A Comprehensive Kinetic Mechanism for C_1 Species Combustion

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30th International Symposium on Combustion, Chicago, IL, July 25-30, 2004

Motivation

❖ C_1 species are of practical importance:
- CO is a primary intermediate of hydrocarbon combustion
- emission of CH_2O from combustion engines has been a great environmental concern because it is a suspected carcinogen and can contribute to photochemical smog
- CH_3OH is a widely used oxygenate additive in reformulated gasoline, and is an attractive alternative to traditional transportation fuels

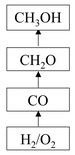
❖ Chemical kinetics of C_1 species plays a critical role in hydrocarbon combustion chemistry:
- the conversion of CO to CO_2 is highly exothermic portion of any hydrocarbon oxidation system
- nearly all carbon atoms in alkyl hydrocarbons and aromatics are converted to CO through CH_2O and HCO
- study of CH_3OH oxidation mechanism lays a foundation for the study of larger alcohols chemistry, and can provide useful information regarding CH_2O reactions

Outline of the Present C_1 Mechanism

❖ The mechanism consists of 85 elementary reactions among 21 species, and is based on the CH_3OH/O_2 mechanism of Held and Dryer (1998).

❖ Revisions encompass recently published kinetic and thermochemical information, while continuing to predict both new experiments and the experimental targets investigated by the original mechanism.

❖ It is developed in a hierarchical manner:



At each level, the sub-mechanism is tested against a wide range of experimental data:
- Species time history in a flow reactor
- Ignition delay data in shock tubes
- Laminar premixed flame speeds
- Other data (stirred reactor, burner-stabilized flame, etc)

Key Mechanism Refinements
Part I: CO + OH = CO_2 + H

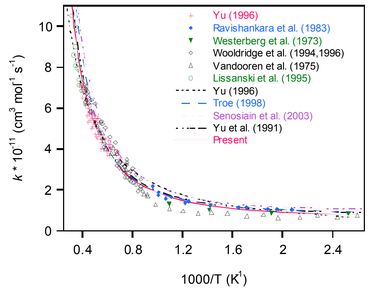
❖ this reaction is the main pathway to convert CO to CO_2 and is responsible for a major fraction of the energy release derived in hydrocarbon oxidation

❖ recent theoretical calculations predict higher rates than experimental measurements at low to intermediate temperature range

❖ the temperature-dependent sensitivity analysis of Zhao et al. (this symposium, poster 1F2-13) demonstrates that the laminar flame speed of CO oxidation systems is most sensitive to this reaction at 300-1900 K

❖ The mechanism uses a new, weighted least squares fit of all of the experimentally measured rate constants available in literature. The expression obtained for the rate constant is:

$$k = 2.23\times10^{5}\, T^{1.89} \exp(-\frac{583}{T})$$



Key Mechanism Refinements
Part II: HCO + M = H + CO + M

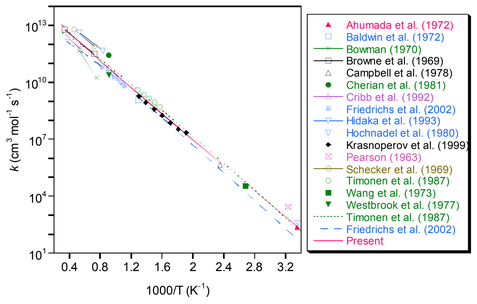
❖ this reaction is the main pathway generating CO during the high temperature combustion of hydrocarbons.

❖ the temperature-dependent sensitivity analysis of Zhao et al. (this symposium, poster 1F2-13) demonstrates that the laminar flame speed of hydrocarbon combustion systems is most sensitive to this reaction at 1300-2000 K, which is above the temperature range of recent experimental studies of this reaction (Friedrichs et al., 2002).

❖ Extrapolation of Friedrichs et al. causes difficulties in reproducing flame speed and flow reactor results for numerous hydrocarbons

❖ In the present study, the method of least squares fitting was applied using experimental data available in literature, and this gives a new expression of the rate constant of this reaction:

$$k = 4.75\times10^{11}\, T^{0.66} \exp(-\frac{7485}{T})$$



Full Set of Updated Kinetic Parameters

❖ Reaction rate coefficients:
- H_2/O_2 sub-mechanism: Li et al. (Int. J. Chem. Kinet. 2004, in press)
- CO + OH = CO_2 + H: this study
  - weighted least squares fitting of experimental results in literature
- HCO + M = H + CO + M: this study
  - weighted least squares fitting of experimental results in literature
- CH_2O decomposition reactions: Friedrichs et al. (Int. J. Chem. Kinet. 2004, 36, 157)
- CH_2O + H = HCO + H_2: Irdam et al. (Int. J. Chem. Kinet. 1993, 25, 285)
- CH_2O + HO_2 = HCO + H_2O_2: Eiteneer et al. (J. Phys. Chem. A 1998, 102, 5196)
- CH_3OH decomposition reactions: GRI-MECH 3.0 (1999)

❖ Thermodynamic data:
- OH: Ruscic et al. (J. Phys. Chem. A 2002, 106, 2727)
- CH_3: Ruscic et al. (J. Phys. Chem. A 1999, 103, 8625)
- CH_2OH: Johnson and Hudgens (J. Phys. Chem. 1996, 100, 19874)

Literature CO Experiments Used for Validation

Method	Source	Mixture	T (K)	P (atm)	ϕ
Shock Tube	Gardiner et al. (1971)	CO/H_2/O_2/Ar	1400– 2500	0.15– 0.3	0.40
	Dean et al. (1978)	CO/H_2/O_2/Ar	2000 – 2850	1.2 – 2.2	1.6– 6.1
Laminar Premixed Flame	McLean et al. (1994)	CO/H_2/air	298	1	0.5 – 6.0
	Huang et al. (2003)	CO/H_2/N_2/air	298	1	0.7– 1.4
Flow Reactor	Yetter et al. (1991)	CO/H_2/O/O_2/N_2	1033	1	0.4 – 1.4
	Kim et al. (1994)	CO/H_2/O/O_2/N_2	960 – 1200	1.0 – 9.6	0.3 – 2.1
	Mueller et al. (1999)	CO/H_2O /O_2/N_2	1038	1.0 – 9.6	1.0

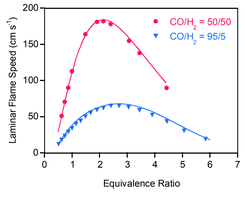
Literature CH_2O Experiments Used for Validation

Method	Source	Mixture	T (K)	P (atm)	ϕ
Shock Tube	Dean et al. (1980)	$CH_2O/O_2/Ar$	1935 – 2150	1.1 – 1.3	pyrolysis – 0.67
	Buxton and Simpson (1986)	CH_2O/Ar	1750 – 2100	0.6 – 3.5	pyrolysis
	Hidaka et al. (1993)	$CH_2O/O_2/Ar$	1240 – 1950	1.5 – 2.9	pyrolysis – 4.0
	Eiteneer et al. (1998)	$CH_2O/O_2/Ar$	1440 – 2120	0.9 – 2.3	pyrolysis – 6.0
	Friedrichs et al. (2002)	CH_2O/Ar	955 – 975	0.3 – 1.8	pyrolysis
Burner-Stabilized Flame	Vandooren et al. (1986)	CH_2O/O_2	300	0.03	0.22
Flow Reactor	Hochgreb and Dryer (1992)	CH_2O /O_2/N_2	945 – 1095	1	0.013– 1.74
	Scire (2002)	CH_2O /$H_2O/O_2/N_2$	850 – 950	1.5 – 6.0	~ 0.005

Literature CH_3OH Experiments Used for Validation

Method	Source	Mixture	T (K)	P (atm)	ϕ
Shock Tube	Bowman (1975)	$CH_3OH/O_2/CO$ /Ar	1545 – 2180	1.2 – 4.7	0.375 – 6.0
Laminar Premixed Flame	Egolfopoulos et al. (1992)	CH_3OH/air	318 – 368	1.0	0.5 – 2.0
Flow Reactor	Aronowitz et al. (1979)	$CH_3OH/O_2/N_2$	1000 – 1010	1.0	0.05 – 1.6
	Norton and Dryer (1989)	$CH_3OH/O_2/N_2$	1027 – 1034	1.0	0.6 – 1.6
	Held (1993)	$CH_3OH/O_2/N_2$	750 – 1040	1.5 – 20.0	0.3 – 2.6

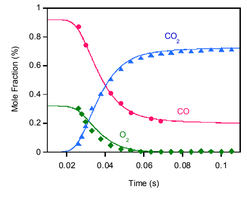
Representative Test Cases
Part I: C_1 Model vs. CO Experiments



Initial Conditions:
298 K, 1 atm, CO/H_2/air mixture

Symbols: laminar flame speed data of McLean et al. (1994)

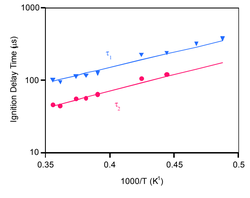
—— : Present model



Initial Conditions:
CO = 0.92%, H_2O = 0.59%, O_2 = 0.32% with balance N_2 at 1034 K and 1 atm

Symbols: flow reactor data of Yetter et al. (1991)

—— : Present model

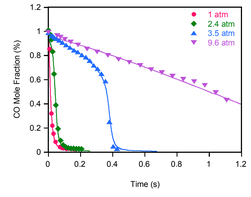


Initial Conditions:
H_2 = 0.049%, O_2 = 1.01%, CO = 3.28% with balance Ar

τ_1 and τ_2 are defined as the time when $[CO_2]$ reaches 2.4×10^{16} and 8×10^{15} molecule/cm^3, respectively.

Symbols: shock tube data of Dean et al. (1978)

—— : Present model

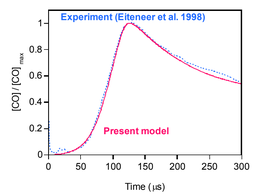


Initial Conditions:
CO = 1.01%, H_2O = 0.65%, O_2 = 0.52% with balance N_2 at 1038 K and 1.0 atm; CO = 1.01%, H_2O = 0.65%, O_2 = 0.50% with balance N_2 at 1038 K and 2.4 atm; CO = 0.99%, H_2O = 0.65%, O_2 = 0.49% with balance N_2 at 1038 K and 3.5 atm; CO = 0.99%, H_2O = 0.65%, O_2 = 0.49% with balance N_2 at 1040 K and 9.6 atm

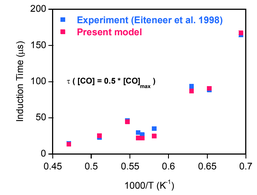
Symbols: flow reactor data of Mueller et al. (1999)

_____ : Present model

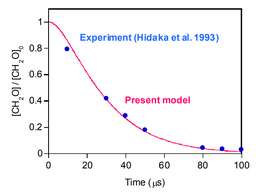
Representative Test Cases
Part II: C_1 Model vs. CH_2O Experiments



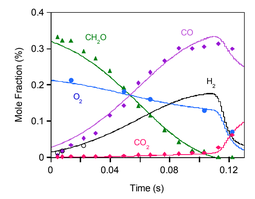
Initial Conditions:
CH_2O = 1.5% , O_2 = 1.5% with balance Ar at 1532 K and 1.35 atm,
CH_2O/O_2/Ar mixture in a shock tube



Initial Conditions:
0.9 – 2.3 atm, CH_2O = 0.5 – 2.0%, ϕ = 0.2 – pyrolysis, CH_2O/O_2/Ar mixture in a shock tube



Initial Conditions:
CH_2O = 4.0% with balance Ar at 1805 K and 2.81 atm, CH_2O/Ar mixture in a shock tube

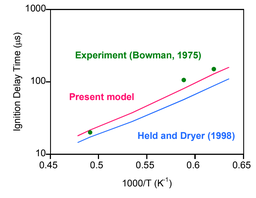


Initial Conditions:
CH_2O = 0.348%, O_2 = 0.223% with balance N_2 at 945 K and 1 atm

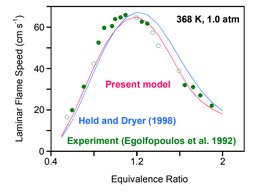
Symbols: flow reactor data of Hochgreb and Dryer (1992)

—— : Present model

Representative Test Cases
Part III: C_1 Model vs. CH_3OH Experiments



Initial Conditions:
2.9 – 3.3 atm, CH_3OH = 1.0%, ϕ = 1.5
CH_3OH/O_2/Ar mixture in a shock tube



Laminar flame speed of CH_3OH/air mixture

- The present mechanism has improved predictive capability over Held and Dryer mechanism (1998)
- The agreement of the present mechanism with other literature experiments is also very good

Summary

❖ A detailed chemical kinetic mechanism for C_1 species (CO, CH_2O, and CH_3OH) combustion has been developed hierarchically

❖ The mechanism has been verified against a wide range of experimental data, and demonstrates very good predictive capabilities for CO, CH_2O, and CH_3OH combustion

❖ Mechanism is available in Chemkin II format from our Web site or by contacting the authors

Acknowledgements

This study was supported by the U.S. Department of Energy, Office of Basic Sciences through Grant No. DE-FG02-86ER-13503, and by NASA under Grant No. NCC3-735.