Electronic Supplementary Information (ESI)

for

Modeling of aromatics formation in fuel-rich methane oxy-combustion with an automatically generated pressure-dependent mechanism

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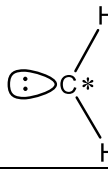
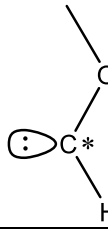
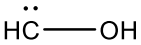
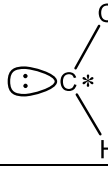
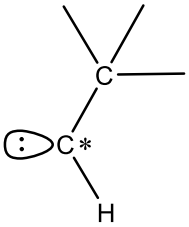
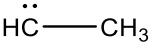
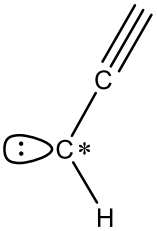
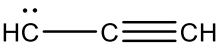
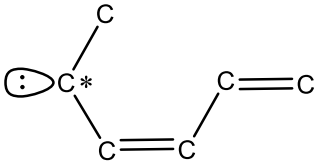
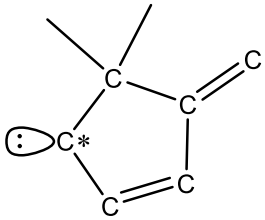
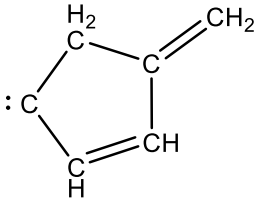
Table S1. Details of singlet carbene thermochemistry group corrections added to RMG

Group	Name	Source of Thermochemistry	Ref.
	CJ2_singlet	CsJ2_singlet-CsH	[1]
	CsJ2_singlet-HH	$:CH_2$	[1]
	CsJ2_singlet-OsH		[1]
	CsJ2_singlet-CH	CsJ2_singlet-CsH	[1]
	CsJ2_singlet-CsH		[1]
	CsJ2_singlet-CtH		[1]
	CsJ2_singlet-(Cds-Cds-Cds-C)C	CsJ2_singlet-(Cds-Cds-Cds-Cds)Cs_6_ring	[2]
	CsJ2_singlet-(Cds-Cds-Cds-Cds)Cs_5_ring		[2]

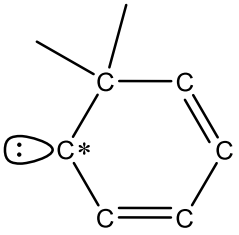
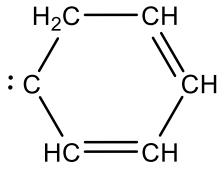
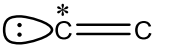
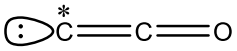
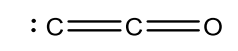
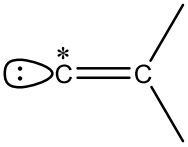
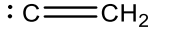
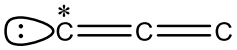
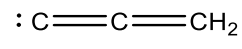
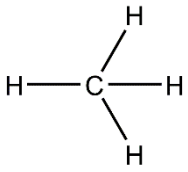
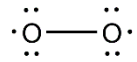
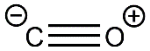
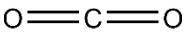
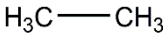
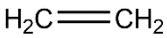
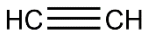
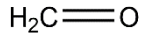
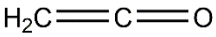
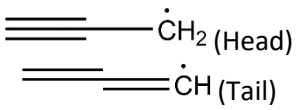
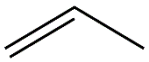
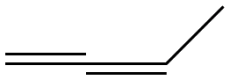
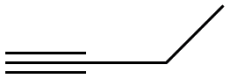
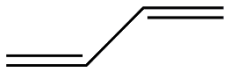
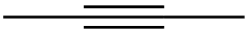
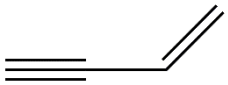
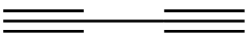
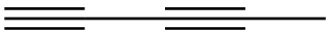
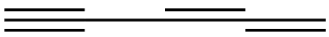
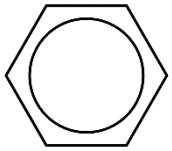
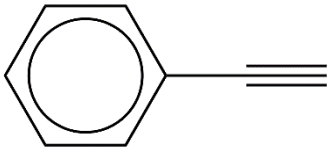
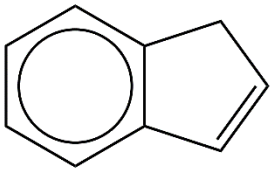
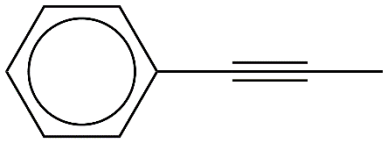
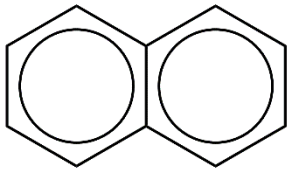
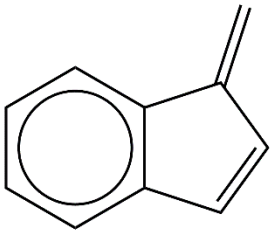
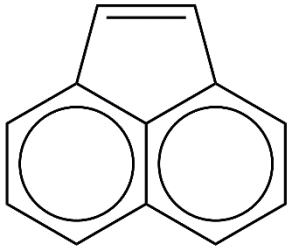
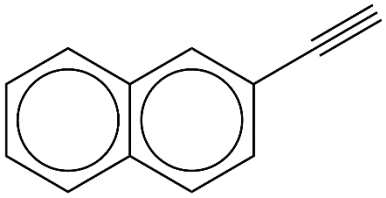
	CsJ2_singlet-(Cds-Cds-Cds-Cds)Cs_6_ring		2
	CdJ2_singlet-Cd	CdJ2_singlet-Cds	1
	CdJ2_singlet-(Cdd-Od)		1
	CdJ2_singlet-Cds		1
	CdJ2_singlet-(Cdd-Cds)		1

Table S2. The name and structure of important isomers in the Chu mechanism

Chemical formula	Species name (in the Chu mechanism)	Structure
CH_4	Methane (CH4)	
O_2	Oxygen (O2)	
CO	Carbon monoxide (CO)	
CO_2	Carbon dioxide (CO2)	
H_2	Hydrogen (H2)	
C_2H_6	Ethane (C2H6)	
C_2H_4	Ethene (C2H4)	
C_2H_2	Acetylene (C2H2-1)	
CH_2O	Formaldehyde (CH2O)	
CH_2CO	Ethenone (C2H2O-1)	
C_3H_3	Propargyl radicals (C3H3-1)	
C_3H_6	Propene (C3H6-1)	
C_4H_6	1,2-Butadiene (C4H6-1)	
	1-Butyne (C4H6-2)	
	1,3-Butadiene (C4H6-5)	
	2-Butyne (C4H6-7)	
C_4H_4	Vinylacetylene (C4H4-1)	
C_4H_2	Diacetylene (C4H2-1)	
C_5H_4	1,3-Pentadiyne (C5H4-1)	
	1,2-Pentadien-4-yne (C5H4-4)	

C_6H_6	Benzene (C6H6-17)	
C_8H_6	Phenylacetylene (C8H6)	
C_9H_8	Indene (C9H8-3)	
	1-Propynylbenzene (C9H8-4)	
$C_{10}H_8$	Naphthalene (C10H8-1)	
	1-Methylideneindene (C10H8-4)	
$C_{12}H_8$	Acenaphthylene (C12H8-2)	
	2-ethynylnaphthalene (C12H8-4)	

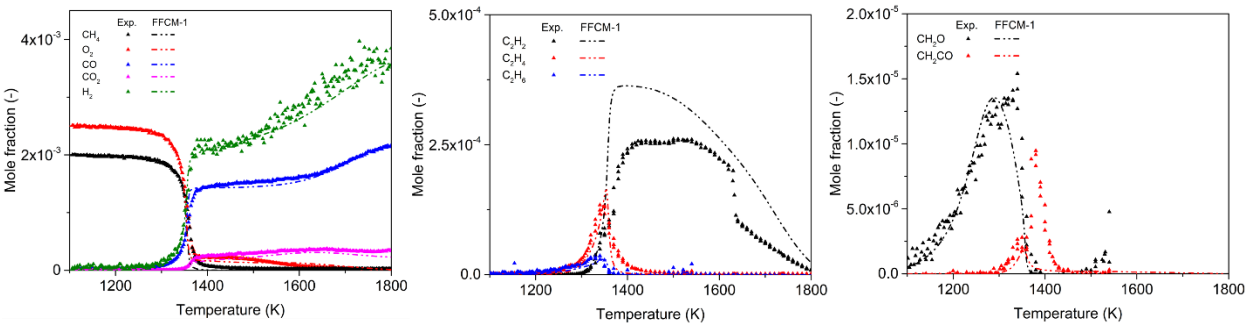


Figure S1. Mole fraction profiles of small molecules for Case I by FFCM-1.

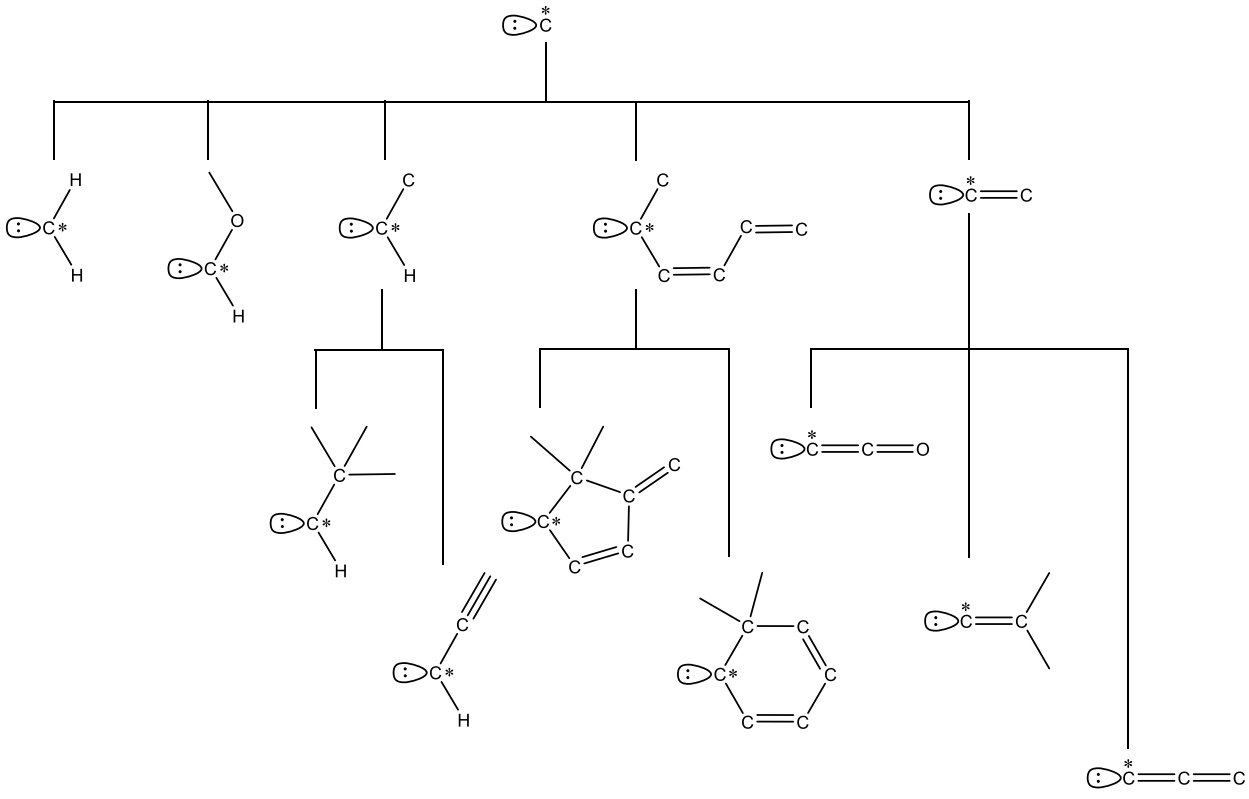


Figure S2. Organization of thermochemistry group corrections for singlet carbenes added to RMG database. Any unspecified ligand or valency is a wild card.

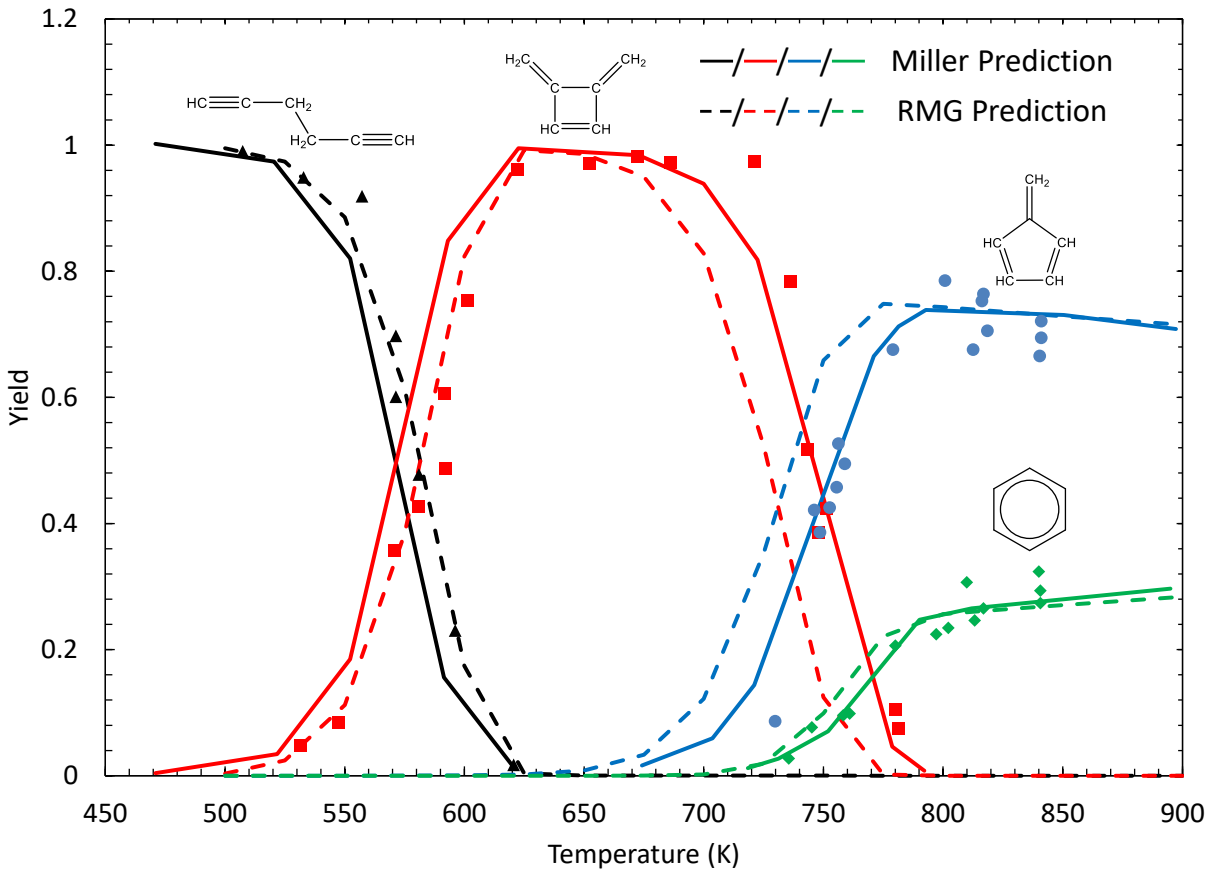


Figure S3. Comparison between predictions of Miller[2] and RMG, following database changes, and 1,5-hexadiyne pyrolysis experiments of Stein *et al.*[3] (symbols).

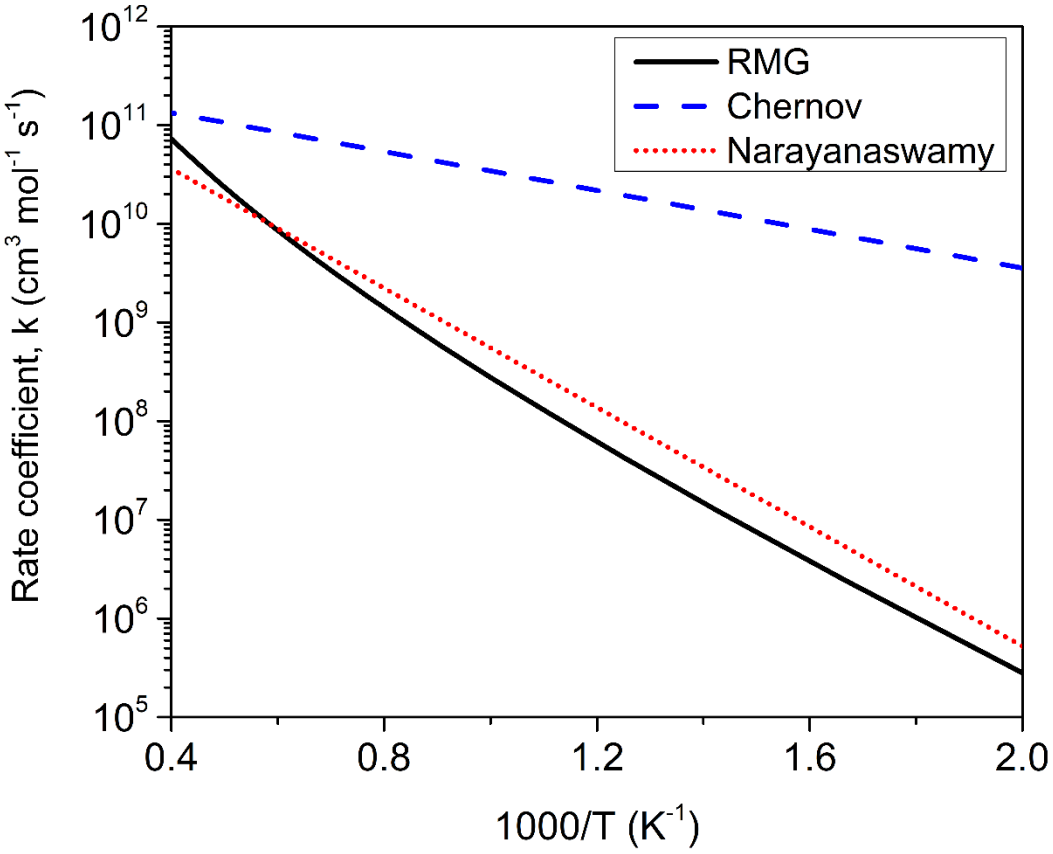


Figure S4. The comparison of rate coefficient k of the reaction $CH_3+O_2 \rightarrow CH_2O+OH$ between the Chu, Chernov, Narayanaswamy mechanism.

Quantification of H_2 by the atom balance method:

The process of converting mass spectrometry signals into mole fractions has a higher uncertainty for H_2 than for the other major species quantified, and as shown below if one just uses the relatively uncertain H_2 mole fractions reported in Ref. 4 the measured number of H atoms coming out of the reactor is apparently significantly lower than the number of H atoms fed into the reactor in Cases II, IV, and V. So we developed a different method, based on atom balance, for determining the H_2 mole fractions from the experimental data.

At the highest temperature in this work (~1800 K), only major species (CH_4, O_2, CO, CO_2, H_2 and H_2O) and acetylene (C_2H_2) have non-negligible signals found in the experiments; therefore, only these species are considered in the atom balance analysis. However, since H_2O could not be directly quantified, O-atom balance is needed to evaluate the mole fraction of H_2O. Next, we use the quantified H_2O concentration to perform H-atom balance, and quantify the mole fraction of H_2. The uncertainty of H_2 is determined by the uncertainty propagation method.

O-atom balance (if no CO or CO_2 in the feed):

$$2x_{O_2,initial} = x_{CO} + 2x_{CO_2} + x_{H_2O} \text{ (at 1800 K)}$$

H-atom balance:

$$4x_{CH_4,initial} + 2x_{C_2H_2,initial} = 4x_{CH_4} + 2x_{H_2O} + 2x_{H_2} + 2x_{C_2H_2} \text{ (at 1800 K)}$$

Putting these together, the H_2 mole fraction inferred from atom balance is given by:

$$x_{H_2(@1800\,K)} = 2x_{CH_4,initial} + x_{C_2H_2,initial} - 2x_{CH_4(@1800\,K)} - x_{C_2H_2(@1800\,K)} + x_{CO(@1800\,K)} + x_{CO_2(@1800\,K)} - 2x_{O_2,initial}$$

To obtain the H_2 mole fraction profiles, the H_2 mole fractions evaluated by the direct measurement and the atom balance method at 1800 K were compared to give a Scaling Factor for H_2 for each Case. The assumption here is that during a single experimental Case the response factor for H_2 is fairly steady. However, apparently the H_2 response factor of the instrument varies a little bit (~20%) between experimental Cases; this Scaling Factor corrects for that variation in absolute response:

Scaling Factor = ($x_{H_2(@1800\,K)}$ from atom balance equation above) / ($x_{H_2(@1800\,K)}$ from Ref. 4)

The results are summarized in Table S3. The atom balance method was not used in Case III because of its very large uncertainty, caused by the uncertainty propagation due to adding and subtracting large mole fractions of CO and CO_2 only known to a few significant figures.

In every case except Case III, the H_2 mole fractions reported in Ref. 4 were scaled by the Scaling Factor in Table S3. The scaled values and the error bars from Table S3 are plotted in Fig. 2 in the main article. For Case III, the experimental H_2 mole fractions and error bars shown in Fig. 2 are directly from Ref. 4 without any adjustment.

Table S3. Summary of H_2 quantification in this work at 1800 K

	H_2 quantified directly (Ref. 4)	**H_2 quantified by atom balance**	**Uncertainty from atom balance**	**Scaling factor**
Case I	3.85E-03	3.90E-03	8.7%	1.01
Case II	1.77E-03	2.21E-03	31.5%	1.25
Case III	1.18E-03	4.75E-04	290.5%	0.40
Case IV	2.61E-03	3.15E-03	10.4%	1.21
Case V	2.90E-03	3.85E-03	9.8%	1.33

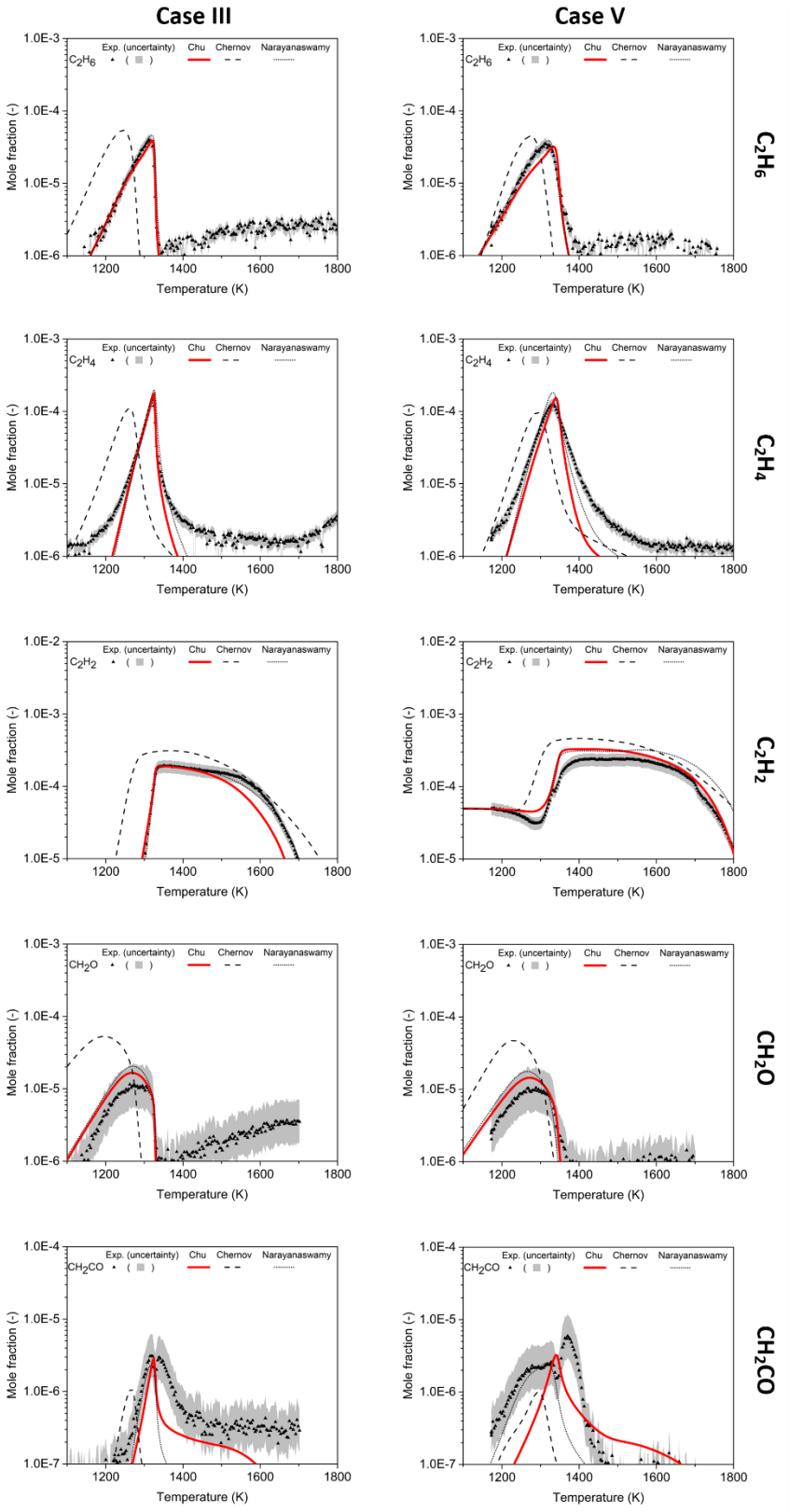


Figure S5. Mole fraction profiles of C_2H_6, C_2H_4, C_2H_2, CH_2O, CH_2CO as a function of oven temperature for Case III and IV, measurements (symbols and uncertainty band) and predictions of three models (lines).

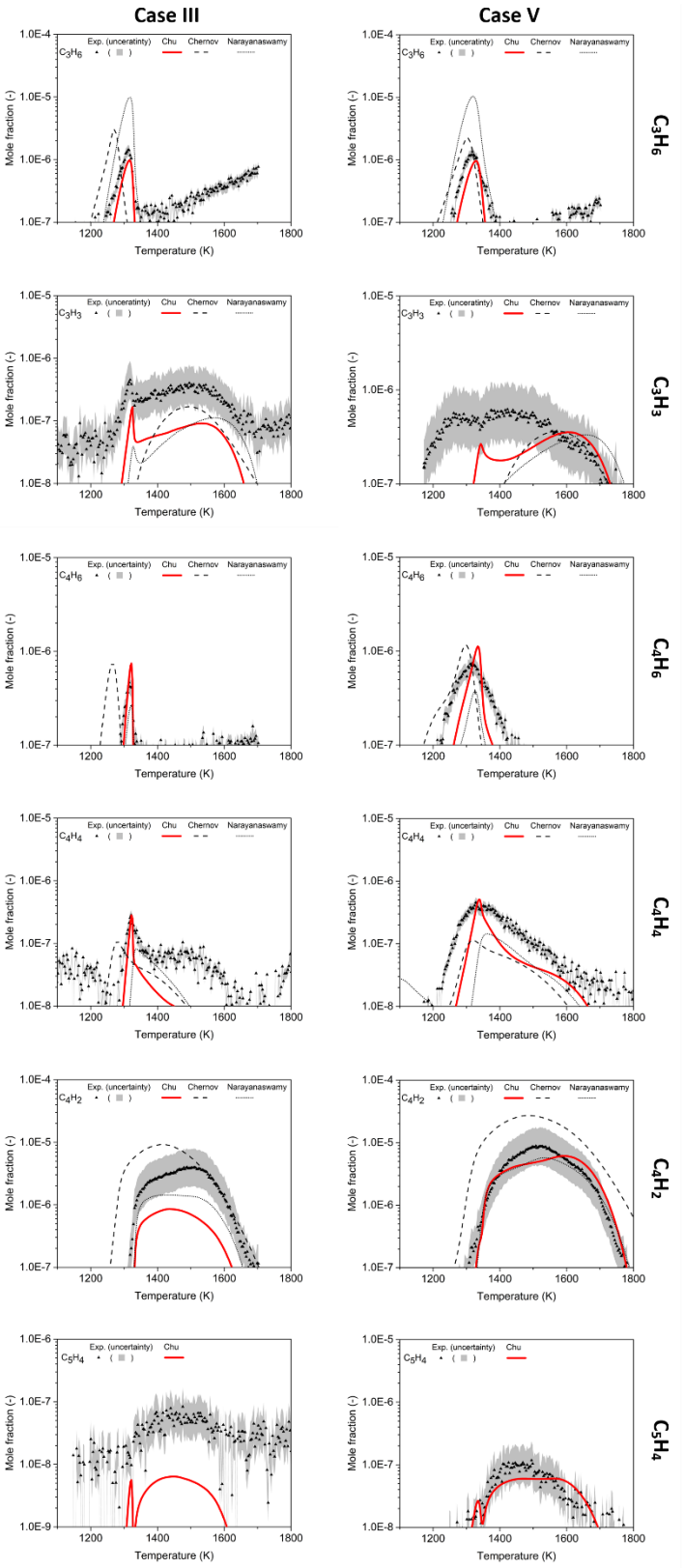


Figure S6. Mole fraction profiles of C_3H_6, C_3H_3, C_4H_6, C_4H_4, C_4H_2, C_5H_4 as a function of oven temperature for Case III and V, measurements (symbols and uncertainty band) and predictions of three models (lines).

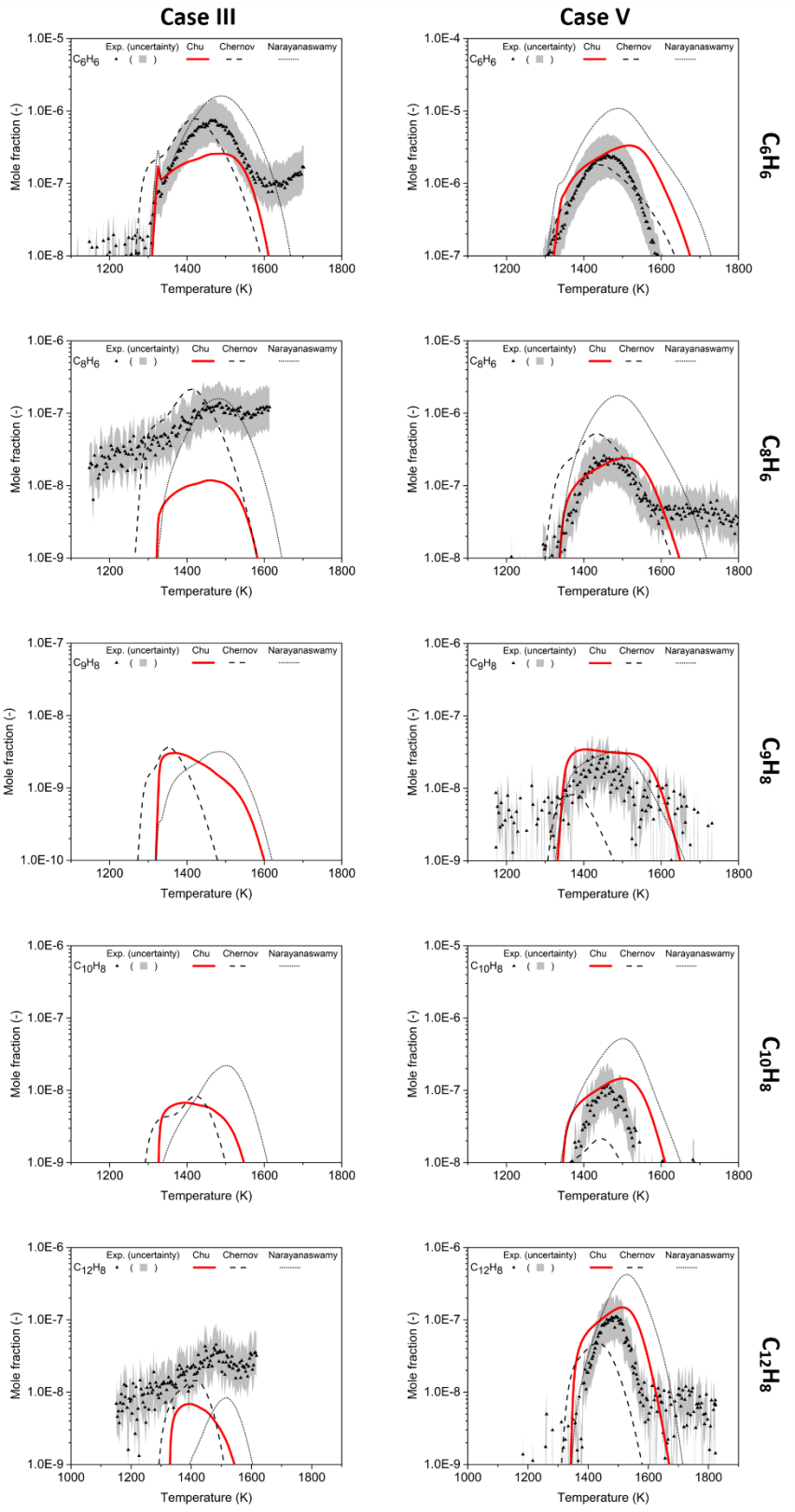


Figure S7. Mole fraction profiles of C_6H_6, C_8H_6, C_9H_8, $C_{10}H_8$, $C_{12}H_8$ as a function of oven temperature for Case III and V, measurements (symbols and uncertainty band) and predictions of three models (lines).

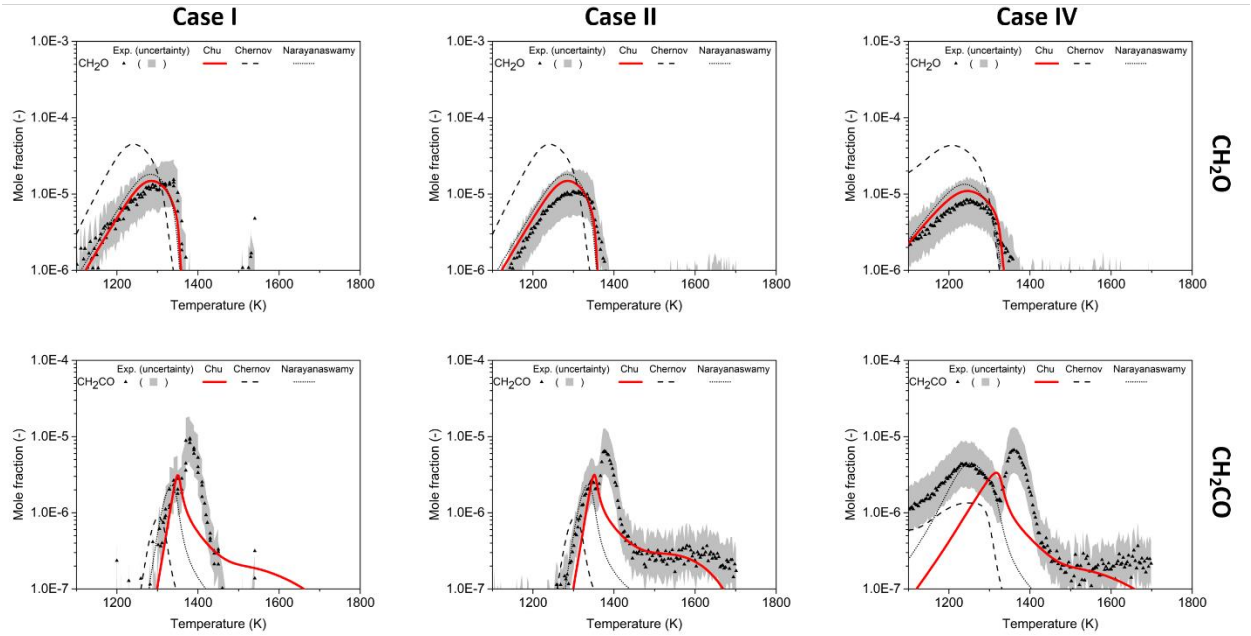


Figure S8. Mole fraction profiles of CH_2O and CH_2CO as a function of oven temperature for Case I, II and IV, measurements (symbols and uncertainty band) and predictions of three models (lines).

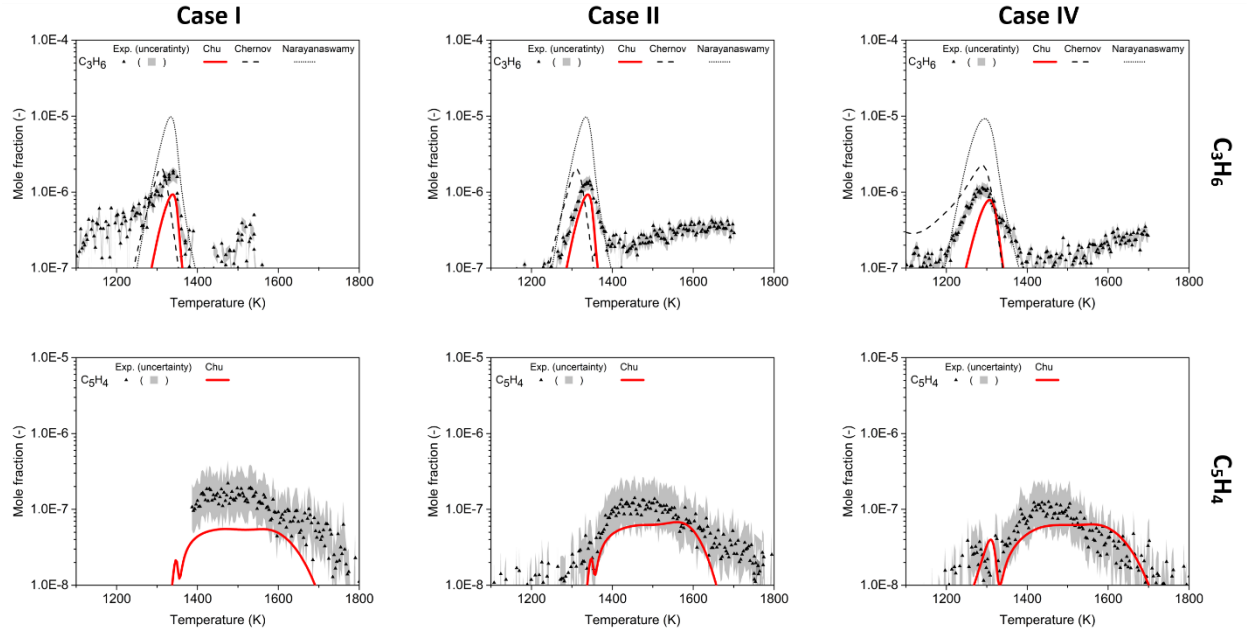


Figure S9. Mole fraction profiles of C_3H_6 and C_5H_4 as a function of oven temperature for Case I, II and IV, measurements (symbols and uncertainty band) and predictions of three models (lines).

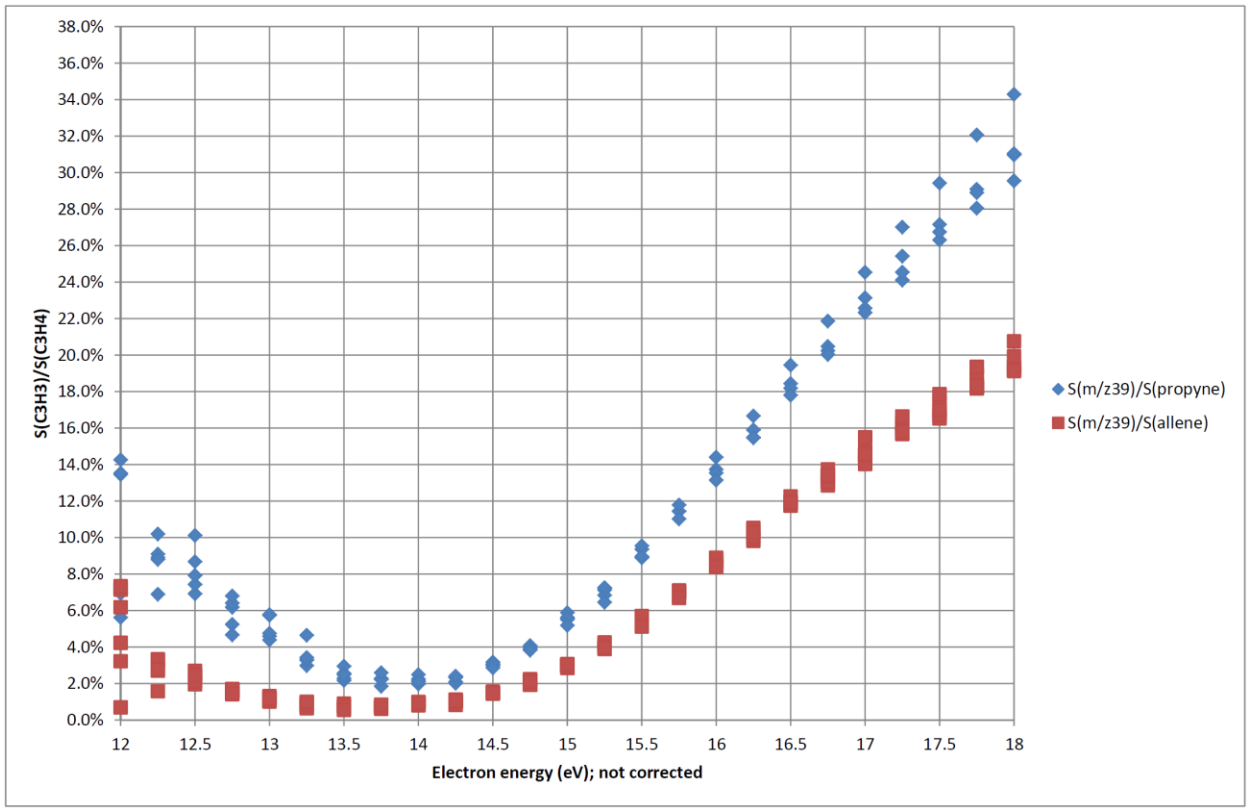


Figure S10. The fragmentation ratio of Signal(C_3H_3)/Signals(C_3H_4) for propyne and allene at various ionization energies.

The contribution of m/z =39 fragments is Atconsidered as follows (at 16 eV):

S(FC3H3) = S(C3H4)*f

S(C3H4) = S(Ar)/x(Ar) * x(C3H4) *k(C3H4, new)

x(FC3H3) = S(FC3H3) * x(Ar)/S(Ar)* 1/k(C3H3, old)

where

S(i): signal of species i, C3H3 = propargyl radicals, C3H4 = propyne or allene, Ar = argon

FC3H3: fragment contribution to the C3H3 signal

f: fragmentation factor (from Figure S10; mean 0.134 for propyne and 0.085 for allene)

x(FC3H3): mole fraction contribution based on C_3H_3 Fragments

k(i): calibration factors (C_3H_3 as used in the original calculation = 3169; C_3H_4 from the new measurements => 1243 for propyne and 1450 for allene)

To combine the equations, we get the following equations:

x(FC3H3) = f*k(C3H4)/k(C3H3) * x(C3H4)

x(FC3H3) = **0.053** * x(propyne)

x(FC3H3) = **0.039** * x(allene)

To validate the effect of fragmentation on the mole fraction profiles, 5.3% of propyne concentration and 3.9% of allene concentration were added to C_3H_3 concentration in the Chu model.

Other supporting information:

1. The full RMG input deck and the RMG version
2. The full mechanism
3. The species dictionary in adjacency list format
4. New experimental quantified in this work

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2. J. A. Miller and S. J. Klippenstein, *The Journal of Physical Chemistry A*, 2003, **107**, 7783-7799.
3. S. E. Stein, J. A. Walker, M. M. Suryan and A. Fahr, *Symposium (International) on Combustion*, 1991, **23**, 85-90.
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