

Supplementary Information:

Experimental observation of molecular-weight growth by the reactions of *o*-benzyne with benzyl radicals

David E. Couch, Myrsini M. San Marchi, and Nils Hansen

1. Calibration of the mass spectrometer

We ran a calibration gas consisting of methane, acetylene, argon, krypton, and xenon in a helium carrier gas through the pyrolysis reactor. By scanning the temperature of the reactor, we found that all 5 test gases had the same temperature-dependent sampling efficiency. The overall efficiency increased with increasing temperature, as shown in Figure S1. This means that all ion signals are artificially elevated somewhat at higher temperatures, but that the effect is the same for all masses. This temperature-dependent sampling has a substantial effect on the signal levels but does not change any of the conclusions of this work.

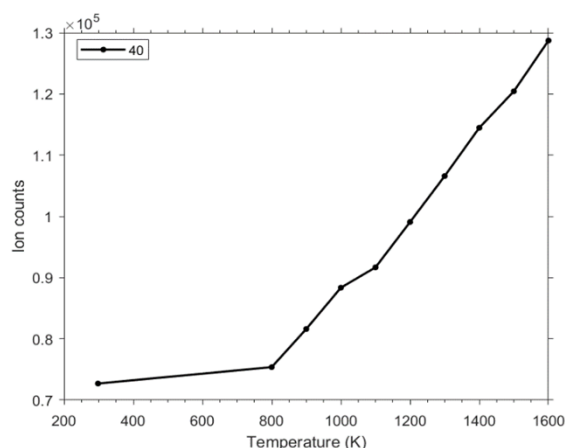


Figure S1. Sampling efficiency increases with temperature, presumably due to alignment of the gas jet with the skimmer.

The temperature-dependent sampling is likely caused by a slight shift in alignment between the reactor and the skimmer. The alignment was set by optimizing total gas throughput through the skimmer at 1500 K. Thus the alignment is quite good at high temperature but may be slightly off at lower temperatures, causing more of the gas jet to miss the skimmer. Due to the increased spread of lighter molecules, this misalignment could in general be mass-dependent, but here any difference between masses is much smaller than the change in overall efficiency with temperature. Another possibility is that the expansion out of the reactor is affected by temperature such that more of the gas reaches the skimmer, or that the reactor opening is closer to the skimmer at higher temperatures. These possibilities were not explored further.

2. Mass spectrum with each precursor individually

In order to verify that the products of interest in this study (m/z 115, 165, 166, 167) were products of cross reactions and not self-reactions, we also ran the pyrolysis of each precursor individually. Each single-component pyrolysis experiment shows several mass peaks, which are not assigned here but are for the most part easily assigned pyrolysis products of the given precursor. The fact that very little signal is observed near m/z 115, 165, 166, and 167 for all three precursors (diiodobenzene Fig. S2, propargyl bromide Fig. S3, benzyl bromide Fig. S4) demonstrates that these products of interest do not arise from repeated reactions of a single precursor at the present conditions (concentrations near 0.1%, temperatures near 1500 K, and pressures near 30 Torr).

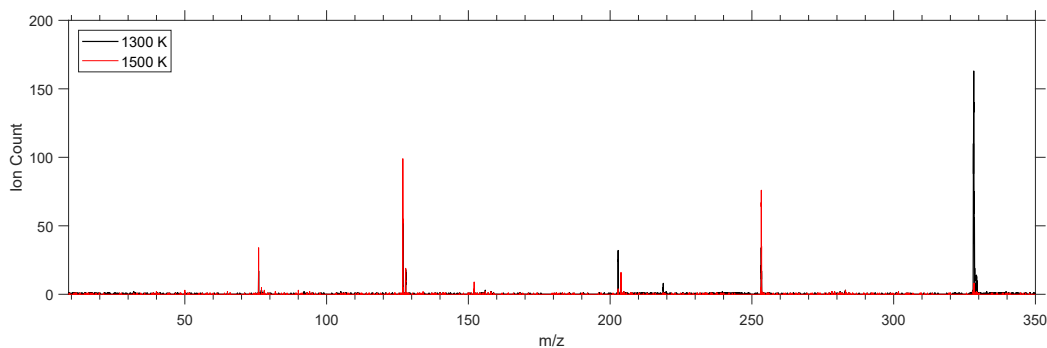


Figure S2. Mass spectrum from the pyrolysis of diiodobenzene at 1300 K (black) and 1500 K (red), showing no m/z 115, 165, 166, 167 which are the products of interest in the present study of benzyne reactions.

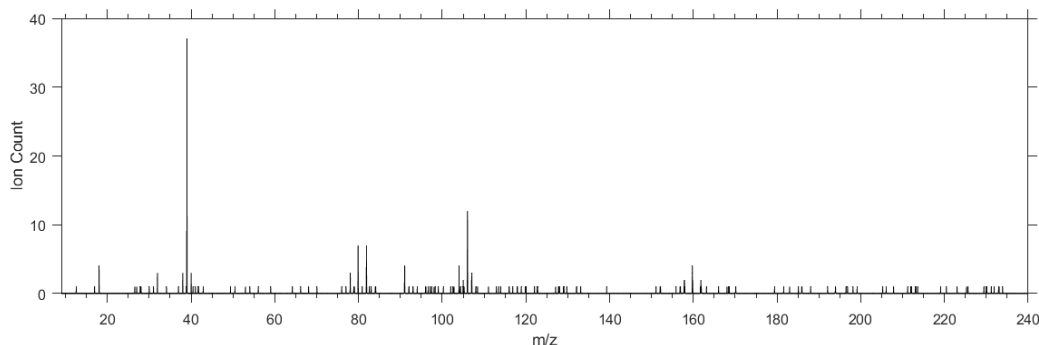


Figure S3. Mass spectrum from the pyrolysis of propargyl bromide at 1500 K, showing no m/z 115, 165, 166, 167 which are the products of interest in the present study of propargyl reactions. Some xylene (m/z 106) is also present in the propargyl bromide sample.

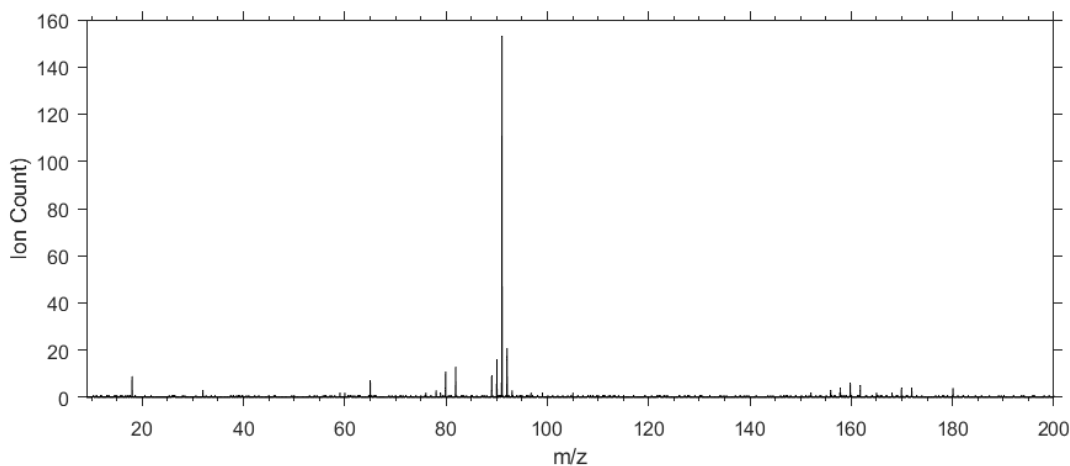


Figure S4. Mass spectrum from the pyrolysis of benzyl bromide at 1500 K, showing no m/z 115, 166, 167 and very little m/z 165. These are the products of interest in the present study of benzyl reactions.

3. Thermal camera images of the reactor

The images shown in Fig. S5 were captured by a MicroEpsilon M-1 thermal imaging camera aimed at the hot reactor tube. The emissivity setting of the camera was set to 0.82, assuming a constant emissivity for all objects in the photo at all wavelengths. The gas flows from left to right in these images, with the skimmer to the high-vacuum chamber visible on the right edge in some of the images. Images are labeled by the highest temperature observed on the reactor, and this temperature is used at the “reactor temperature” in the figures in the manuscript. The hottest part of the reactor is generally between the two electrodes but close to the second electrode, that is, closer to the exit of the reactor. Gas is supplied through Swagelok connections on the left. The reactor is heated by passing electrical current along the center section of the tube. Silicon carbide becomes a conductor at high temperatures, allowing the reactor itself to be part of the electrical circuit. Current is supplied by copper wires bolted to molybdenum clips which support graphite annular disks which fit snugly on the cylindrical silicon carbide tube. All of the components are visible in the higher-temperature images due to light scattering off the components. These images provide a trustworthy temperature measurement (± 50 K) for the silicon carbide reactor tube and the graphite disks that serve as electrodes contacting the tube. Everything else in the image is reflecting or scattering light emitted from the tube and is generally at a lower temperature than indicated. The lowest temperature that can be recorded by this camera with the present settings is 454 K.

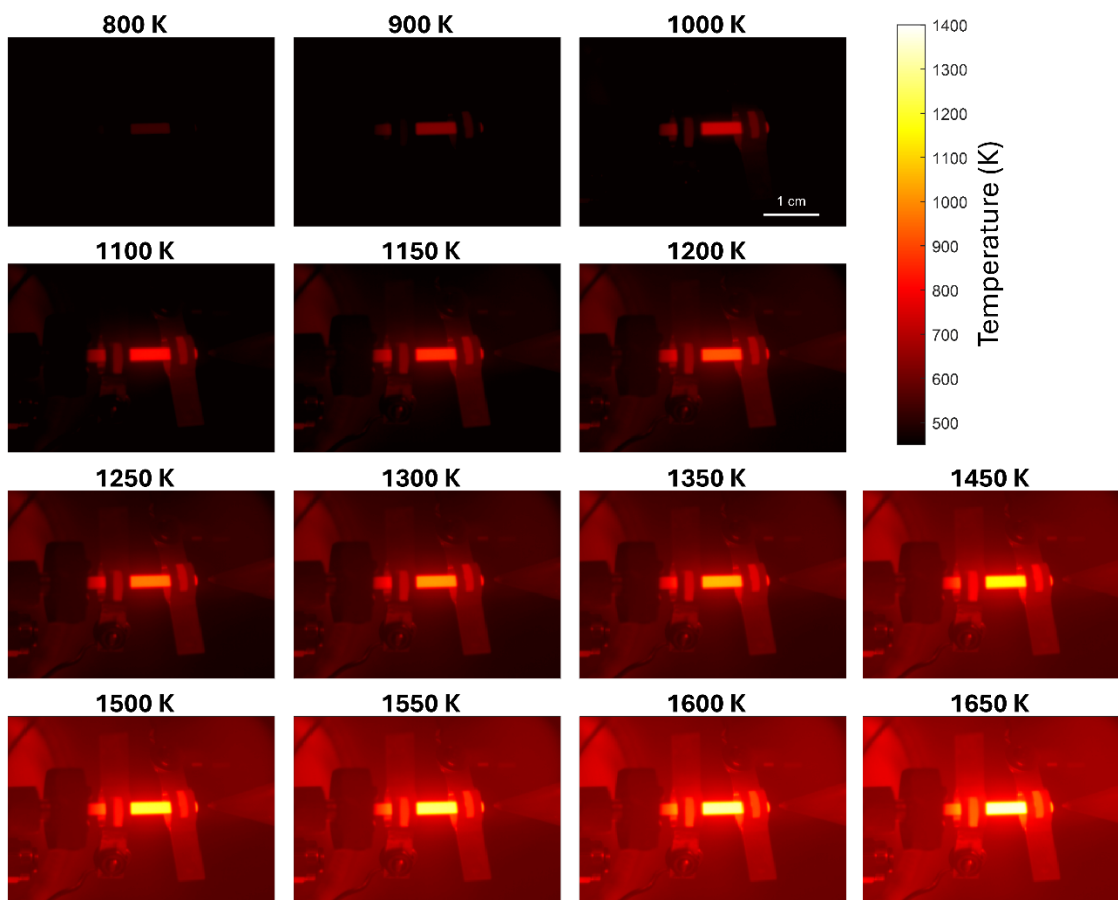


Figure S5. Thermal camera images of the silicon carbide reactor for each recorded temperature. Each image is labeled with the highest temperature in the image.

4. Simulated pressure profile of the reactor

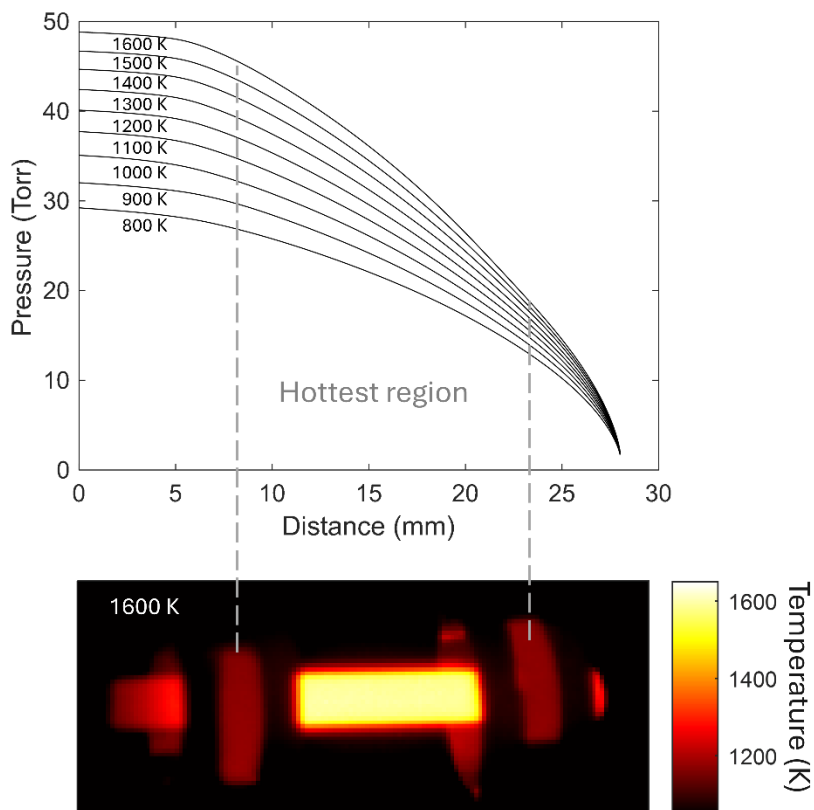


Figure S6. Simulated pressure profile over a range of temperatures, with the hottest portion of the reactor where most of the pyrolysis chemistry occurs indicated.

The pressure profile through the reactor (Fig. S6) was calculated using a boundary layer flow model developed by Weddle et al. [1]. The pressure drops throughout the reactor, especially near the exit where the flow is most choked. Higher inlet pressure occurs at higher temperatures due to the increased viscosity of helium.

In the lab, the inlet pressure was monitored during experiments, and at 800 K the inlet pressure was generally slightly lower (up to 20%) than predicted by the simulation while at 1600 K the inlet pressure was higher (up to 40%). At high temperatures, the reactor was found to be filling with soot which further lowered the conductance in the hottest part of the reactor. The remainder of the discrepancy may arise from imperfect treatment of the temperature-dependent viscosity of helium. Since the pressure dependence of kinetic rates tends to vary logarithmically, uncertainties in pressure should not greatly impact predicted rates and hence the conclusions of this study. Most of the pyrolysis chemistry of interest here occurs at pressures of 20-45 Torr.

References

1. P. J. Weddle, C. Karakaya, H. Zhu, R. Sivaramakrishnan, K. Prozument and R. J. Kee, *International Journal of Chemical Kinetics*, 2018, **50**, 473-480.