

# Photochemical bistability and oscillations in isothermal closed systems. Substances in dimer–monomer equilibrium

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## Abstract

New reaction schemes showing photochemical instabilities in closed isothermal conditions are proposed. Bistability and oscillations are predicted for a system in which one reactant is in rapid dimer–monomer equilibrium. The necessary feedback originates from the light absorption law at high total absorption of a stirred solution. For the experimental observation of instabilities, the rates of thermal and photochemical reactions must be comparable. The necessary relations of the parameters are obtained from the presented equations.

**Keywords:** Bistability; Kinetics; Oscillations; Photoreaction; Reaction schemes

## 1. Introduction

“Exotic” kinetic behaviour, i.e. bistability and oscillations, involves chemical instabilities. In some systems [1–7], instabilities have been observed experimentally in reactions incorporating a photochemical step. In most cases, unusual kinetics have been studied in a continuous flow stirred tank reactor (CSTR), i.e. in systems open to mass flow, or at thermokinetic conditions, when the necessary feedback involves heating by light and the temperature dependence of the equilibrium constant.

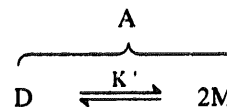
So far, no experimental observations of instabilities in an isothermal closed system on light exposure have been obtained. In Ref. [8], the photochemical transformation of products into reactants has been introduced into the model reaction scheme to obtain a closed system. In the model, the autocatalytic step, or substratum inhibition of the enzyme reaction, is used as the feedback. The possibility of photochemical instabilities in closed photochemical systems has been shown [9–11]. Known bistable photoreaction schemes include [10,11]: (1) thermally reversible photochemical reactions in which the reactant is subject to concentration quenching; (2) three-membered cyclic reaction with a thermoreversible photochemical step; competitive light absorption is the feedback in the second case. Oscillatory behaviour has been observed for a more complicated scheme in which the system contains two independent photochemical reactions induced by light with two different wavelengths. One of the

reactions is bistable and the other reaction is connected with the first by the absorption of light at both wavelengths.

Bistability in a CSTR and in thermokinetic experiments is observed for molecules which form associates or, in the simplest case, dimeric particles [1–5]. In the present work, we have considered photochemical reactions which include a substance in rapid dimer–monomer equilibrium. This is a simple example of a system with bistable and oscillatory behaviour.

## 2. Results

Let us consider a substance A which is in rapid dimer–monomer equilibrium with a constant  $K'$



The concentrations of dimer and monomer are

$$D = \frac{A - M}{2}; \quad M = \frac{\sqrt{1 + 8AK'} - 1}{4K'} \quad (1)$$

where  $A$  is the total concentration of monomer and dimer expressed in moles of monomer.

Now, let us suppose that both monomeric and dimeric molecules absorb light. The light intensity absorbed by the monomer in a stirred solution is

$$I_M/I_0 = D_M \frac{[1 - \exp(-D_\Sigma)]}{D_\Sigma}$$

$$D_M = M\epsilon_M l; \quad D_\Sigma = M\epsilon_M l + D_{\epsilon_D} l \quad (2)$$

where  $\epsilon_M$  is the molar absorptivity of the monomeric form of A,  $\epsilon_D$  is the molar absorptivity of the dimeric form,  $D_\Sigma$  is the total absorbance,  $D_M$  is the absorbance of the monomer (here the molar absorptivities and absorbances are multiplied by a factor  $\ln 10$ ),  $I_M$  and  $I_0$  are the intensity of light absorbed by the monomer and the incident light intensity respectively and  $l$  is the optical path length.

The concentration dependence of the light intensity absorbed by the monomer is shown in Fig. 1. It can be seen that the dependence is substantially non-linear. A maximum is observed at a sufficiently high total absorption. The maximum occurs when the molar absorptivity of the monomer is larger than that of the dimer, and vice versa. It is clear that the absorption maximum is related to the screening effect, i.e. the shielding of light by the dimer as the concentration of

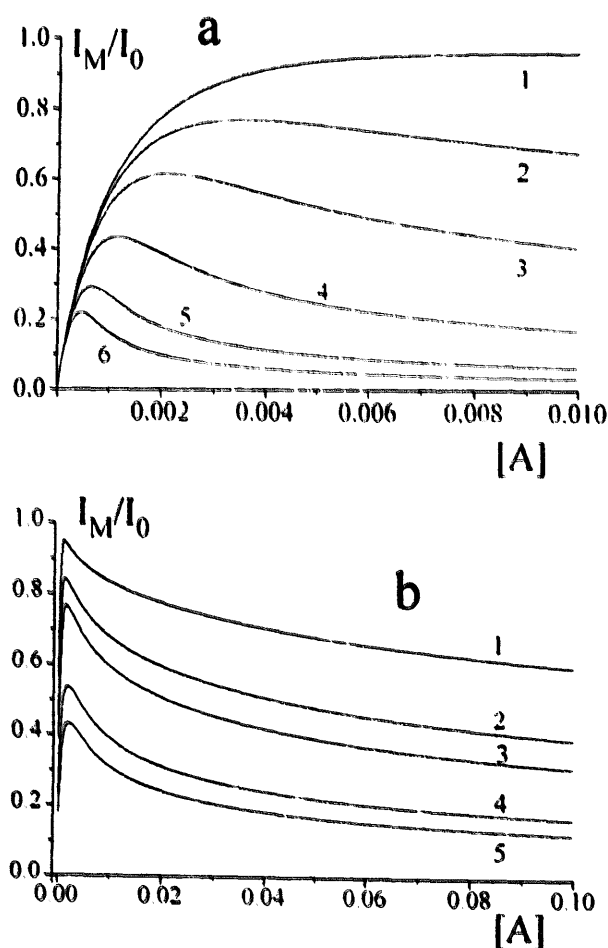
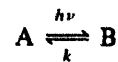


Fig. 1. Concentration dependence of the light intensity absorbed by the monomer (in accordance with Eq. (1)): (a)  $\epsilon_M = 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ ;  $K' = 100 \text{ l mol}^{-1}$ ;  $\epsilon_D/\epsilon_M = 0.1$  (1), 1 (2), 3 (3), 10 (4), 30 (5), 60 (6); (b)  $\epsilon_M = 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ ;  $\epsilon_D = 0.1\epsilon_M$ ;  $K' (\text{l mol}^{-1})$ :  $10^3$  (1),  $5 \times 10^3$  (2),  $10^4$  (3),  $5 \times 10^4$  (4),  $10^5$  (5).

A increases and the fraction of dimer in the total concentration increases.

The non-linearity of the absorbed light intensity as a function of concentration allows bistability in the isothermal closed condition to be predicted. The simplest reaction involving substance A is



Scheme 1.

Let us assume that only the monomeric form of A reacts with the substance produced (B) and the dimeric form is unreactive. The kinetic equation for this reaction is

$$\frac{dA}{dt} = -I_0\phi D_M \frac{[1 - \exp(-D_\Sigma)]}{D_\Sigma} + kB \quad (3)$$

where  $\phi$  is the quantum yield of the photochemical reaction of the monomer and  $B = A_0 - A$  in accordance with the conservation condition.

Let us introduce the dimensionless variables

$$X = A/A_0; \quad K = 4K'A_0; \quad \tau = kt; \quad \epsilon = \frac{\epsilon_D}{2\epsilon_M}$$

The dimensionless representation of Eq. (3) is

$$\frac{dX}{d\tau} = -i_0 g(X) + 1 - X \quad (4)$$

where

$$g(X) = D_M \frac{[1 - \exp(-D_\Sigma)]}{D_\Sigma}; \quad i_0 = I_0\phi/k$$

$$D_\Sigma = D_0 \left[ \epsilon X + (\epsilon - 1) \frac{\sqrt{1 + 2KX} - 1}{K} \right]$$

$$M/A_0 = \frac{\sqrt{1 + 2KX} - 1}{K}$$

The steady state equation

$$i_0 = \frac{1 - X}{g(X)} \quad (5)$$

can be numerically or graphically solved (Fig. 2). Three stationary states are found in the system. Further examination indicates the first and third stationary points to be stable and the second point to be unstable. This means that bistability must occur in the system, and two distinct stationary states with different concentrations of A can be observed. The transition from one stationary state to another can be induced by a variation in the incident light intensity. The feedback is a result of the light absorption by the dimeric form of A.

The same kind of bistability can be obtained in other closed photochemical systems. For example, the cycle model



$$\begin{aligned} dX/d\tau &= -i_0g(X) - (1-\alpha)X - (1-\beta)Y + 1 \\ dY/d\tau &= \alpha X - \beta Y \end{aligned} \quad (8)$$

$$g(X) = \frac{1 - X(1 + \alpha/\beta)}{i_0} \quad (9)$$

where

$$Y = P/A_0; \quad \alpha = k_2/k_1; \quad \beta = k_3/k_1; \quad \tau = k_1 t$$

We can choose parameters  $i_0$  and  $\alpha/\beta$  so that the steady state equation has one solution in the falling part of the  $g(X)$  curve (Fig. 3). In this case, oscillatory kinetics are observed by numerical solution of Eq. (8) (Fig. 4). The oscillatory behaviour can be explained in the following manner. Let us assume that  $k_2$  and  $k_3$  are small. Then the bistable subsystem rapidly achieves one of the two stationary states and the concentrations of the substances vary slowly according to the switch equilibrium. If, according to the ratio  $k_2/k_3$ , the equilibrium concentration of A ( $X_s$  in Fig. 3) falls near the unstable stationary point of the bistable subsystem, the global stationary state is unattainable. On moving to  $X_s$ , the system will transfer from one stable branch to another, i.e. oscillation will be observed.

By a similar method, oscillatory mechanisms can be constructed for an arbitrary bistable photochemical system (for example, for Scheme 2). Suitable parameters can be obtained

by immediate Lapunoff analysis of the corresponding equations.

### Acknowledgements

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