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## Inherent Pitfalls in the Simplified Evaluation of Kinetic Curves

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It is shown and explained in detail by four examples generated from known kinetic models that simplified evaluation procedures—initial rate studies, individual exponential curve fitting method—may inherently lead to inappropriate chemical conclusions, even in the case of relatively simple kinetic systems. It is also shown that in the case of all four examples the simultaneous curve fitting immediately reveals the defectiveness of the kinetic model obtained from the simplified evaluation procedures. We therefore propose the extensive usage of the simultaneous curve fitting of all the kinetic traces to avoid these pitfalls and to find the appropriate kinetic models.

### Introduction

Evaluation of the kinetic curves based on the methods of initial rates and/or the individual exponential fit of the (pseudo-) first-order kinetic curve is a widely accepted procedure to unravel the kinetics and mechanism of a chemical system. Systematic search among the articles published in leading journals from 1997—such as *The Journal of the American Chemical Society*, *The Journal of Physical Chemistry A and B*, and the *Inorganic Chemistry*—have provided more than three-thousand research papers containing the phrase of “initial rate” or “pseudo-first order”. All the textbooks of physical chemistry treat these simplified evaluation techniques as almost an exclusive choice to determine the governing rate equation of the chemical system in question because the analytical solution (concentration–time series) of the ordinary differential equation system rarely exists.<sup>1</sup> Before the era of the personal computers, however, these procedures were indeed the only way to successfully obtain a rate equation and to suggest a plausible mechanism of a chemical system. The barrier of these evaluation methods was already noticed in the early 1950s by Awtrey and Connick.<sup>2</sup> The lack of powerful computational technique prevented their explanation of the unexpected iodide dependence of the apparent rate coefficients of the iodine–tetrathionate reaction. In their own words “... It is therefore concluded that the system is more complicated than was assumed. ... These results are being reported now because further work could not be carried out at this time ...”. Although the shortcomings of these evaluation procedures were already discovered more than half a century ago, they have fallen into oblivion and even nowadays thousands of research articles have been published in the field of chemical kinetics leaning solely on the simplified evaluation techniques.

The past couple of decades have witnessed revolutionary development in the instruments collecting concentration–time data pairs (or proportional to concentration such as absorbance, potential, etc.) and computational techniques as well. This development made it possible to measure the actual values of the characteristic quantities by powerful and precise data-acquisition systems and to evaluate many kinetic traces mea-

sured in the system at different experimental circumstances (concentration ratios, wavelength, pH, etc.) simultaneously. The evaluation procedures, however, have neglected this revolutionary development. Even nowadays the software provided with brand-new instruments does not offer evaluation procedures that point beyond the usual chemistry textbook.<sup>1</sup> To follow the possibilities of the new instrumentations and the increasing computational power we have developed different methods to determine the number of absorbing species in kinetic systems or in a system in equilibrium state.<sup>3–5</sup> Besides, we have also developed a program package ZiTa for the simultaneous evaluation of the kinetic curves.<sup>6</sup> Its main advantage is that it not only simulates the experimental data but also fits the kinetic parameters of the ordinary differential equation system rigorously by minimizing the average deviation between the measured and calculated data of the kinetic curves practically in the case of all types of possible measurements. Having these powerful evaluation techniques, we have published the results of several kinetic studies<sup>7–15</sup> and some other laboratories have also utilized the possibilities of the program.<sup>16–18</sup> One of us has recently pointed out<sup>19</sup> that exclusive usage of the simplified evaluation techniques might result in false conclusions in determining the kinetics of a real chemical system. Stanbury and Figlar have also shown<sup>20</sup> that inappropriate handling of kinetic data may also lead to contradictory results in real chemical systems. Our latest result<sup>21</sup> has just provided the long-awaited answer about the iodide dependence of the iodine–tetrathionate system raised<sup>2</sup> by Awtrey and Connick. As was already pointed out, the simplified evaluation methods were not sufficient to resolve the problem, it was only the simultaneous curve fitting method that was able to give the proper explanation. Recently, a series of papers have been published,<sup>22–25</sup> mainly in the field of gas kinetics, clearly indicating that a more reliable reaction mechanism may be obtained if several different experimental data are handled simultaneously. The high number of the papers published in leading journals in the past decade and the possible misinterpretations of the results obtained by simplified evaluation methods have convinced us of the necessity of publishing this paper. More than fifteen years of experience with the programs and with other evaluation techniques of the kinetic curves have led us to the results presented in this paper. Based on real experiments but illustrated

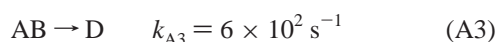
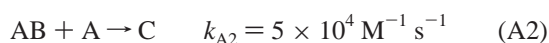
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on model calculations, we show that the simplified evaluation of the kinetic curves may inherently lead to false chemical conclusions even in the case of relatively simple kinetic models. Moreover, it is shown that the pitfalls may be avoided if the whole time series measured at different concentration ratios and different concentrations are evaluated simultaneously and the kinetic data cover at least 60–95% conversion.

### “Experimental” Section

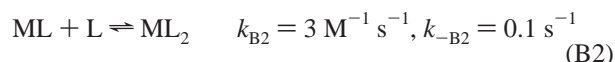
The “experimental data” in all four examples presented below were in fact generated from realistic kinetic models. The reason for choosing to imitate the experiments with simulations is to make sure of the exact kinetic model to be determined from the simplified evaluation procedures. The theoretically calculated “experimental data” are then altered by 0.5% experimental error obeying Gaussian error-distribution to imitate the real experiments. These “experimental curves” are used for further evaluation including the simplified techniques, i.e., the individual curve fitting based on pseudo-first-order approach or initial rate studies. A kinetic model in each case has been suggested from the results of the simplified techniques that can be concluded by any competent chemist.

**Case A.** A branching mechanism is considered in which the adduct formed from the reactants reacts further in parallel pathways.



All the steps are supposed to be elementary reactions. The initial concentration of reactant B was kept constant at 0.001 M and the initial concentration of reactant A was varied between 0.03–0.2 M to fulfill pseudo-first-order conditions. The concentration of reactant B is followed throughout the “experiments”. This example remarkably resembles the kinetic models obtained by our previous works<sup>3,14</sup> and other research groups<sup>20,26,27</sup> in different chemical systems.

**Case B.** A simple stepwise complex formation is considered in this example.



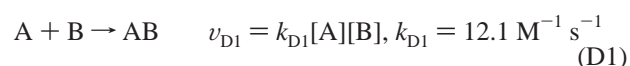
All the rate equations in the model follow the law of mass action. The initial metal concentration (M) was kept constant at  $3 \times 10^{-4}$  M and the initial ligand concentration was varied between 0.003 and 0.06 M to fulfill pseudo-first-order conditions. The concentration of the metal ion was followed during the “experiments”. This example is a simplified version of our recently studied  $\text{Fe}^{3+}$ – $\text{SO}_4^{2-}$  system.<sup>28</sup>

**Case C.** A complex formation is studied in this example, where the law of mass action is valid for all the rate equations.



The initial concentration of the ligand was kept constant at 0.01 M, and the metal concentration was varied between 0.05 and 0.30 M to maintain the pseudo-first-order condition. The ligand concentration was followed during the “experiments”, but the data were evaluated only from 0.007 M, as the reaction is fast. The reaction can conveniently be followed by stopped-flow technique; thus the first part of the signals should be neglected due to the well-known instrumental parameters (dead time, mixing time).<sup>29</sup> This example is also based on a real chemical system, namely the copper(II)–bipyridyl system determined by the T-jump relaxation technique.<sup>30</sup> All the rate coefficients have been decreased by 6 orders of magnitude to reach the convenient stopped-flow time scale.

**Case D.** A branching mechanism is considered in which the rate determining step is pH-independent but the branching ratio strongly depends on pH.

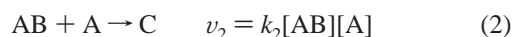


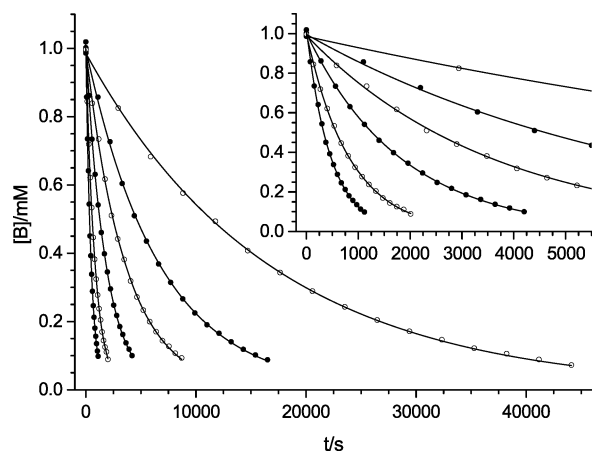
The initial concentration of the reactants A and B were kept constant at  $[A]_0 = 0.0015$  M and  $[B]_0 = 1 \times 10^{-4}$  M, respectively and the  $[H^+]$  was varied between  $(3 \text{ and } 100) \times 10^{-5}$  M. In each single run, however,  $[H^+]$  was kept constant throughout the whole time interval. The reaction was followed throughout the initial rate of formation of the product C. The final example is based on the proposed kinetic model of the reaction between iodide and periodate ion published in detail recently.<sup>19</sup>

As one may notice, Cases A and D or Cases B and C are quite similar examples, respectively. The main difference between Cases A and D is that Case A is evaluated by individual exponential fit of the pseudo-first-order kinetic curves whereas the kinetic model of Case D is determined from initial rate studies. Cases B and C differ from each other in the time scale thus the first part of the kinetic curves in Case C is excluded due to instrumental parameters (dead-time, mixing time). Additional to that in Case B and Case C, the concentrations of the metal and ligand are followed, respectively.

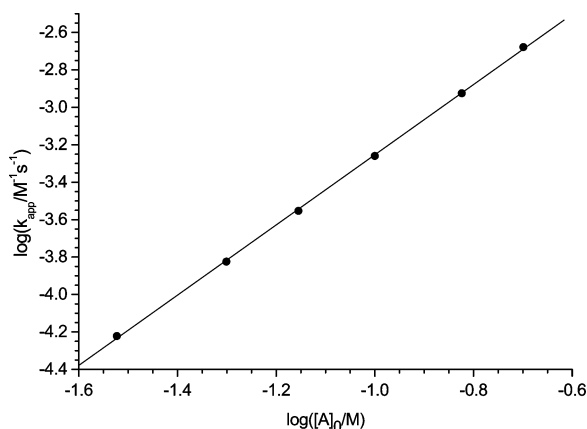
### Results and Discussion

**Case A. Individual Curve Fitting.** Figure 1 shows the decrease of concentration of reactant B in excess of different amount of reactant A as a function of time. The individual exponential fitting of the kinetic traces is perfect thus the exponent gives the pseudo-first-order rate coefficients ( $k_{app}$ ). The logarithm of these rate coefficients is then plotted as a function of  $\log [A]_0$  in Figure 2 that shows perfect linear dependence having a slope to be  $1.88 \pm 0.04$ . It clearly indicates that the kinetic order of reactant A is 2. The straightforward conclusion from these figures is that the reaction takes place through a fast pre-equilibrium (shifted to the left) between reactants A and B, and the encountered complex reacts further with A producing C, i.e.:





**Figure 1.** “Measured” (symbols) and calculated (solid lines) kinetic curves at  $[B]_0 = 0.001$  M in case of individual curve fitting (Case A).  $[A]_0/M$  (left to right) = 0.03 (●), 0.05 (○), 0.07 (●), 0.1 (○), 0.14 (●), 0.2 (○). The inset shows the early stage of the kinetic curves.

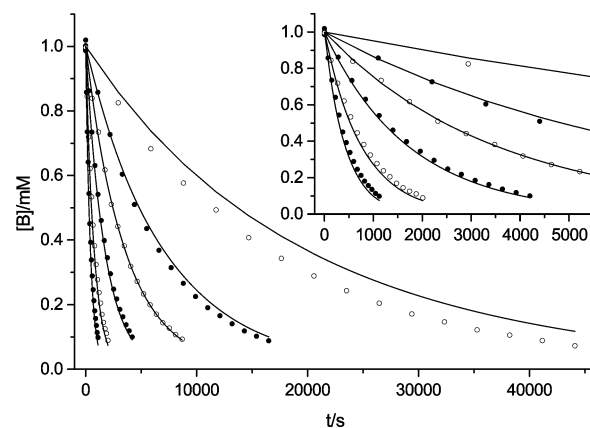


**Figure 2.** Logarithm of the apparent rate coefficient as a function of  $\log[A]_0$  (Case A). The slope and the intercept were calculated to be  $1.88 \pm 0.04$  and  $-1.38 \pm 0.03$ , respectively.

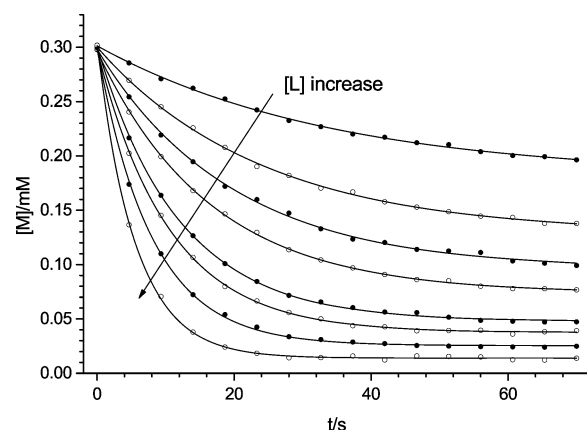
From these experiments only the product of  $k_2K_1 = (4.2 \pm 0.4) \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$  could be determined from the intercept of the linear regression obtained from the log–log representation in Figure 2.

**Simultaneous Curve Fitting.** As one may easily notice, the evaluation with a simplified method has provided a slightly lower value for  $k_2K_1 = 4.2 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$  than for  $k_{A2}k_{A1}/k_{-A1} = 0.05 \text{ M}^{-2} \text{ s}^{-1}$  from which the “experimental” data were generated. Though the difference is not striking (16%) it is expedient that such an excellent fit of the transformed data may provide the same value within the “experimental” error. Nevertheless, the simplified evaluation procedure has resulted in a loss of an important chemical step A3. If, however, we try to fit the experimental data simultaneously with eqs 1 and 2 the results of the best fit achieved can be seen in Figure 3. It clearly indicates that the model determined from the simplified evaluation procedure is not working properly; it requires assumption of other process(es).

**Case B. Individual Curve Fitting.** Figure 4 shows the experimental data of the concentration of metal ion as a function of time. It is clearly seen that even 40-fold ligand excess does not lead to a complete complexation; i.e., the kinetic curves should be evaluated by the following equilibrium process:



**Figure 3.** “Measured” (symbols) and calculated (solid lines) kinetic curves at  $[B]_0 = 0.001$  M in case of simultaneous curve fitting (Case A).  $[A]_0/M$  (left to right) = 0.03 (●), 0.05 (○), 0.07 (●), 0.1 (○), 0.14 (●), 0.2 (○). The inset shows the early stage of the kinetic curves.



**Figure 4.** “Measured” (symbols) and calculated (solid lines) kinetic curves at  $[M]_0 = 0.3$  mM in case of individual curve fitting (Case B).  $[L]_0/mM$  = 3.0 (●), 6.0 (○), 9.0 (●), 12.0 (○), 18.0 (●), 22.0 (○), 30.0 (●), 45.0 (○).

This simple equilibrium model leads to the following analytical solution:

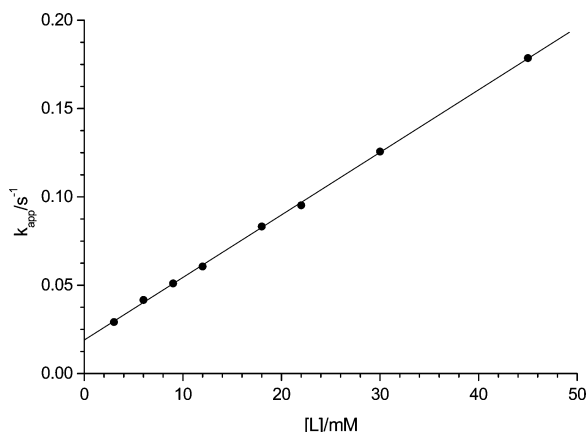
$$[M]_t = \frac{T_M k_3 [L]}{k_3 [L] + k_{-3}} + \frac{T_M k_{-3}}{k_3 [L] + k_{-3}} e^{-(k_3 [L] + k_{-3})t} \quad (4)$$

i.e.,

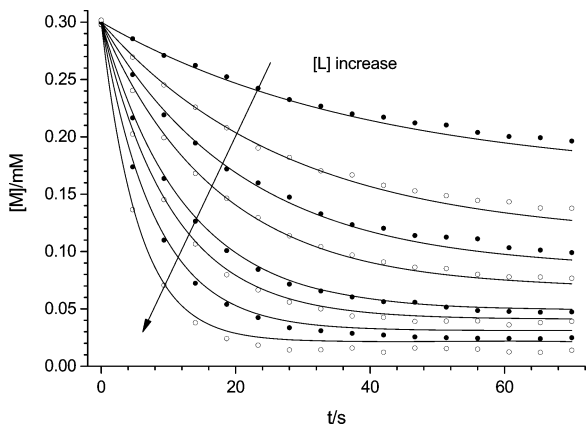
$$[M]_t = a + b e^{-k_{app}t} \quad (5)$$

where  $T_M = [M]_t + [ML]_t = 3 \times 10^{-4} \text{ M}$  and  $k_{app} = k_3 [L] + k_{-3}$ . The solid lines in Figure 4 show the best fits<sup>31</sup> if the experimental data are evaluated individually by eq 5. The calculated pseudo-first-order rate coefficients ( $k_{app}$ ) are plotted as a function of the ligand excess in Figure 5. The straight line seems to be perfect with an intercept  $0.019 \pm 0.002$  and with a slope  $3.54 \pm 0.07$ , from which even the equilibrium constant of ML may be calculated,  $K_{ML} = k_3/k_{-3} = 186 \pm 20$ .

**Simultaneous Curve Fitting.** It is easy to realize that the simplified evaluation procedure has hidden the second step of the complexation process by nice individual fits of the kinetic curves and by a perfect straight line of the apparent pseudo-first-order rate coefficient as a function of the ligand concentration. Although the stability constant of ML is not so bad if one compares  $K_3 = 186 \text{ M}^{-1}$  with  $K_{B1} = k_{B1}/k_{-B1} = 200 \text{ M}^{-1}$ , the simultaneous curve fitting method suggests (see Figure 6) that the kinetic model may contain other processes because system-



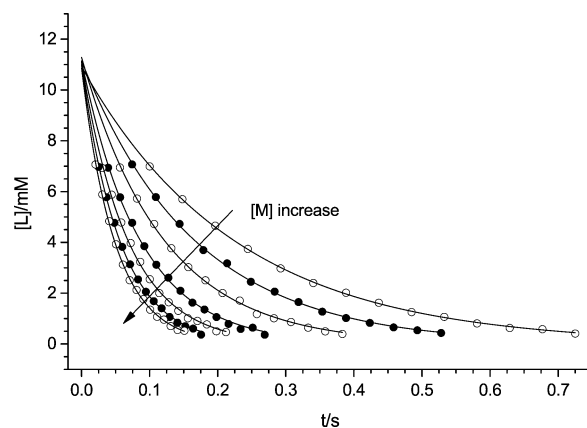
**Figure 5.** Dependence of the apparent rate coefficient on the ligand concentration (Case B). The slope and the intercept were calculated to be  $3.54 \pm 0.07$  and  $0.019 \pm 0.002$ , respectively.



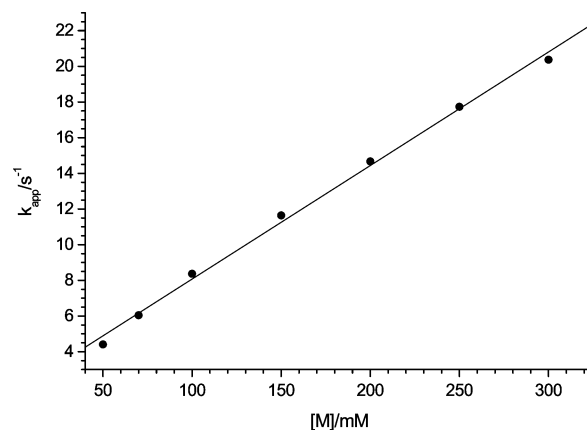
**Figure 6.** “Measured” (symbols) and calculated (solid lines) kinetic curves at  $[M]_0 = 0.3$  mM in case of simultaneous curve fitting (Case B).  $[L]_0$ /mM = 3.0 (●), 6.0 (○), 9.0 (●), 12.0 (○), 18.0 (●), 22.0 (○), 30.0 (●), 45.0 (○).

atic deviation can be noticed especially at the end of the kinetic curves. If we compare the results of the simultaneous and the individual fits (see Figures 4 and 6), the difference becomes more striking. The deviation stems from the following fact: according to the “experimental” section, four parameters would give a perfect description of the kinetic curves. In case of individual fits, three parameters ( $a$ ,  $b$ , and  $k_{app}$ ) are calculated for each kinetic trace and parameters  $a$  and  $b$  are also adjusted to find the best results. The eight kinetic curves are described by 24 parameters altogether but only the eight  $k_{app}$  values are used to reach the final conclusion. That is why the formation of  $ML_2$  is not even “detected” despite the fact that at the highest ligand concentration  $ML_2$  is the dominating complex. In the case of the simultaneous fitting procedure (Figure 6) only  $k_3$  and  $k_{-3}$  are calculated, i.e., there are no surplus parameters to cover the model error. It strengthens the fact again that the simplified evaluation procedure may lead to an incorrect conclusion. Besides, it shows that before the kinetic experiments it is important to carry out detailed stoichiometric studies to determine the composition of a reacting system when it reaches the equilibrium state. This example is given as a simplified version of our recently studied  $Fe^{3+}-SO_4^{2-}$  system.<sup>28</sup>

**Case C. Individual Curve Fitting.** Figure 7 shows the decrease of the ligand concentration in excess of different amounts of metal ion. The calculated pseudo-first-order rate coefficients as a function of excess metal ion give a fairly acceptable straight line (see Figure 8). It indicates that a complete complex formation takes place and, because of the

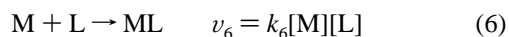


**Figure 7.** “Measured” (symbols) and calculated (solid lines) kinetic curves at  $[L]_0 = 10.0$  mM in case of individual curve fitting (Case C).  $[M]_0$ /mM = 50.0 (○), 70.0 (●), 100.0 (○), 150.0 (●), 200.0 (○), 250.0 (●), 300.0 (○).



**Figure 8.** Dependence of the apparent rate coefficient as a function of the metal concentration (Case C). The slope was calculated to be  $64.5 \pm 6.3$ .

metal ion excess, only  $ML$  complex is formed; i.e., the appropriate model is



with a  $k_6 = 64.5 \pm 6.3 \text{ M}^{-1} \text{ s}^{-1}$  calculated from the slope of the straight line in Figure 8.

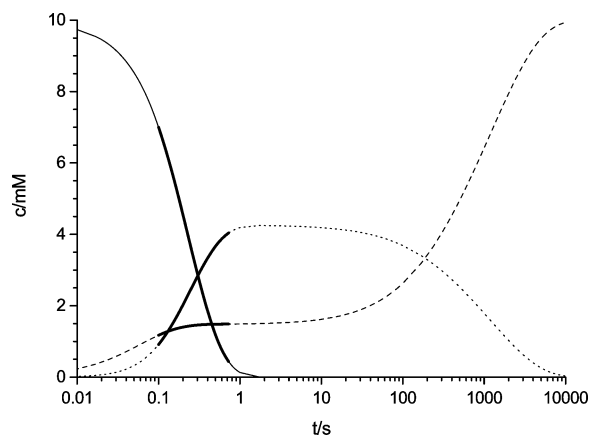
**Simultaneous Curve Fitting.** Comparing the kinetic model obtained from the individual curve fitting method with the original model reveals surprising difference. The real two-step complexation process (D1–D2) is falsely reduced to a single reaction (eq 6). Figure 9 provides a simple explanation for how it may be interpreted. The striking feature of this kinetic model is that, in spite of the metal excess,  $ML_2$  is the dominating complex that is formed from a practically constant  $[ML]$  in the stopped-flow time scale. The majority of  $ML$  is, however, formed throughout the slow dissociation of  $ML_2$ , not from the direct association process. As the concentration–time curves suggest, in fact the



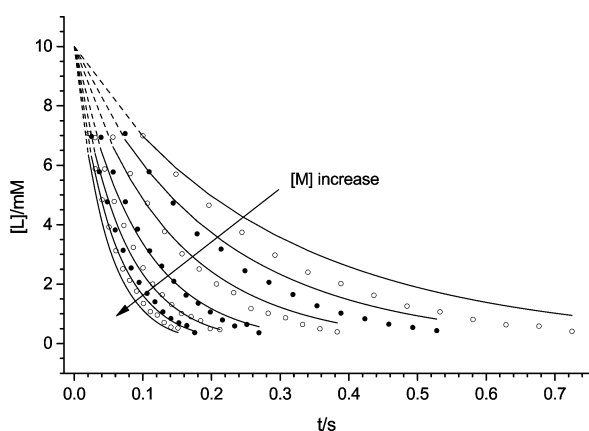
process takes place; therefore

$$\frac{d[L]}{dt} = -k_8[ML][L] \quad k' = k_8[ML] \quad (8)$$





**Figure 9.** Calculated concentration–time curves based on the kinetic model of Case C. The concentrations of L, ML, and  $ML_2$  as a function of time are indicated by solid, dashed, and dotted lines, respectively.  $[M]_0 = 50.0$  mM,  $[L]_0 = 10.0$  mM.



**Figure 10.** “Measured” (symbols) and calculated (solid lines) kinetic curves at  $[L]_0 = 10.0$  mM in case of simultaneous curve fitting (Case C).  $[M]_0$ /mM = 50.0 (○), 70.0 (●), 100.0 (○), 150.0 (●), 200.0 (○), 250.0 (●), 300.0 (○).

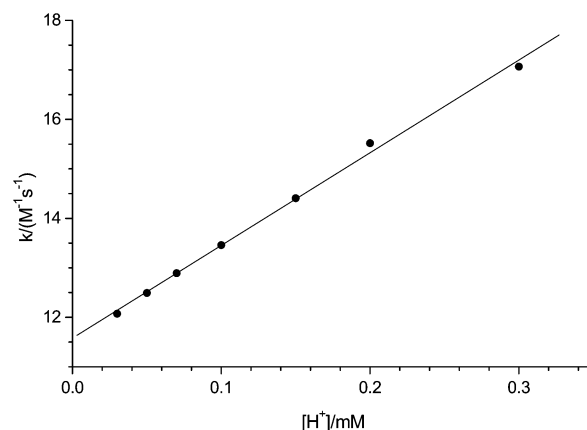
It clearly means that constancy of  $[ML]$  provides such a condition in the reacting system that the disappearance of the free ligand obeys first-order kinetics. This decay may easily be misinterpreted by eq 6 using metal excess. If, however, we try to fit the “experimental” data with eq 6 simultaneously (as seen in Figure 10) the systematic deviations between the measured and calculated data unambiguously indicate the deficiency of the model obtained from the individual fit of the kinetic curves.

**Case D. Individual Curve Fitting.** Figure 11 shows the dependence of the apparent second-order rate coefficient, calculated from the initial rate and the initial concentrations of A and B, on the concentration of  $[H^+]$ . The perfect straight line with a nonzero intercept clearly indicates that the rate-determining step has both a  $[H^+]$ -dependent and  $[H^+]$ -independent part, i.e.,

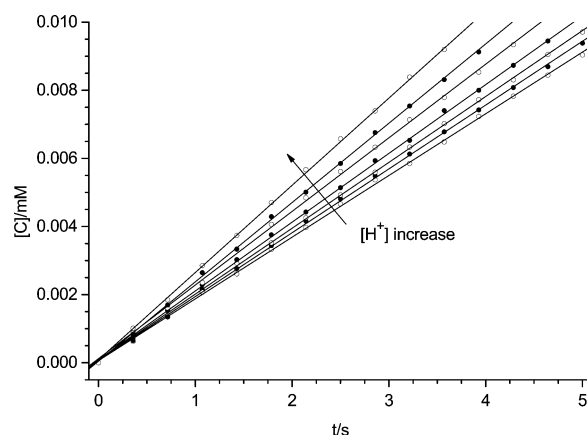


where  $k_9 = 11.6 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$  and  $k'_9 = (1.87 \pm 0.11) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ .

**Simultaneous Curve Fitting.** In contrast to the results of the initial rate study, which indicates both pH-dependent and pH-independent parts of the rate equation (see eq 9), the “experimental” data are generated from such a kinetic model where the initial rate-determining step is independent of pH but the stoichiometry strongly depends on it; thus the formation of product C also depends on pH (see Figure 12). This fact may



**Figure 11.** Dependence of the apparent second-order rate coefficient on the concentration of  $H^+$  (Case D). The intercept and the slope were calculated to be  $11.6 \pm 0.2$  and  $(1.87 \pm 0.11) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ , respectively.



**Figure 12.** “Measured” (symbols) and calculated (solid lines) kinetic curves at  $[A]_0 = 1.5$  mM and  $[B]_0 = 0.1$  mM in case of individual curve fitting (Case D).  $[H]/\text{mM} = 0.03$  (○), 0.05 (●), 0.07 (○), 0.1 (●), 0.15 (○), 0.2 (●), 0.3 (○).

be misinterpreted as if the rate-determining step has a pH-dependent part if only the initial rate is used to generate the kinetic model. If, however, the simultaneous curve fitting is applied and we try to fit the data with a single stoichiometry by pH-dependent and pH-independent processes, then we evidently run into trouble as the model strictly keeps the stoichiometry. This situation happened in the case of investigating the kinetics and mechanism of the periodate–iodide reaction, where Indelli and their co-workers were misled,<sup>32,33</sup> although others have already shown that the rate-determining step of the reaction is pH-independent.<sup>34,35</sup>

**Additional Remarks.** It should be emphasized that the pitfalls may also be avoided if we have an experimental possibility to measure the time series of the products also or at least to measure their final concentrations. In cases A and D the final stoichiometry depends on the branching ratio, meaning that the kinetic traces can only be evaluated by simplified techniques if extreme concentration ratios are applied in both reagent excesses. The main advantage of the simultaneous curve fitting over the individual evaluation of the kinetic traces is that it does not require extreme concentration conditions for determining both pathways. Even if one of the routes has only 20–30% (see Case A lowest A concentration) contribution to a couple of kinetic traces, the simultaneous curve fitting immediately sheds light on the existence of a branching kinetic model. In case B the kinetic measurements should be preceded by careful equilibrium work to identify the complexes formed. Once the

formation constants of ML and ML<sub>2</sub> are known, then the false conclusion that only ML is formed may be avoided. In case C, however, the preceding equilibrium study will indicate the exclusive formation of ML in metal ion excess, thus the pitfall is unavoidable unless the kinetic curves are evaluated simultaneously.

## Conclusion

It is clearly demonstrated throughout four examples that simplified evaluation procedures may be misleading in drawing the chemical conclusion. Each of the examples chosen is connected to real chemical systems. As was convincingly shown in the case of the branching mechanism, an important pathway may be lost or the rate equation of the rate-determining step can be misinterpreted by the simplified evaluation procedures or, in the case of equilibrium systems, the signal detected can be assigned to a completely different process than it belongs to. Moreover, it is also shown that simultaneous curve fitting in all cases can call attention to the defectiveness of a proposed model based on simplified evaluation procedures. Because these misinterpretations may occur even in relatively simple kinetic models, it is strongly recommended to use a simultaneous evaluation procedure to unravel the kinetics and mechanism of an unknown chemical system.

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