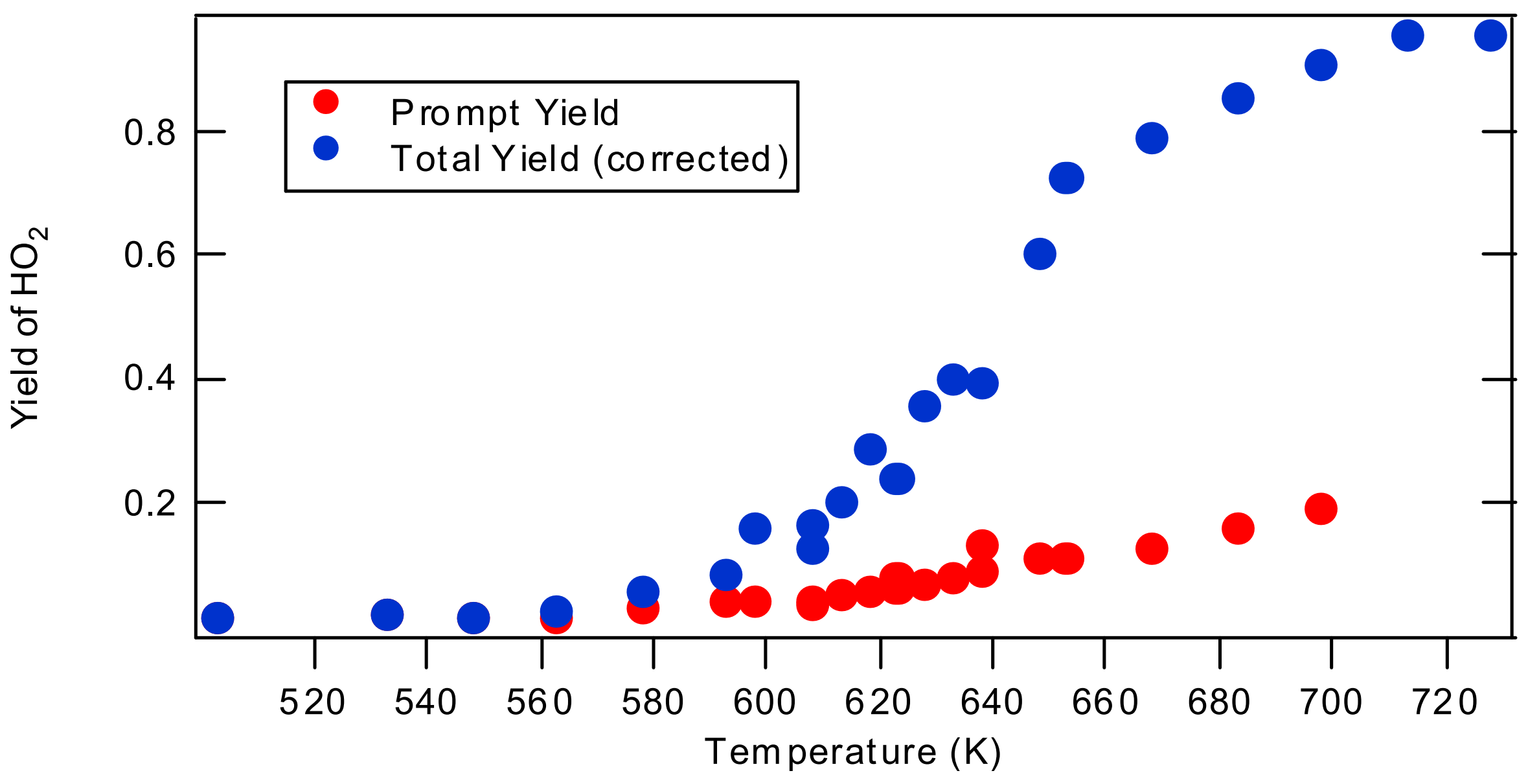
- •Product channels with every transition state below reactant energy are expected to be significant
- •HO_2 is directly formed from RO_2
- •Ring fission channel allow efficient formation of OH
- •Other channels, with higher barriers, contribute less to product formation

HO_2 Signals Are Corrected for Loss Due to Self-Reaction and Compared to Reference Amplitude



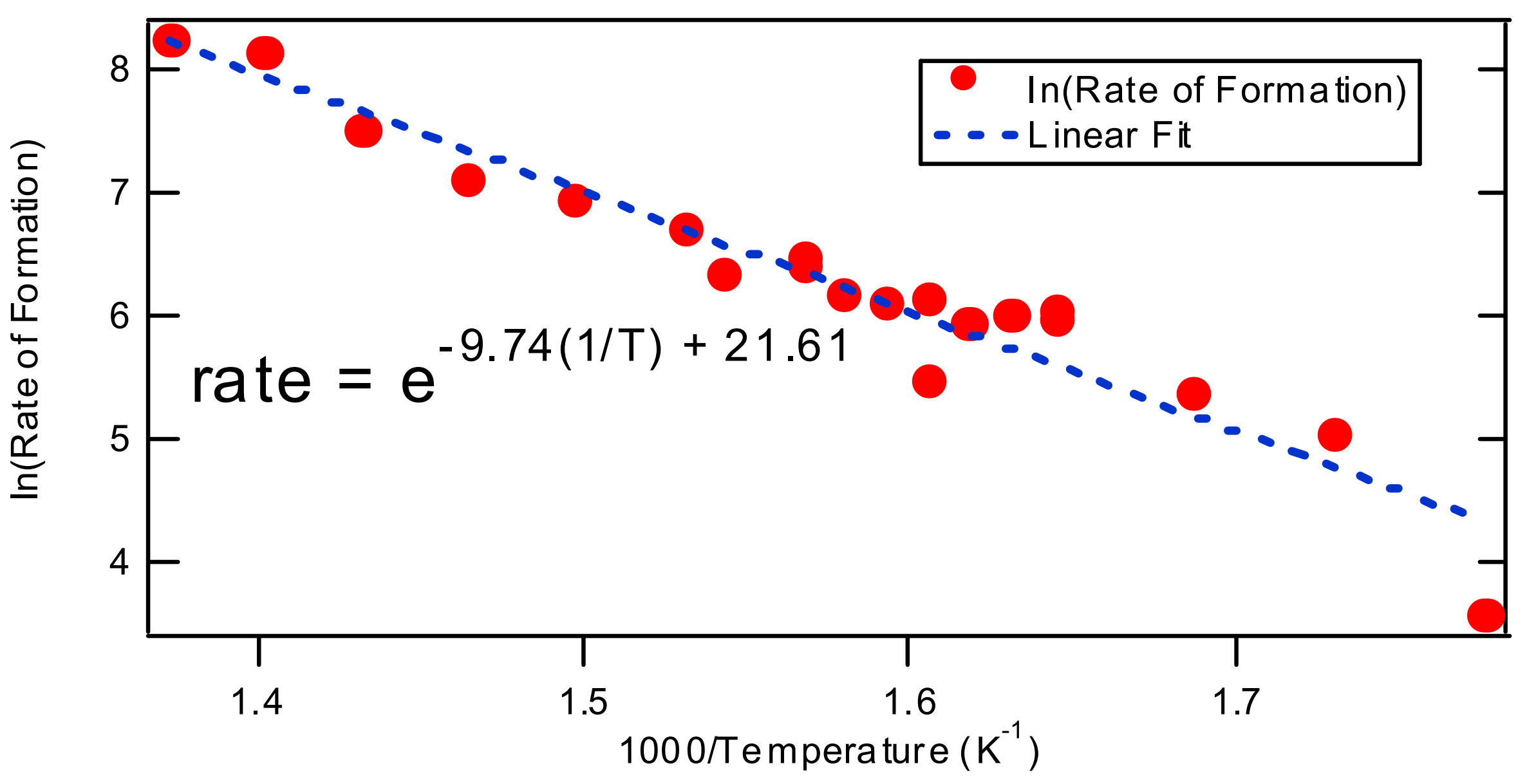
- •Phenomenological rate coefficient for HO_2 self-reaction from reference reaction signal decay
- •Experimental signal is corrected for recombination
- •Corrected signal is a lower bound to actual HO_2 production, as other less significant removal pathways also contribute

Temperature Dependence of HO_2 Yield



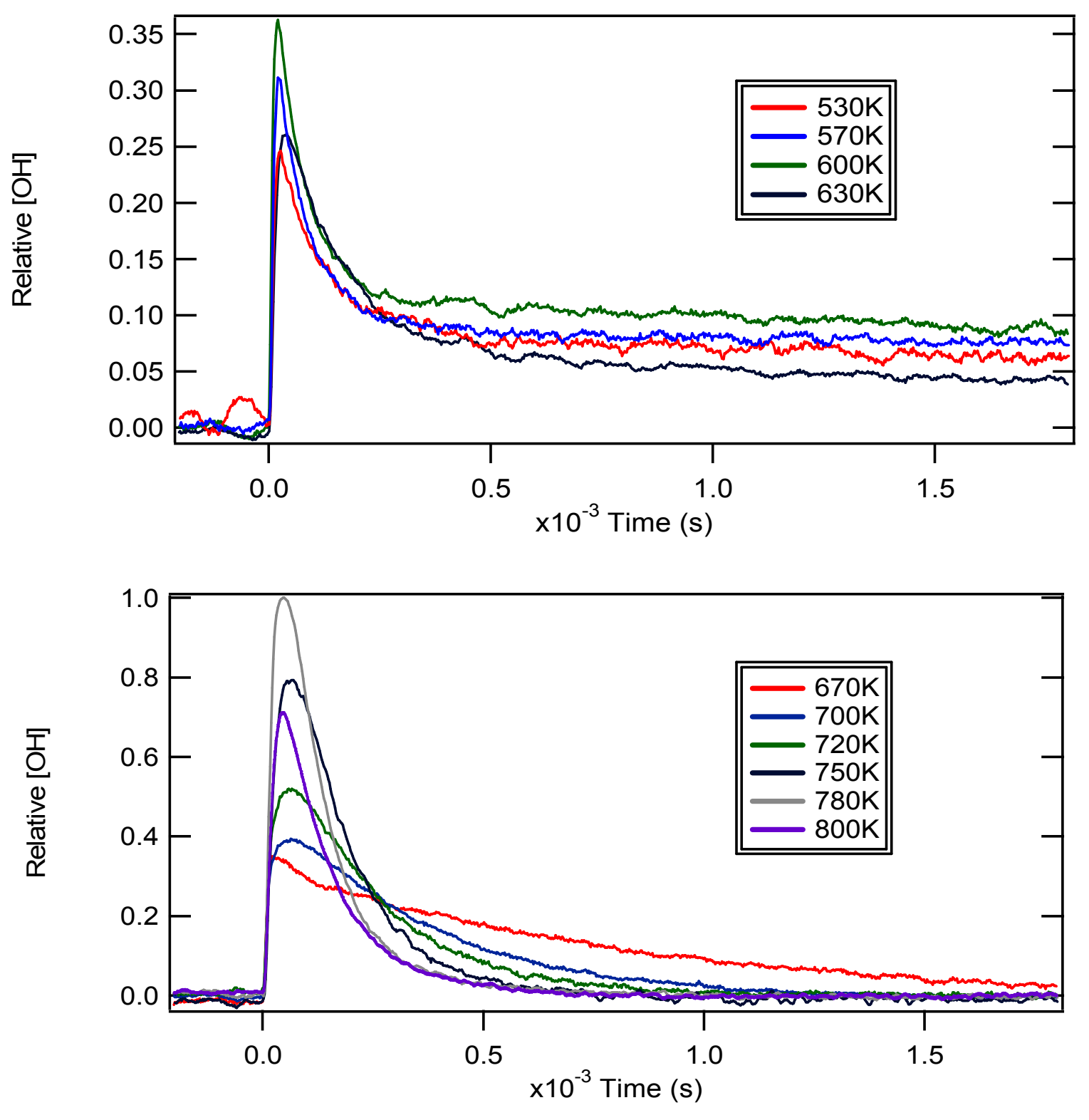
- •HO_2 produced by two mechanisms
  - •prompt formation from initial activated RO_2*
  - •slower production via stabilized RO_2 intermediate
- •Prompt yield steadily increases with temperature
- •Sharp increase in delayed yield observed near 600 K, where RO_2 becomes thermally unstable
- •At higher temperatures, total yield approaches but does not reach 1
- •Less than 100% yield of HO_2 at high temperatures suggests substantial branching to OH
- •Above 700 K, "delayed" rise indistinguishable from the prompt rise

Temperature Dependence of Delayed HO_2 Formation



- •Arrhenius plot suggests effective energy of activation of approximately 22 kcal mol^{-1}
- •Slightly less than the apparent activation energies for C_2H_5 + O_2, C_3H_7 + O_2, and c-C_5H_9 + O_2
- •Apparent A-factor, which is inversely related to the change in entropy between reactants and transition state, is high (as in c-C_5H_9)
- •Relatively small entropy change from reactants to ring intermediate because cyclohexylperoxy is already restricted rotationally

OH Formation Between 530 and 800 K



- •Detailed kinetic modeling is underway to glean information from OH formation measurements
- •Contributions of side and secondary reactions are more significant than for HO_2 because of the reactivity of OH

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