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Short Communication

Reaction Rate View on Autocatalysis

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Discussions on autocatalysis rarely inspect rates of reactions though autocatalysis is a kinetic phenomenon. This contribution uses a recently published example of the autocatalytic mechanism and shows how the rate versus concentration profiles support clarification and refinement of the classification and identification of autocatalysis.

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Introduction

Autocatalysis is an interesting example of catalysis where a given reaction product plays the role of catalyst. The general textbook statement, "A reaction whose rate is proportional to the concentration of a product is said to be autocatalytic."[1], can be broadened to more complex reaction schemes: "...a product of one reaction appears as a catalyst in the same or another coupled reaction."[2] Horváth in recent works[3][4] discussed the correct classification and identification of autocatalysis. He stressed the importance of the proper parametrization to arrive at real autocatalysis. This requires proper (relative) values of the rate parameters (rate constants) in the mass action law formulation of the reaction rates. To support his analysis, results of mathematical modeling of several potential autocatalytic reaction schemes were given in terms of the concentration-time profiles during the reaction. It was illustrated that sigmoidal product concentration-time profiles, which are often considered as an indicator or even proof of autocatalysis, are not unique to an autocatalytic course. The modeling results demonstrated accelerated product formation when the product's initial concentration was non-zero and increased progressively. Consequently, the product served as a catalyst in the given reaction system which was thus used to refine the definition of autocatalysis (and of autocatalyst).

Autocatalysis is a kinetic phenomenon – a reaction is accelerated by its product. Interestingly, perhaps no attention has been paid to reaction rates in discussions and modeling of autocatalytic schemes though the reaction rate is a core quantity in kinetics. Although rate equations are given in, e.g., ref.[4] no rates are addressed in it, and discussion applies only to concentration-time profiles. This short article aims to extend the recent analyses by inspecting reaction rate profiles and thus to show how the rates contribute further clarification and refinement of the classification and identification of autocatalysis from an authentic and direct kinetic viewpoint. The main tool is the very definition of autocatalysis, in the sense of the dependence of a reaction rate on product concentration, particularly of the rate increasing with rising product concentration. Modeling was performed with the Chemical Reaction Engineering Module of the COMSOL Multiphysics package, version 5.6; the model of a batch reactor was used.

Results and Discussion

Horváth used[3][4] (among others) a simple but realistic autocatalytic scheme – a Landolt-type reaction system written generally as a 3-step scheme:

$$A + B \rightarrow C, \qquad (1)$$

$$B + C \rightarrow D, \qquad (2)$$

$$A + D \rightarrow 2C. \qquad (3)$$

The first step is, in fact, a direct route to the formation of the product C. The sum of the second and third steps is formally the first reaction again but, in this case, the product C formation can be of (two-step) autocatalytic type, particularly due to the third step and its formal stoichiometry.

Let us briefly analyze the kinetics of the first step alone. When there is no product initially ($c_C^0 = 0$) its formation rate is $r_C = k_1(c_A^0 - c_C)(c_B^0 - c_C)$. The

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product concentration can change (in a batch system) from zero to $\min\left(c_A^0, c_B^0\right)$. The formation rate as a function of the product concentration has derivative $k_1\left[-\left(c_A^0 + c_B^0\right) + 2c_C\right]$; it is an easy task to show that this derivative is negative, thus the function is decreasing and no acceleration of the reaction rate by the product is observed. It is noteworthy that, being proportional to the concentration of the product, the rate still fulfills the above textbook autocatalysis definition by Berry et al. [1] which is thus seen to be insufficient. There is, however, a subtle difference – although the rate is (mathematically) proportional to the product concentration, it is not (chemically) controlled and increased by this concentration.

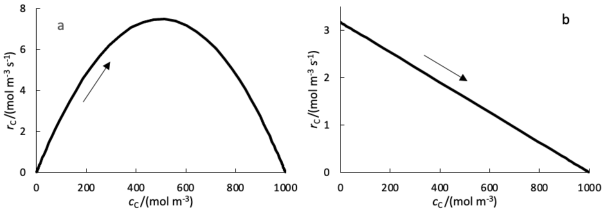

Figure 1. The product formation rate versus the product concentration calculated with the set Nr. 1 (a) and 2 (b) in Table 1. The arrow shows the course of time.

The formation rate of C in the full Landolt-scheme (1)-(3) is $r_C = r_1 - r_2 + 2r_3$. The product concentration directly participates in the mass-action kinetic expression for r_2, further, the concentration of the intermediate D is hidden in r_3, with the rate of the step also giving the product C.

Figure 1a shows the relationship between r_C and the product concentration calculated with the set of the rate parameters Nr. 1 (Table 1; corresponds to the black curve in Fig. 1b of ref[3]). The increase of the rate (in the first half) is evident and can be accepted as a strong indicator of autocatalysis in the sense of a product accelerating, i.e. catalyzing, its formation. The decrease in the second half is caused by the progressive exhaustion of the (initial) supply of reactants A and B which are also necessary for the product C formation. Figure 1b shows a similar situation for the set Nr. 2 (Table 1; corresponds to the cyan curve in Fig. 1 of ref[4]). The product formation rate is steadily decreasing with the product concentration. Thus, no autocatalysis is observed which is the consequence of the too low value of k_2 relative to k_1. This is further illustrated in Figure A1 (Appendix) obtained with a slightly higher value of k_2 (set Nr. 3 in Table 1) and a smaller (in comparison with Figure 1a) autocatalytic rate increase. The importance of the proper parametrization in autocatalysis[3][4] is confirmed directly by the behavior of reaction rate. Let us note that the original works[3][4] show a sigmoidal and concave-only product C concentration profile for the sets Nr. 1 and 2, respectively.

In contrast to the supposition $k_3 \gg k_2, k_3 \gg k_1$ used mostly in ref.[3] and exclusively in ref. [4], the rate approach shows autocatalysis also for higher values of k_2. An example is given in Figure 2 for the set Nr. 4 from Table 1. Equal values of all rate constants did not show autocatalytic behavior (Figure A2 in Appendix).

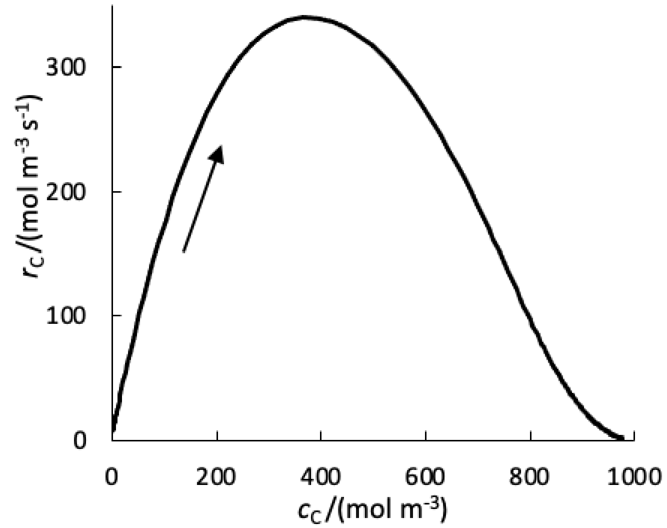

Figure 2. The product formation rate versus the product concentration calculated with the set Nr. 4 in Table 1. The arrow shows the course of time. Inset shows the concentration-time profile.

Table 1. Values of rate parameters used in the modeling of reaction system (1)-(3) in a batch reactor. Initial conditions (mol m^{-3}): $c_A^0 = c_B^0 = 1000$, $c_C^0 = 0$ except set 6 where $c_A^0 = 700$.

set	k_1	k_2	k_3	note
	$mol^{-1}m^3s^{-1}$			
1	10^{-8}	$3×10^{-5}$	10^4	corresponds to the black curve in Fig. 1b of ref.[3]
2	$3.16×10^{-6}$	$3.16×10^{-6}$	10^4	corresponds to the cyan curve in Fig. 1 of ref.[4]
3	$1.58×10^{-6}$	$6.33×10^{-6}$	10^4	Figure A1 in Appendix
4	10^{-5}	$5×10^{-3}$	$5×10^{-3}$	–
5	10^{-3}	10^{-3}	10^{-3}	Figure A2 in Appendix
6	10^{-9}	$5×10^{-5}$	10^4	corresponds to Fig. 2b of ref.[3]
7	10^{-5}	10^{-4}	10^{-5}	–

A rather intricate rate-concentration relationship is found for set 6 (Table 1) which corresponds to Fig. 2b of ref.[3] (see Figure 3). The initial autocatalytic rate increase reverses to a negative production rate due to the decrease of the rate of the step (3) because the supply of A had been exhausted. The component C is then only consumed in step (2) at a decreasing rate (corresponding to the decreasing supply of B). Figure 3 also shows that the rate r_c is not a true function of the C concentration because there is not a one-to-one correspondence at all points. This rate-concentration relationship is “only” a useful indicator of the occurrence of autocatalysis.

An interesting “delayed” autocatalysis is observed for set 7 (Table 1) with (to a certain extent) a higher value of k_2 relatively to k_3 (which, in turn, is equal to k_1), see Figure 4a. The product formation rate decreases with its concentration, at first, then a temporary increase is observed rising a local maximum; the increasing segment is the interval of the autocatalytic course. On the product concentration profile this becomes evident as a sigmoidal shape “with a delay” (Figure 4b). It should be noted that refs.[3][4] correctly emphasize that the sigmoidal shape itself is not a (sufficient) proof of autocatalysis.

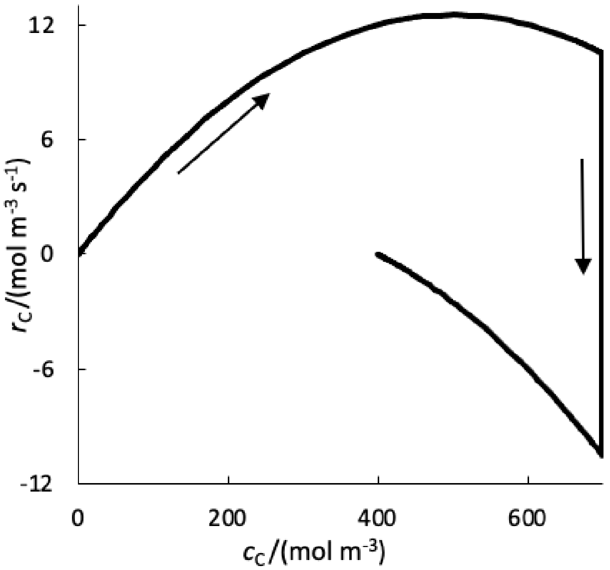

Figure 3. The product formation rate versus the product concentration calculated with the set Nr. 6 in Table 1. The arrow shows the course of time.

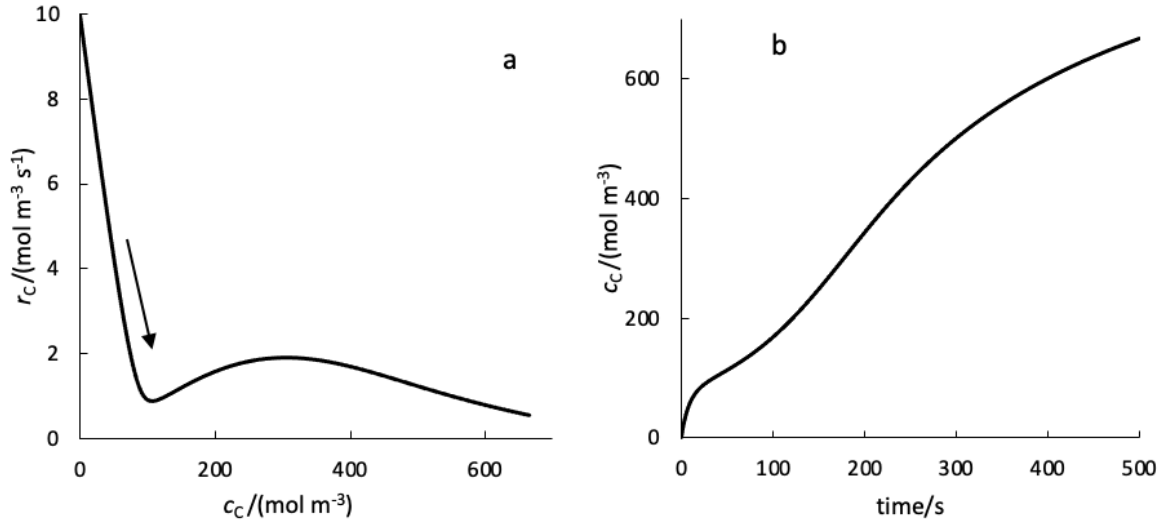

Figure 4. The product formation rate versus the product concentration (a) and the product concentration-time profile (b) calculated with the set Nr. 7 in Table 1. The arrow shows the course of time.

Conclusion

In conclusion, especially in mathematical modeling studies of reaction kinetics, it is very easy to follow the reaction rates and their change in time and in relation to (product) concentrations. Autocatalysis can be thus seen directly as a reaction course in which the product formation rate increases with its concentration. This increase in rate needs not occur during the entire reaction time. The rate approach is quite general, based on the very definition of autocatalysis and can be used regardless of the initial concentration of the (potentially autocatalytic) product. The rates should not be ignored in favor of concentrations. The concentration-time profiles should be used as an additional tool.

Appendix

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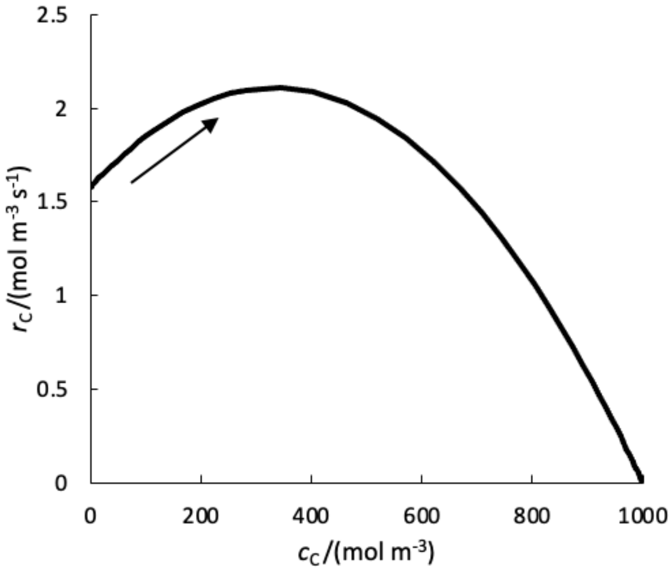

Figure A1. The product formation rate versus the product concentration calculated with the set Nr. 3 in Table 1 in the main text. The arrow shows the course of time.

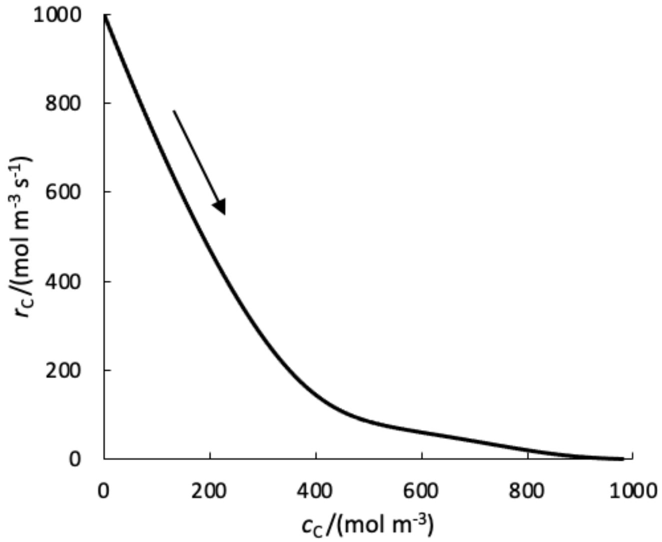

Figure A2. The product formation rate versus the product concentration calculated with the set Nr. 5 in Table 1 in the main text. The arrow shows the course of time.

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Declarations

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