

An Information-Rich Graphical Representation of Catalytic Cycles

ABSTRACT: Catalytic reactions are limited in their turnover by certain steps in the cycle. We present a free, web-based interface where the rate constants of various steps in a cycle can be visualized. Population of a web form using known data will generate a highly customizable graphic for annotation by the user to represent their chemistry.

The way in which catalytic reactions are depicted schematically has barely changed in decades.¹ A cycle is constructed, in which intermediates are arranged in sequence joined by arrows, which are in turn decorated with reagents (Figure 1):

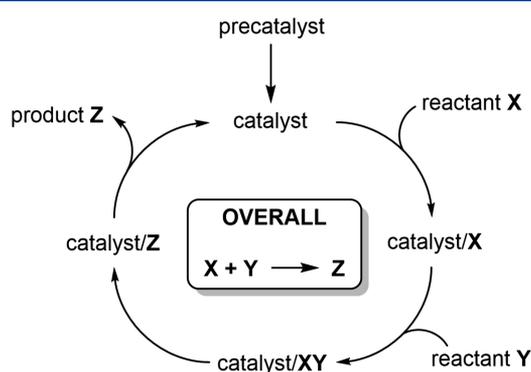


Figure 1. Typical depiction of a catalytic cycle.

However, there is little visual information conveyed about the rate constants of the various steps, the catalyst resting state, and so on. We sought to remedy this by constructing a web-based tool that uses information about the reaction to generate an information-rich, high-quality graphical depiction that the user can then annotate with their chemistry. By visualizing the kinetic information on each step, the audience can, at a glance, assess the characteristics of a catalytic reaction. The utility of such catalytic infographics is particularly useful at a time when powerful experimental, simulation, and computational methods are increasingly capable of extracting rate constants, energy barriers, and/or intermediate identities from complex catalytic systems.²

The goal was a web-based, Python-powered system whereby users could input their data by specifying basic parameters: number of steps, reversibility of each step, relative rate for each step, and the addition of a reactant or the elimination of a product for a given step. Python is an open-source programming language popular among chemists for its flexibility, ease of use, and abundance of modules.³ We frequently use Python ourselves for data analysis and presentation and have shared some of that work previously in open-source form.⁴

Graphically, the look of the cycle can be modified according to a wide number of parameters. The code is hosted at <https://catalyticcycle.com/>, and no programming skills are required. The user simply needs to specify parameters and the code operates behind the scenes to generate downloadable vector graphics ready for further annotation by whatever graphics program the user typically employs for constructing chemical schemes.

Users are able to tweak a host of parameters, as detailed below.

Number of Steps. Catalytic cycles feature different numbers of steps, depending on their complexity. This parameter is specified in the first tab of the tool, by adding a step using the + button. By default, steps are irreversible (Figure 2).

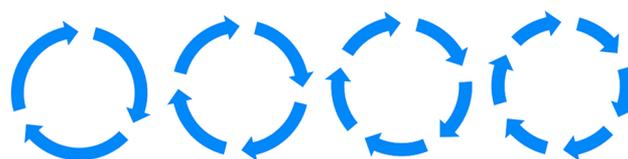


Figure 2. Different numbers of steps in integer values; shown here $n = 3-6$.

Colors. The colors of each arrow can be specified using hexadecimal form (e.g., red = #FF0000), allowing over 16 million color options. The 16 HTML color names (black, silver, gray, white, maroon, red, purple, fuchsia, green, lime, olive, yellow, navy, blue, aqua, teal) can also be entered directly into the form and will be converted into the correct hexadecimal code, and colors can also be selected manually from a pop-up palette (Figure 3).

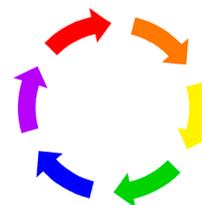


Figure 3. The color of arrows can be easily altered for each step.

Reversibility. Any step can be made reversible by specifying a reverse reaction. The reverse arrow appears on the inside and its color is by default a lighter version of the outer color (Figure 4). That default can be overwritten by entering the desired color.

Gaps and Arrow Thickness. Space needs to be left for structures in the cycle, and the arrow thickness can be tuned to keep relative proportions at whatever level is desired (Figure 5).

In cases where additional space needs to be left for a larger structure, the gaps between arrows can be individually customized.

More Arrows. Many steps in catalytic cycles involve the addition of a reagent, and that can be accommodated by checking the “Add reagent?” box. Similarly, if the step extrudes a product, the “Generate product?” box should be checked (Figure 6). Side reactions producing off-loop species can also be

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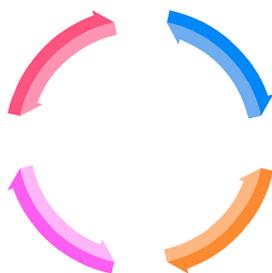


Figure 4. Catalytic cycle with four reversible steps.



Figure 5. Adjustment of gaps (small, medium, large) with narrow arrow widths; the last two have increasing arrow thickness.

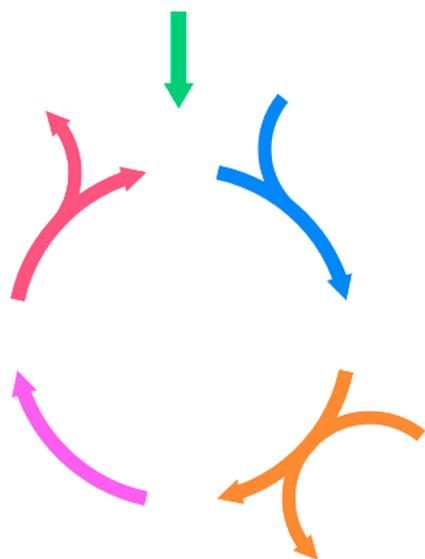


Figure 6. A catalytic cycle with additional off-cycle steps (green), reagents entering the cycle (blue), entering and leaving (orange), and leaving (pink).

included, as there is a separate tab for making straight arrows with all of the functionality of the main cycle arrows (width, reversibility, etc.).

The tool offers a great deal of control over the appearance of the cycle. Figure 7 shows the options available under the “Styling” tab.

Rate Constants. In a catalytic cycle at steady state, the *rate* of each step of the cycle is the same. Reactions with small rate constants accumulate enough of the reactant(s) to proceed as quickly as reactions with much higher rate constants that do not hang around long enough to accumulate appreciable amounts of intermediate.⁵ We indicate individual steps with a large rate constant (low barrier) by a wide arrow, and steps with a small rate constant (high barrier) by a narrow arrow.

Presently, we offer five different rate constants for both forward and reverse reactions: very low, low, moderate, high, very high. What these actually mean will depend a good deal on the actual reaction under study, and users of the program may prefer to specify actual ranges of rate constant or energy barrier for each arrow thickness.

General Settings

Gap: Thickness:

Arrowhead Width: Arrowhead Length:

Incoming/Outgoing Arrows

Thickness: Radius:

Total Length: Arrowhead Length:

Shackleford Angle:

Figure 7. Available options under the “Styling” tab.

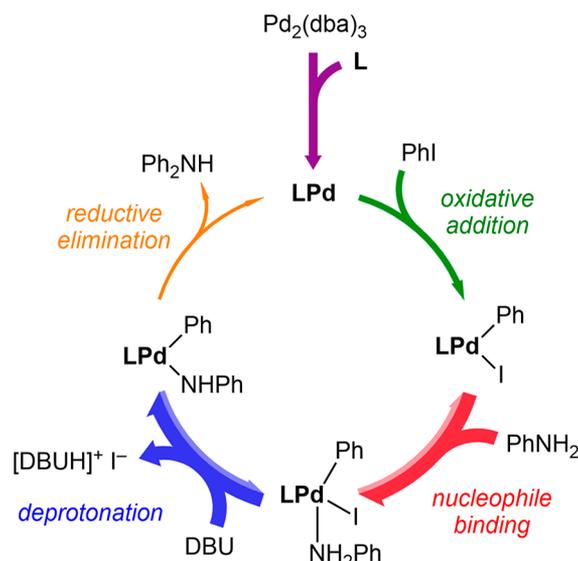


Figure 8. Catalytic cycle for the Buchwald–Hartwig amination. Catalyst activation (fuschia) is relatively slow, as is oxidative addition (green). Addition of the aniline (red) and deprotonation (blue) are both very fast and reversible. The reductive elimination (orange) is the slowest step and is the point at which the catalyst rests.

An obvious complication is that individual steps can be unimolecular (first order) or bimolecular (second order), and these have very different rate constants that are not directly comparable. Bimolecular reactions are often conducted under pseudo-first-order conditions (excess of one reagent), in which case the pseudo-first-order rate constant can be used as a point of comparison. If not, comparing the half-lives of the first- and second-order reactions may be useful, though for second-order transformations these depend on concentration and will necessarily change continuously over the course of the reaction.

If no information about the rate constants or energy barriers is available, arrow sizes should be kept the same. If some information is known, e.g. the identity of the step with the highest barrier/smallest rate constant, it can be depicted with a narrow arrow to indicate that that step is the bottleneck and the

preceding intermediate (or species in equilibrium with that intermediate) is the resting state.

Putting It All Together. Figure 8 draws together the various components of the tools for a real cycle, in this case a Buchwald–Hartwig amination reaction.⁶ We have studied this in our laboratory⁷ using real-time mass spectrometric methods.⁸

CONCLUSIONS

The arrows generated by our tool conveys more chemical information about the catalytic cycle than a typical traditional schematic (Figure 1). The utility of such depictions becomes particularly useful as modern experimental, simulation, and computational methods are increasingly capable of probing the individual steps in complex catalytic systems.

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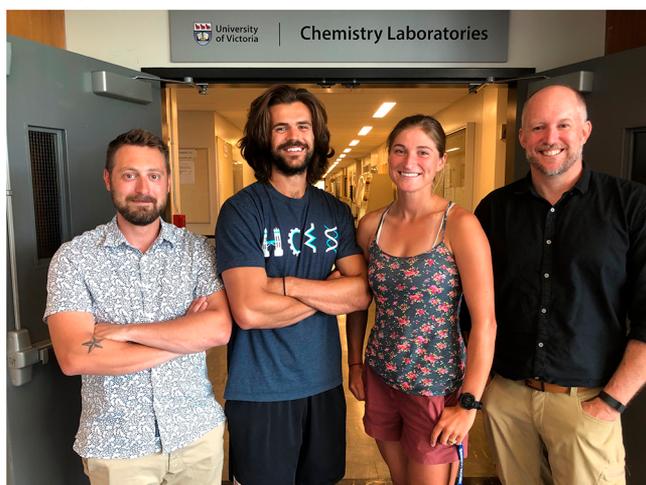
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Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

Biography



The McIndoe group investigates challenging inorganic and organometallic catalytic systems using real-time mass spectrometric methodologies. Graduate students James McFarlane, Brett Henderson, and Sofia Donnecke were responsible for developing the Python code to

visualize the cycles as well as the web implementation of the utility. They are all currently working as computational chemists under Irina Paci with Sofia cosupervised by Scott McIndoe.

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