From microkinetic model to process: Understanding the role of the boron nitride surface and gas phase chemistry in the oxidative dehydrogenation of propane

Electronic Supplementary Information

ESI Table 1 available from MINDS@UW Subcollection entitled "MINDS@UW Madison / College of Engineering, University of Wisconsin--Madison / Department of Chemical and Biological Engineering / Data and Supplementary Materials."

Ozone Generation and Measurement

Ozone was generated using a VMUS-DG ozone generator. In a typical experiment, ca. 2L/min of UHP O_2 was flown through the ozone generator to produce an ozonated oxygen feed with ca. 10 psig of backpressure. This feed was then directed into the reactor through a Bronkhorst EL-Flow Select mass flow controller.

Ozone concentration was measured prior to reaction using UV-Vis absorbance measurements with a Maya 2000Pro spectrometer using a combined deuterium and halogen light source. A 0.1cm path length quartz cuvette was placed in line with the generator outlet prior to any heated sections of the reactor. Ozonated oxygen was introduced to the cuvette via mass flow controllers and decomposed using an ozone destroyer after the cuvette. O_3 absorption measurements at 253.6 nm were collected for at least 500 seconds. An exemplar spectrum is shown in Figure 1. Absorptivity at 253.6 nm was taken to be 1130E-20 molecules cm^{-2}.[1] The Beer-Lambert law was used to estimate the O_3 concentration.

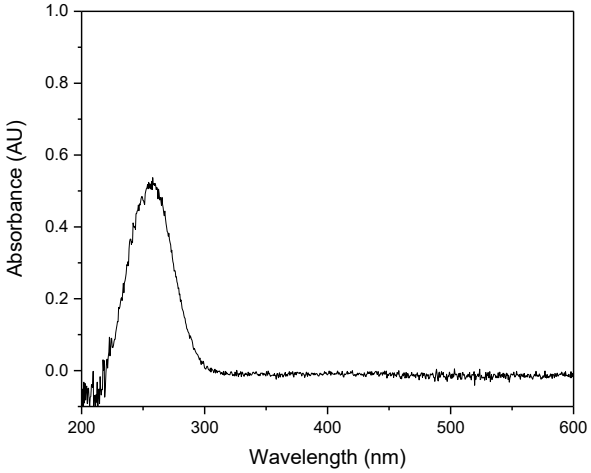

Figure 1: Exemplar absorbance measurement for undiluted ozonated O_2 stream.

Ozone Reactor Tube

Ozone is highly reactive and decomposes rapidly. To minimize non-isothermal reactivity, a reactor tube was constructed that had minimal dead-volume outside the isothermal region. The tube consisted of a central 9mm ID reactor portion and two 4mm ID quartz tube sections that were packed either with a thermowell or a quartz spacer rod to minimize dead volume. This tube was used for O_3, NO, and some background reactions. The temperature profile was found to vary within a 14°C range within this region at a setpoint of 475°C.

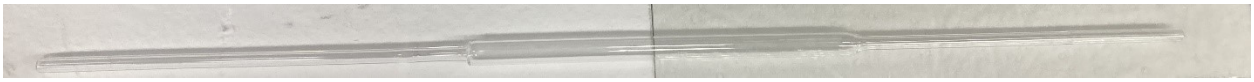

Figure 2: Tube used for ozone reactions. Central tube portion where gas-phase reactions occurred is 18cm in length and 9mm in inner diameter.

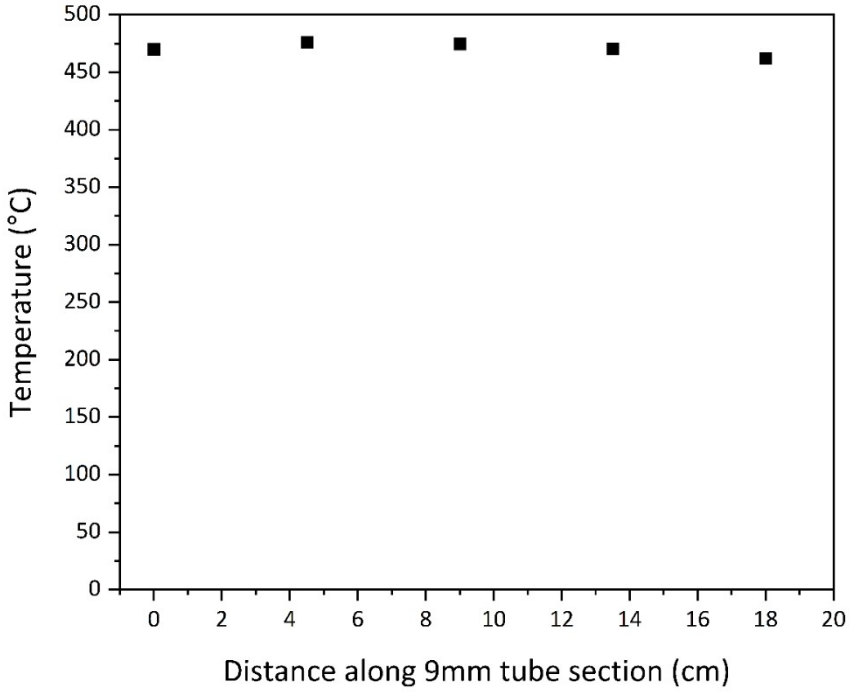

Figure 3: Temperature along 9mm section of reactor tube at 475°C setpoint.

B_2O_3 Reactivity

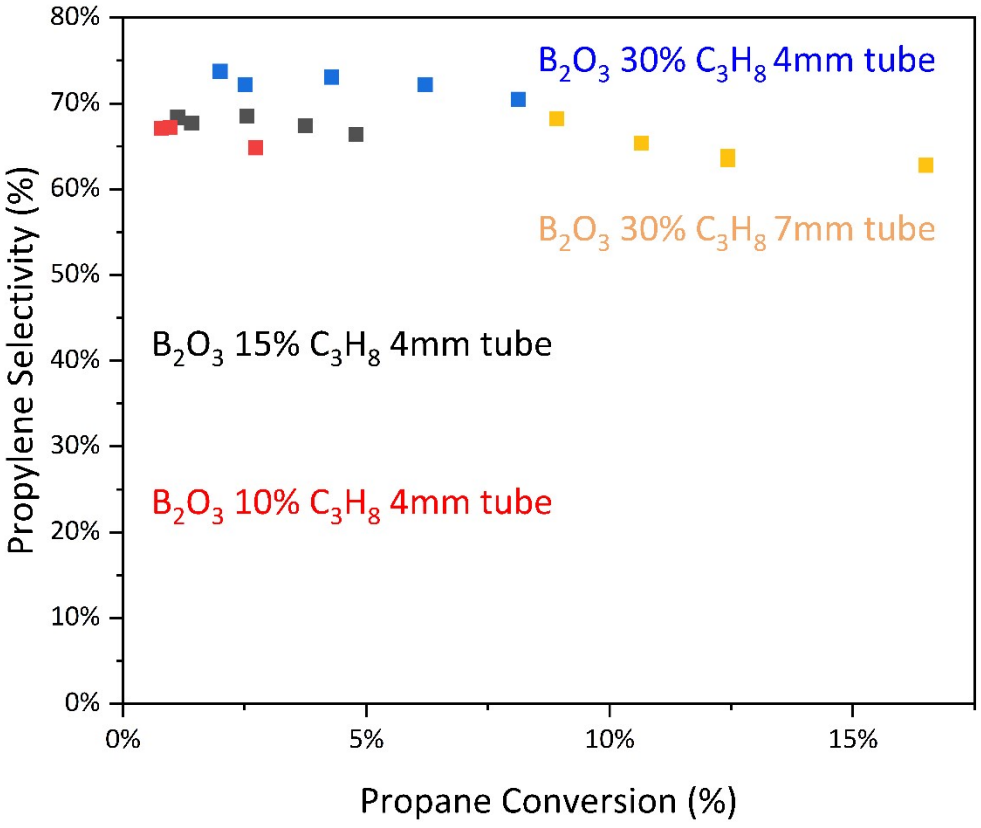

Figure 4: B_2O_3 reactivity in 4mm and 7mm tubes. Conditions: 550°C, 25-70 mLn min^{-1} total flow, 2:1 C_3H_8:O_2 ratio with various dilutions in N_2.

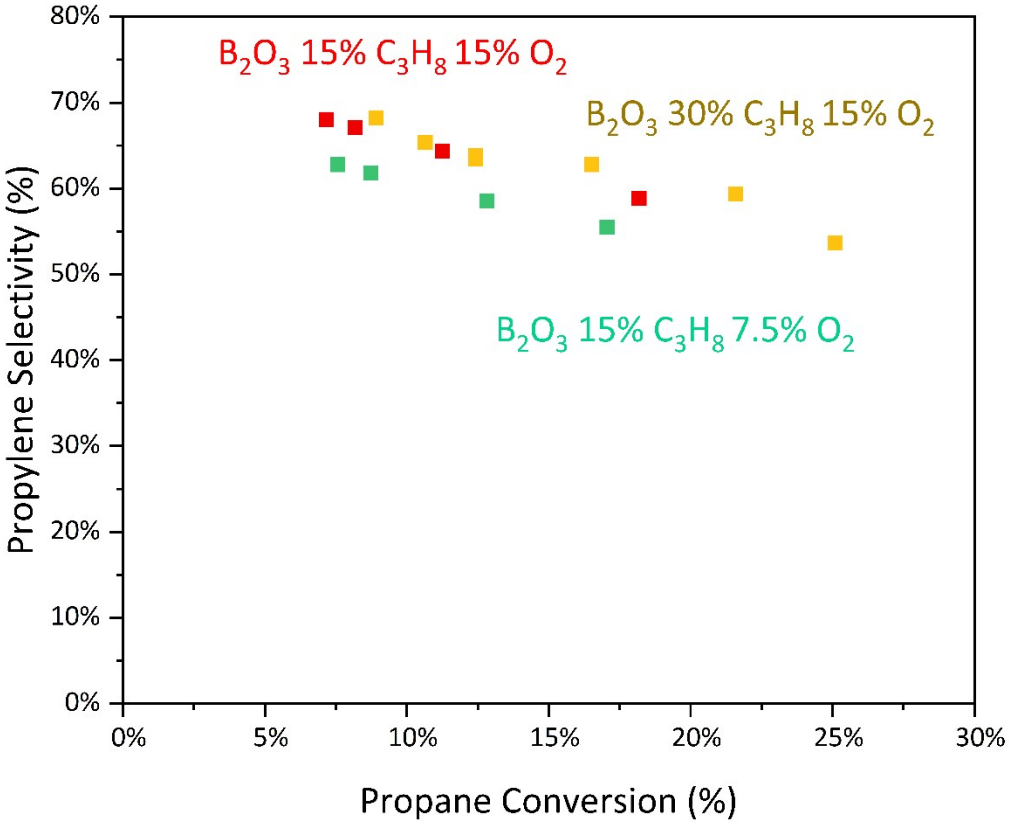

Figure 5: B_2O_3 reactivity in 7mm tube. Conditions: 550°C, 30-80 mLn min^{-1} total flow, 50mg B_2O_3 diluted in 950mg quartz chips. C_3H_8 and O_2 feed fractions specified in figure with balance of feed containing N_2.

Effect of low Partial Pressure of Propane

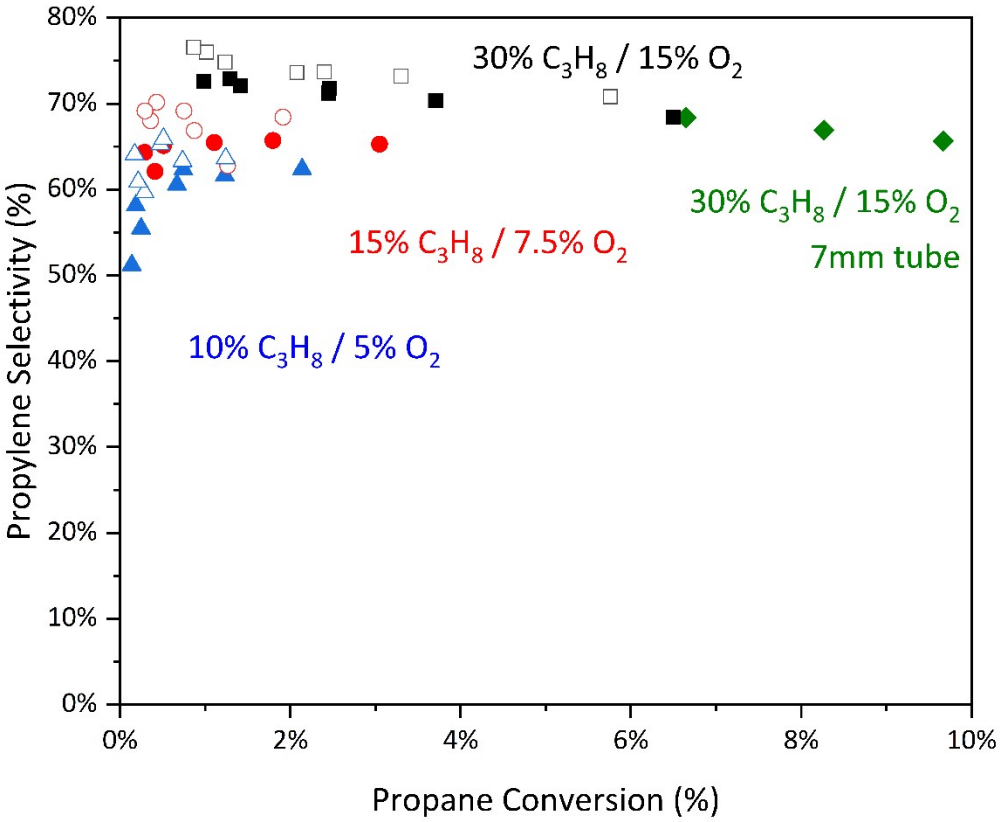

Figure 6: Propylene selectivity vs propane conversion over boron nitride (solid) and in empty tube (hollow) at various feed dilutions. Each run maintained a 2:1 C3H8 : O2 ratio but with a different feed dilution to achieve the stated feed fraction of C3H8. Conditions: 550°C, 20-80 mLn min-1, 1:5 dilution of boron nitride in passivated silicon carbide (50mg hBN in 4mm tube and 100mg hBN in 7mm tube) or 9cm of empty tube. All runs were performed in a 4mm tube unless otherwise noted.

Role of hydrogen peroxide dissociation

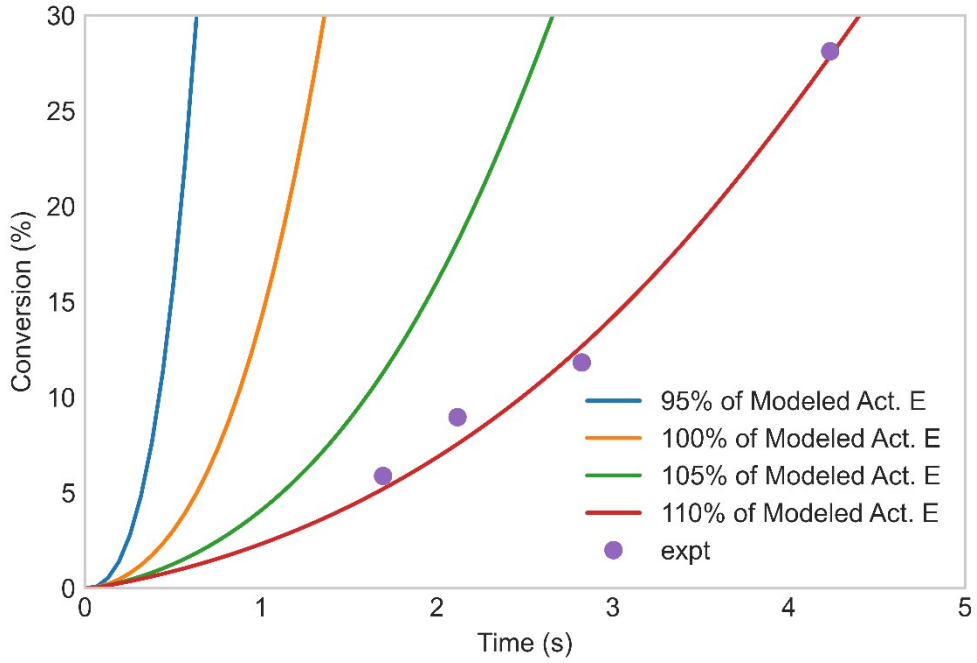

Figure 7: Conversion versus time in reactor tube, experiment vs model with different multipliers applied to the modeled activation energies for hydrogen peroxide dissociation. Modifying the activation energy improves the accuracy of the model in capturing the conversion as a function of contact time. Conditions: 550°C, 30% C_3H_8 / 15% O_2 / 55% N_2.Figure generated using Matplotlib.[2]

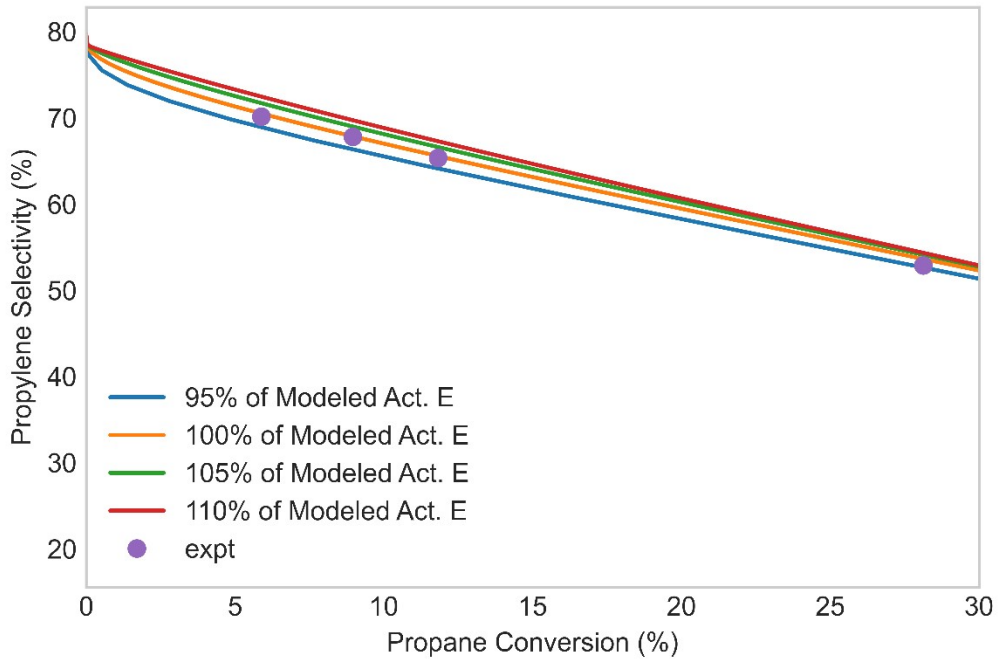

Figure 8: Selectivity versus conversion in reactor tube, experiment vs model with different multipliers applied to the modeled activation energies for hydrogen peroxide dissociation. Modifying the activation energy reduces the accuracy of the model in capturing the selectivity vs conversion. Conditions: 550°C, 30% C3H8 / 15% O2 / 55% N2. Figure generated using Matplotlib.[2]

Effect of O_2 Feed Percentage

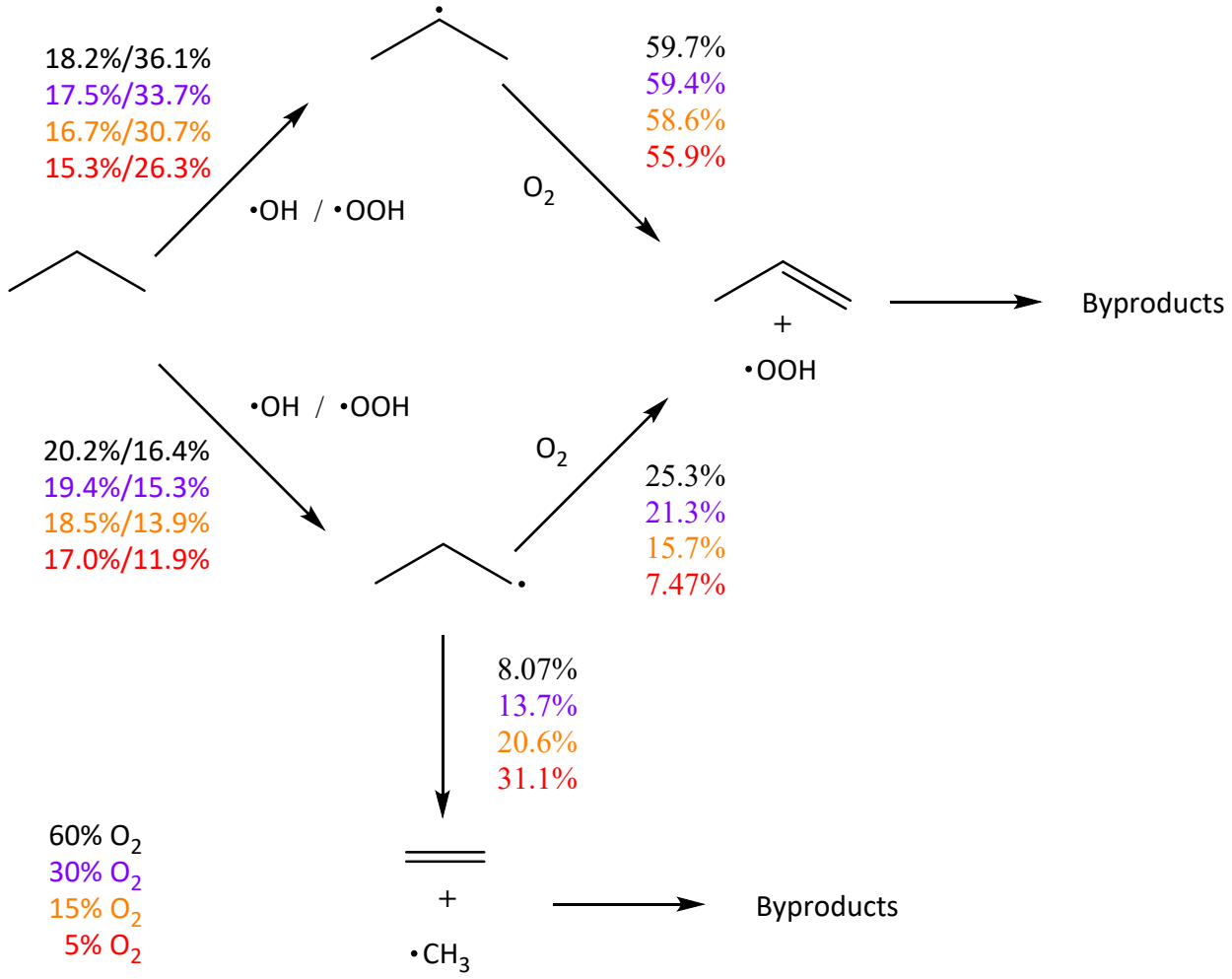

Figure 9: Major pathways for carbon flux in the gas-phase as predicted by the microkinetic model. Percentages represent the percentage of total carbon flux from C3H8 that goes through a specific pathway when measured at 5 % conversion. Note that minor flux pathways are not included in this simplified diagram. Conditions: 550°C, 30 % C_3H_8 / x% O_2 / balance % N_2.

Works Cited

(1) Orphal, J.; Staehelin, J.; Tamminen, J.; Braathen, G.; De Backer, M.-R.; Bais, A.; Balis, D.; Barbe, A.; Bhartia, P. K.; Birk, M.; Burkholder, J. B.; Chance, K.; von Clarmann, T.; Cox, A.; Degenstein, D.; Evans, R.; Flaud, J.-M.; Flittner, D.; Godin-Beekmann, S.; Gorshelev, V.; Gratien, A.; Hare, E.; Janssen, C.; Kyrölä, E.; McElroy, T.; McPeters, R.; Pastel, M.; Petersen, M.; Petropavlovskikh, I.; Picquet-Varrault, B.; Pitts, M.; Labow, G.; Rotger-Languereau, M.; Leblanc, T.; Lerot, C.; Liu, X.; Moussay, P.; Redondas, A.; Van Roozendael, M.; Sander, S. P.; Schneider, M.; Serdyuchenko, A.; Veefkind, P.; Viallon, J.; Viatte, C.; Wagner, G.; Weber, M.; Wielgosz, R. I.; Zehner, C. Absorption Cross-Sections of Ozone in the Ultraviolet and Visible Spectral Regions: Status Report 2015. *Journal of Molecular Spectroscopy* **2016**, *327*, 105–121. https://doi.org/10.1016/j.jms.2016.07.007.

(2) Hunter, J. D. Matplotlib: A 2D Graphics Environment. *Comput. Sci. Eng.* **2007**, *9* (3), 90–95. https://doi.org/10.1109/MCSE.2007.55.