

CH₂O and HCO Chemistry

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Introduction

Formaldehyde [CH₂O] is a key intermediate in the combustion of fuels like natural gas and methanol, see Figure 1. However, even though CH₂O decomposition and oxidation chemistry are of importance in the overall hydrocarbon oxidation process, there still exists much uncertainty in the high-temperature rate coefficients of several of the key reactions involving CH₂O. Accurate measurements of these critical rates at elevated temperatures are needed to develop and refine detailed chemical kinetic mechanisms of combustion chemistry.

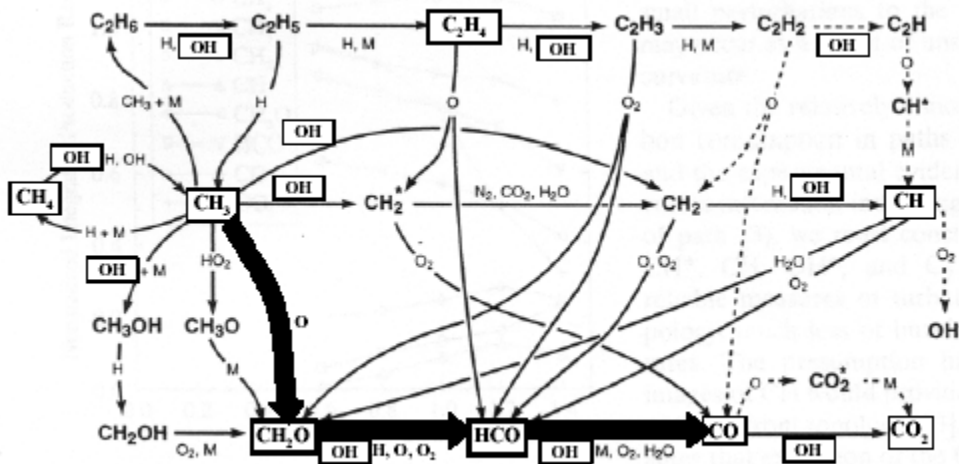


Figure 1: Methane oxidation pathways

Rate coefficients of the following reactions are targets of the current work:

- $\text{CH}_2\text{O} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$
- $\text{CH}_2\text{O} + \text{Ar} \rightarrow \text{HCO} + \text{H} + \text{Ar}$
- $\text{CH}_2\text{O} + \text{Ar} \rightarrow \text{H}_2 + \text{CO} + \text{Ar}$
- $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{HCO} + \text{HO}_2$

Our measurement strategy and experimental results are summarized below.

CH₂O + OH → HCO + H₂O

The reaction of hydroxyl [OH] radicals with formaldehyde [CH₂O] was studied at temperatures ranging from 934 K to 1670 K behind reflected shock waves at an average total pressure of 1.6 atm. OH radicals were produced by shock-heating tert-butyl hydroperoxide [(CH₃)₃-CO-OH], while 1,3,5 trioxane [(CH₂O)₃] was used in the pre-shock mixtures to generate reproducible levels of CH₂O. OH concentration time-histories were inferred from laser absorption using the well-characterized R1(5) line of the OH A-X (0, 0) band near 306.7 nm.

An example experiment is presented in Figure 2, while a comparison of the current measurements with previous work is shown in Figure 3.

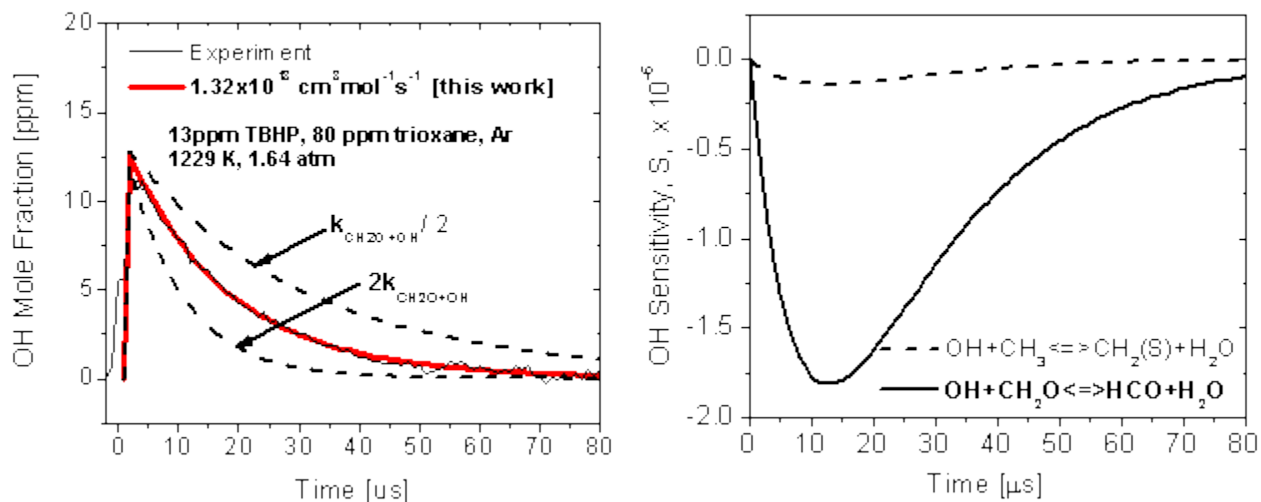


Figure 2: $\text{CH}_2\text{O}+\text{OH} \rightarrow \text{HCO}+\text{H}_2\text{O}$: Example experiment and sensitivity

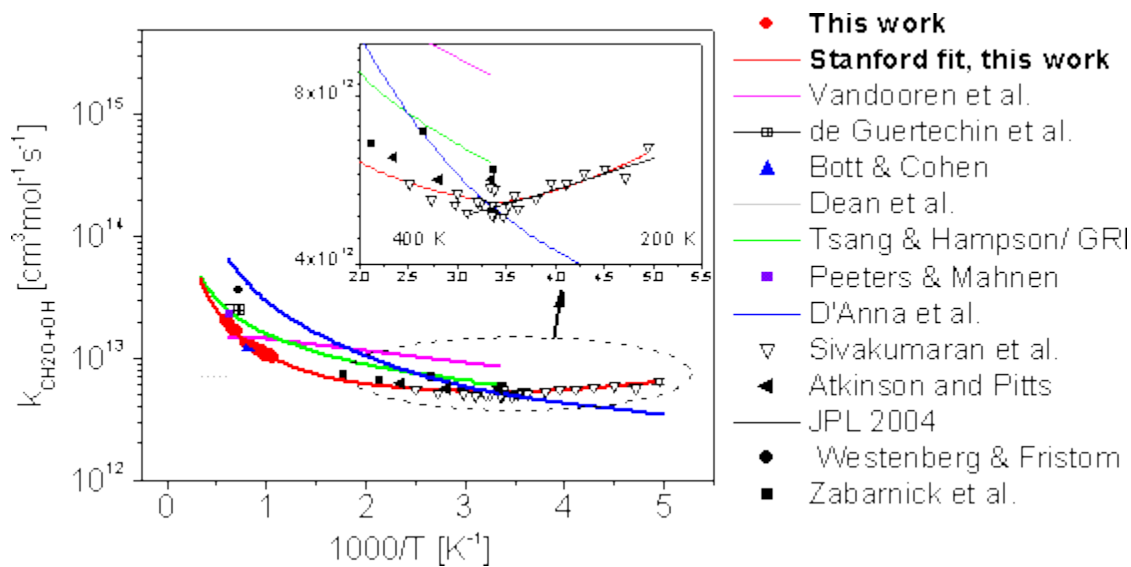


Figure 3: $\text{CH}_2\text{O}+\text{OH} \rightarrow \text{HCO}+\text{H}_2\text{O}$: Comparison with previous work

The reaction of OH with CH_2O was also studied using quantum chemical methods at the CCSD(T) level of theory using the 6-311++G(d,p) basis set. The transition state for the H-atom metathesis reaction was located, and reaction rate coefficients were calculated. Reasonable agreement with the experimental measurements was obtained. Figure 4 presents a comparison of theory and experiment.

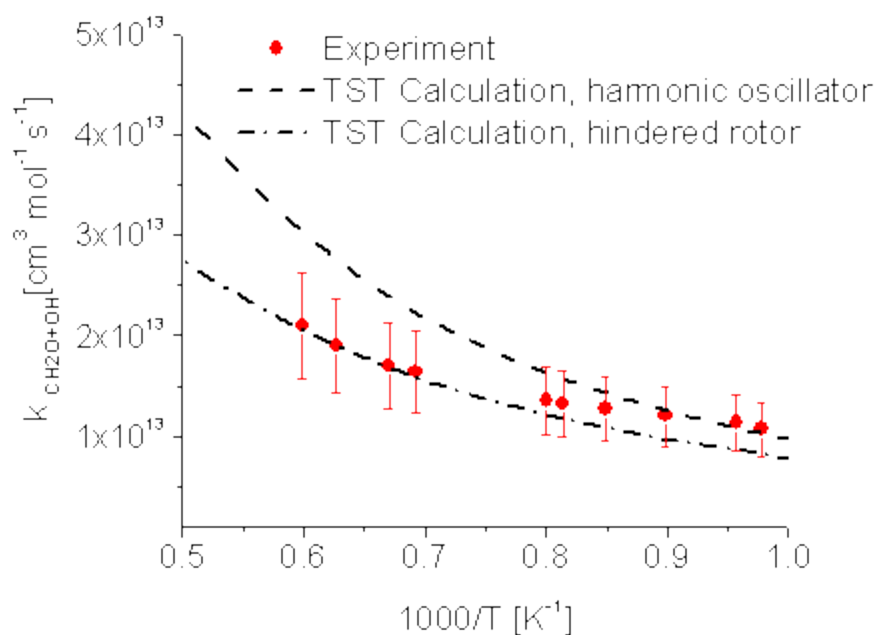


Figure 4: CH₂O+OH → HCO+H₂O: Theory vs. experiment

CH₂O + Ar → Products

The two-channel thermal decomposition of formaldehyde [CH₂O], (1a) CH₂O + Ar → HCO + H + Ar, and (1b) CH₂O + Ar → H₂ + CO + Ar, was studied in shock tube experiments in the 2258-2687 K temperature range, at an average total pressure of 1.6 atm. OH radicals, generated on shock heating trioxane-O₂-Ar mixtures, were monitored behind the reflected shock front using narrow-linewidth laser absorption. 1,3,5 trioxane [C₃H₆O₃] was used as the CH₂O precursor in the current experiments. H-atoms formed upon CH₂O and HCO decomposition rapidly react with O₂ to produce OH via H + O₂ → O + OH. The recorded OH time-histories show dominant sensitivity to the formaldehyde decomposition pathways. The second-order reaction rate coefficients were inferred by matching measured and modeled OH profiles behind the reflected shock.

An example experiment is presented in Figure 5, while a comparison of the current measurements with previous work is shown in Figure 6. The OH traces were fit in terms of the overall decomposition rate coefficient, k_{1a}+k_{1b}, and the branching ratio (α) = k_{1a}/(k_{1a}+k_{1b}). The time dependence of the OH sensitivity to the overall decomposition rate coefficient and the branching ratio allows for the separation of these two parameters. The overall rate of decomposition is determined by fitting the early-time behavior of the OH profile. At longer times, sensitivity to k_{1a}+k_{1b} decreases, and OH is primarily sensitive to the branching ratio – this facilitates a simple determination of α.

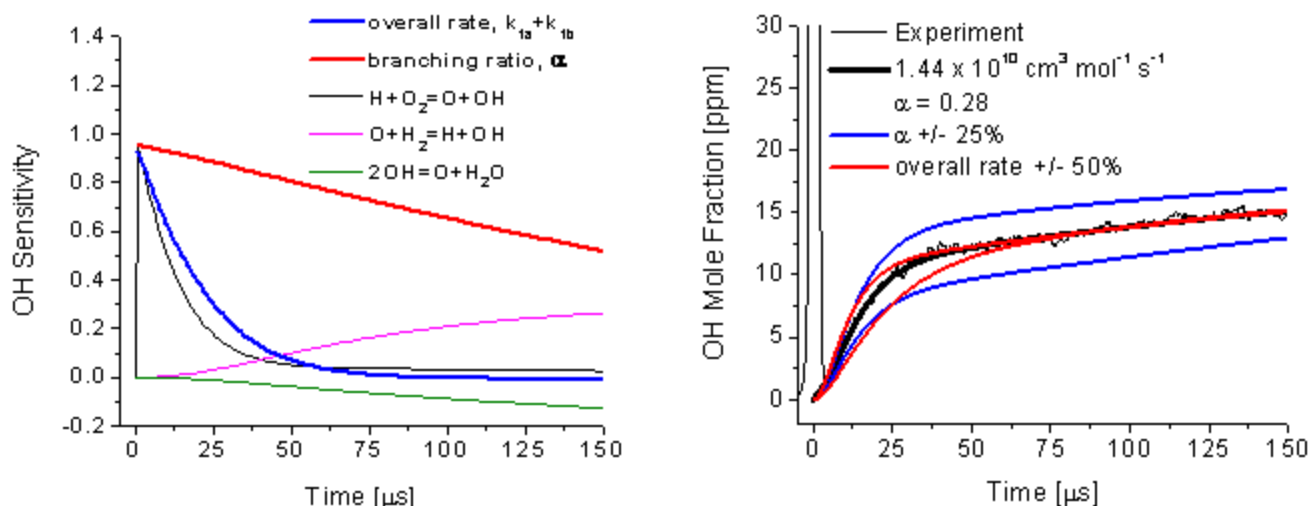


Figure 5: CH₂O+Ar → Products: Example experiment and sensitivity. Left: 2687 K and 1.52 atm. Right: 6.5 ppm (CH₂O)₃, 0.5% O₂, Ar

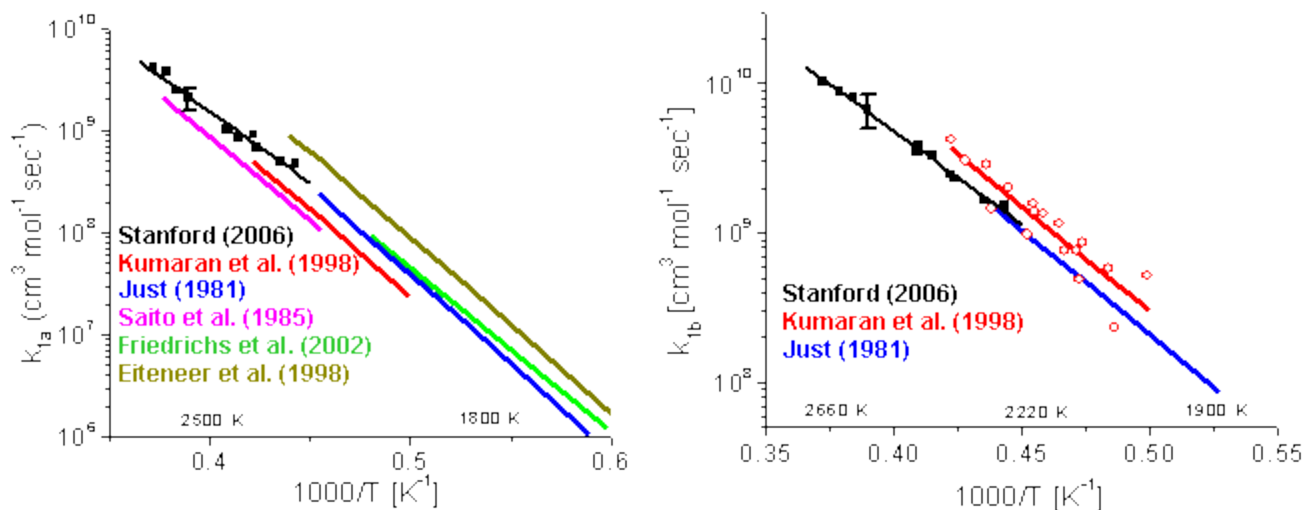


Figure 6: CH₂O+Ar → Products: Comparison with previous work

CH₂O + O₂ → HCO + HO₂

The reaction between CH₂O and O₂, (2) CH₂O + O₂ → HO₂ + HCO, was investigated in shock tube experiments. The rapid thermal decomposition of HCO and HO₂ generate H-atoms that react with O₂ to produce OH. Rate coefficients were inferred by matching measured and modeled OH time-histories behind the reflected shock, under conditions where interference from secondary chemistry is minimal. As in the formaldehyde decomposition measurements, trioxane was used as the formaldehyde precursor and OH was monitored by narrow linewidth laser absorption at 306.7 nm.

An example experiment is presented in Figure 7, while a comparison of the current measurements with previous work is shown in Figure 8.

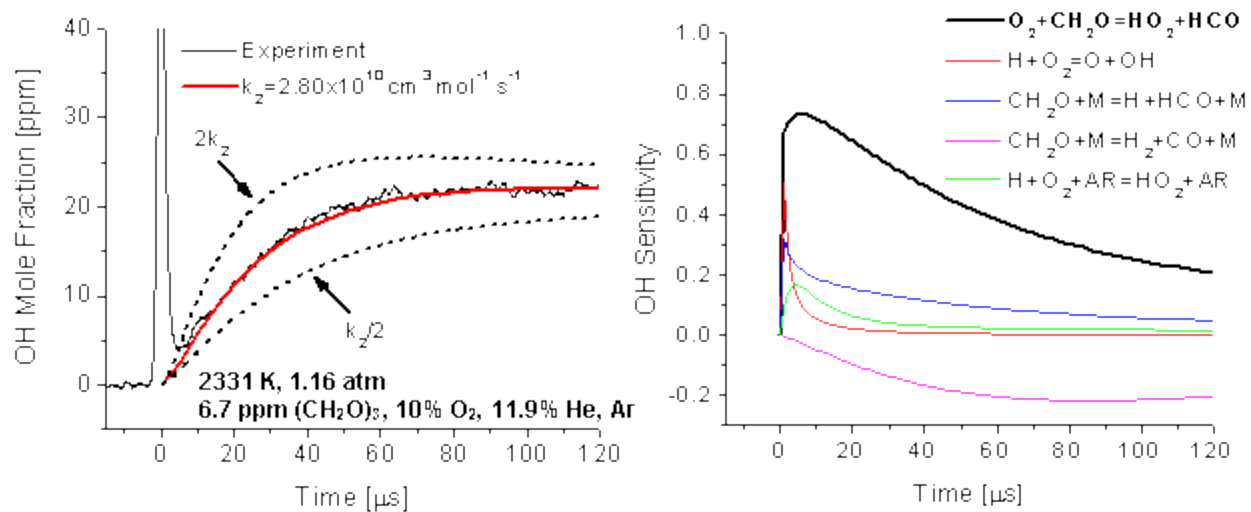


Figure 7: $\text{CH}_2\text{O}+\text{O}_2 \rightarrow \text{HCO}+\text{HO}_2$: Example experiment and sensitivity

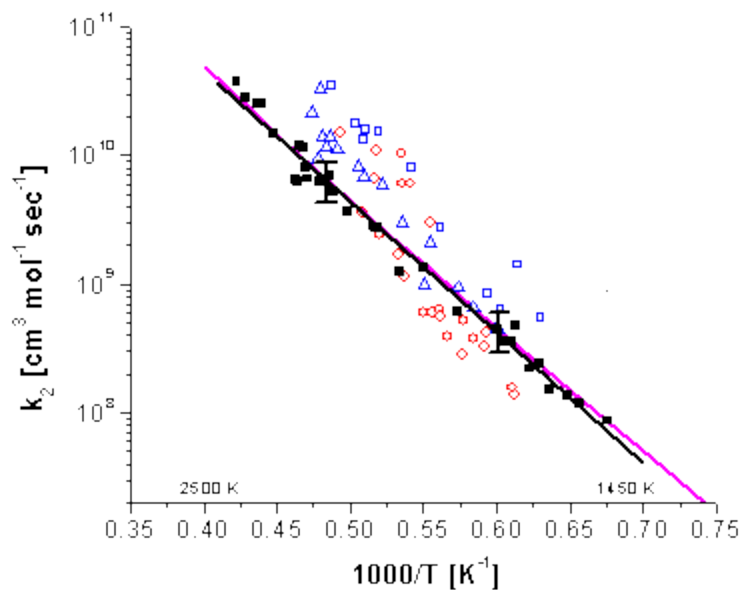


Figure 8: $\text{CH}_2\text{O}+\text{O}_2 \rightarrow \text{HCO}+\text{HO}_2$: Comparison with previous work

References

1. V. Vasudevan, D.F. Davidson, R.K. Hanson, C.T. Bowman, and D.M. Golden, "High-Temperature Measurements of the Rates of the Reactions $\text{CH}_2\text{O}+\text{Ar}$? Products and $\text{CH}_2\text{O}+\text{O}_2$? Products," Proc. Comb. Inst 31, 2006 (in press).
2. V. Vasudevan, D.F. Davidson, and R.K. Hanson, "Direct Measurements of the Reaction $\text{OH} + \text{CH}_2\text{O} \rightarrow \text{HCO} + \text{H}_2\text{O}$ at High Temperatures," Int. J. of Chem. Kinetics 37, 98-109 (2005).