# 248. Hyperbolic Reaction Curves with Concentration-Independent Relaxation Times

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*Summary*

Hyperbolic reaction curves with concentration-independent relaxation times are obtained from the simple reaction scheme $A \rightleftharpoons I + P$; $A + I \rightarrow P$. While a mathematically perfect hyperbola is only obtained, if two of the three rate constants are accidentally degenerate, the same function can still be used as a very close approximation in the general case, and the differences may go unnoticed even for well-defined stopped-flow experiments. In view of the simplicity of the reaction scheme, it is suggested that reaction curves with second-order (hyperbolic) shapes, but concentration-independent relaxation times may be a common feature in chemical kinetics.

**Introduction.** – According to elementary kinetics, reaction curves that can be described by a generalized hyperbola (*1*) are obtained from simple bimolecular processes (*2*) (or (*2a*), if the components A and B are present in equal concentrations).

$$Y = a/(1 + bt) + c \tag{1}$$

$$2A \xrightarrow{k_2} P(roducts) \tag{2}$$

$$A + B \xrightarrow{k_{2a}} P(roducts) \tag{2a}$$

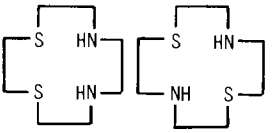
The integrated rate law is given by *Eqn. 3* and if reaction (*2*) is followed spectrophotometrically, a plot of the absorbance E *vs.* time will be described by *Eqn. 3a*. *Eqn. 1, 3, 3a* are identical in structure, and we expect a half-life time $t_{1/2} = 1/([A]_0\, k_2)$ which is inversely proportional to the initial concentration $[A]_0$.

$$[A] = [A]_0/(1 + [A]_0 k_2 t) \tag{3}$$

$$E = d\,(\varepsilon_A\,[A] + \varepsilon_p\,[P]) = d\left(\frac{(\varepsilon_A - \varepsilon_p)\,[A]_0}{1 + [A]_0\, k_2 t} + \varepsilon_p\,[A]_0\right) \tag{3a}$$

Recently, we have come across two completely independent kinetic systems for which the individual reaction curves could be perfectly described by the hyperbolic

function (*1*). The relaxation times were, however, independent of the total concentration, or, the second-order rate constants calculated with *Eqn. 3a* were inversely proportional to the total concentration of the reactive species. The two systems are *i*) the oxidation of ascorbate by $Cu^{2+}$ in the presence of chloride [1], and *ii*) the autoxidation of the Cu(I) complexes with the two 12-membered macrocyclic ligands 1,4-diaza-7,10-dithiacyclododecane (**1**) and 1,7-diaza-4,10-dithiacyclododecane (**2**) [2] [3].




**1** **2**

While the detailed kinetic studies will be published elsewhere [1] [3], we want to describe here, how perfectly hyperbolic reaction curves with relaxation times independent of the total concentration indeed can be obtained under some specific conditions. More important, reaction curves which can be rather closely approximated by hyperbolic functions and also have concentration-independent relaxation times, are likely to be found in many low-molecular and also biochemical systems.

**Experimental.** – The macrocyclic ligands **1** and **2** were synthesized according to [4]. Stopped-flow measurements were done at 25° on a *Durrum D 110* spectrophotometer which was connected to a *Datalab Dl 901* transient recorder and controlled by a *Rockwell AIM 65* microprocessor. Numerical treatment of the data was done on a *Apple II* with a modified version of ELORMA [5] as described in [3]. Model calculations were carried out on a *Hewlett Packard HP 9835* calculator. Full account of experimental details will be given elsewhere [1] [3].

**Results and Discussion.** – In the course of our studies on the copper-catalyzed oxidation of ascorbate by dioxygen [6], we were interested in the reduction of $Cu^{2+}$ by ascorbate in the absence of $O_2$ but in the presence of high concentrations of chloride [1]. In these experiments, we obtained a series of kinetic curves which could be described perfectly by *Eqn. 1*, as shown in *Fig. 1*. The reactions were done using a relatively high excess of ascorbate, and thus it was reasonable to describe the kinetics according to *Eqn. 2* ($A = Cu^{2+}$) and to assume the differential rate law (*4*). However, upon variation of the initial concentration of $Cu^{2+}$ it became obvious that *Eqn. 4* cannot be the correct description, since the relaxation times (of half-life times) were independent of $[Cu^{2+}]_0$. As shown in *Fig. 2*, the second-order rate constants calculated with the aid of *Eqn. 3* are inversely proportional to the initial copper concentration. In other words, the denominator in *Eqn. 3* has to be replaced by $1 + k_2\,t$.

Recently, we have observed the same phenomenon in the autoxidation of the cuprous complexes with the 12-membered macrocyclic ligands **1** and **2** [2] [3].

$$-\,d[Cu^{2+}]/dt = k_{bim}\,[Cu^{2+}]^2 \tag{4}$$

$$2\,Cu^{2+}_{aq} + ascH^- + 4\,Cl^- \rightarrow 2\,CuCl_2^- + asc + H^+ \tag{5}$$

$$2\,CuL^+ + O_2 + 2H^+ \rightarrow 2\,CuL^{2+} + H_2O_2 \tag{6}$$

The stoichiometries of the two reactions mentioned above are given by *Eqn. 5* and *6*, respectively ($ascH^-$: ascorbate monoanion, asc: dehydroascorbic acid). Several

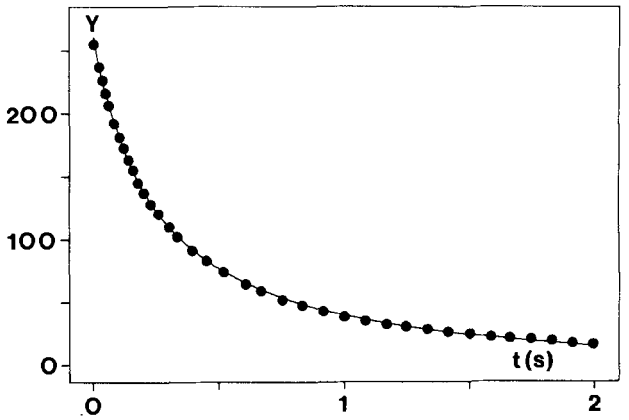



Fig. 1. *Reduction of $Cu^{2+}$ by ascorbate.* Absorbance Y in arbitrary units from an 8-bit transient recorder. $[Cu^{2+}] = 0.002$M, $[ascH_2] = 0.01$M, $[Cl^-] = 0.6$M, pH = 2.05, T = 25°C. ● Experimental points, —— curve calculated according to *Eqn. 3*, $k = 2040 M^{-1}s^{-1}$, Y(0) – Y(inf) = 280, $\sigma(Y) = 1.1$.

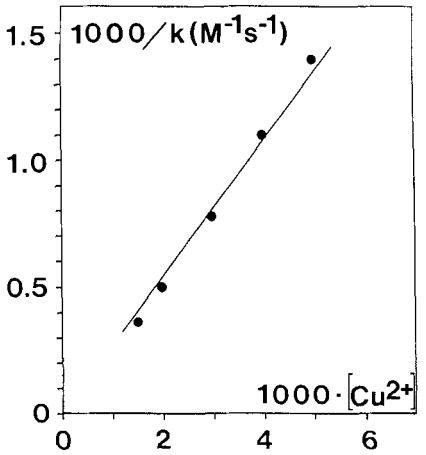



Fig. 2. *Reduction of $Cu^{2+}$ by ascorbate showing inverse proportionality of* $k(M^{-1}s^{-1})$ vs. $[Cu^{2+}]$. $[ascH_2] = 0.01$M, $[Cl^-] = 0.6$M, pH = 2.05, T = 25°C. ● Experimental points.

mechanisms can be invoked for reactions (*5*) and (*6*), and we want to show in the following that the mechanistic schemes (*5a*) and (*6a*) will lead to identical kinetic behaviour, suitable to describe the experimental facts for a given pH.

$$
\begin{aligned}
&ascH^- \rightleftharpoons asc^{2-} + H^+ \quad \text{(fast)} \\
&Cu^{2+}_{aq} + asc^{2-} \underset{k_{-5}}{\overset{k_{+5}}{\rightleftharpoons}} Cu^{+}_{aq} + asc^- \qquad (5a) \\
&Cu^{2+}_{aq} + asc^- \xrightarrow{k_5} Cu^{+}_{aq} + asc \\
&Cu^{+}_{aq} + 2Cl^- \rightleftharpoons CuCl_2^- \quad \text{(fast)}
\end{aligned}
$$

$$\begin{aligned} CuL^+ + O_2 &\underset{k_{-6}}{\overset{k_{+6}}{\rightleftharpoons}} CuL^{2+} + O_2^- \\ CuL^+ + O_2^- &\xrightarrow{k_6} CuL^{2+} + O_2^{2-} \qquad (6a) \\ O_2^{2-} + 2H^+ &\rightleftharpoons H_2O_2 \qquad \text{(fast)} \end{aligned}$$

It should be added that in our experiments the components ascorbate (*5a*) and $O_2$ (*6a*) were present in large excess over $Cu_{aq}^{2+}$ and $CuL^+$, respectively, so that pseudo-first-order conditions can be assumed for the steps $k_{+5}$ and $k_{+6}$.

Neglecting the fast equilibria which have no effect on the shape of the individual reaction curves, the mechanistic schemes (*5a*) and (*6a*) can be replaced by (*7*). Recalling that $[B]_0 \gg [A]_0$ this can be further simplified to (8).

$$\begin{aligned} A + B &\underset{k_{-7}}{\overset{k_{+7}}{\rightleftharpoons}} P + I(\text{ntermediate}) \qquad (7) \\ A + I &\xrightarrow{k_7} P + P' \end{aligned}$$

$$\begin{aligned} A &\underset{k_-}{\overset{k_+}{\rightleftharpoons}} P + I \qquad (8) \\ A + I &\xrightarrow{k} P + P' \end{aligned}$$

Steady state approximation ($d[I]/dt = 0$) yields *Eqn. 9* and *9a*.

$$k_- [I][P] = k_+ [A] - k [I][A] \qquad (9)$$

$$[I] = k_+ [A]/(k_- [P] + k [A]) \qquad (9a)$$

With *Eqn. 9*, *9a* and $[A]_0 = [A] + [P]$, we obtain the rate law in differential (*10*) and in integrated form (*11*) ($K = k_-/k$).

$$\begin{aligned} d[A]/dt &= -k_+ [A] + k_- [I][P] - k [A][I] \\ &= -2k [A][I] \\ &= -2k_+ k [A]^2/(k_- [A]_0 - k_- [A] + k [A]) \qquad (10) \end{aligned}$$

$$K([A]_0/[A] - 1) + (1 - K) \ln([A]_0/[A]) = 2k_+ t \qquad (11)$$

$$t_{1/2} = (K(1 - \ln 2) + \ln 2)/2k_+ \qquad (12)$$

$$[A]_0/[A] - 1 = 2k_+ t \quad \text{or} \quad [A] = [A]_0/(1 + 2k_+ t) \qquad (13)$$

Quite obviously, the half-time of such a reaction *(Eqn. 12)* does not depend on the initial concentration of A, $[A]_0$. Perfect hyperbolic functions are indeed obtained, if $K = k_-/k = 1$. In this case *Eqn. 11* reduces to (*13*) or (*1*) and from individual spectro-

photometric runs we cannot differentiate between proper second-order reaction (*Eqn.2* and *3*) and the mechanistic scheme (*8*) and (*11*), the only difference being that the half-time $t_{1/2} = 1/(2\ k_+)$ is independent of the concentration in the latter case.

Perfect degeneracy of $k_-$ and $k$ and thus exact hyperbolic behaviour would be fortuitous and is not expected to be met in reality. We have, therefore, studied the influence of different values for the ratio $K = k_-/k$. Inspection of *Eqn. 11* shows that a simple exponential is obtained for $K \ll 1$. Such cases were, therefore, not included in our calculations.

Model data were obtained with the complete function (*11*). An error of 1.1 units as obtained experimentally *(cf. Fig. 1)* was superimposed. This is characteristic for well-defined stopped-flow curves obtained with an 8-bit transient recorder [7]. Subsequently, the data were subjected to least-squares treatment using the second-order *Eqn. 3* as the matching function. As expected, a perfect fit is obtained for $K = 1$ (*Fig. 3*, curve *a*). More important, however, is the observation that the goodness of fit does not depend strongly on the value of $K$. The standard deviation $\sigma(Y)$ increases from 1.1 to 1.28 (F = 1.36) or 1.62 (F = 2.19), when $K$ is increased from 1 to 2 or 5, resp. (curves *b*, *c*, *Fig. 3*). For very high values of $K$ (curve *d*, *Fig. 3*), $\sigma(Y)$ converges to 1.87 (F = 2.87) with the present model data ($t_{1/2} = 0.5$ s).

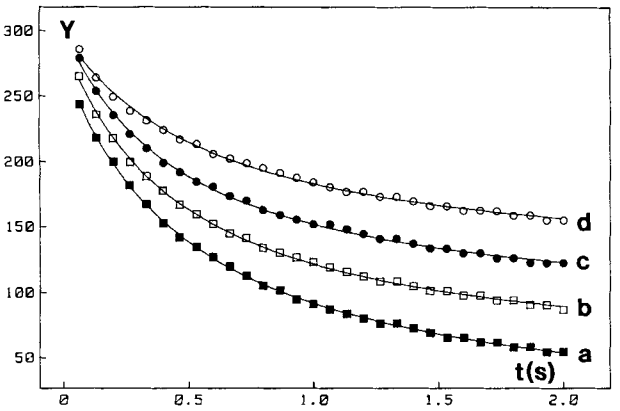



Fig. 3. *Model calculations.* Representation of points obtained from *Eqn. 11* by second-order reaction curves, *Eqn. 3*. Y(0) – Y(inf) = 280, $\sigma$(Y, data) = 1.1 as in *Fig. 1*; $t_{1/2} = 0.5$. a, ■: $K = k_-/k = 1$, $\sigma$(Y, calc.) = 1.1; b, □: $K = 2$, $\sigma$(Y, calc.) = 1.28, F = 1.36; c, ●: $K = 5$, $\sigma$(Y, calc.) = 1.62, F = 2.19; d, ○: $K = 1000$ or 10000, $\sigma$(Y, calc.) = 1.87, F = 2.87. —— Curves calculated according to *Eqn. 3*.

According to the F-test [8] the above F-values are not or barely significant on the 99% confidence level ($F_{lim} = 2.7$). It must be added that the model data used in the present case (standard error 0.4%) correspond to stopped-flow data of rather high quality. Distinction between the complete function (*11*) and the simple hyperbola (*1*) becomes completely impossible, if data with higher noise levels have to be processed. Hence, for $K \geq 1$, kinetic curves obtained from reactions of type (*8*), will in general be quite well described by the hyperbolic function (*1*), suggesting second-order kinetics with relaxation times independent of the total concentration. In view of the simplicity

of (*8*), we assume that our two systems (*5a*) and (*6a*) are by no means unique and that similar kinetic behaviour can be obtained in many fields of chemistry, despite the fact that this type of kinetic behaviour does not seem to have been reported so far.

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