

# A New Formulation of the Lindemann Mechanism of Unimolecular Reactions

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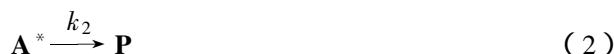
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A new formulation of the Lindemann mechanism of unimolecular reactions in gaseous phase is presented, without the use of steady state hypothesis. It is hereby shown that the nature of applicability of steady state hypothesis in the regime of high reactant gas pressure is different from that in the regime of low gas pressure. In the former case it is an equilibrium approximation, while in the latter case it is a highly reactive intermediate approximation in no connection with a steady state. Furthermore for the latter case it is shown that in the classical formulation of Lindemann mechanism the use of steady state hypothesis is an *ad hoc* assumption. A highly reactive intermediate in the sense that its concentration is very small during the whole course of reaction is a necessary condition for the applicability of very reactive intermediate approximation. When the two distinctive nature of the applicability of steady state hypothesis is mixed-up, wrong or useless conclusion may be arrived at. The only possible case of realizing a true steady state in a complex reaction is pointed out.

**Keywords** chemical kinetics, unimolecular reaction, Lindemann mechanism, steady state hypothesis

## Introduction

The collision mechanism for a unimolecular reaction in gaseous phase with the formulation of its chemical kinetics using the steady state hypothesis is now classical, which appears in all textbooks and monographs as follows:



where  $\mathbf{A}$  is the reactant molecule,  $\mathbf{A}^*$  the reactant molecule in activated state via collision and  $\mathbf{P}$  the product molecule. The corresponding concentrations of these molecules in this gaseous reaction system as functions of time are represented by  $A(t)$ ,  $A^*(t)$  and  $P(t)$  respectively in the kinetic equations:

$$dA(t)/dt = -k_1A^2 + k_{-1}A^*A \quad (3)$$

$$dA^*(t)/dt = k_1A^2 - k_{-1}A^*A - k_2A^* \quad (4)$$

$$dP(t)/dt = k_2A^* \quad (5)$$

where  $k_1$  and  $k_{-1}$  are bimolecular rate constants of the reversible activation and deactivation of  $\mathbf{A}$ , and  $k_2$  is the unimolecular rate constant of the conversion of  $\mathbf{A}^*$  to  $\mathbf{P}$ . The analytical solutions of these equations are not known, while the relation

$$dA/dt + dA^*/dt + dP/dt = 0 \quad (6)$$

is satisfied for all  $t$  from Eqs. (3)–(5), being a result of mass conservation of the reaction system.

## The classical formulation

In the classical formulation of the kinetics of Lindemann mechanism it starts from the application of the so called steady state hypothesis, that is, by putting

$$dA^*/dt = 0$$

Then, we have  $A^* = k_1A^2/(k_{-1}A + k_2)$  by Eq. (4), and  $dP/dt = -dA/dt$  by Eq. (6).

Now, under the condition (i)

$$k_{-1}A \gg k_2, dP/dt = (k_2k_1/k_{-1})A = -dA/dt \quad (7)$$

and under the condition (ii)

$$k_{-1}A \ll k_2, dP/dt = k_1A^2 = -dA/dt \quad (8)$$

When the reactant gas pressure is high, the rate of deactivation of  $\mathbf{A}^*$  is high, so the condition (i) applies, the decay of  $A(t)$  follows the first order kinetics by Eq. (7). As the reactant gas pressure decreases the rate of deactivation of  $\mathbf{A}^*$  will decrease, and when reaching the limit so that the condition (ii) applies, the decay of  $A(t)$  will follow the second order kinetics by Eq. (8). The derivation seems fine. However, the application of the hypothesis

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$dA^*/dt = 0$  under the condition (ii) is rather difficult to be justified.

## A new formulation

A new formulation of the Lindemann mechanism, starting directly from the conditions (i) and (ii) without the use of steady state hypothesis  $dA^*/dt = 0$ , is to be presented as follows.

Under the condition (i),  $k_{-1}A \gg k_2$ , the reaction (2) of the conversion of  $A^*$  to  $P$ , can be considered as a small perturbation to the reversible activation-deactivation reaction (1), so that in the kinetic equation (4) the last term could be neglected,

$$dA^*/dt \approx k_1A^2 - k_{-1}A^*A \quad (9)$$

At activation-deactivation equilibrium,  $k_1A^2 = k_{-1}A^*A$ , thus  $dA^*/dt \approx 0$ . Therefore the use of steady state hypothesis in the classical formulation under the condition (i) is an **equilibrium approximation**, leading to the first order kinetics for the decay of  $A^*$ .

Under the condition (ii),  $k_{-1}A \ll k_2$ , the reverse reaction (deactivation) of (1) can be considered as a small perturbation to the bi-molecular two-step consecutive reaction shown below:



Analytical solutions to this two-step reaction (10) have been obtained by the author long time ago,<sup>1</sup> they are, under the condition (ii),

$$A(t)/a_0 = 1/(1 + a_0k_1t) = 1/\tau \quad (11a)$$

$$A^*(t)/a_0 = \exp(-k_2t) + J - (1/\tau) \quad (11b)$$

$$P(t)/a_0 = 1 - \exp(-k_2t) - J \quad (11c)$$

where  $a_0 = A(t=0)$ ,  $J = \kappa \exp(-\kappa\tau) \int Ei(\kappa\tau) - Ei(\kappa)$ ,  $\kappa = k_2/a_0k_1$ ,  $\tau = 1 + a_0k_1t$ , and  $Ei(x)$  is the exponential integral

$$Ei(x) = \int_{-\infty}^x \exp(\xi/x) d\xi.$$

It is to be noted that mass conservation is observed for this analytical solution of the reaction system Eq. (10), that is,  $[A(t) + A^*(t) + P(t)]/a_0 = 1$  for all  $t$ .

Under an additional condition (iii)  $\kappa \gg 1$ , that means  $k_2 \gg a_0k_1$ , we can use the series expansion of  $Ei(x)$ ,  $Ei(x) = (1/x) \exp(x) [1 + 1!/x + 2!/x^2 + \dots]$ ,  $|x| \gg 1$ .

Taking only the first term of the expansion we have

$$Ei(\kappa\tau) \approx (1/\kappa\tau) \exp(\kappa\tau), \text{ as } \tau > 1,$$

$$\text{and } Ei(\kappa) \approx (1/\kappa) \exp \kappa.$$

Thus  $J \approx (1/\tau) - \exp(-k_2t)$ , conditions (ii) and (iii).

Substituting into Eq. (11) we obtain

$$A^*(t)/a_0 \approx 0 \text{ and } P(t)/a_0 \approx 1 - 1/\tau = a_0^2 k_1 t / (1 + a_0 k_1 t), \text{ conditions (ii) and (iii) } \quad (12)$$

This shows that under the conditions (ii) and (iii) the formation of  $P$  follows the second order kinetics.

For a two step consecutive reaction as expressed in Eq. (10) the concentration of the intermediate product  $A^*(t)$ , starting from  $A^*(t=0) = 0$ , increases with  $t$  to a maximum at certain time  $t_m$ , and then falls to  $A^*(t \rightarrow \infty) = 0$ . Consequently a steady state,  $A^*(t) = \text{const}$ , actually does not exist. On the other hand, when  $A^*$  is highly reactive,  $A^*(t) \neq \text{const}$  but very small numerically for all  $t$ .  $A^*(t)$  is usually non-oscillatory, as chemical oscillation can only happen under very special conditions, then the magnitude of  $|dA^*/dt|$  will also be very small, so that it could be considered as  $|dA^*/dt| \approx 0$  numerically. Therefore, the applicability of the "steady state hypothesis" in the classical formulation under the condition (ii) is actually a **highly reactive intermediate approximation**, in nothing connected with a steady state. In this sense the term steady state approximation is conceptually rather misleading, although its use leads numerically to approach the results of steady state approximation.

## Discussion

From the foregoing derivation it is seen that the transition of the formation of  $P$  to a second order kinetics comes under the conditions (ii) and (iii), while in the classical formulation it comes under the condition (ii) and the assumption of  $dA^*/dt = 0$  (the so-called "steady state hypothesis"). The fallacy of the classical formulation lies in the point that under the condition (ii) alone, the "steady state hypothesis" may not be applicable. For example, for this case the values of  $A(t)/a_0$ ,  $A^*(t)/a_0$  and  $P(t)/a_0$  calculated from the analytical solutions given in Eq. (11) at  $\tau$  values of 1.2, 1.5, 2.0 and 2.5 are listed in Table 1, if  $\kappa$  is taken as unity, i. e.  $k_2 = a_0k_1$ .

**Table 1** Calculated values of Eq. (11) for  $\kappa = 1$

$\tau$	$A(t)/a_0$	$A^*(t)/a_0$	$P(t)/a_0$	$\Delta m$
1.2	0.83	0.15 (0.69)	0.02	(0.69)
1.5	0.67	0.25 (0.44)	0.08	(0.44)
2.0	0.50	0.28 (0.25)	0.22	(0.25)
3.0	0.33	0.20 (0.11)	0.47	(0.11)

In Table 1, the values listed in the round brackets are values calculated from using the "steady state hypothesis", where  $[A(t) + P(t)]/a_0 = 1$ , and  $\Delta m = [A(t) + A^*(t) + P(t)]/a_0 - 1$  showing the deviation from mass conservation as a criterion for the applicability of the steady state hypothesis.<sup>2</sup> It is thus evident that under the condition (ii) and  $\kappa \leq 1$ , the "steady state hypothesis" is not valid, the mass conservation being seriously violated. Consequently the condition  $dA^*/dt = 0$  used in the classical formulation under the condition (ii) is an *ad hoc* assumption, as the condition (iii) is lacking here. Only when  $\kappa \gg 1$ , *i. e.* the condition (iii), the "steady state hypothesis" becomes applicable under the condition (ii).

From what we have discussed above, it is also important to recognize the possible two distinctive nature of the applicability of "steady state hypothesis", the equilibrium approximation and the highly reactive intermediate approximation. When the two different nature of applicability are mixed up, false conclusion could crop up. For example, in the analysis of "validity of the steady state approximation in unimolecular reactions" Shin and Giddings<sup>3</sup> arrived at a conclusion that "in general the smallness of  $A^*/A$  can be considered neither as a necessary nor as a sufficient condition for the smallness of error introduced by the use of steady state hypothesis". This statement is not true. If the case of equilibrium approximation is excluded, the smallness of  $A^*(t)/a_0$  for all  $t$  is a necessary condition for highly reactive intermediate approximation. For complex reactions other than Lindemann mechanism, the reactive intermediate is better written as **B**. In the analysis of the applicability of "steady state hypothesis" to the two-step organic reactions of  $S_N1$ ,  $S_N2$ ,  $E_1$ ,  $E_2$  and  $E_2cb$  types of Ingold classification of reaction mechanisms, Frei and Günthard<sup>4</sup> also arrived at a wrong and useless conclusion that small  $B(t)$  for all  $t$  is neither a necessary nor a sufficient condition for the applicability of "steady state hypothesis" for the same reason.

Now, it is interesting to see if there is any possible case of a true steady state in a complex reaction? This question has never been explored so far in literature. In the original proposition of the "steady state hypothesis" by Bodenstein<sup>5</sup> in his study of photochemical chain reactions, the steady state was really meant that the rate of creation of the reactive intermediate **B** from a starting molecule **A** is equal to the rate of decay of **B**. From the view point of consecutive reactions the rate of decay and the rate of creation of **B** are independent, generally it will not be possible to maintain these two rates equal for a considerable length of the reaction time. However if the reactive intermediate **B** is created at a constant rate while its decay rate will increase, from zero at  $t = 0$ , with the building up of  $B(t)$ , following the whatever its kinetic law of decay, till the de-

cay rate balances the creation rate and a true steady state is realized. This actually occurs in the vinyl polymerization reaction by free radical mechanism, with an almost constant initiation rate from an added chain initiator at the early stage of the polymerization, whence the initiator and monomer concentration have not consumed appreciably. It is followed by chain propagation and chain termination say by radical combination. A steady state of the total radical concentration will be set up<sup>6,7</sup> during the course of polymerization reaction. Similar situation may also apply for photochemical chain reactions in an analogous way.

To sum up, the applicability of "steady state hypothesis" for complex reactions falls in two distinct categories. (a) Equilibrium or true steady state approximation: The concentration of the reactive intermediate after an initial transient becomes a constant value,  $B(t) = (B_{eq} \text{ or } B_{ss}) \neq 0$ , being not necessary to be small, and hence  $dB/dt = 0$ . The initial transient is the time needed to establish the equilibrium or steady state. (b) Highly reactive intermediate approximation: Here  $B(t)$  is not constant, being a single-peaked curve and non-oscillatory, but its value is very small for all  $t$ , and hence  $dB/dt$  is also very small so that it could be considered as  $dB/dt \approx 0$  numerically in Eq. (6). For this case no initial transient period could be defined, as  $B(t)$  does not become a constant value, although in the literature it was often stated just otherwise, being entirely misled by the term "steady state hypothesis". The only condition for its applicability is smallness of  $B(t)$  for all  $t$ , a condition of very low stringency, and consequently it has very wide range of applications covering various categories of complex reactions.

## References and note

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