An Autocatalytic Constant Sensitivity Detection System for Catalysts and Infectors

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(Received February 6, 1995)

Mathematical model calculation shows that the shape of the reactant concentration-time curves of autocatalytic reaction system at their inflection time is similar to each other even for different initial concentrations of catalysts. It should be of great value as a theoretically infinite sensitivity detection system for catalysts or its infectors. This model has been demonstrated by the use of oxidative destruction of cobalt complexes of 2,4-(2-pyridylazo)benzenediolate and phthalocyaninetetrasulfonate with peroxomonosulfate in aqueous phosphate buffer solution (pH 7) at 25°C.

Kinetic methods for trace analysis of metal ions by the use of induction period of various kinds of reaction systems have been extensively studied.[1-4] Characteristic S-shape reaction time curves of autocatalytic systems were also well known. However, it was very recently that detailed kinetic mechanisms of autocatalytic reaction were studied.[5-7] But no analytical method was proposed based on a nature of the reactant concentration-time profile as shown in Figure 1, which was calculated based on the reaction (equation 1) and the integrated second order rate equation 2,

$$R + C \xrightarrow{k} 2C + P \qquad (1)$$

$$[R] = \frac{[R_0]([R_0] + [C_0])}{[R_0] + [C_0]\exp(k([R_0] + [C_0])t)} \qquad (2)$$

where R, C, P, k, and subscript 0 indicate reactant, catalyst, product, rate constant, and initial condition, respectively. On the course of analysis of such curves, we have found that they have a constant slope at the inflection time, t_i, given by equation 3, so that they provide a constant sensitivity detection system for any concentrations of catalysts and infectors, even at infinite concentrations.

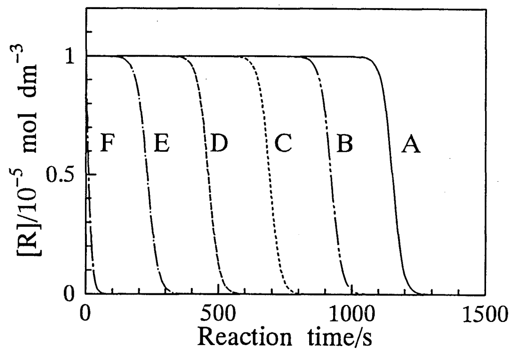

Figure 1. A model calculation of autocatalytic reaction based on equation 2, where rate constant k/mol^{-1} dm^3 s^{-1} is 5000, [R$_0$]/mol dm^{-3} is 1x10^{-5}, and [C$_0$] are A: 10^{-30}, B: 10^{-25}, C: 10^{-20}, D: 10^{-15}, E: 10^{-10}, and F: 10^{-5} mol dm^{-3}.

$$t_i = \frac{\ln([R_0]) - \ln([C_0])}{k([R_0] + [C_0])} \qquad (3)$$

Noteworthy descriptions have not been found in any analytical journals about such an important nature of autocatalytic reaction system. This finding prompts us to realize it, even though the real systems should have some proper limitations in sensitivity due to the production of the catalyst itself by the non-catalytic path of the indicator reaction, as well as the contamination level of traces of catalysts.

One of the promising system is an oxidative destruction of metal complex [ML$_n$] which produces a metal catalyst, M, as the reaction proceeds (equations 4 and 5).

$$[ML_n] + ox \xrightarrow{k_1} M + P \qquad (4)$$

$$[ML_n] + M + ox \xrightarrow{k_2} 2M + P' \qquad (5)$$

$$[ML_n] + L + ox \xrightarrow{k_3} M + P'' \qquad (6)$$

where L, ox, P, P' and P'', and k_x indicate a ligand, oxidant, reaction products, and rate constant, respectively. The system A is proposed based on equations 4 and 5, and the system B is proposed based on equations 4,5, and 6, where excess ligand L acts as an infector for catalyst M^{n+} ion by reducing its activity with complextaion.

Cobalt ion was found to catalyze the oxidative decomposition of azo-dye complexes and water soluble phthalocyanine metal complexes in the presence of peroxomonosulfate ion at room temperature. An azo-dye ligand, 2,4-(2-pyridylazo)benzenediol (4-(2-pyridylazo)resorcinol: PAR, H$_2$par), was chosen as a chelating reagent taking into account the stability of the complex and its detection sensitivity. The cobalt(III)-PAR complex (Co(par)$_2$) was synthesized and was purified to eliminate the trace amount of free cobalt ion by repeated precipitation with an aqueous ammonia and hydrochloric acid. The Co(par)$_2$ solution is prepared by dissolving it in 2 cm^3 of 0.01 mol dm^{-3} sodium hydroxide solution and diluting it to 1x10^{-4} mol dm^{-3} with water. The standard procedure is as follows: To a 1 cm light-path cell with a small stirrer bar, 2 cm^3 of sample solution containing cobalt(II) ion and 0.4 cm^3 of the Co(par)$_2$ solution are added, and the cell is settled on a spectrophotometer equipped with a cell stirrer. Then, 0.1 cm^3 of 0.25 mol dm^{-3} phosphate buffer solution (pH 7) is added[8], and after 10 s, 0.2 cm^3 of 0.2 wt% oxidizer (OXONE® (ox): $2KHSO_5 \cdot K_2SO_4 \cdot KHSO_4$; Aldrich inc.) aqueous solution is injected to the mixture to start the reaction. The absorbance vs. time curve is measured (Figure 2). According to the increase of the initial concentration of the catalyst (cobalt ion), the inflection time decreases. Therefore, cobalt(II) ion concentration can be determined based on the inflection time dependence. As can be seen from the data in

Figure 2, detection limit of this system can reach at least down to 10^{-8} mol dm^{-3} of cobalt ion.

In the system B, where the excess ligand is added to the reaction mixture, the inflection time increases as the ligand concentration increases. Such system has been realized by the use of PAR as the inhibitor ligand and well-defined shift of inflection time are observed according to the PAR concentration as shown in Figure 3. The inflection time decreased as a function of the metal ion concentration (Figure 4), therefore, this system also can be used for the determination of metal ions.

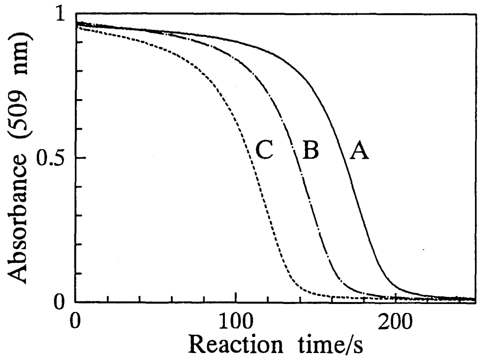

Figure 2. Absorbance-reaction time curve. [ox]/wt% = 0.015, initial concentration of cobalt(II) ion/mol dm^{-3} are A: blank, B: 3.6×10^{-8}, C: 9.1×10^{-8}.

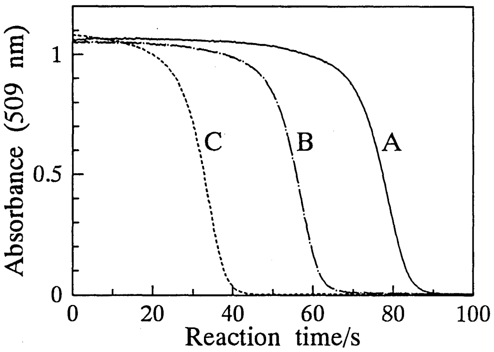

Figure 3. Absorbance-reaction time curve in the presence of excess ligand. [Co(par)$_2$]/mol dm^{-3} = 1.7×10^{-5}, [ox]/wt% = 0.14, PAR concentration/mol dm^{-3} are A: 1.8×10^{-6}, B: 4.4×10^{-7}, and C: blank.

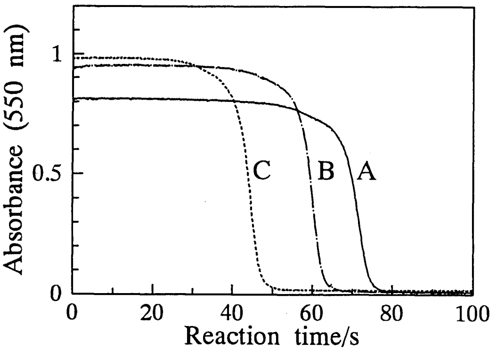

Figure 4. Absorbance-reaction time of the Co(par)$_2$-PAR system . [Co(par)$_2$]/mol dm^{-3} = 2×10^{-5}, [PAR]/mol dm^{-3} = 1.2×10^{-5} , [ox]/wt% = 0.072, concentrations of added cobalt(II) ion/mol dm^{-3} are A: blank, B: 2×10^{-6} , and C: 4×10^{-6} .

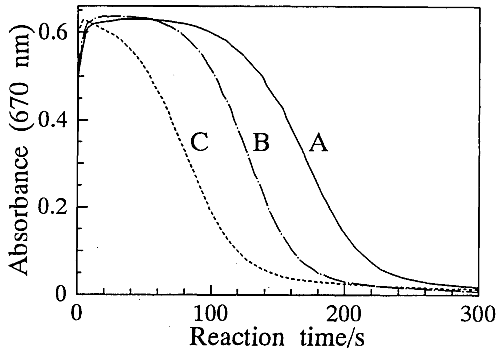

Figure 5. Absorbance-reaction time curve of Co(pts)-8-quinolinol system. [ox]/wt% = 0.033, concentration of cobalt(II) ion/mol dm^{-3} are A: blank, B: 8.5×10^{-8} , and C: 2×10^{-7}.

The kinetic behavior of the system B in the presence of different kind of ligand (for example, 8-quinolinol) from that in the mother complex (for example, cobalt(III)-phthalocyanine-tetrasulfonate: Co(pts)), was also examined [9,10] by the use of the same oxidant and buffer solution as that for Co(par)$_2$ system. If 8-quinolinol acts as inhibitor, the inflection time should be extended as the concentration of 8-quinolinol increases. This was confirmed by the data shown in Figure 5.

It has been demonstrated that a constant sensitivity detection system can be realized by the use of autocatalytic reaction. This method can be applied to the determination of various kinds of species which act as catalysts (either those are the same ions of analytes or the other metal ions which act as triggers) and infectors (such as complexation reagents for metal ions or ion-interaction reagent for metal complexes and ligands). Detailed studies on the forms of the active cobalt species as well as the reaction mechanisms for infectors are now under way.

References and Notes

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8 Phosphate ion accelerates the reaction rate.
9 Chloride ion accelerates the reaction rate.
10 This complex can not be used as the reagent for the system A because the blank reaction rate is large.