

Autocatalysis in a Hierarchically Organized Inorganic Chemical Network

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Abstract

One of the salient features of living systems is presence of autocatalytic chemical reaction networks. Here we present a stochastic model of an inorganic autocatalyst, which is derived directly from empirical results. Using the model, we can explore the emergence of autocatalysis and its consequences on the larger, hierarchical, chemical network. This model provides a useful tool to study the emergence and organization of autocatalytic chemical networks and the effect autocatalysis has on the global system dynamics.

A characteristic feature of living systems is the existence of autocatalytic cycles, which enables the exponential growth of individuals and thus evolutionary dynamics (Cronin & Walker 2016, Kauffman 1992). Accordingly, a primary goal of origins of life and artificial life research is the design and synthesis of autocatalytic chemical reaction networks (Ashkenasy et al, 2017, Ashkenasy et al 2004, Kauffman 1992). Here we demonstrate a stochastic kinetic model of network autocatalysis based on an inorganic chemical system (Miras et al 2010). This model provides mechanistic insights into how autocatalytic cycles can be stabilized in real chemical systems and how their emergences effects the large-scale dynamics of hierarchically organized chemical networks. Our goal is to use this model to generate design constraints for observing autocatalytic reactions in the experimental system.

We model the formation of large molybdenum nano-structures, known as Mo-Blue wheels (Miras et al 2010). In experimental platforms, these large structures are synthesized using flow through systems fed with Molybdate (MoO_4^-) monomers in a reduced solution (Miras et al 2010). Current analytical techniques cannot elucidate the exact assembly mechanism for large structures such as the Mo_{154} wheel (Miras et al 2010). It is hypothesized that Molybdenum intermediates (Mo_6) are stabilized around a Mo_{36} structure. This mechanism would imply that the Mo_{36} structure would be capable of templating both Mo_6 building blocks, and the larger wheel structure. This introduces the possibility that the Mo_{36} structure is both autocatalytic (since it is formed from the Mo_6 structures it templates) and cross-catalytic in that it templates the larger Mo_{154} structure. Structural studies suggest that the Mo_{36} can be ejected from the larger scale structure enabling it to participate in further templating reactions. These mechanisms may lead to the exponential amplification of the wheel after the emergence of the Mo_{36} template.

The Mo-Blue wheel system presents an interesting chemical system because it contains three clear hierarchical levels of organization: small intermediates (Mo_1 - Mo_6), small templates (Mo_{36}) and larger structures (Mo_{154}). The existence of these clearly delineated levels of organization enables us to explore the consequences of autocatalysis on the levels above and below the proposed autocatalytic entity.

To explore the consequences of this proposed mechanism we developed a model of the Mo-Blue dynamics. Our model is implemented using a kinetic Monte Carlo algorithm (Gillespie, 1977). This technique represents all reactions as either uni-molecular degradation reactions ($A \rightarrow B + C$) or bimolecular ($A + B \rightarrow C$). Structures and intermediates form as the products of bimolecular reactions between building blocks and other intermediates. We assume that all molecules (besides Molybdate monomers, Mo_1) can degrade into component parts. We initialized the system with 10^6 Mo_1 molecules. The model uses Mo_1 , Mo_2 , and Mo_6 , as building blocks, which are given a different degradation rate. Both the Mo_{36} (template) and Mo_{154} (Wheel) form in these simulations. The Mo_{36} templates host intermediate compounds and act to enhance the net rate of bimolecular reactions with those intermediates. This is included in the model by increasing the reaction rate constant of bimolecular reactions when one of the reactants is bound to a template.

To characterize the formation of Mo Blue structures, simulations were run using different sets of bimolecular rate constants. We first modeled the system by inhibiting templates and setting the rate constant to 1.0 for all bimolecular reactions, such that the only differences in propensities were due to the differences in the reduced mass and the relative abundances of molecules. In this setting the only structure which formed was Mo_{36} , albeit in relatively low abundance. We next included the effect of templating for the formation of Mo_6 (templated by the Mo_{36}) and the formation of Mo_{154} (also templated by Mo_{36}). We found that while including the effect of templating did result in dramatic increase in the formation of Mo_{36} (both in rate and in steady state abundance), it did not ensure the formation of Mo_{154} or Mo_{132} . While intermediate compounds between the Mo_{36} and the Mo_{154} or Mo_{132} formed readily, those intermediates always degraded before forming complete structures, resulting in many “frustrated attempts.” We propose several mechanisms which overcome this limitation without *fine-tuning* the model. Including any one of these mechanisms in the model results in

the robust formation of larger structures over a large range of parameters.

The model recovers the dynamical characteristics of the experimental system. In typical simulations the abundance of Mo₁₅₄ remains 0 for a time followed by a period of explosive growth. This feature is also seen in experimental data when the solution is not seeded with Mo₃₆. An example time series of this effect is shown in figure 1.

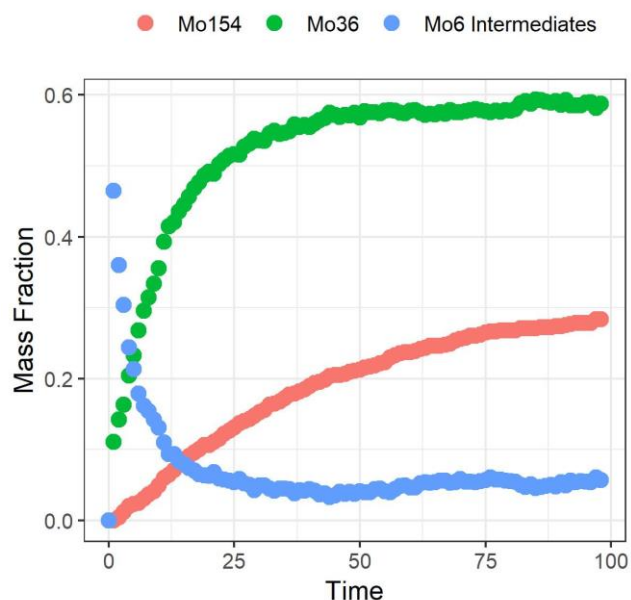


Figure 1: Typical time series from the stochastic simulation. The mass fractions of different molecular species are shown over time. At the beginning of the simulation small intermediates (blue) form rapidly but are transformed into the Mo₃₆ template (green), which then enables the emergence of the larger Mo₁₅₄ wheel (red).

We are currently using this model to investigate alternative mechanisms which could reproduce these dynamical features. We expect to generate new testable hypotheses from the proposed mechanistic pathway which can ultimately be tested in the lab. We are exploring the interactions between the three levels of organization and identifying the most dramatic observable differences between alternative mechanistic pathways.

By interweaving experimental constraints and computational studies we will be able to characterize and explore autocatalysis in a purely inorganic chemical reaction network. Thanks to the hierarchical organization of this particular chemical system we hope to develop new theoretical insights related to how autocatalytic processes drive dynamics within and between different levels.

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