Kinetics of a Reversible, First–Order, Consecutive Reaction

Last week in my PChem Lab, we performed an experiment to study the kinetics of a reversible, first-order, consecutive reaction. I’m just going to go over the general reaction that took place during the experiment without getting too much detail on the analytic part. The concept was the formation of intermediate and how it affects the reaction. So here we go. In the experiment, we studied the double–exponential time dependence of the reduction of Cr(VI) by using glutathione in an aqueous system. The rate constants for the process was obtained by monitoring the absorbance of the reactant and the intermediate. The data was then analyzed by methods of nonlinear regression. The reactant in this reaction was being consumed continuously, while the reaction intermediate was first formed and consumed to produce the final product. The kinetics of the redox reaction between tripeptide glutathione, L-glutamyl-L-cysteinylglycine (GSH), and Cr(VI) was studied. The thio groups link the two GSH units, while oxidizing them to glutathionyl disulfide (GSSG). As the oxidation takes place, the oxidation state of the Chromium ion reduces from +6 to +3. The reaction looked like this:

$$2\text{CrO}_4^2+6\text{GSH}+10\text{H}^+ \rightarrow 2\text{Cr}+3\text{GSSG}+8\text{H}_2$$

The reaction mechanism is expected to involve Cr(VI) to reversibly form the thioester intermediate. The final product was formed form when the thioester intermediate combines with a second GSH molecule. The reaction was broken down in two steps:

$$\text{CrO}_4^2+\text{GSH} \rightarrow \text{CrO}_4^2\text{GSH} \text{ (thioester)}$$

$$\text{thioester}+\text{GSH} \rightarrow \text{GSSG}+\text{Cr}$$

The fact that it is difficult to characterize real life rate processes by simple kinetic models gives rise to reversible, multi-step, consecutive reaction mechanisms. The reaction mechanism proposed in this experiment follows the process in which the reactant, forms an intermediate, and intermediate is reversibly converted to back to reactant while forming product. This is essentially what was happening in the above reactions. The thioester was the intermediate. To visually grasp the concept of intermediates, the blue line was the product, the black line was the reactant, and the
red line was the intermediate. The intermediate was formed and consumed because the concentration curve increases and decreases at the end. The product was constantly formed and the reactant was continuously consumed.

Source: http://lehighcheme.wordpress.com/2014/04/07/kinetics-of-a-reversible-first-order-consecutive-reaction/