Supplemental Material

Figure S1. Mass spectra on a linear scale taken with MgF_2 window ~150 μs after the shock front arrival in a 0.06% C_8H_8/99.94% Ar mixture. Mass spectra are integrated from 8 – 10.5 eV.

Figure S2. Mass spectra on a linear scale from photoionization (top) and electron impact (bottom) TOF-MS experiments ~150 μs post-shock. PI spectra were taken at 1875 ± 25 K, 11.3 ± 0.2 atm, 0.25% C_8H_8/99.75% Ar, and integrated from 8 – 10.5 eV. EI spectra were taken at 1830 ± 25 K, 368 ± 7 Torr, 0.5% C_8H_8/1.0% Ar/98.5% Ne and 21 eV.

Figure S3. Mass spectra on a linear scale from photoionization (top) and electron impact (bottom) TOF-MS experiments pre-shock/non-reactive. PI spectra were taken at 1875 ± 25 K, 11.3 ± 0.2 atm, 0.25% C_8H_8/99.75% Ar, and integrated from 8 – 10.5 eV. EI spectra were taken at 1830 ± 25 K, 368 ± 7 Torr, 0.5% C_8H_8/1.0% Ar/98.5% Ne and 21 eV.

Figure S4. EI time history of m/z 74 at 1830 ± 25 K, 368 ± 7 Torr, 0.5% C_8H_8/1.0% Ar/98.5% Ne and 21 eV. Symbols represent the data, lines are experimental fits for clarity only, and shading is the 95% confidence interval of the experimental fit.

Figure S5. PI time history of m/z 74 with the MgF_2 filter at 1875 ± 25 K, 11.3 ± 0.2 atm, 0.25% C_8H_8/99.75% Ar, and integrated from 8 – 10.5 eV. Symbols represent the data, lines are experimental fits for clarity only, and shading is the 95% confidence interval of the experimental fit.

Figure S6. Simulation of $[C_8H_6]/[C_8H_8]$ at 150 μs in a constant volume reactor showing the effect of pressure.

Figure S7. Percentage that R2: $C_8H_8 \rightarrow \beta\text{-}C_8H_7 + H$ comprises of the total styrene decomposition rate based upon the current mechanism. The conditions of the current study and literature studies are emphasized.

Figure S8. Percentage that R3: $C_8H_8 \rightarrow o\text{-}C_8H_7 + H$ comprises of the total styrene decomposition rate based upon the current mechanism. The conditions of the current study and literature studies are emphasized.

Figure S9. Percentage that R4: $C_8H_8 \rightarrow m\text{-}C_8H_7 + H$ comprises of the total styrene decomposition rate based upon the current mechanism. The conditions of the current study and literature studies are emphasized.

Figure S10. Percentage that R5: $C_8H_8 \rightarrow p\text{-}C_8H_7 + H$ comprises of the total styrene decomposition rate based upon the current mechanism. The conditions of the current study and literature studies are emphasized.

Figure S11. CHEMKIN-based normalized $[C_8H_8]$ sensitivity of the current mechanism while simulating the Müller-Markgraf and Troe study.

Table S1. Species name translations for mechanism names, chemical names, and InChI. InChiKey is suitable for internet and PubChem database searching.

Table S2. List of density, refractive index, and molar refractivity for mixture species.

Table S3. List of LS experimental conditions and rate coefficients for k_{decomp} (the total rate of styrene decomposition) at 60 Torr.

Table S4. List of LS experimental conditions and rate coefficients for k_{decomp} (the total rate of styrene decomposition) at 120 Torr.

Table S5. List of LS experimental conditions and rate coefficients for k_{decomp} (the total rate of styrene decomposition) at 240 Torr.

Table S6. Stationary point energies for the thermal decomposition reactions of Styrene.

Table S7. Structures and frequencies for relevant molecules and reactions on the C_8H_8 PES at the M06-2X/cc-pvtz level of theory.

Styrene - PLOG.ck– Full mechanism