Electronic Supplementary Information

Unimolecular isomerization of 1,5-hexadiyne observed by threshold photoelectron photoion coincidence spectroscopy

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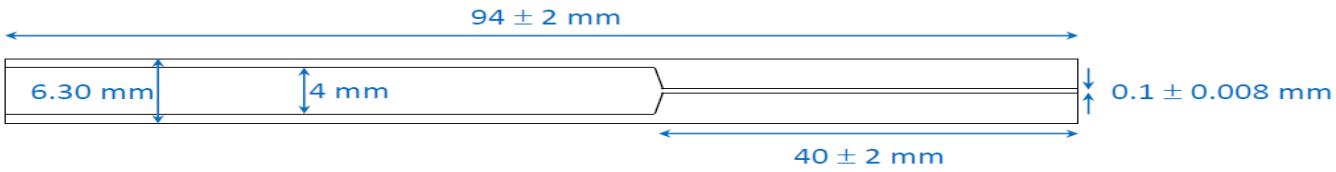

Figure S1: Drawing of the borosilicate pyrolysis reactor. The 32 mm long heated zone is located immediately before the reactor ID decreases from 4 to 0.1 mm.

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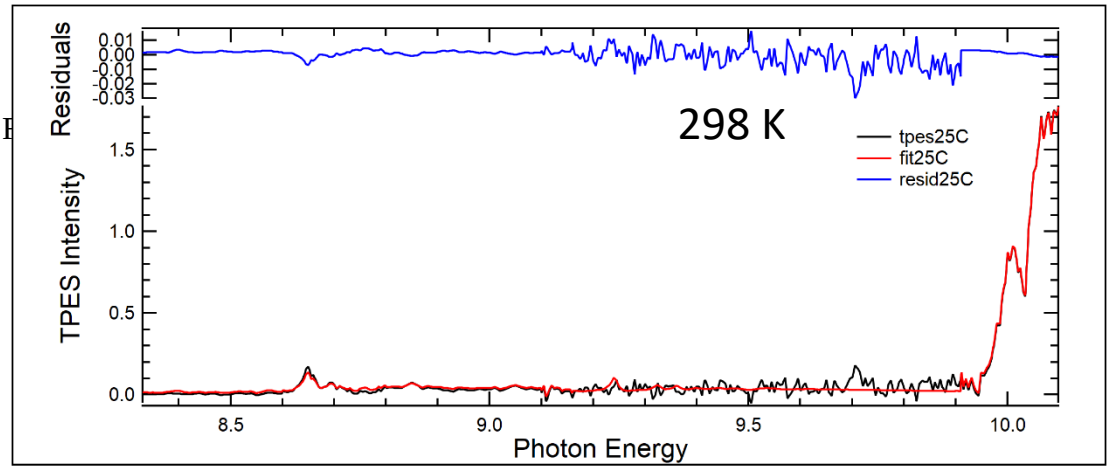
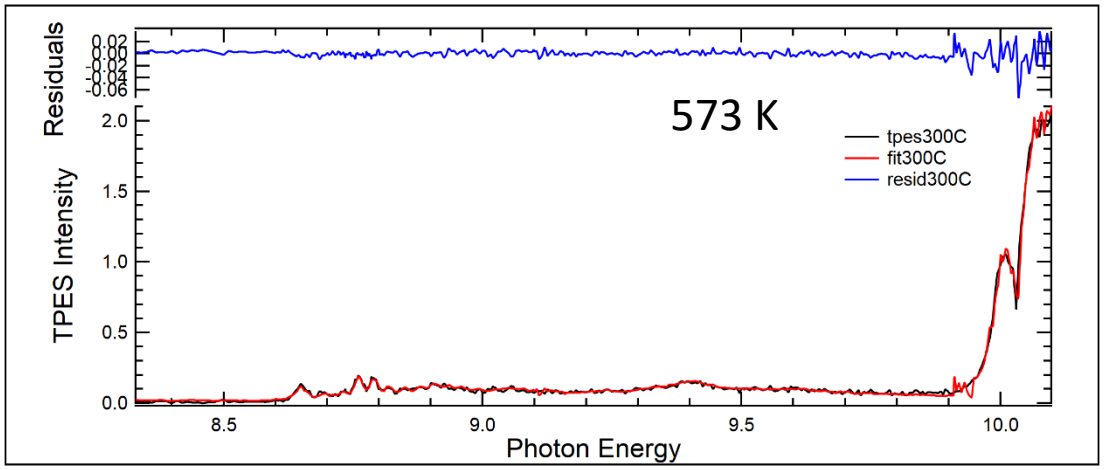
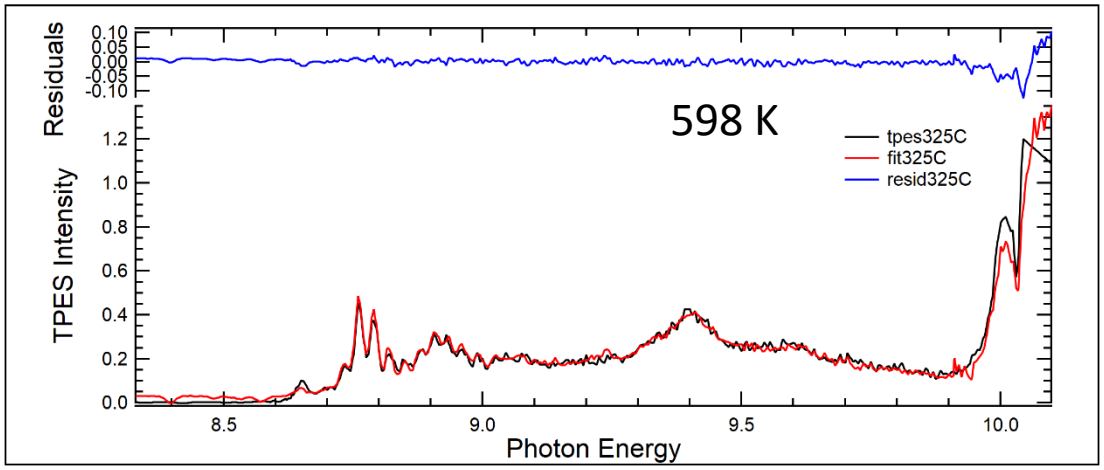
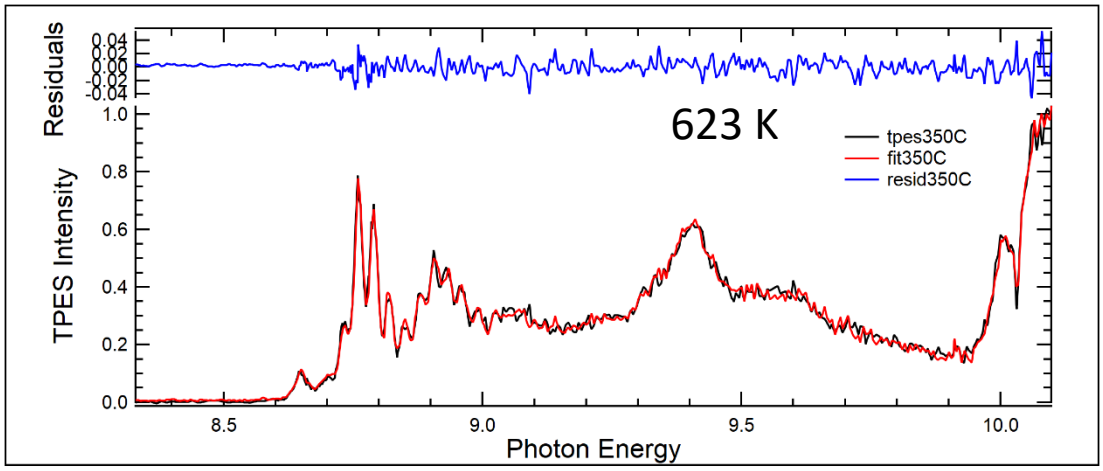
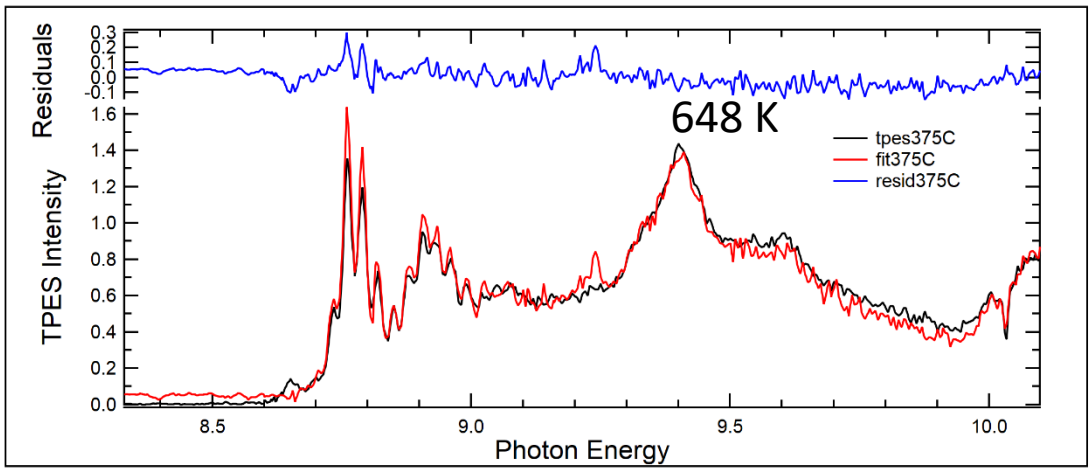
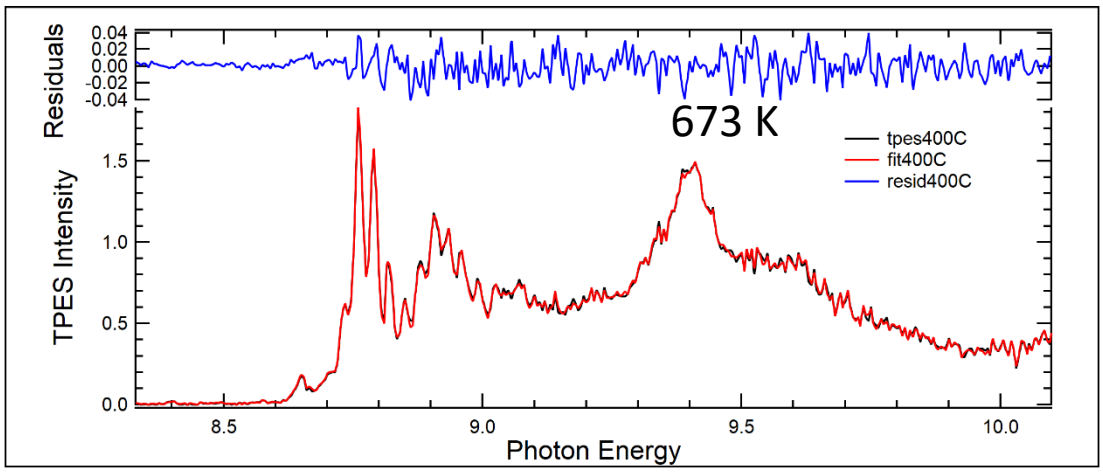

Residuals
TPES Intensity
298 K
tpes25C
fit25C
resid25C
Photon Energy

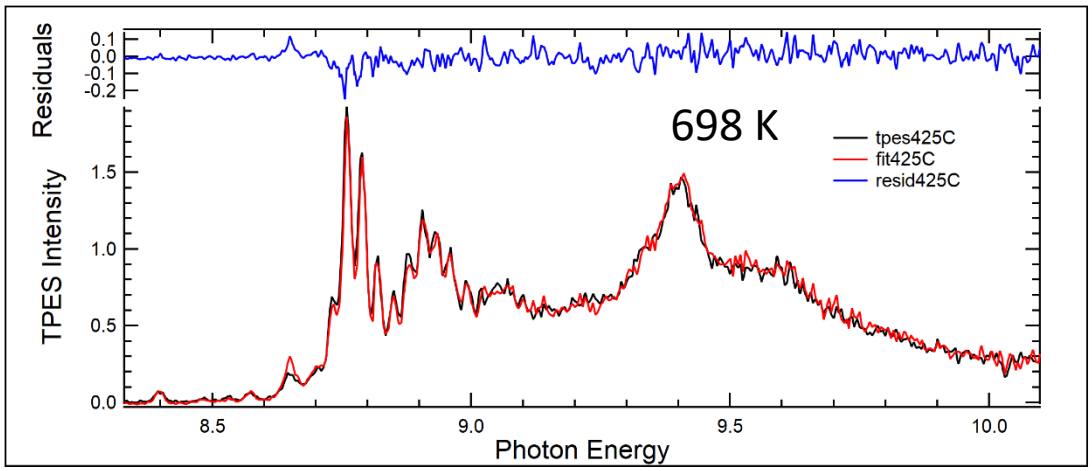

Residuals
TPES Intensity
573 K
tpes300C
fit300C
resid300C
Photon Energy

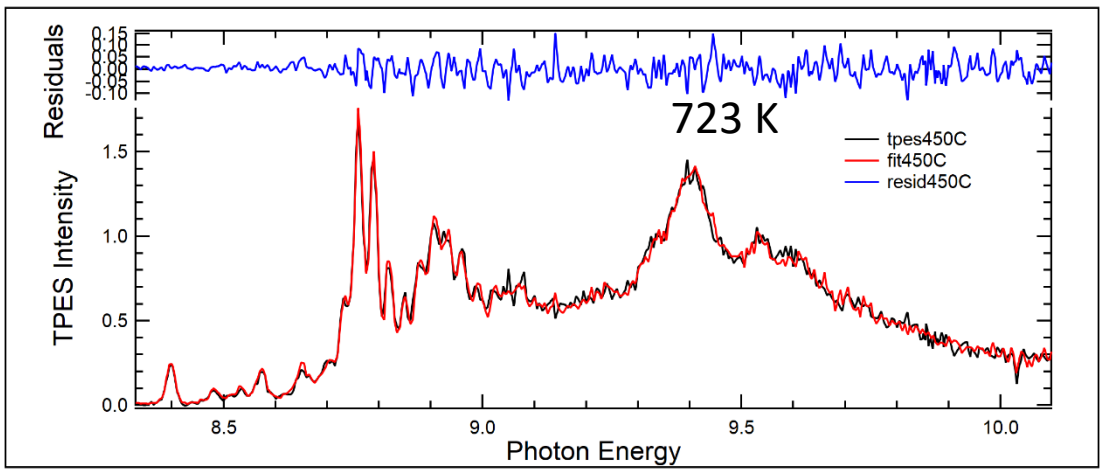

Residuals
TPES Intensity
598 K
tpes325C
fit325C
resid325C
Photon Energy

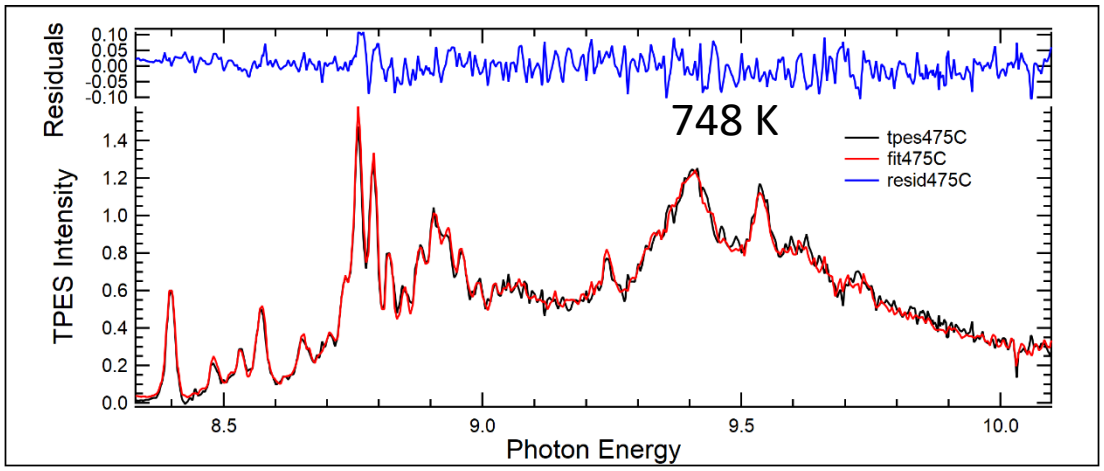

Residuals
TPES Intensity
623 K
tpes350C
fit350C
resid350C
Photon Energy


Residuals
TPES Intensity
648 K
tpes375C
fit375C
resid375C
Photon Energy


Residuals
TPES Intensity
673 K
tpes400C
fit400C
resid400C
Photon Energy


Residuals
TPES Intensity
698 K
tpes425C
fit425C
resid425C
Photon Energy


Residuals
TPES Intensity
723 K
tpes450C
fit450C
resid450C
Photon Energy


Residuals
TPES Intensity
748 K
tpes475C
fit475C
resid475C
Photon Energy

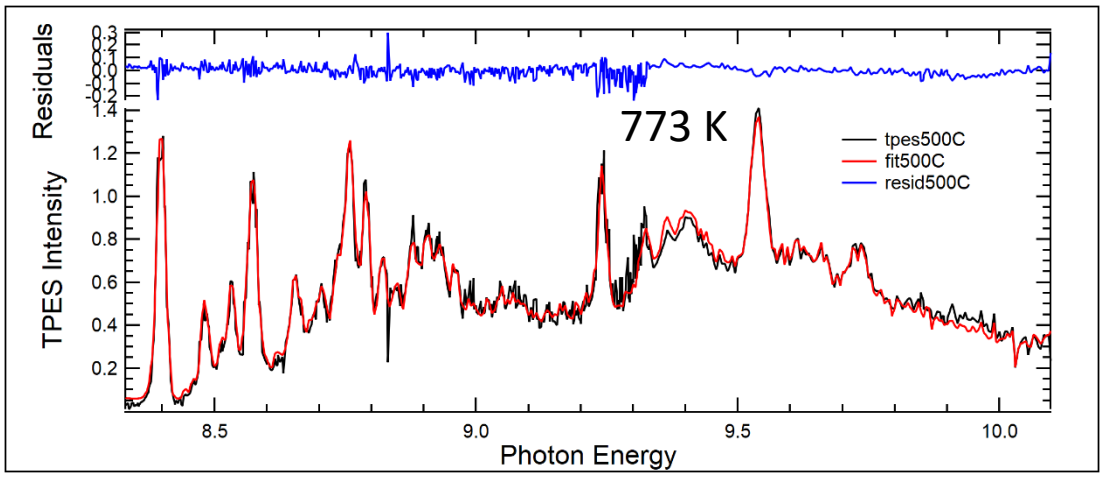


Figure S2: Threshold photoelectron spectra of C_6H_6 isomers (black), fits to the reference functions (red), and fit residuals (blue) for the 10 temperatures used in this study.

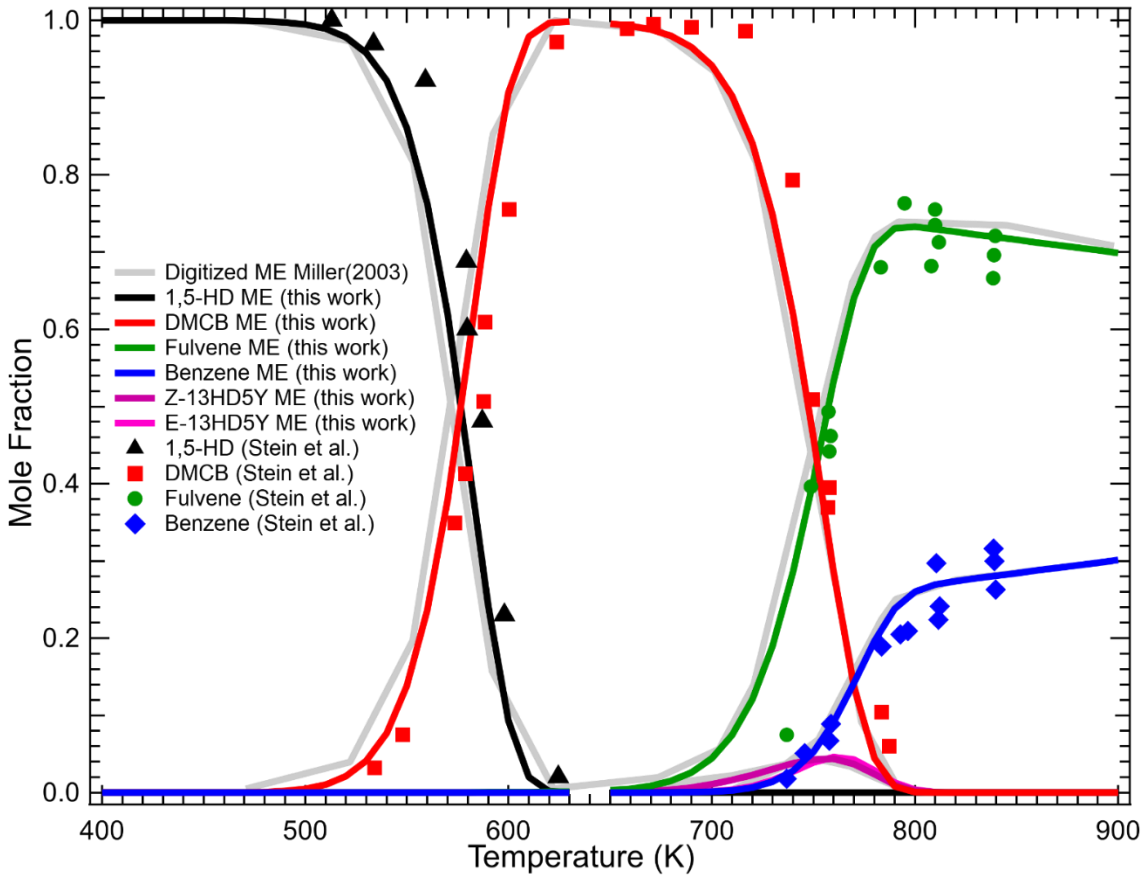


Figure S3: Digitized master equation simulations of Miller and Klippenstein from Fig. 5 of their 2003 paper (grey). Solid lines show the present master equation simulations for a residence time of 30 seconds, corresponding to the experimental data of Stein et al., digitized from their 1990 paper.

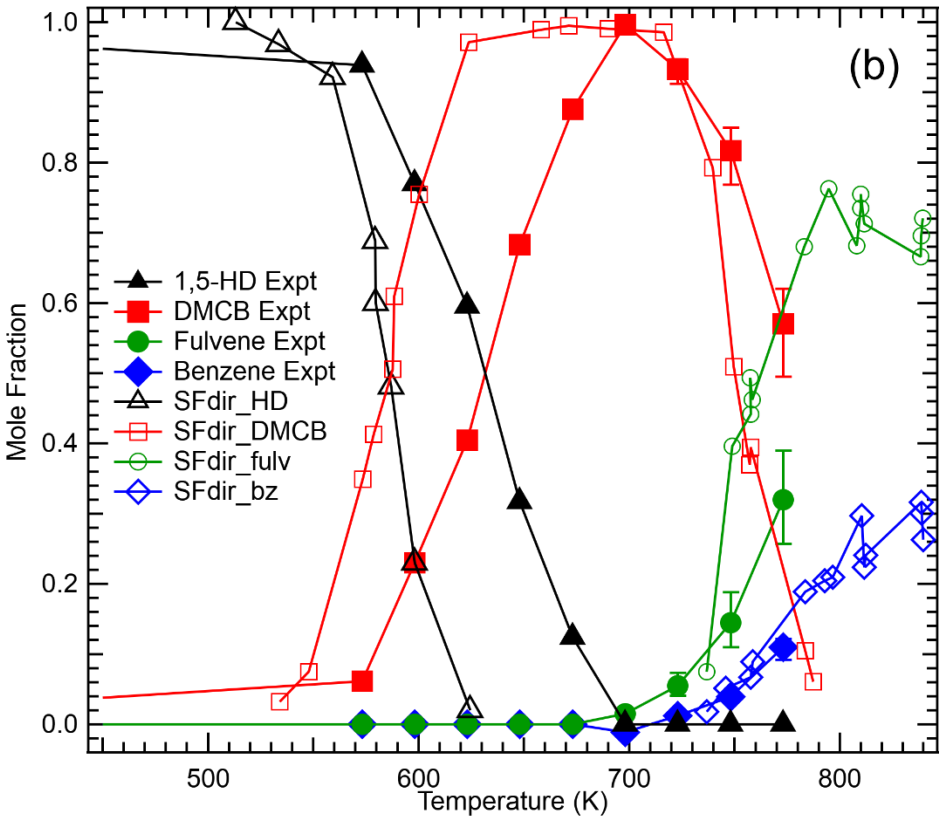


Figure S4: Comparison of the experimental data from Stein et al. (1990, open symbols) to the present experimental data (closed symbols). Note that the residence time for the former data is reported as 30 s, whereas the average residence time of the present data is 11.8 s.

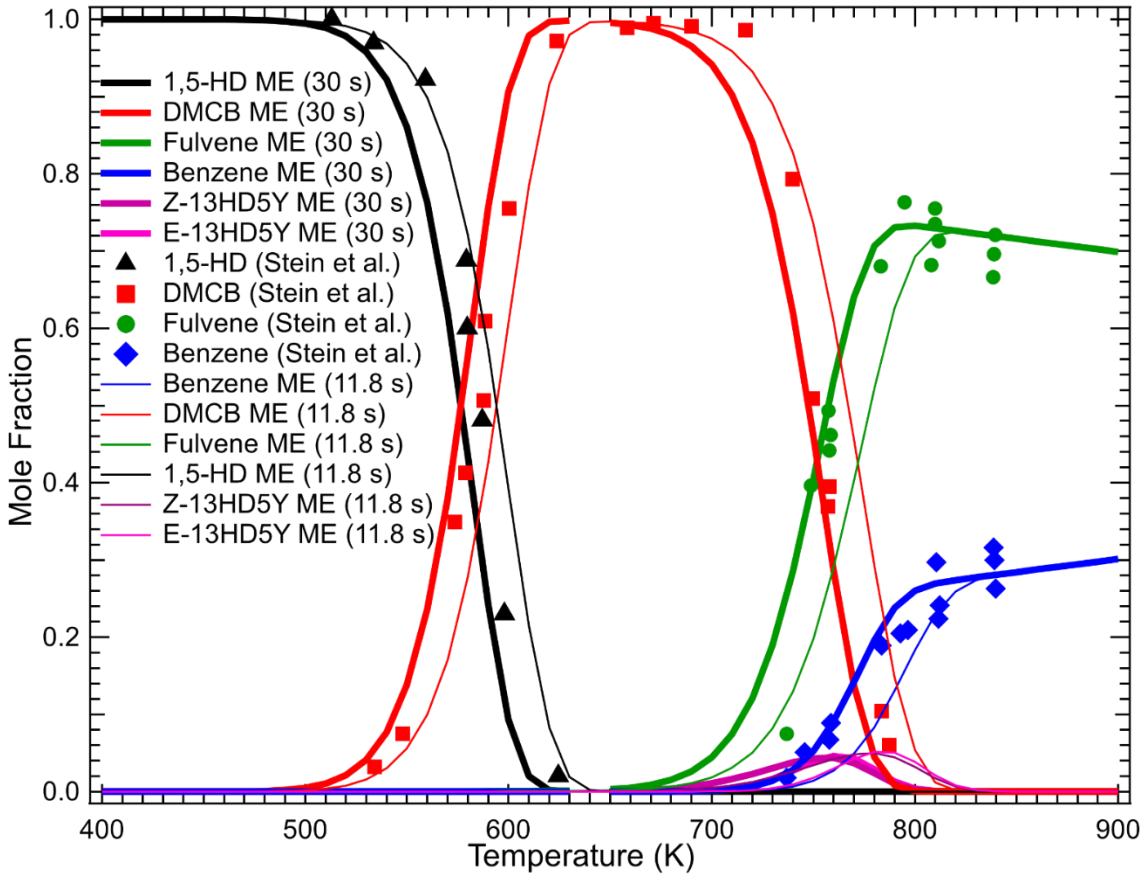


Figure S5: The master equation simulations of Miller and Klippenstein for a residence time of 30 s (thick solid lines), which were used by MK to model the Stein et al. experiments (symbols), are compared with the same master equation model with only the residence time shortened to 11.8 s (thin solid lines). Note that all profiles are nearly uniformly shifted ~ 20 K to higher temperature by the decrease of residence time from 30 to 11.8 s.