

An Information-Rich Graphical Representation of Catalytic Cycles

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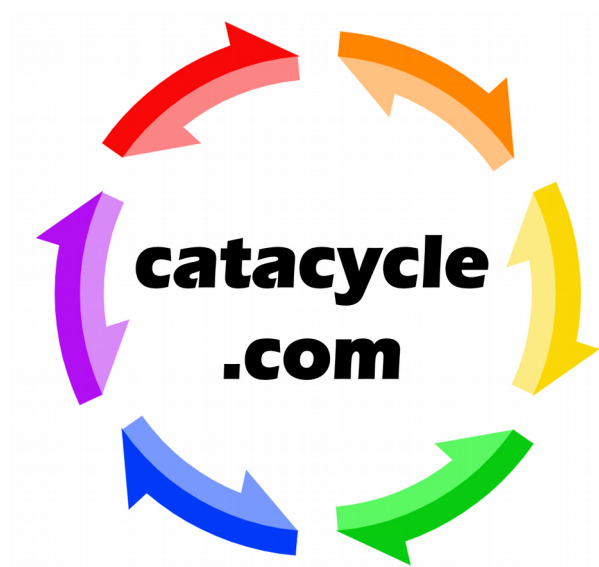
An information-rich graphical representation of catalytic cycles

James McFarlane, Brett Henderson, Sofia Donnecke and J. Scott McIndoe*

Department of Chemistry, University of Victoria, PO Box 1700 STN CSC, Victoria, BC V8W 2Y2, CANADA

Abstract

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Introduction

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

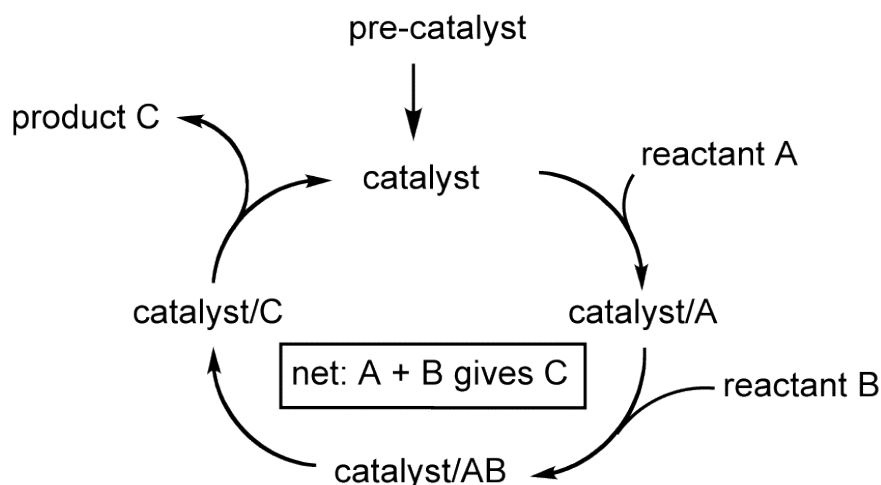


Figure 1. A typical depiction of a catalytic cycle, from https://en.wikipedia.org/wiki/Catalytic_cycle.

However, there is little visual information conveyed about the rate constants of the various steps, which species is the catalyst resting state, and so on. We sought to remedy this by construction of a web-based tool that allows input of information on the reaction and generates in return an information-rich, high quality graphical depiction that can be custom annotated with structure/formula data in conventional fashion. It provides an at-a-glance way of assessing 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.¹

Approach

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, the relative rate for each step, whether a given step involves the addition of a reactant or the elimination of a product. Python is an open-source programming language popular among chemists for its flexibility, ease of use and abundance of modules.² We frequently use Python ourselves for data analysis and presentation, and have shared some of that work previously in open-source form.³

Graphically, the look of the cycle can be modified according to a wide number of parameters. The code is hosted at <https://catacycle.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).

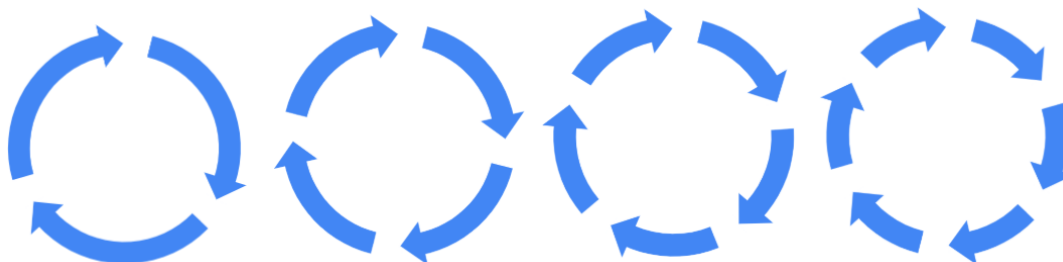


Figure 2. Different numbers of steps in integer values; shown here $n = 3$ to 6.

Colors

Colors of each arrow can be specified using the web color palette, i.e. in RGB hexadecimal form (e.g. **red** = #FF0000) specifying over 16 million colors. The 16 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 spectrum.

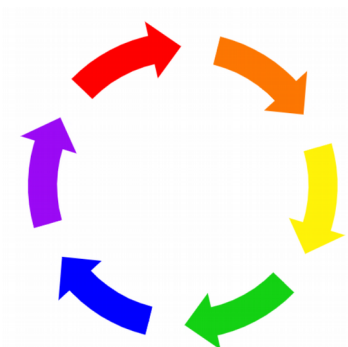


Figure 3. Color of arrows can be easily altered for each step.

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.

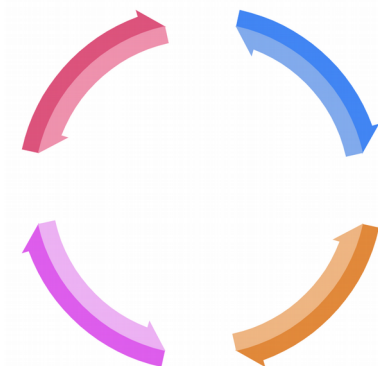


Figure 4. Catalytic cycle with 4 reversible steps

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).

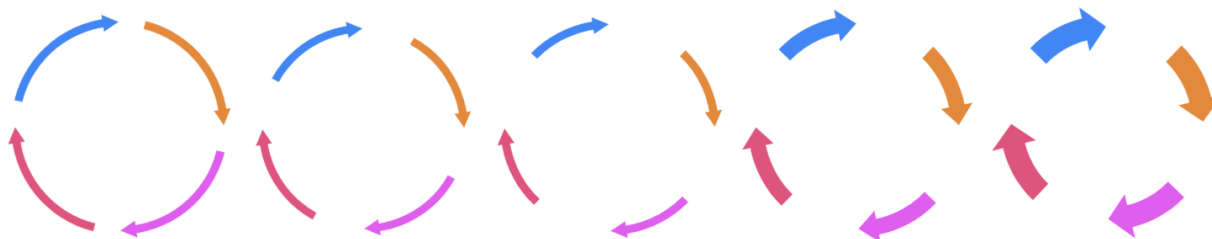


Figure 5. Adjustment of gaps (small, medium, large) with narrow arrow widths; last two have increasing arrow thickness.

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

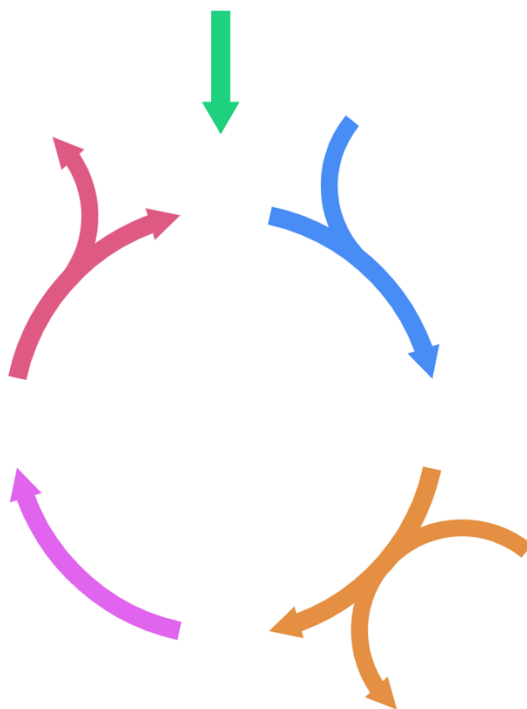


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The tool offers a lot of control over the appearance of the cycle. Figure 7 shows the options available under the “Styling” tab.

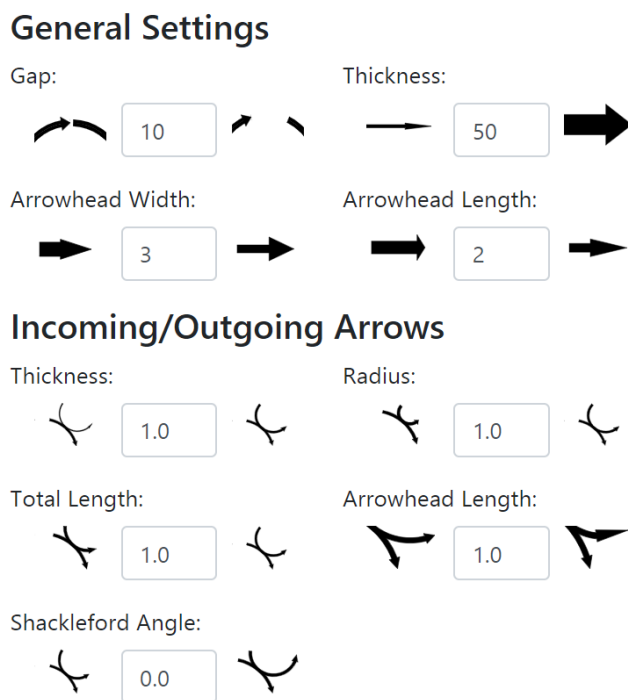


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Rate constants

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.⁴ 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 lot 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.

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.

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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.⁵ We have studied this in our laboratory⁶ using real-time mass spectrometric methods.⁷

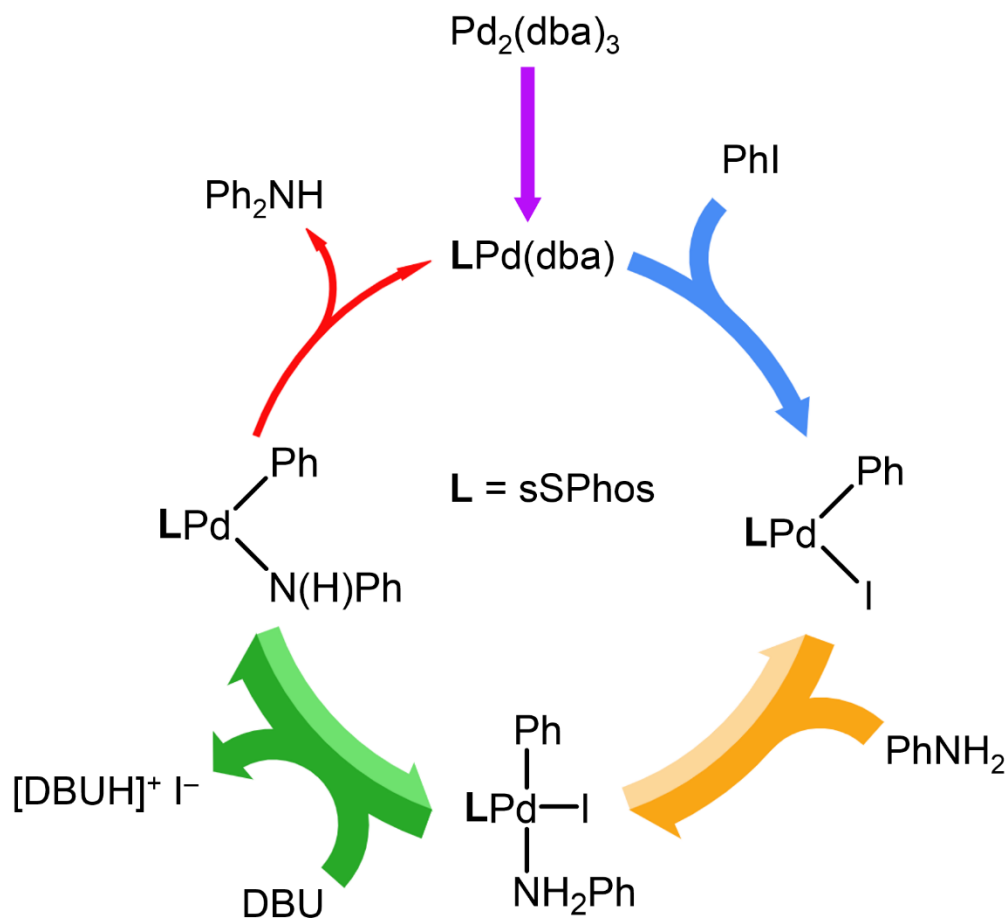


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References

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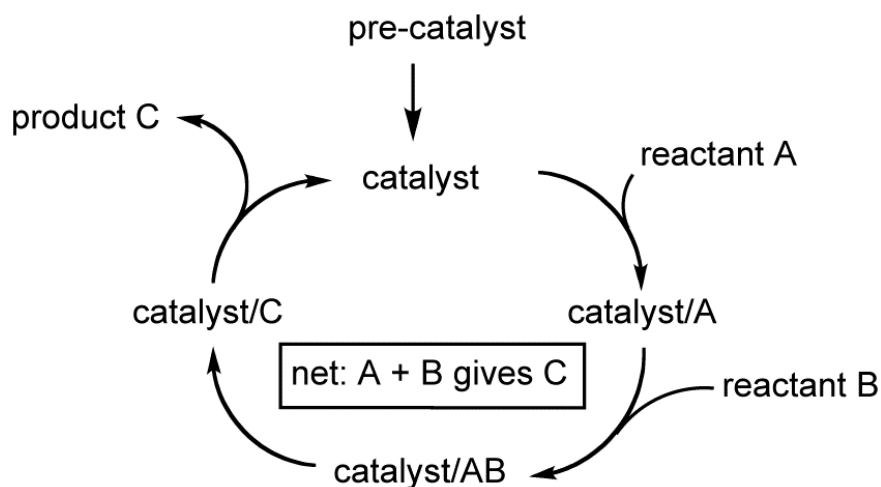


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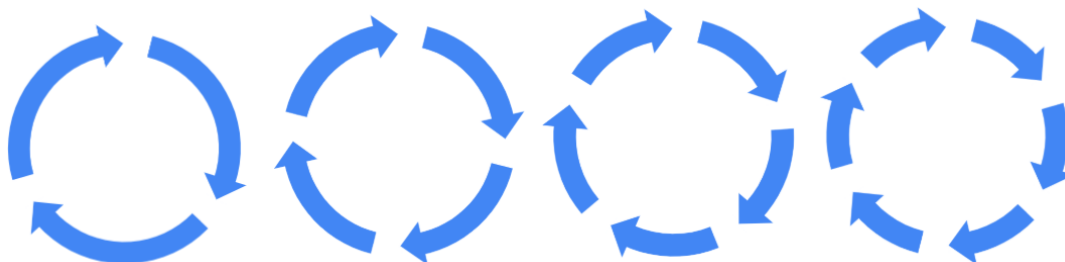


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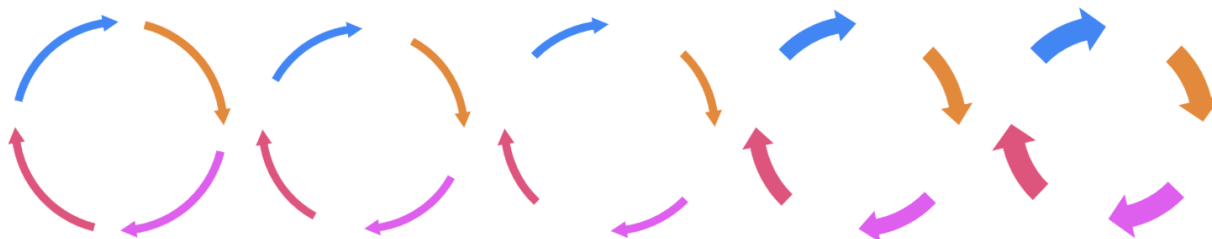


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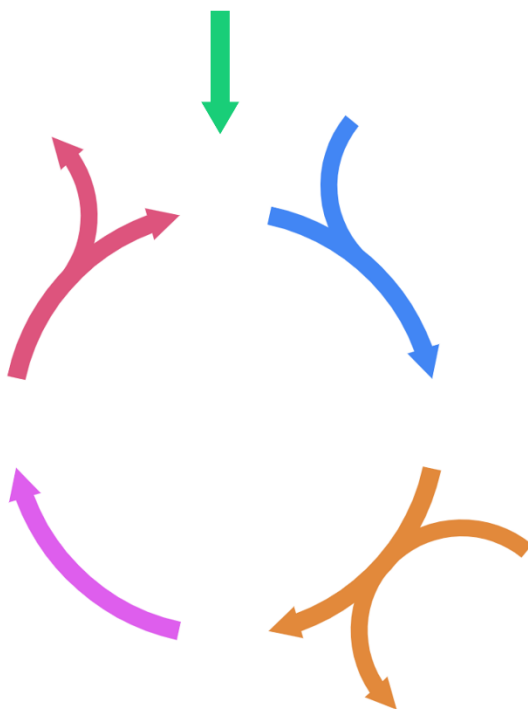








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General Settings



Gap:  



Thickness:  



Arrowhead Width:  



Arrowhead Length:  

Incoming/Outgoing Arrows

Thickness:  

Radius:  

Total Length:  

Arrowhead Length:  



Shackleford Angle:  

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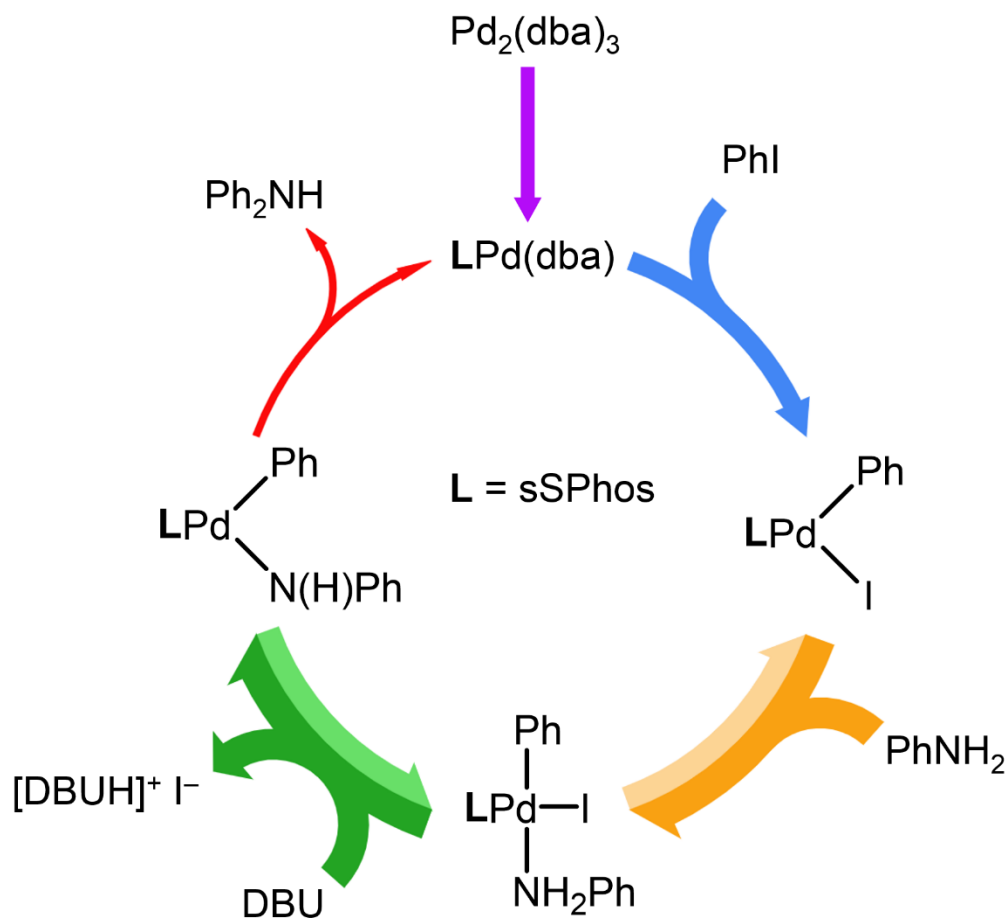


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